

**ABSTRACT BOOK
AACD2016**

Çanakkale / TURKEY

AACD 2016 is Coming Home

Dear AACD Attendees,

Welcome to Çanakkale and to the 10th Aegean Analytical Chemistry Days (AACD 2016). It was a pleasure to invite you to the “AACD 2016”. In 1998 Professor Gürel Nişli initiated the first AACD conference in Izmir. Sixteen years later, passing a series of nine exciting AACD conferences held at wonderful destinations in Turkey and Greece, it has been an honor for us to continue this long tradition and to organize the AACD 2016 in Çanakkale. The conference will provide a forum among Analytical Chemistry researchers from many different countries.

AACD 2016 will be a three and half day event combining invited lectures, parallel oral sessions and poster presentations. In this edition, there will be 14 invited lectures, 45 contributed oral presentations and 331 poster presentations, making a total of 390 presentations.

We would like to express our gratitude to all the people who contributed to the AACD 2016 conference.

We are particularly thankful to the members of the continuation committee for the continuity of the AACD and scientific committee for reviewing numerous abstracts and of course to the invited speakers - outstanding scientists who are willing to share their expertise with us. Also, as you can see from our webpage, a severe number of sponsors and exhibitors are here to support this event. We express our great gratitude to all of them.

Last but not least, we would like to thank many enthusiastic students and members of the organizing committee who supported us in the organization of this event and did an outstanding job throughout last year.

We are sure you will have a productive and enjoyable stay in Çanakkale and wish you all the best for your time at 10th Aegean Analytical Chemistry Days.

Yusuf Dilgin and Ayşem Arda

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Analytical Chemistry at the Service of Food Quality

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A few decades ago, most of the research in Analytical Chemistry was focused on the discovery and development of new **techniques** which could provide sensitive and hopefully selective results. Typical examples are new detectors and columns for HPLC and GC, flow injection analysis, ICP, atomic fluorescence, atom traps for atomic spectroscopy, molecular emission cavity analysis and many others. Some of these techniques were successful and were further developed by Analytical Instruments Companies.

During the last decade, analytical research is focused to the development of **methods** for sample preparation, preconcentration of analyte and sensitive and selective measurement. Method validation is now part of our everyday life and results should be presented for limit of detection, limit of quantitation, ruggedness, within day and between day repeatability, etc.

Food is a typical sample where Analytical Chemistry can be applied. Consumers should be very careful for the quality of food and this is an area of application where Analytical Chemistry can make miracles! A typical example is the 2008 Chinese Milk Scandal where melamine was added to milk for babies in order to increase the nitrogen content. Another example is the detection and measurement of dichlorobenzene in honey.

Nowadays Analytical Methods are used extensively for the estimation of food quality. Typical examples which will be presented and discussed are the effect of thermal treatment on quality parameters of honey, antioxidant activity of pomegranate juice and measurement of antioxidant activity of edible oils by the CUPRAC method.

Nanomaterials for Elemental Speciation

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Trace element determination in various types of samples (industrial, environmental, pharmaceutical, biological, food, beverages) is an important field of application of modern analytical methods. Nowadays, it is widely recognized that a large number of elements can naturally exist under various forms with considerably different behavior and properties. Due to the significant distinctions in toxicity, mobility and bioavailability of the particular chemical species, a determination of total element concentrations is generally not sufficient for comprehensive clinical and environmental considerations. Therefore, the speciation analysis has reasonably become an important topic of the present-day analytical research. Various types of nanomaterials such as magnetic nanoparticles, carbon nanostructures, metal oxides and noble metal nanoparticles, ion imprinted polymers have been incorporated in new innovative approaches for speciation analysis. Small size, high surface to volume ratio, high chemical reactivity are the properties which makes them ideal sorbents for selective separation of chemical species. Nanostructures based on different modification of the nanoparticles and combinations between them additionally increased the nanostrategies employed for on-line or off-line determination of particular chemical species of elements. The presented lecture is focused on the summary and good examples of the application of nanomaterials for speciation analysis, analytical procedures developed and their application for analysis of environmental, food and biological samples. Critical view point on the current limitations as well as the future perspective will be presented.

Keywords: Nanomaterials, Speciation, Trace Elements

Recent Trends in High-Performance Liquid Chromatographic Separation of Enantiomers

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This presentation summarizes the recent trends in separation of enantiomers by high-performance liquid chromatography (HPLC). Aspects such as new kinds of chiral selectors, carrier materials [1, 2], mobile phases, and mobile phase additives will be discussed. The effect of optimizing of these parameters on separation efficiency, selectivity and analysis time will be demonstrated. After overviewing the most promising recently introduced chiral selectors, polysaccharide-based chiral selectors will be discussed in more detail. In this part, our newest results on the adjustment of the enantiomer elution order based on the chemistry of the chiral selector, the nature of the mobile phase, mobile phase additives and the separation temperature will be reported [3]. Furthermore, some uncommon effects based on the content of water in aqueous-organic mobile phases on the separation of enantiomers of acidic and basic analytes will be shown. In addition, an unusual increase of the separation selectivity based on the optimization of the structures of the analytes and the chiral selectors will be presented as well as baseline enantioseparations within a few seconds by using common HPLC instrumentation. In the final part, examples of chip-based enantioseparations will be shown and the advantages and disadvantages of this separation mode will be discussed [4].

Keywords: Enantioseparations, Chiral Stationary Phases, High-Performance Liquid Chromatography.

References:

1. Q. Kharashvili, G. Jibuti, T. Farkas, B. Chankvetadze, J. Chromatogr. A (2016) in press.
2. L. Bezhitashvili, A. Bardavelidze, T. Ordjonikidze, G. Jibuti, M. Chity, T. Farkas, B. Chankvetadze, J. Chromatogr. A (2016) in press.
3. Kh. Gogaladze, L. Chankvetadze, M. Tsintsadze, T. Farkas, B. Chankvetadze, Chirality, (2015) 27 228-234.
4. S. Thürmann, C. Lotter, J. J. Heiland, B. Chankvetadze, D. Belder, Anal. Chem. (2015) 87 5568-5576.

Development of Bioanalytical Methods for Mass Spectrometry-Based Glycoproteomics and Glycomics

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Mass spectrometry-based glycoproteomics and glycomics studies provide vital knowledge for in-depth characterization of glycosylation including site and protein identification, and glycan profiling at the level of glycopeptide and released glycans. Glycosylation studies led to discover novel biomarkers for most diseases and understand their progress in cellular systems. For the efficient analysis of glycoconjugates by mass spectrometry, enrichment and purification steps play a crucial role. Several enrichment techniques based on different interactions between glycoconjugates and solid supports have been developed for this purpose. In this communication, several bioanalytical methods consisting of fast, efficient and easy applications were developed, which based on different interactions such as hydrophilic and chelation. The glycopeptide profiles covering glycosylation site and glycan structure knowledge of standard glycoproteins were determined in mass spectrometric analysis using novel bioanalytical methods. Some glycoproteins were analyzed by MALDI-MS and ESI-MS to examine their glycosylation site and glycan profile using developed bioanalytical methods after the enrichment and the purification. Also, 2-AA labelled human plasma N-glycans were used to test purification performance of the methods at the glycan level. A workflow including a facile application for determining glycosylation sites and site heterogeneity in glycoproteins by mass spectrometry will be discussed in detail.

Keywords: Glycoproteomics, Glycomics, Mass Spectrometry, Enrichment.

Target and Non-Target LC-HRMS Strategies for the Detection of Emerging Contaminants in the Aquatic Environment

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The analysis of environmental samples by liquid chromatography - high resolution mass spectrometry (LC-HRMS) reveals a high number of peaks in the samples. Reversed phase liquid chromatography (RPLC) does not cover all the polarity range of micro-contaminants present in these samples. Hydrophilic interaction liquid chromatography (HILIC) is an important complementary technique for the identification and determination of polar compounds. Two wide-scope target screening methods, RPLC- and HILIC-QToFMS, were developed and applied in wastewater samples. The methods were validated with a novel approach involving advanced chemometrics. Through their application in real environmental samples, it was proved that additional compounds can be detected only under HILIC conditions and that the two chromatographic modes have complementary domains. Therefore, our next aim was to incorporate both techniques, along with additional analytical strategies, in suspect and non-target HRMS screening of environmental samples with the ultimate aim to explore deeper their polar fraction. Towards this aim, we have developed an integrated workflow for the identification of suspect and unknown compounds, comprising mainly of the following steps: (1) analysis of the extracts by RPLC-QToFMS and HILIC-QToFMS in both electrospray ionization modes; (2) automated comparison of the peak lists and recording of the common and unique peaks in each chromatographic system; (3) prioritization of polar compounds, i.e. unique peaks in HILIC or with high retention time in HILIC; (4) interpretation of the MS/MS spectra in both ionization modes and study of the common fragmentation patterns of structurally related analogues; (5) application of quantitative structure-retention relationship (QSRR) models for the accurate prediction of retention time of tentatively identified compounds in both chromatographic systems, and development of a universal RT index system for RPLC mode; and (6) diurnal or weekly trend analysis or study of the time profile of the detected peaks in related experiments, using statistical platforms. This strategy was applied in several case studies, such as non-target screening of influents and effluents from the WWTP of Athens, or treatment experiments, such as the identification of transformation products from ozonation studies, or exposure of zebrafish to xenobiotics and study of the xenometabolome. The application of this integrated workflow supported the identification of new compounds in wastewater or it was able to separate and identify new transformation products of emerging contaminants, hidden from the RPLC-QToFMS analysis.

Acknowledgements: My research team (<http://trams.chem.uoa.gr>), our Eawag collaborators (J. Hollender, E. Schymanski, K. Fenner, H. Singer) and Bruker (A. Drury, C. Baessmann) are gratefully acknowledged. This research has been co financed by the European Union and Greek national funds through the Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF)-ARISTEIA 624 (TREMEPOL project; tremepol.chem.uoa.gr).

Bio(mimetic) Electrochemical Sensors: *Present, Past and Future*

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Biosensors represent the technical counter part of sense organs by coupling enzymes, antibodies, nucleic acids, receptors, organelles, cells, and tissues with a chemical or physical sensor.

Inaugurated by L.C. Clarck in the sixties the development of electrochemical biosensors mainly focused on glucose oxidase and (PQQ) glucose dehydrogenase for blood glucose measurement. Ten years later direct heterogeneous electron transfer has been achieved by us for cytochrome c, hemoglobin and different P450 enzymes. This approach has been extended to develop sensors for the reactive oxygen species (ROS) superoxide and peroxide or for different xenobiotics and drugs. At present, electrochemical glucose sensors cover almost 75 percent of the 17 billion US Dollars world market of biosensors. On the other hand, electrochemical immunosensors or nucleic acid chips reached not a comparable acceptance and optical principles are considerably more applied in these fields.

In order to mimic the active sites of antibodies or enzymes by synthetic mimics so-called „molecularly imprinted polymers” (MIPs) have been developed. Functional monomers are polymerised in the presence of the target analyte and after polymerisation the template molecules are removed, providing binding sites ideally complementary in size, shape and functionality to the template. So far the affinity and catalytic activity of MIPs have in general been lower than those of their biological counterparts. MIP-based electrochemical sensors have the potential to complement biosensor and biochips for the measurement of low molecular weight substances, proteins, viruses and living cells.

Enhancement of Catalytic Activity on Conducting Polymers or Carbon Based Electrodes via Metal Particles Modification for Electrochemical Applications

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Electrocatalysis is an important field in electrochemistry that has achieved a remarkable progress in the three last decades due to application of new characterization techniques. The main part of electrocatalysis has been modified the electrode surface. In order to prepare ideal catalytic surface for electrochemical oxidation and reduction reactions, conductive polymers or carbon-based materials after modification with metal/bimetallic/metal oxide systems have been generally used. The unique chemical and physical properties of metal/metal oxide particles make them extremely suitable for designing new and improved sensing devices, especially as in electrochemical systems like for electrocatalytic reactions and electroanalytical applications. A well-dispersed Au, Ag, Pt mono metallic and Au–Ag and Au–Pt bimetallic nanoparticles have been successfully synthesized on conductive polymers or carbon based electrodes via electrochemical reduction process. In the present study, the electrocatalytic activity of metal particles modification of conductive polymers and carbon based electrodes for boron compounds toward oxidation and oxygen reduction were evaluated in alkaline medium. On the other hand, the metal nanoparticles modified electrodes were used for simultaneous determination of compounds which were pharmacologically and biologically important. The surface morphology and chemical composition of all electrodes were examined by scanning electron microscopy, transmission electron microscopy, electrochemical impedance spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy.

Volatile Compound Generation Strategies in Analytical Chemistry

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One of the main aspects for analytical chemists is to develop sensitive and accurate analytical methods for the determination of analytes without matrix interferences. In order to perform trace and ultratrace determination of elements, production of volatile analyte species has been commonly used in literature as one of the most powerful and widely employed method. There are some strategies in literature for the generation of volatile species. Chemical generation of volatile hydride species by derivatization with borane complexes has been applied not only for total element determination but also for speciation purposes for hydride forming elements such as Pb, Cd, Sb, Te, As, Se, Bi, Hg (1). Electrochemical hydride generation is another alternative to chemical hydride generation to obtain lower detection limits. Scientists have spent great efforts to create new vapor generation systems to replace or reduce the use of chemical reagents. UV vapor generation has been proved as a useful alternative to the commonly employed chemical and electrochemical hydride generation methods for the determination of hydride forming elements, transition metals (Ni, Co, Cu, Fe), noble metals (Ag, Au, Rh, Pd, Pt) and nonmetals (I, S). In UV-photochemical vapor generation system, production of volatile analyte species is achieved by UV-irradiation of aqueous analyte solution including low molecular weight carboxylic acids (formic, acetic, propionic) (2). In addition, different sorts of traps have been applied to volatile analyte species prior to atom cell in order to improve the sensitivity and reduce the interferences (3,4).

Keywords: Volatile Compound Generation, Chemical Hydride Generation, Transition Element, Photochemical Vapor Generation

References:

1. D'Ulivo, A., Dědina, J., Mester, Z., Sturgeon, R.E., Wang, Q., Welz, B., Pure and Applied Chemistry (2011), 83, 1283-1340.
2. Guo, X., Sturgeon, R.E., Mester, Z., Gardner, G.J. Analytical Chemistry (2004), 76, 2401-2405.
3. Kula, İ., Arslan, Y., Bakırdere, S., Titretir, S., Kendüzler, E., Ataman, O.Y. (2009) Talanta 80, 127-132.
4. Titretir, S., Kendüzler, E., Arslan, Y., Kula, İ., Bakırdere, S., Ataman, O.Y. Spectrochimica Acta Part B, (2008), 63, 875-879.

Electrochemistry – the Flexible Tool Box for the Construction of Hyphenated Instrumental Analytical Systems

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Instrumental analytical methods have experienced a rapid development during recent years. Miniaturization, the increasing impact of mass spectrometry and the implementation of hyphenated systems have become trend-setting routes towards enhanced performance characteristics. Concerning electrochemistry, the design of tailor-made electrochemical systems with a wide variety regarding size, geometry and materials is an essential strength that can be exploited for the construction of hyphenated analytical arrangements. The present contribution presents several examples that illustrate the possibilities of implementation of electrochemical components into more or less complex hyphenated systems.

Electrochemical detection (ED) operated in the amperometric mode offers very low limits of detection even in miniaturized detector configurations. Such ED systems can be coupled with capillary-based separation techniques enabling studies of extremely small sample volumes down to the femtoliter range [1]. The combination of electrochemical techniques with mass spectrometry (MS) paves the way for new research directions in material and life sciences [2]. Another strength of electrochemical methods is the high spatial resolution that can be realized using scanning electrochemical microscopy for studies of single cells or nanostructured bioactive objects [3]. Finally it will be shown that electrochemical components can easily be integrated into very complex instrumental systems such as comprehensive two-dimensional separation techniques [4, 5]. In this way electrochemical devices are serving as tools for optimization and interpretation of analytical studies.

Keywords: Hyphenated Techniques, Electrochemical Detection, Mass Spectrometry, Miniaturized Electrochemical Systems, Separation Methods

References:

1. J.J.P. Mark, R. Scholz, F.-M. Matysik, J. Chrom. A (2012) 1267 45.
2. R. Scholz, P. Palatzky, F.-M. Matysik, Anal. Bioanal. Chem. (2014) 406 687.
3. S. Bergner, P. Vatsyayan, F.-M. Matysik, Anal. Chim. Acta (2013) 775 1.
4. A. Beutner, S. Kochmann, J.J.P. Mark, F.-M. Matysik, Anal. Chem. (2015) 87 3134.
5. A. Beutner, R.R. Cunha, E.M. Richter, F.-M. Matysik, Electrophoresis (2016) 37 931.

Electrochemical Aptasensors

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Aptamers are synthetic nucleic acid sequences that could selectively bind to their target molecules (e.g, proteins) similar to antibodies (1,2). The synthesis and selection of aptamers are done by using SELEX (*Systematic Evolution of Ligands by Exponential enrichment*) method. The improved stability properties including resistant to denaturation and degradation, easy modification, target adaptability and easy-to-stock make them more advantageous comparison to antibodies and ideal candidates as protein recognition elements in a wide range of bioassays and for diagnostic applications (3-5).

The development of advanced biosensor platforms could impact significantly the areas of genomics, proteomics, biomedical diagnostics and drug discovery (6-9). Electrochemical biosensors coupling the inherent specificity of biorecognition reactions with the high sensitivity of physical transducers, hold great promise for detection of sequence-specific nucleic acids, or proteins for clinical, environmental or forensic investigations (2-9).

An overview to aptamer based biosensors (aptasensors) developed for electrochemical detection of aptamer-protein interactions has been presented herein with their advantages and further applications.

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Keywords: Aptasensors, Electrochemical Biosensors, Aptamer-Protein Interactions.

References

1. J. Muller, B. Isermann, C. Ducker, M. Salehi, M. Meyer, M. Friedrich, T. Madhusudhan, J. Oldenburg, G. Mayer, B. Potzsch, *Chem. Biol.* (2009) 16 442-451.
2. M. Mascini, I. Palchetti, S. Tombelli, *Angew. Chem. Int. Ed.* (2012) 51 1316-1332
3. A. Erdem, H. Karadeniz, G. Mayer, M. Famulok, A. Caliskan, *Electroanalysis* (2009) 21 1278-1284.
4. A. Erdem, G. Congur, E. Eksin, Chapter 13: Voltammetric aptasensor based on magnetic beads assay for detection of Human Activated Protein C, In: Ed. G. Mayer, *Nucleic Acid Aptamers, Selection, Characterization, and Application, Methods in Molecular Biology* (2016) pp. 163-170, Springer Protocols, Humana Press. UK.
5. E. Eksin, G. Congur, A. Erdem, Aptasensor Technologies Developed for Detection of Toxins, In: Ed. D.P. Nikolelis, G-P. Nikoleli (eds.) *Biosensors for Security and Bioterrorism Applications* (2016) pp. 249-259, Springer, Ottawa, ON, Canada
6. E. Palecek, M. Bartosík, *Chem. Rev.* (2012) 112 3427-3481.
7. J. Wang, *Electroanalysis* (2005) 17 7-14.
8. A. Erdem, *Talanta*, (2007) 74 318-325.
9. A. Erdem, Chapter 8: Electrochemical Sensors for Biomolecular Recognitions, In: Ed. A. Vaseashta, *Life Cycle Analysis of Nanoparticles: Risk, Assessment, and Sustainability* (2015) pp.203-229, Destech Publications, Inc. USA.

Microanalytical Systems for Personalized Medicine

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The development of lab-on-chip systems will enhance the diagnostics in personalized medicine. After an introduction of personalized medicine a short overview of microbiosensors for monitoring metabolic parameters will be given and with a look on the history and commercialization of such devices. For future applications special microfluidic lab-on-chip chip based systems will be highlighted for RNA based pathogen detection using only 5µl analyte volumes. Enrichment, lysis, purification and isothermal amplification of RNA can be done using phaseguide structures for performing free flow electrophoresis, gel electrophoresis and electrothermal lysis on chip¹.

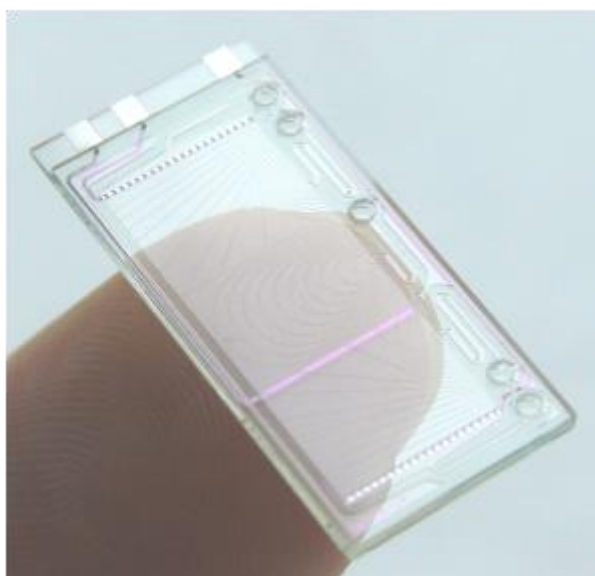


Fig.1: Point of Care biochip for RNA biomarker detection

Keywords: Point Of Care Testing, Lab-On-Chip, Microbiosensors, Personalized Medicine, RNA Biomarker Detection

References:

1. Hakenberg S, Huegle M, Weidmann M, Hufert F, Dame G, Urban G, A Phaseguided Passive Batch Microfluidic Mixing Chamber for Isothermal Amplification, (2012) Lab Chip 12, 21, 4576 - 4580

Direct Atomic Absorption Spectrometric determination of Se in Biological Fluids by Graphite Filter Furnace Atomizer with Graphite Thread

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Electrothermal atomic absorption spectrometry (ET AAS) is one of the most effective methods (**tool**) for the direct determination of Se in biological fluids (blood, urine, saliva and breast milk and other) that is important for studying of element effect on human body status as well as at diagnostic some of diseases. Although ET AAS method offers high sensitivity and require low volume of sample to be analyzed, however Se determination can cause significant difficulties from spectral and matrix interference effect as well as serious risk of it losses during the sample preparation stage. For solving these problems the “filter furnace atomizer” (FFA) with graphite thread (GT) and Pd-Mg chemical modifiers (CM) are appears as promising tools for the direct ET AAS analysis materials with a high content of organic matter [1-4]. Unfortunately, in analytical practice of clinical, toxicological and etc. laboratories it is not widely used.

This paper are devoted to investigation of operation parameters of graphite furnace (with longitude heating) with FFA, graphite thread and Pd-Mg CM as well as established of corresponding analytical characteristics for direct ET AAS determination Se in blood, urine, saliva and breast milk samples.

The interferences effect from mineral (chlorides, sulfates, phosphates of Na, K, Ca and Mg) and organic (protein, carbohydrates, animal fat, urea) macro-components on atomic absorption values and background signal of Se are established. Compared with technique of evaporation analyte from L’vov platform, the FFA with CM and Pd-Mg CM allows to 1,5-2 times to increase the sensitivity of Se determination, to improve mineralization process by rising furnace temperature on the pyrolysis step of analyte up to 1100°C and at the same time to significantly reduce nonselective absorption of light.

In the optimized conditions of FFA heating and taking into account dilution of biological fluids in 2-3 times (to reduce their viscosity) the limits of Se quantification (LOQ) - 2,5 µg·L⁻¹ Se.

The proposed method was use in some of medical, clinical and toxicological laboratories activity.

The accuracy of the results obtained checked in accordance with the basic rules of mathematical statistics. Time of Se determination in one of biological fluid sample does not exceed 10 minutes and value of the relative standard deviation (S_r) does not exceed 8%.

Keywords: Selenium, Biological Fluids, Interferences, ET AAS, Filter Furnace Atomizer, Graphite Thread, Pd-Mg Chemical Modifier

References:

1. D. Katskov Spectrochim. Acta Part B. (2007) 62 897-917.
2. C. Canário, P. Ngobeni J. Anal. At. Spectrom. (2004) 19 1468-1473.
3. P. Ngobeni, C. Canário J. Anal. At. Spectrom. (2003) 18 762-768.
4. A.Zhuravlev a, A.Zacharia, S.Gucer, A.Chebotarev, M.Arabadji, A.Dobrynin. Journal of Food Composition and Analysis 38 (2015) 62–68

Superporous Cryogel/Conductive Composite Systems for Potential Sensor Applications

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Cryogels that are prepared under cryogenic conditions as superporous hydrophilic polymer networks are used as template for in situ synthesis of conductive polymers such as poly(aniline) (p(An)), poly(pyrrole) (p(Py)), and poly(thiophene) (p(Th)) via oxidative polymerization technique to obtain superporous cryogel/conductive polymer semi-interpenetrating polymer networks (IPN). In addition to p(An), p(Py), p(Th) conductive polymers, other conductive moieties such as graphene oxide (GO), reduced-GO (r-GO), and a dye, methyl blue were embedded within the networks of neutral, anionic and cationic superporous cryogel networks to prepare different conductive composite systems. The potential sensor application of the prepared superporous cryogel/conductive composite were evaluated for different analytes such as HCl, NH₃, various dyes, and some toxic organic contaminants.

Keywords: Cryogel-Conductive Polymer Composite; GO-Cryogel Sensors; Gas/Liquid Sensors; Ionic/Electrical Conductivity.

R&D STUDIES IN TÜPRAŞ

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Tüpraş is the largest industrial enterprise in Turkey operating 4 oil refineries with a 28.1 million tons annual crude oil processing capacity. It is the only oil refining company in Turkey and refineries are located in Batman (1955), İzmit (1961), İzmir (1972) and Kırıkkale (1986). Kırıkkale and Batman Refineries have connection with Baku-Tiflis-Ceyhan pipeline across Azerbaijan, Georgia and Turkey. Tüpraş process crude oil from various regions. In 2015, Tüpraş purchased 21 different types of crudes from 11 countries. Regarding Tüpraş latest and biggest investment in its history, Tüpraş commissioned the Residuum Upgrading Facility (RUP) in 2015 with a total capital investment of US\$ 3.1 billion.

Tüpraş R&D Center was established in 2010 in order to reach global competitive power and success in interested areas. R&D Center is composed of three different buildings which are administrative and offices building, R&D laboratories and pilot plant building. In R&D there are six different research groups which are Process Development and Optimization, Modelling and Control, Product Development, Catalyst Management and Development, Materials Development and Reaction, Modelling and Characterization.

Some of the projects being conducted in product development related groups are as follow. In one project, the physical properties of refinery distillates which are measured using different international and national standard procedures (ASTM, EN-ISO, IP) are tried to be estimated using chemometric model with the help of data obtained from faster instruments such as NIR, FT-IR and NMR. In other project, the refinery spent gas, H₂S, is studied to be converted to elemental sulfur and H₂ gas using photo, electrochemical and photo-electrochemical methods. Another ongoing project is synthesis of light and middle distillates by olefin oligomerization.

In R&D center, other than synthesis and reaction projects, modelling and optimization studies are also carried out for the production processes to increase the process and energy efficiency. One of the projects made for that purpose is the Tüpraş Energy Network Tracking and Optimization System Project. Additional to these projects mentioned above, important and ongoing project about pilot plant facility is hydrocracker pilot plant system which is going to create a good place to study the catalyst performance and effect of different variables on the selected catalyst.

Keywords: Tüpraş, Refining, Chemomerty, Oligomerization, Energy Optimization, Hydrocracker

Advanced Mass Spectrometry (MS) Technologies

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Ant Teknik Cihazlar Ltd., Istanbul

LC/MS is becoming an increasingly indispensable tool in many application fields. It provides the solution to the high reliability, productivity and sensitivity demanded in the areas of pharmaceuticals, food science, chemicals, and environmental analysis.

An MS detector has benefits like its high sensitivity, high detection selectivity, and high qualitative capability that bring improved productivity to HPLC analysis; high sensitivity measurements of compounds with almost no UV absorption like macrolide antibiotics, by utilizing selected ion monitoring (SIM) mode; and selective detection by component in a multi-component simultaneous analysis; using LC-MS, even multi-component simultaneous analysis can be performed without spending time and effort on investigating separation conditions.

The aim of this study is to get a brief explanation that are summarized above, and support them with some real data.

Q-TOF: Need More Confirmation ?

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The use accurate mass measurements provides a better confidence in identification of unknowns and confirmation. Agilent has MS systems and solutions for regulations and beyond this. Analyses using MS systems (QQQ, TOF, or Q-TOF) require some rules (depending on EC 2002/657 The performance of analytical methods and the interpretation of results, Or SANTE 11945/2015 for pesticides) for results positive for confirmation.

Agilent 6500 Q-TOF series and 6400 series QQQ systems are used for more confidence in determination. TMRM for QQQ systems and Library search and Molecular Structure Correlator (MSC) softwares allow us to be more confident about positive results. MSC uses accurate mass product ion data to predict structural pattern of the compound by using “Systematic Bond-Breaking” approach as described by Hill and Mortishire-Smith.

Keywords: Q-TOF, MSC, Screening of Unknowns, Toxicology

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ORAL PRESENTATIONS

***Plantago holosteum* Scop. (Plantaginaceae) as a Candidate for Monitoring of Metal Pollution Around the Abandoned Tungsten Mine Work: A Case Study of Inductively Coupled Plasma Spectrometry Applications in Environmental Pollution**

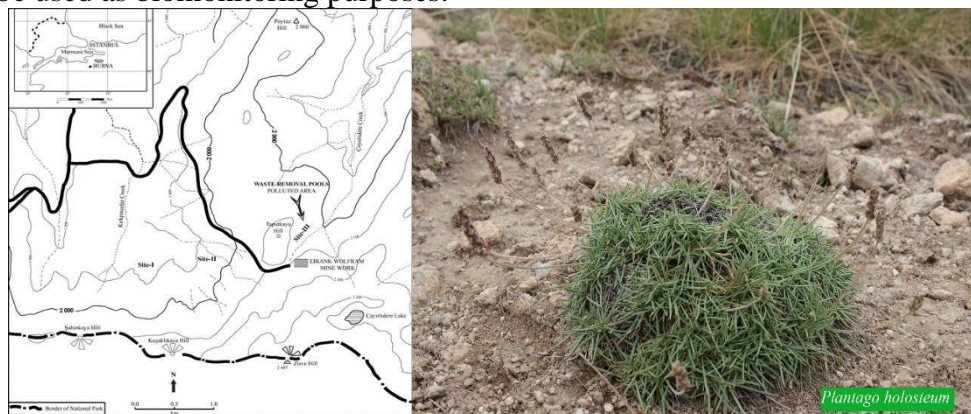
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This study evaluates the influence of tungsten on uptake and translocation of essential elements (Cu, Fe, Mo, Mn and Zn) of *P. holosteum* around the abandoned tungsten mine work on Uludağ Mountain, Turkey. In earlier work, *P. holosteum* was evaluated for phytoremediation purposes over a wide range of elements¹. ICP-MS was used to analyze different elements from different organs (roots, leaves and flowers) of plant and soil samples. Three sample sites were selected around the mine for soil and plant sampling. Two sites approximately 500 m from the mine work were assumed to be unpolluted sites whereas a polluted sample were selected from a waste removal pool (WRP) from mine area. Open wet and Kjeldahl digestion procedures were applied to the samples. Accuracy was evaluated using at least two kind of standard reference materials. Interday and intraday precisions were determined over one week period during analysis. Possible matrix interferences were screened by analyzing different isotopes of any elements. Although the elemental levels of mentioned elements were increased in soil samples from the waste removal pools compared with the unpolluted sites; all elements except manganese were found to be increased in plant samples possibly due to mining activities. As a result, *P. holosteum* may be considered a bioaccumulator species for W, Mn, Cu, Cd, and Fe and can be used as biomonitoring purposes.



Investigation area and sampling sites² and *Plantago holosteum* Scop. (photo by G. Güleriyüz)

Acknowledgements: This work is supported by the Commission of Scientific Research Projects of Uludağ University [to H. Arslan, Project No KUAP(F)-2015/64], it is part of MSc. thesis of H. Kiazolu (advisor G.Güleriyüz).

Keywords: *Plantago*, ICP-MS, Tungsten Mine Work, Uludağ.

References:

1. H.Arslan, G.Güleriyüz, Hawa Kiazolu, Ümran Seven Erdemir, Second Symposium on EuroAsian Biodiversity (SEAB-2016), proceedings book, page 371.
2. G.Güleriyüz, H.Arslan, S.Kırmızı, Ş. Güçer, Environmental Pollution (2002) 120 707-716.

Sample Preparation for Determination of Therapeutic Natural Compounds in Medicinal Plants

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Abstract

There is growing interest in medicinal botanicals as part of complementary medicine in the World. Considerable peoples from both developed and developing as well as undeveloped countries use alternative remedies, including herbal medicine, for disease prevention and therapy. The high cost, side effects and therapeutic limitations of conventional medications are key factors in this state. Recently, there is interest in a scientific approach to this subject, by using extraction/isolation of the active compound from botanicals and its use in drug form. Among the commonly studied compounds, curcumin, quercetin and resveratrol are called as miraculous chemicals. To determine these reagents, they should be extracted from samples plant at high efficiency. Several new extraction techniques for improving efficiency and selectivity are now replacing the traditional methods of extraction such as soxhlete extraction and similars. These novel extraction methods include Supercritical Fluid CO₂ Extraction (SCFE), Accelerated Solvent Extraction (ASE) and Microwave Assisted Extraction (MAE).

Keywords: Natural Compounds; Extraction Methods; Herbal Medicine.

Introduction

During last years, the interest on polyphenols and other molecules with antioxidant activity has increased among agricultural and food scientists, nutritionists, food industry professionals and consumers (1-3). Among them, resveratrol is called as miraculous component because it have the antiinflammatory, antimicrobial, antioxidant, antimutagenic, antidepressants, cardio-protective, anti-angiogenic, anti-proliferative as well as anticancer properties and recently stated to be useful for skin whitening agent (in cosmetic), against hair loss, neurodegenerative and diabete diseases (4-6). Thus, the effects of resveratrol have been widely studied (7-8). Subsequent reports have shown that resveratrol suppresses proliferation of several types of cancers, such as colon, breast, pancreas, prostate, ovarian and endometrial cancers, as well as lymphoma, and affects diverse molecular targets (9). Resveratrol is produced by a restricted number of plants such as grapes (*Vitis* spp.), peanuts (*Arachis* spp.) [11] and berries [12]. It is not normally present in large amounts and is produced in response to stress; resveratrol belongs to a class of defense molecules called phytoalexins that protect against infection and damage from exposure to ultraviolet (UV) irradiation.

After a long studied period, it is knowledge that curcumin have the antiinflammatory, antibacterial, pro-apoptotic, chemopreventive, chemotherapeutic, anti-proliferative, wound healing, anti-nociceptive, antiparasitic and anti-malarial properties (10-11). Further, it was reported that curcumin may be active against a wide range of human diseases, including diabetes, obesity, neurologic and psychiatric disorders, and cancer, as well as chronic illnesses affecting the eyes, lungs, liver, kidneys, and gastrointestinal and cardiovascular systems as well

as curcumin has potential as both a chemopreventive and a chemotherapeutic agent against cancer (12).

Nowadays, quercetin is largely utilized as a nutritional supplement and as a phytochemical remedy for a variety of diseases like diabetes/obesity and circulatory dysfunction, including inflammation as well as mood disorders (13). The therapeutic applications of quercetin is illustrated in Figure 1. Strong antioxidative capacities of quercetin are primarily described to the presence of two antioxidant pharmacophores within the molecule that have the optimal configuration for free radical scavenging: the catechol group in the B ring and the OH group at position 3 of the A ring (Fig. 2) (13).

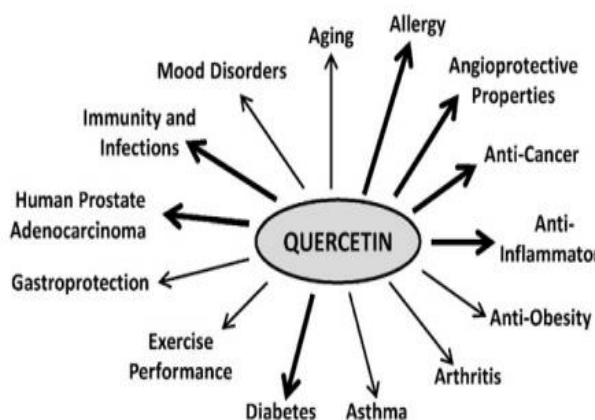


Figure 1. Therapeutic applications of quercetin (13).

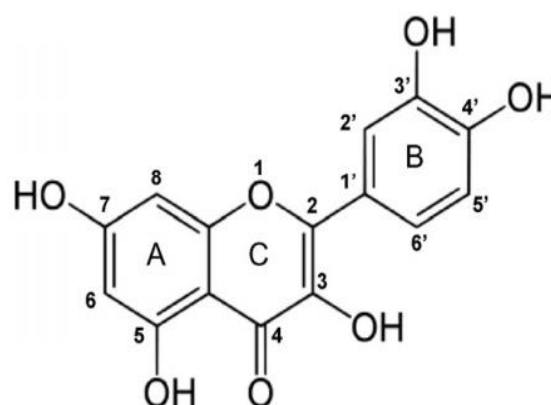


Figure 2. Structure of quercetin

In this study, novel extraction methods were evaluated and concentrations of resveratrol, curcumin and quercetin in food samples using these methods were summarized.

Materials&Methods

Obtaining an appropriate sample is an obvious first step in an analytical procedure. When developing analytical protocols, a key step is the determination of the analyte recovery for the overall method and for each individual procedure. Recently, a few novel extraction techniques are more popular:

1. Accelerated Solvent Extraction (ASE): Accelerated solvent extraction (ASE) or sometime called pressurized solvent extraction (PSE) or pressurized liquid extraction (PLE) is a technique which has been developed as an alternative to classical extraction methods such as Soxhlet, maceration, percolation or reflux, offering advantages with respect to extraction time, solvent consumption, extraction yields and reproducibility. It uses organic solvents at elevated pressure and temperature in order to increase the efficiency of the extraction process. Increased temperature accelerates the extraction kinetics and elevated pressure keeps the solvent in the liquid state, thus enabling safe and rapid extractions. High temperatures decrease the viscosity of the liquid solvent, allowing a better penetration of the matrix and weakened solute matrix interactions. Also, elevated temperatures enhance diffusivity of the solvent resulting in increased extraction speed. Solvents can be selected based on the polarity of the analyte and compatibility with any post-extraction processing steps and quantification equipment (14-15).

2. Subcritical water extraction (SWE): Subcritical water extraction (SWE) is the extraction using hot water under pressure. SWE is an environmentally-clean technique that provides

higher extraction yields to extract solid samples. SWE is carried out using hot water (from 100 °C until 374 °C, the latter being the water critical temperature) under high pressure (usually up to 10 bar) enough to maintain water in the liquid state.

Supercritical Fluid Extraction (SCFE): A supercritical fluid is an element or compound above its critical pressure and temperature. In this state, it is compressible and possesses both the properties of a gas and a liquid, providing the supercritical fluid with improved solvating power and has an edge over conventional liquids. The main attraction of SCFE is the use of carbon dioxide (CO₂) as the solvent. Unlike most organic solvents, CO₂ is not as harmful environmentally and has been described as a “green solvent”. It is an inexpensive, relatively inert and non-inflammable gas of low toxicity, with easily achievable supercritical conditions (Fig. 3). Polar modifiers such as water or methanol are usually added to improve the solubility of the more polar analyte in the supercritical fluid or to competitively displace the analyte from the matrix active sites. The addition of a modifier is reported to increase the yield of the analyte of interest by up to three-fold (16-17).

3. Microwave assisted extraction (MAE): Using MAE (Fig. 4), heating occurs in a targeted and selective manner with practically no heat being lost to the environment as the heating occurs in a closed system. This unique heating mechanism can significantly reduce the extraction time (usually less than 30 min) as compared to Soxhlet. The principle of heating using microwave is based upon its direct impact with polar materials/solvents and is governed by two phenomenons: ionic conduction and dipole rotation. Both of them are responsible for heating of substances, which in most cases occurs simultaneously. Only dielectric material or solvents with permanent dipoles do get heated up under microwave. The efficiency with which different solvents heat up under microwave depends on the dissipation factor, which is the measure of the ability of the solvent to absorb microwave energy and pass it on as heat to the surrounding molecules (18-19).

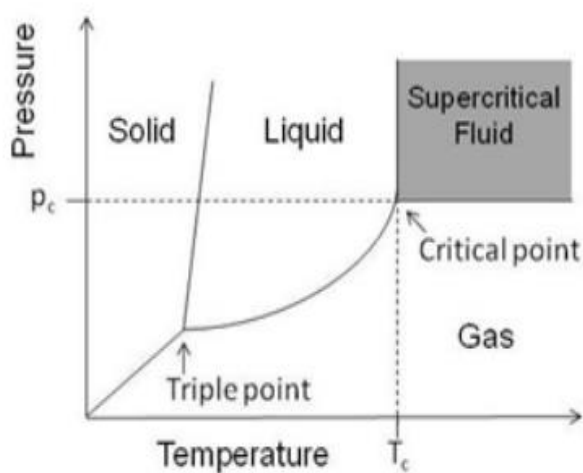


Figure 3. Supercritical conditions



Figure 4. Microwave assisted extraction

Results and Discussion

The polyphenols can be divided, depending on their basic chemical structure into at least 10 different classes. The flavonoids constitute one of the most important group, and they can be further subdivided into 13 different classes, with more than 5000 compounds described (20). During last years, the interest on polyphenols and other molecules with antioxidant activity has increased among agricultural and food scientists, nutritionists, food industry professionals and consumers. In the analysis scheme, extraction serves to isolate analytes from potentially interfering sample components while getting these analytes into a form suitable for analysis. Enhanced extraction methods are generally instrumental systems, and the enhanced efficiency of these methods comes from elevated solvent temperature. This temperature elevation leads to favorable kinetic, diffusion, solubility, and other parameters. Temperature increases lead to the improved extraction capabilities of more traditional techniques such as Soxhlet extraction. Ultrasonic-assisted extraction possesses enough potential than conventional techniques for the extraction of plants secondary metabolites. It has been least exploited in comparison to other techniques. Ultrasonication overcomes all the disadvantages of high cost, post process concentration, low recovery, and others. The time required for the extraction stage is reduced to some 40 min in the ASE method (representing a considerable reduction when compared with the traditional methods of maceration) (14). The efficiency of ASE was 1.2–1.5 times higher than the Soxhlet extraction and time consumed was very less. It can be evaluated that, maximum recovery/efficiency is achieved using ASE and MAE.

Conclusion

It can be concluded that various factors influence the polyphenol extraction in terms of content, efficiency, composition, and purity of polyphenols. These factors include technique used for extraction, duration of extraction, solvent used, solvent to solid ratio, and intensity of waves. Microwave-assisted and Accelerated Extraction techniques seem to be more promising and have shown a greater potential and better efficiency for the extraction of polyphenols as compared to other techniques.

References

1. Surh YJ. *Nat Rev Cancer* (2003) 3 768-80.
2. Park, EJ, Pezzuto, JM. *Cancer and Metastasis Reviews* (2002) 21 231–255.
3. Dixon, RA. *Nature* (2001) 411 843-847.
4. Signorelli, P, Ghidoni, R. *Journal of Nutritional Biochemistry* (2005) 16 449-466.
5. Das, S, Das, DK, *Recent Patent Cardiovascular Drug Discovery* (2007) 2 2 133-8.
6. Falchetti R, Fuggetta, MP, Lanzilli G, Tricarico M, Ravagnan G, *Life Sciences* (2001) 70 1 81-96.
7. Gusman J, Malonne H, Atassi G, *Carcinogenesis* (2001) 22 8 1111-7.
8. Jang M., L, Udeani G.O., Slowing K.V., Thomas C.F., Beecher C.W., Fong H.H., Frasnfort N.R., Kinghorn AD, Mehta RG, Moon RC, Pezzuto JM, *Science* (1997) 10 275(5297) 218-220.
9. Zulueta A, et al. *World J Gastroenterol* (2015) 21 37 10636-10643
10. Kuttan R, Bhanumathy P, Nirmala K, George MC, *Cancer Lett* (1985) 29 197-202.
11. Limtrakul P, Lipigorngoson S, Namwong O, Apisariyakul A, Dunn FW, *Cancer Lett* (1997) 116;197-203.
12. Busquets S, Carbo N, Almendro V, Quiles MT, Lopez-Soriano FJ, Argiles JM, *Cancer Lett*, (2001) 167 33-8.
13. D'Andrea G, *Fitoterapia* (2015) 106 256–271.
14. Piñeiro Z, Palma, M, Barroso, CG, *Journal of Chromatography A* (2006) 1110 61–65.
15. Pasrija D, Anandharamakrishnan C, *Food Bioprocess Technol* (2015) 8 935–950.
16. Pascual-Martí MC, Salvador A, Chafer A, Berna A, *Talanta* (2001) 54 735–740.
17. Benova B, Adam M, Pavli'kova, P, et al., *Journal of Supercritical Fluids* (2010) 51 325–330.
18. Raynie DE, *Anal Chem* (2006) 78 3997.
19. Otero-Pareja MJ, Casa L, Fernández-Ponce MT, Mantell C, Martínez de la Ossa EJ, *Molecules*, (2015) 20 9686-9702.
20. Pereira Lima GP et al. *Food and Nutrition Sciences* (2014) 5 1065-1082.

Simultaneous Preconcentration of Some Metal Ions on Fluorescein Loaded Silica Gel and Determination by ICP-OES

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Industrial effluents raise municipal water pollution and contamination monitoring gains more importance for water sources¹. Separation and/or preconcentration of trace elements are very important prior to their accurate and precise determination²⁻³.

In present study, a solid phase extraction procedure was suggested for simultaneous preconcentration of trace levels of Ba(II), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II), Sr(III) and Zn(II) on fluorescein loaded silica gel. Modification of silica gel was confirmed with scanning electron microscope (SEM) and X-ray diffraction (XRD) analyses. The influences of analytical parameters, including pH, sample volume, flow rate of solutions, eluent type, volume and concentration on recovery of certain ions were studied. Determination of the analytes was achieved by inductively coupled plasma optical emission spectrometry (ICP-OES). The accuracy of the method was tested with Lake Ontario water and multi-element standard solution. The proposed method was also applied to various natural water samples and satisfactory results were obtained. The suggested methodology can be alternatively applied in separation/preconcentration of Ba(II), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II), Sr(III) from water based natural samples.

Keywords: Multielement Preconcentration, Silica Gel, Fluorescein, ICP-OES

References:

1. F. TOKAY, S. BAĞDAT, Water Air and Soil Pollution (2015) 226 48.
2. F. TOKAY, S. BAĞDAT, International Journal of Food Science and Technology (2015) 50 2694-2699.
3. F. TOKAY, S. BAĞDAT, Applied Spectroscopy (2016) 70(3) 1-9.

Microchip Based Determination of Bacteria by in-Chip Sandwich Immunoassay

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Bacteria detection is still a challenging issue and conventional bacterial detection methods are time consuming. In this study, a passive microchip design was used for fast and sensitive determination of *Escherichia Coli* (*E. Coli*) based on sandwich immunoassay. Gold coated magnetic nanoparticles (MNPs) and cadmium telluride (CdTe) quantum dots (QDs) were synthesized, surface modified and functionalized using *E.coli* specific antibody and they were used to form an in-chip sandwich immunoassay. The developed microchip consists of four micro-chambers connected to each other by microchannels, which act as capillary valves. First the magnetic separation and preconcentration of the *E.coli* from the sample solution in the vial was performed and then, the first chamber was filled with MNP-bacteria conjugate. The second microchamber was filled with QD-antibody conjugate, the third and fourth chambers were filled with washing buffer (phosphate buffered saline, pH=7.4). The MNP-bacteria conjugates were transferred from the first chamber through the microchannel using a magnet and being interacted with the QDs and then, washed in the third chamber in order to eliminate free QDs. Signal measurement was performed at the forth chamber using hand held spectrofluorometer equipped with a 295 nm LED source for excitation and fiber optic reflection probe. Amount of MNP and QDs injected to the microchambers were optimized. The calibration was linear in the range of 10^1 - 10^5 cfu/mL with a correlation coefficient higher than 0.988. River water samples were analyzed with a recovery of 92 ± 10 %. The detection limit of the method in PBS was calculated as 1 cfu/mL. The proposed technique provides an inexpensive, rapid and sensitive method for the determination of *E. coli*.

Keywords: *E .coli*, Magnetic Nanoparticle, Quantum Dots, Microchip

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Synthesis of a Molecularly Imprinted Polymer for Clean-up of the Fungicide Carbendazim in Water and Fruit & Vegetable Extracts

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The global occurrence in water resources of organic micropollutants, such as fungicide has raised concerns about potential negative effects on aquatic ecosystems and human health ¹. A new selective material based on molecularly imprinted polymers (MIP) have been synthesized by precipitation polymerization using carbendazim as template, methacrylamide as functional monomer, ethyleneglycol dimethacrylate as cross-linkers and an acetonitrile as porogen ²⁻³. The new MIP was used as solid phase extraction (SPE) sorbent for sample enrichment of carbendazim residues prior to high performance liquid chromatography. Various parameters affecting on the extraction efficiency of the imprinted polymers were evaluated to optimize the selective preconcentration of carbendazim from water and fruit & vegetable samples. Under the optimized conditions, the developed MIP-SPE method showed excellent linearity in the range of 0.05–5.00 mg L⁻¹ with coefficient of determination (R^2) > 0.995 and good recovery of >80.9% and limit of detection (LOD) was 0.008 mg kg⁻¹ which is much lower than the maximum residue limits (MRL) set by the EU legal limit (> 0.01 mg kg⁻¹) ⁴⁻⁵. The developed method was successfully applied to the analysis of carbendazim in selected water and fruit & vegetable samples. MIP-SPE showed superior extraction efficiency towards the carbendazim as compared to non-imprinted polymer solid-phase extraction (NIP-SPE).

Keywords: Molecularly imprinted polymers, Carbendazim, Water and Fruit & Vegetable Samples and HPLC-DAD.

References:

1. Alaaeddin Alsbaiee, Brian J. Smith, Leilei Xiao, Yuhang Ling, Damian E. Helbling, William R. Dichtel. *Nature* (2015) 16185 1–5.
2. Andrea Bereczki, Antal Tolokan, George Horvai, Viola Horvath, Francesca Lanza, Andrew John Hall, Borje Sellergren. *Journal of Chromatography A* (2001) 930 31–38.
3. Mohd Marsin Sanagi, Syairah Salleh, Wan Aini Wan Ibrahim, Ahmedy Abu Naim, Dadan Hermawan, Mazidatulakmam Miskam, Iqbal Hussain, Hassan Y. Aboul-Enein. *Journal of Food Composition and Analysis* (2013) 32 155–161.
4. Michelangelo Anastassiades, Wolfgang Schwack. *Journal of Chromatography A* (1998) 825 45–54.
5. Sumitra Arora, Irani Mukherjee, Aman Kumar, D. K. Garg. *Environmental Monitoring and Assessment* (2014) 186 361–366.

Assessment of μ -SPE Methods for Endocrine Disruptor Pesticide Analysis

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More than seventy years, many reports have stated some of natural and synthetic chemicals can cause adverse effects by altering the hormones in the endocrine systems of animals. Since, these chemicals are capable of disrupting the endocrine system, are known as endocrine-disrupting chemicals (EDCs) [1]. EDCs consist of pharmaceuticals, steroids, industrial chemicals, personal care products and pesticides. More recently, pesticides have been linked to ecological impacts at trace concentrations and have been detected in various surface and ground waters. Therefore, there is an urgent need to develop methods to be able to detect concentrations of these chemicals at ng L⁻¹ level.

Apart from the conventional liquid-liquid extraction, solid phase extraction (SPE), using different stationary phases, have been employed for the sample preparation step of pesticide determinations in environmental samples as a standard method. However, SPE displays some drawbacks such as multistage operation, large consumption of reagent, low enrichment factor and time consuming. These problems can be accomplished by using micro-SPE (μ -SPE) extraction technique developed in 2006 [2]. In this technique, the interfacial area between the solid adsorbent and sample solution was increased and by improving the surfaces, selectivity of the proposed method was also improved [3].

In this study; different μ -SPE methods including dispersive and micropipette tipped type were used for fast analysis of EDC pesticides in different samples. Different nano particles namely, TiO₂, ZnO, SiO₂, carbon nanotube and different clay types were utilized in fast micro extraction of pesticides. These nanofiller surfaces were used in sonication-assisted emulsification microextraction combined with vortex assisted μ -SPE and in micropipette tips extraction. The performances of dispersive μ -SPE and micropipette tipped μ -SPE were also compared in this study.

The parameters related to the extraction procedure namely; pH, sorbent amount, extraction solvent type and volume, washing and elution solvent type, sample volume effect on the extraction efficiency were also screened. The performance of extraction of Chlorpyrifos, Chlorpyrifos-oxon, Penconazole, Procymidone, Bromopropylate and Lambda Chyalothrin were compared by using GC-ECD and GC-MS systems. The regression coefficients relating to linearity were at least 0.99. Recoveries from spiked well water sample range from 80 to 97% and relative standard deviations were no higher than 15% in the most unfavourable case.

Keywords: Dispersive Micro-SPE, Micropipette Tipped SPE, Pesticides, Endocrine Disruptors.

References:

1. Munaretto J. S., Ferronato G., Talanta (2013) 116 827–834.
2. C. Basheer, A.A. Alnedhary et al. Anal. Chem. (2006) 78 2853-2858
3. C. Aftafa, F.O. Pelit et al., Journal of Chromatography A (2014) 1361 43–52

Determination of Carbidopa, Levodopa and Droxidopa in Pharmaceutical Preparations by Liquid Chromatography Tandem Mass Spectrometry

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New drugs have become available in recent years such as Carbidopa (Carbi), and Droxidopa (Droxi) for the treatment of Parkinson's disease. However, since the demand of dopamine supplementation during the treatment, levodopa has been considered treatment for motor symptoms. Therefore, their simultaneous analyses are important. Liquid chromatography- tandem mass spectrometry (LC-MS/MS) is a powerful technique for the sensitive, selective and accurate analyses of drug molecules in pharmaceutical formulations and in various biological matrixes.

This study is aimed to develop a new LC –MS/MS method for the simultaneous determination of Carbi, Droxi and Levo in pharmaceutical dosages. Accordingly, performances of two types of analytical columns namely, ODS and HILIC were tested and the detection limits were calculated according to S/N =3 criterion as 0.007,0.003 and 0.007 ng/mL for ODS column and 0.003, 0.0015, 0.007 ng/mL for HILIC column, for Carbi, Droxi and Levo respectively.

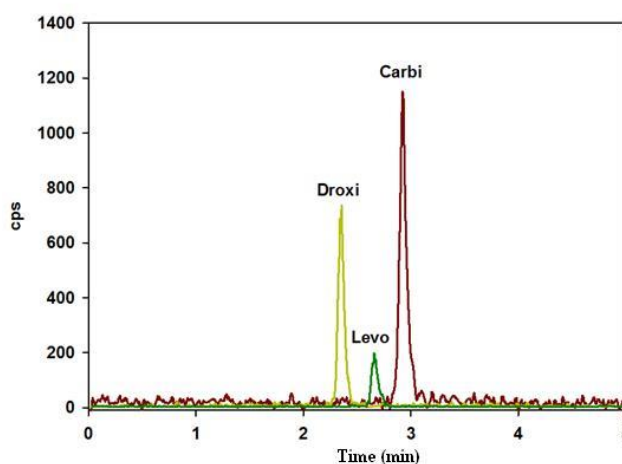


Figure 1 LC –MS/MS chromatogram for 5 ng/mL Carbi, Droxi and Levo obtained by using ODS column

Keywords: Liquid Chromatography- Tandem Mass Spectroscopy, Droxidopa, Levodopa, Carbidopa,

References:

1. R. de O. Vilhena, F. L. D. Pontes, B. M. Marson, R. P. Ribeiro, K. A. T. de Carvalho, M. A. Cardoso, R. Pontarolo Journal of Chromatography B, (2014) 967 41–49

Simultaneous Determination of Selected Hormones, Endocrine Disruptive Compounds and Pesticides in Water Samples by GC-MS after Dispersive Liquid-Liquid Microextraction

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The need to enhance food safety has led to major advancements in pesticide productions and though many benefits have been gained, environmental contamination has also risen from these chemicals that tend to persist in the environment. Some pesticides, together with other chemicals commonly called endocrine disruptive compounds, block the receptor sites of hormones or mimic displaced hormones, leading to imbalanced hormonal levels that result in health disorders and diseases. These chemicals occur at trace levels and are not directly detected by conventional analytical methods (1,2). A dispersive liquid-liquid microextraction method was therefore developed for preconcentration of 12 analytes including hormones, endocrine disruptive compounds and pesticides, to be analyzed by GC-MS. This was achieved by optimizing the parameters that affect extraction output such as extractor solvent type and amount, dispersive solvent type and amount, pH and salt effect. The limits of detection and quantification of the method were between 0.09 – 5.69 ng mL⁻¹ and 0.31 – 18.96 ng mL⁻¹, respectively. The calibration plots of the analytes also showed good linearity. Recovery studies were performed for water matrice and the percentage recoveries recorded were between 85-110%.

Keywords: DLLME, Endocrine Disruptor Compounds, Pesticides, Hormones, Gc-Ms

References:

1. Rezaee, M., Assadi, Y., Milani Hosseini, M.R., Aghaee, E., Ahmadi, F., Berijani, S., Journal of Chromatography A (2006) 1116 1–9.
2. Morgan, D., Tsai, S.C., Critical Care Clinic (2015) 31 403-418.

Optimization of Liquid Chromatography/Quadrupole Time-of-Flight Mass Spectrometry for Metabolomic Profiling of Breast Cancer

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Today's innovative technologies permit comprehensive screening of the genome, transcriptome, proteome, and metabolome. Detailed knowledge of genomic, proteomic and metabolomics processes converged in the integrated "omics" approach holds an immense potential for understanding mechanism of diseases, for their early diagnostics, choosing personalized therapeutic strategy and assessing its effectiveness. In metabolomics, the purpose is to identify and quantify as much as metabolites in a biological system.

Breast cancer is the most common type of cancer among women is 12% lifetime risk of developing the disease; the risk of death from the diseases is increasing up to 5%. Metabolomics analysis has a great potential in the elucidation of the mechanism and the early diagnosis of breast cancer as well as other diseases (1-2).

In this study, we aimed to find best analyses conditions in order to analyse metabolites. For that reason, we create a plasma pool samples made by mixing of plasma samples obtained from healthy individuals (n=20) and patients (n=20) for method optimization. Three different chromatographic columns were tested for LC-qTOF-MS based metabolomics profiling. The optimal separation was achieved on ZIC-HILIC column (100x4.6mm I.D., 5 µm) at a column temperature of 40 °C using a mobile phase of 0.1% formic acid in acetonitrile and 0.1% formic acid in water (80:20, v/v) by gradient elution at a flow rate of 0.3 mL/min. The analyses were carried out at both positive and negative ionization mode. Mass feature detection, retention time correction, alignment, annotation and statistical analysis were performed with XCMS software. Around 600 peaks were achieved in negative ionization techniques, while about 2000 peaks in positive ionization techniques (Table 1). The highest number of mass feature was detected in the column 2 with shortest analysis time. This column was used screen analysis of 300 patient's plasma sample in order to investigate biomarker candidates for early diagnosis of breast cancer. The possible new biomarkers has been identified and their predictivity index on early diagnosis of breast cancer were discussed.

Table 1: The number of mass features detected in different experimental conditions

	Positive ionization mode*	Negative ionization mode*
Column 1	1580 / 2162	433 / 673
Column 2	1494 / 2171	511 / 782
Column 3	792 / 2592	275 / 508

* The number of evaluable peaks / The number of peaks

Keywords: LC-qTOF-MS, Metabolomic Profiling, Breast Cancer

References:

1. Anthony, L., Angelina, N., Tony, K., Kristina, C.O., Tina, M. C., Journal of Chromatography B (2014) 944 166–174.
2. Nemutlu E, Zhang S, Gupta A, Juranic NO, Macura SI, Terzic A, et al. Physiol Genomics (2012) 44 386-402.

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Determination of Melatonin in Milk with Liquid Chromatography Tandem Mass Spectrometry

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Melatonin (N-acetyl-5methoxytryptamine) is a neurohormone synthesized from L-tryptophan via serotonin and naturally present in foods. Besides playing an important role in circadian rhythmicity and photoperiodic responses, it also has therapeutic properties, such as anti-tumor, anti-aging and protects the immune system (Mostafavi et al). It has been proven that melatonin has a strong influence on the sleep–wake cycle in humans. Moreover melatonin is more powerful than other antioxidants, namely carotenoids, vitamin E, ascorbic acid and glutathione probably due to its small size and amphipathic nature that makes it easily permeate all tissues and subcellular compartments. It has also been suggested for clinical use to treat diseases, including neurodegenerative diseases (Alzheimer's, Parkinson's disease), heart disease, metabolic disorders, tumors, and accidental nuclear radiation. (Feng et al) Melatonin was first discovered in plants in 1995. Since then, numerous studies have been reported the presence of melatonin in foods. The aim of this study is to develop reliable analytical method to detect melatonin in milk. The method includes extraction of melatonin with ethylacetate from milk and analyzing with LC-MS/MS. d7-Melatonin was used as internal standard. In House validation of analytical method was performed by carrying out, linearity, limit of detection, limit of quantification, precision and recovery. Calibration curve was linear between 0.05 and 20.0 ng/ml with correlation coefficient >0.99. Recovery values of the method were 100% and 106% for 1 µg/L and 5 µg/L spike respectively. Interday and intraday precisions were 4,11% and 3,92% for 1 µg/L spike and 4,35% and 2,15% for 5 µg/L spike respectively.

Keywords: Melatonin, LC-MS/MS, Milk

References:

1. Elham Oladi, Maryam Mohamadi, Tayebbeh Shamspur, Ali Mostafavi, Spectrochimica Acta part A: Molecular and Biomolecular Spectroscopy (2014) 132 326-329

The Electrochemical Properties of Dopamine and Serotonin Neurotransmitters at a Poly(amino acid) Modified Carbon Paste Electrode: Their Voltammetric Determination in Rat Brain after Microdialysis Sampling

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Dopamine (DA) and serotonin (5-hydroxytryptamine, 5-HT) are important and major biogenic monoamine neurotransmitters, which are released to extracellular fluids from the neurons widely distributed in the brain. In order to realize the pharmacological, physical and biological roles of these biomolecules, measuring their concentration in brain tissue is an important task. Voltammetry is preferable among the traditional methods for the determination of monoamine neurotransmitters *in vivo* or *in vitro* in experimental neuropharmacology and neuroscience for its simplicity and rapidity. However, the major problem is the strong interference arising from many other electroactive species which often coexist in biological tissues or fluids. Another problem is that several macromolecules, mainly proteins, present in brain can foul the electrode surface. To resolve the first difficulty, electrodes have been modified with various materials. In order to overcome the latter one, *in vivo* sampling by microdialysis can be used. Hence, if voltammetry is combined with microdialysis, some advantages, such as high sensitivity, selectivity and effective anti-fouling ability, will be possibly obtained [1].

Bearing in mind the aforementioned facts, the current work aims to describe the fabrication and application of a novel chemically modified electrode for the measurements of DA and 5-HT in rat brain after using of microdialysis sampling. For this purpose, the carbon paste electrode (CPE) modified with electropolymerized films of glutamic acid (PGA) known as an amino acid was used. Using square-wave mode, the modified electrode (PGA/CPE) exhibited linear voltammetric responses for DA and 5-HT at +0.27 and 0.36 V (vs. Ag/AgCl) in the ranges from 5×10^{-8} M to 6×10^{-7} M, and 2×10^{-8} M to 9×10^{-7} M, with detection limits of 1.1×10^{-8} M (1.53 ng mL^{-1}), and 3.4×10^{-9} M (0.85 ng mL^{-1}), respectively. Taking advantage of the enhanced electrochemical response of PGA/CPE, the proposed method was applied to the microdialysis samples deriving from *corpus striatum* of rat brain.

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Keywords: Dopamine, Serotonin, Poly(Glutamic Acid) Modified Carbon Paste Electrode, Square-Wave Voltammetry, Microdialysis, Rat

References:

1. M. Perry, Q. Li, R.T. Kennedy. Anal. Chim. Acta (2009) 653 1-22.

Protein Imprinting for Sensing

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Selective determination of the low amounts of the target analyte in the presence of interfering substances is one of the major problems in analytical chemistry. The high specificity of the biological macromolecules like enzymes and antibodies has been exploited for more than 50 years in clinical analysis, food control and environmental analysis. However, the analytical use of bioreceptors can be restricted due to their incompatibility and limited stability under analysis conditions. In order to overcome these problems, biomimetic binders and catalysts have been generated using “evolution in the test tube” of non-natural nucleic acids (aptamers) or total synthesis of (molecularly imprinted) polymers (MIPs) [1].

The essential prerequisite of macromolecular imprinting to create accessible binding sites amenable for free target-exchange between the MIP and the sample phase has been fulfilled by controlling the binding site generation solely at the surface of the polymer, i.e. surface imprinting. The development of MIPs for proteins started from 1995 with only a few papers up to 2004 but it exploded in 2005 and covers at present almost ten percent of all publications on MIPs. Protein-MIPs have great potential in both diagnostic and therapeutic applications.

We present in this talk the preparation and the performance (Table 1) of electrochemically prepared MIPs by using scopoletin or a novel carboxylate-modified derivative of 3,4-propylenedioxythiophene (ProDOT-COOH) as monomers for three very different protein targets: The iron storage protein ferritin, tetrameric acetylcholine esterase (AChE) and the Hexameric Tyrosine-coordinated Heme Protein (HTHP)-a peroxidase.

Table 1.

Template	MW (KDa)	Number of Subunits	Imprinting Factor	Linear range (μM)	Read-Out
HTHP	50	6	12	30-100	Direct Electron Transfer, Catalysis
AChE	280	4	9.9	0.04-0.4	Catalysis, AFM
Ferritin	450	24	13	Up to 0.5	SPR, AFM, Redox Marker

Keywords: Molecularly Imprinted Polymers, Biomimetic Sensors, Ferritin, Acetylcholine Esterase, HTHP

References:

1. Erdőssy J., Horváth V., Yarman A., Scheller F.W., Gyurcsányi R.E. Trends Anal. Chem., (2016) 79 179-190.

Voltammetric Determination of Boron in Eye Lotion and Water Samples Using Gold and Copper Nanoparticles and Multiwalled Carbon Nanotube Modified Electrode

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This study describes a sensitive and accurate voltammetric determination of boron in eye lotion and various water samples using gold or copper nanoparticles and multiwalled carbon nanotube modified glassy carbon electrode (Au or CuNP/MWCNT/GCE). The oxidation of Alizarin Red S (ARS) at -0.59 V in the boron-ARS complex formed in ammonium/ammonia buffer solution (pH 8.5) was evaluated as a response. The parameters affecting the peak current such as gold and sulfuric acid concentration, scan rate and cycle number for modification of electrode and the other parameters such as pH and concentration of supporting electrolyte, concentration of ARS, ionic strength, step amplitude, interval time, pulse time, pulse amplitude, deposition potential and time were optimized. Modified electrodes were characterized by Electrochemical Impedance Spectroscopy (EIS) and Scanning Electron Microscope (SEM). The limit of detection ($3s_{y/x}$) is 55 µg/L for 40 s accumulation time and calibration graph is linear between 100 µg/L and 1500 µg/L of boron concentration for AuNP/MWCNT/GCE and the limit of detection ($3s_{y/x}$) is 81 µg/L for 40 s accumulation time and calibration graph is linear between 200 µg/L and 1000 µg/L of boron concentration for CuNP/MWCNT/GCE. The relative standard deviation values were found to be 2.14%, 2.38%, 2.57% and 2.99% for 0.4, 0.7, 1.0 and 1.5 mg/L boron concentration levels with AuNP/MWCNT/GCE and 6.43%, 2.14% and 5.56% for 0.2, 0.5 and 0.8 mg/L boron concentration levels with CuNP/MWCNT/GCE. The recovery results changed between 97.2% and 101.2% for various water samples and 100.5% for eye lotion with AuNP/MWCNT/GCE. The recovery results changed between 103.5% and 105.7% for various water samples and 100.0% for eye lotion with CuNP/MWCNT/GCE. The results obtained from the developed method with two modified electrodes were compared with those obtained from ICP-MS method and no statistically significant difference between the methods was found for 95% confidence level.

Keywords: Boron, Alizarin Red S, Nanoparticles, Modified Electrode, Multiwalled Carbon Nanotubes, Voltammetry.

References:

1. Şahin, İ., Nakiboğlu, N., Anal. Chim. Acta, (2006) 572 253-258.
2. Lee, S. W., Kim, B. S., Chen, S., Shao-Horn, Y., Hammond, P. T., J. Am. Chem.Soc. (2009) 131 671-679.
3. Etesami, M., Salehi Karoonian, F., Mohamed, N., J. Chin. Chem. Soc., (2011) 58-5 688-693.
4. Ceylan Koçak, Ç., Dursun, Z., J. Electroanal. Chem. (2013) 694 94-103.

Amperometric Determination of Tyramine Using Poly(3-methylthiophene) Film

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Tyramine (p-hydroxyphenylethylamine, Tyr) being one of the important biogenic amines is produced by both the decarboxylation of tyrosine and degradation of food products resulting from microbial activity. Tyr can cause unnatural and toxic effects when ingested in more quantities than certain legal limits that have been established 100-800 mg of Tyr/kg of food. For these reasons, determining the amounts of Tyr is important for our health. Electrochemical methods may be a better option because of their simplicity, rapidity and high sensitivity. But Tyr is known to polymerize and passivate the electrode surfaces and detecting it at conventional electrodes is limited^[1-3].

Poly(3-methylthiophene) (P3MT), which can be easily electrodeposited onto different electrode surfaces by electrochemically methods, is one of the most promising conductive polymers, which has high conductivity, good redox reversibility, and environmental stability. P3MT modified electrodes have shown an improvement for detecting catecholamines and other molecules of biological importance over the traditional electrode materials^[4,5].

In this study, Pt/P3MT modified electrode were prepared using electrochemically method for Tyr electroanalysis. Black adherent P3MT film was deposited on Pt electrode by potentiodynamically at -0.4V to 1.8V range in the dichloromethane solution containing 0.50M 3MT monomer and 0.1M tetrabutylammonium perchlorate. The experiments were carried out in a buffer solution (pH 2) consisting NaHSO₄/Na₂SO₄. The amperometric results obtained good analytical values in aqueous media at applied potential of 0.80V that there was no any current response on bare platinum electrode and polymerization of Tyr monomer. The limit of detection (LOD), limit of quantification (LOQ), linear dynamic range and the regression coefficient (R²) of Pt/PF modified electrode determined as 4.06x10⁻³, 1.40x10⁻², 1.40x10⁻² to 10.0 mM and 0.998, respectively.

Keywords: Poly(3-Methylthiophene), Biogenic Amine, Tyramine, Amperometri

References:

1. B.Brink ten, C.Damink, H. Joosten, J. Huis in't Veld, Int. J. Food Microbiol. (1990) 11 73 -84
2. E. Khudaish, M. Hinaai, S. Al-Harthy, K. Laxman, Electrochimica Acta (2014) 135 319–326
3. X.Yang, B. Feng, Xiulan He, F. Li, Y. Ding, Junjie Fei, Microchim Acta (2013) 180 935–956
4. Wang J, Li R Anal Chem(1989) 61 2809–2811
5. M. Kavanoz, U. Bük, E. Ülker, Inc. J. Appl. Poly m. Sci (2014) 131 40859- 40867

The Biological Activities and Essential Oil Profiles of Some Endemic *Salvia* Species from Anatolia

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Salvia L. (Lamiaceae) genus is represented more than 900 species in the world and about 98 species in Turkey. Fifty-three of them are endemic. *Salvia* genus is a member of the Lamiaceae family. These plants have trichomes and aromatic qualities. As they contain various essential oils, they are used in perfumery and medicine. Medicinal plants are biologically active materials traditionally used in the treatment of a variety of diseases since ancient times. Essential oils derived from many plant species are known to have antimicrobial, antioxidant and anticholinesterase activities, and attempts to characterize their bioactive principles have increased in many pharmaceutical and food-processing applications (1-5). The aim of this study was to determine the essential oil profile of five endemic *Salvia* species (*Salvia cerino-pruinosa* var. *cerino-pruinosa*, *Salvia cerino-pruinosa* var. *elazigensis*, *Salvia pseudeuphratica*, *Salvia siirtica* and *Salvia rosifolia*) by GC/MS. Additionally, the essential oil of these *Salvia* species were tested for antioxidant (β -Carotene-linoleic acid test system, DPPH free radical scavenging activity, ABTS cation radical decolorisation and cupric reducing antioxidant capacity) and anticholinesterase (Acetyl- and butyrylcholinesterase enzymes) activities. The major component of the essential oils was identified as Germacrene D (38.3%) for *S. cerino-pruinosa* var. *cerino-pruinosa*, Camphor (43.1%) for *S. pseudeuphratica*, Germacrene D (32.7%) for *S. siirtica*, 1,8-Cineole (26.3%) for *S. rosifolia*, Germacrene D (21.6%) for *S. cerino-pruinosa* var. *elazigensis*. Generally, the essential oil of these *Salvia* species exhibited weak antioxidant activity in the four tested methods but good anticholinesterase activity in the two method.

Keywords: *Salvia* species, Essential Oil, Antioxidant, Anticholinesterase

References:

1. Baytop T. Therapy with medicinal plants in Turkey. University of İstanbul Press. İstanbul; 1984.
2. Davis PH, Leblebici E. Miller L. (1982) Flora of Turkey and East Aegean Islands, (Editor Davis, P.H), p. 323-329, University Press, Edinburgh.
3. Lu Y, Foo LY. Phytochemistry (2002) 59 114-140.
4. Tepe B, Daferera D, Sokmen A et al. Food Chem (2005) 90 333-340.
5. Gülaçtı Topçu, Abdulsalam Ertaş, Ufuk Kolak, Mehmet Öztürk and Ayhan Ulubelen Arkivoc (vii), (2007) 195 - 208

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fitting models

1 Ampholytes $k = (k_0 + k_1 \cdot 10^j \cdot (\text{pH} - \text{pK1}) + k_2 \cdot 10^j \cdot (\text{pK2} - \text{pH})) / (1 + 10^j \cdot (\text{pH} - \text{pK1}) + 10^j \cdot (\text{pK2} - \text{pH}))$

2 Monoprotic acids/bases $k = (k_0 + k_1 \cdot 10^j \cdot (\text{pH} - \text{pK1})) / (1 + 10^j \cdot (\text{pH} - \text{pK1}))$

3 Diprotic acids/bases $k = (k_0 + k_1 \cdot 10^j \cdot (\text{pH} - \text{pK1}) + k_2 \cdot 10^j \cdot (\text{pH} - \text{pK1}) + 10^j \cdot (\text{pK2} - \text{pH})) / (1 + 10^j \cdot (\text{pH} - \text{pK1}) + 10^j \cdot (\text{pK2} - \text{pH}))$

where $k_0 = \exp(-c_0 \cdot 10^j)$, $k_1 = \exp(-c_1 \cdot 10^j)$, and $k_2 = \exp(-c_2 \cdot 10^j)$

System features	Gradient	solute:	ANA	HANA	HIA	HTRP	KYNA	TRP	HT	KYN
$t_0 = 0.73$	$\varphi_1 = 0.020$	$c_0 = 3.07$	2.24	3.44	2.94	4.65	5.14	2.42	1.03	
$t_0 = 0.983$	$\varphi_2 = 0.030$	$c_1 = 9.46$	16.75	19.73	38.51	27.48	28.99	12.51	0.00	
	$\varphi_3 = 0.100$	$c_{10} = -25.03$	-24.97	1.01	1.16	2.69	2.10	1.98	1.29	
Functions features	$\text{pH1} = 2.0$	$c_{11} = 0.00$	0.00	0.00	3.78	20.53	10.40	22.48	0.00	
$N = 50$	$\text{pH2} = 7.9$	$c_{20} = 0.68$	-0.22	5.11	6.25	1.77			2.23	
	$\text{pH3} = 11.4$	$c_{21} = 0.00$	0.00	1110.71	334.34	23.31			26.64	
	$t_1 = 0.51$	$\text{pK1} = 1.81$	1.74	3.93	2.09	1.67	1.10	9.23	7.41	
	$t_2 = 8.54$	$\text{pK2} = 4.29$	4.35	11.17	10.75	9.87			2.28	
	$t_3 = 15.69$	$j = -1$	2	1	3	3	1	1	1	2
		$j_1 = 2$	2	3	3	3	1	1	1	2
		$dt(\text{min}) = 0.29$								
		$t_{\text{max}} = 10.946$								
		$NP_{\text{opt}} = 7.708$	5.659	7.997	5.080	10.946	8.543	5.368	4.629	

optimal gradient profile

Pseudo optimal chromatogram

References:

- 43

Determination of Mycotoxin in Rat Plasma Samples by Ultra High Performance Liquid Chromatography with Fluorescence Detection

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Mycotoxins are toxic metabolites produced by fungi and they are potentially hazardous to humans and animals. Ochratoxin A (OTA) is a common mycotoxin and its main toxic effects are nephrotoxicity, hepatotoxicity, immunotoxicity, teratogenicity and neurotoxicity [1, 2]. Besides that, OTA has been classified as a possible human carcinogen by the International Agency for Research on Cancer (IARC) [3]. Therefore, quantification of OTA concentration in the blood sample is very important for evaluation of the possible human health risks of OTA [4]. In this study, a new, efficient and rapid Ultra High Performance Liquid Chromatography with Fluorescence Detection (UHPLC-FLD) method was developed and validated for OTA analysis in rat plasma samples. The rat blood samples were collected simultaneously after intra-peritoneal injection (i.p.) of OTA (5 mg kg⁻¹) during a period of 12 h. Calibration curve obtained with spiked biological matrices showed good linearity with a high correlation coefficient. Plasma samples were analyzed after a simple, one-step protein precipitation with methanol. Diflunisal (DIF) was used as the internal standard (IS). OTA and IS were separated on a Zorbax Eclipse Plus C8 (150 mm x 3.0 mm ID, 1.8 µm particles) column and were isocratically eluted in the mobile phase consisting of acetonitrile:water:phosphoric acid (50:50:0.1, v/v). The flow rate was 0.6 ml min⁻¹. The signals were detected at 330 nm excitation and 450 nm emission wavelengths. Under these conditions, OTA and IS were separated in 5 min. The method was successfully validated in terms of linearity, precision, accuracy, limit of detection, limit of quantification, robustness, and stability. This method was successfully applied for monitoring of OTA levels in rat plasma.

Keywords: Mycotoxin, Ochratoxin-A, UHPLC, Rat Plasma, Validation

References:

1. Nicholas W. Turner, Sreenath Subrahmanyam, Sergey A. Piletsky *Analytica Chimica Acta* (2009) 632 168–180.
2. Sylvie Beláková, Karolína Benešová, Renata Mikulíková, Zdenek Svoboda *Food Chemistry* (2011) 126 321–325.
3. International Agency for Research on Cancer (IARC) (1993) *Some Naturally Occurring Substances: Food Items and Constituents, Heterocyclic Aromatic Amines and Mycotoxins* (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, vol. 56), Lyon, France.
4. Bernhard Zimmerli, Rudolf Dick *Journal of Chromatography B*, (1995) 666 85-99.

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New Standard Flow UPLC Method for Identification of CaCo2 Cell Line Proteome

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Colorectal cancer (CRC) is the third most common cancer and the second most common cause of cancer related deaths in the world. Great effort is being made to treat and detect this disease at early stages¹. Especially genomic and post genomic studies *in vivo* or *in vitro* supplies huge amount of information to support clinically treatment. Proteomic that is a post genomic area provide proteome based changing in cancer cell lines, tissues and body fluids with every stage of disease and treatment. Proteomic is the one of the main tools to understand mechanism of CRC and the effect of drug candidate molecules on CRC.

Mass spectroscopy coupled with nano liquid chromatography has been used extensively to study proteome. Nano liquid chromatograph (nLC) gives more sensitivity than regular liquid chromatography and limited amount of samples like tissue proteome could be analyzed with nLC. Although nLC is a very useful tool for proteomics; system has some drawbacks that are dead volume and robustness². Especially robustness is a main parameter in analytical system validation process. In recent years regular UPLC system has been used in proteomics and it has been observed that standard flow UPLC gives better yields in target proteomics and comparable results with nLC about protein identification *in vitro*³. Especially in terms of chromatographic metrics UPLC is better than nLC system.

In our study we developed new standard flow UPLC method to identify Caco 2 cell line proteome. Our gradient took 150 minutes and our flow rate 0.2 mL/min. Peptide mixtures were loaded onto C18 column (2.1mm x 100mm, 2.7 µm). Our mobile phase was water containing %0.1 formic acid and acetonitrile containing %0.1 formic acid. We used maxquant software for identification and our database was human uniprot. We injected three replicate and identified 741 proteins. Our results showed that loading capacity is the main point in UPLC system for proteomics studies. We increased amount of sample up to the 100 µg of proteins. We can conclude that UPLC could be used in proteomics researches if there is no problem with amount of sample. Also maxquant search engine works very well with data that obtained from UPLC-QTOF

Keywords: Proteomics, Colorectal Cancer, Loading Capacity, UPLC, Maxquant

References:

1. Madhavan, S., Gusev, Y., Natarajan, T. G., Song, L.; Bhuvaneshwar, K., Gauba, R., Pandey, A., Haddad, B. R., Goerlitz, D., Cheema, A. K., Juhl, H.; Kallakury, B., Marshall, J. L., Byers, S. W., Weiner, L. M. Front Genet. (2013) 236
2. Mitulovic, G. J Liq Chromatogr R. T.(2015) 390-403
3. Gonzalez Fernandez-Nino, S. M., Smith-Moritz, A. M., Chan, L. J.; Adams, P. D., Heazlewood, J. L., Petzold, C. J. Front Bioeng Biotechnol. (2015) 44

Lab-on-a-Membrane Foldable Devices for Duplex Drop-Volume Electrochemical Biosensing Using Quantum Dot Tags

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Herein we describe a new type of integrated lab-on-a-membrane foldable device suitable for on-site duplex electrochemical immunosensing using drop-size sample volumes. The devices are fabricated entirely by screen-printing on a nylon membrane and are composed of two assay zones, which are located symmetrically on either side of a three-electrode voltammetric cell featuring a bismuth citrate-loaded graphite working electrode. After the completion of two spatially separated drop-volume immunoassays on the two assay zones using antibodies labeled with Pb- and Cd-based quantum dots (QDs), respectively, the QD labels are dissolved releasing Pb(II) and Cd(II) in the assay zones. Then, the two assay zones are folded over, and brought in contact, with the voltammetric cell for simultaneous anodic stripping voltammetric (ASV) determination of Pb(II) and Cd(II) at the bismuth nanostructured layer formed on the working electrode, by reduction of the bismuth citrate during the preconcentration step. In order to demonstrate their applicability to the analysis in complex matrices, duplex ASV-QDs determination of bovine casein and bovine gamma-globulin G was carried out in milk samples yielding limits of detection of $0.04 \mu\text{g mL}^{-1}$ and $0.02 \mu\text{g mL}^{-1}$, respectively. The potential of the devices to detect milk adulteration is further demonstrated. These new membrane devices enable duplex biosensing with distinct advantages in terms of cost, fabrication and operational simplicity and rapidity, portability, sample size, disposability, sensitivity and suitability for field analysis.

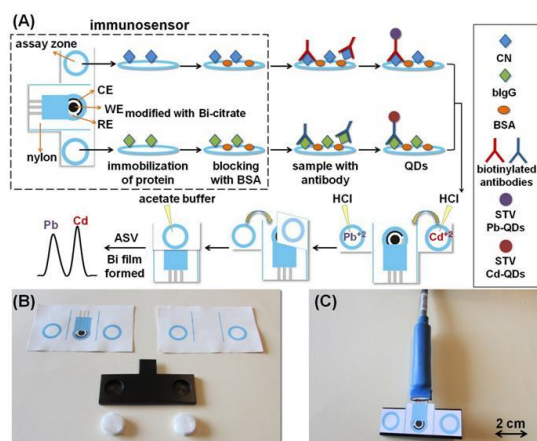


Figure 1. (A) Schematic illustration of the duplex protein immunosensing, (B) Photograph of both sides of the membrane and of the PVC holder along with the hydrophilic tabs used for the collection of the liquid waste. (C) Photograph of the complete device (membrane mounted on the PVC holder) plugged into the cable connecting to the potentiostat.

Keywords: Lab-on-a-Membrane, On-Site Duplex Electrochemical Immunosensing, Drop-Size Sample Volumes, Screen-Printed Analytical Devices

Functionalized Reduced Graphene Oxide/Pd/Gox/Nafion Nanocomposites Film for Glucose Biosensing

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In the study, we have demonstrated the fabrication of a novel glucose biosensor based on amine functionalized reduced graphene oxide (rGO-NH₂) and Pd nanocomposites modified glassy carbon electrode (GCE) for glucose detection in serum samples. The electrocatalytic properties of the biosensor were investigated using electrochemical impedance spectroscopy, cyclic voltammetry, and amperometry. The resulting nafion/Pd@rGO-NH₂/GOx/GCE composites showed good electrocatalytic response to glucose. The nafion/Pd@rGO-NH₂/GOx/GCE exhibited a linear range for glucose concentration from 0.05 to 3.8745 mM with a correlation coefficient of 0.999 and a detection limit of 0.03 mM. Also, nafion/Pd@rGO-NH₂/GCE showed a linear range for H₂O₂ concentration from 0.03 to 8.2986 with a correlation coefficient of 0.997 and a detection limit of 4 µM. Besides, the fabricated biosensors have a sensitivity of 63.79 µA mM⁻¹ cm⁻² and an acceptable selectivity for glucose and a sensitivity of 471.2 µA mM⁻¹ cm⁻² for H₂O₂.

Keywords: Amine Functionalized Reduced Graphene Oxide, Pd, Gox, Nafion, H₂O₂, Nafion.

References:

1. M. F. Hossain and Jae Y. Park. *Electroanalysis* (2014) 26 940-951.
2. Keerthy Dhara, Ramachandran Thiagarajan, Bipin G. Nair, Gopalakrishnan Satheesh BabuThekkedath. *Microchim Acta* (2015) 182 2183–2192.
3. Muhammet Guler, Vedat Turkoglu, Arif Kivraf. *Int. J. Biol. Macromol* (2015) 79 262–268.

Label-Free Impedimetric Immunosensor for Ultrasensitive Detection of Cancer Biomarker RACK1 in Human Serum

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The Receptor for Activated C Kinase 1 (RACK1) is a protein which is belonged to the tryptophan-aspartate repeat (WD-repeat) family¹ and a homologue of the β -subunit of G-protein.^{2,3} It is responsible of cell growth, movement, and division. Also, RACK1 can be an effective cancer biomarker for some tumor types, such as oral squamous cell carcinoma,^{5,6} melanoma, colon cancer, non-small cell lung cancer, and hepatocellular carcinoma, breast cancer.⁴ A new quite sensitive disposable immunosensor, based on the anti-RACK1 antibody, was developed for determination of Receptor for Activated C Kinase 1 (RACK1) for the first time. Moreover, indium tin oxide (ITO) PET films were modified by using an aldehyde ended silane 11-(triethoxysilyl)undecanal (TESU) self-assembled monolayers (SAMs) for immobilizing anti-RACK1 antibody via covalent bonds. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and square wave voltammetry (SWV) methods were used for characterizing the immobilization steps and for determining RACK1 concentration. To obtain a successful immunosensor, experimental factors were optimized. This quite sensitive biosensor was able to detect concentration as low as fg/mL. The detection principle was based on the change in charge transfer resistance and Nyquist plot diameter and these changes were monitored by using electrochemical impedance spectroscopy (EIS)^{5,6}. This impedimetric immunosensor had perfect repeatability and reproducibility. We proved that the new silane agent, TESU had an excellent performance in the biosensor application⁷. The feasibility of the fabricated immunosensor was experienced by determining of RACK1 in an artificial and human serum samples.

Keywords: Receptor For Activated C Kinase 1 (RACK1), Electrochemical Impedance Spectroscopy, 11-(Triethoxysilyl)Undecanal

References:

1. D. R. Adams, D. Ron, P. A. Kiely Cell Commun. Signaling (2011) 9 22 1-24.
2. R. Nagashio, Y. Sato, T. Matsumoto, T. Kageyama, Y. Satoh, R. Shinichiro, N. Masuda, N. Goshima, S. Jiang, I. Okayasu Lung Cancer (2010) 69 54–59.
3. Q. Ren, J. Zhou, X. Zhao, J. Wang Dev. Comp. Immunol. (2011) 35 629–634.
4. X. Cao, J. Xu, X. Liu, J. Xu, W. Wang, Q. Li, Q. Chen, Z. Xu, X. Liu Int. J. Cancer (2010) 127 1172–1179.
5. M. Ç. Canbaz, M.K. Sezgintürk Anal. Biochem. (2014) 446 9–18.
6. M. N. Sonuç, M. K. Sezgintürk Curr. Anal. Chem. (2016) 12(1) 43-53.
7. B. Ibarlucea, C. Fernandez-Sanchez, S. Demming, S. Büttgenbach, A. Llobera, Analyst (2011) 136 3496-3502.

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A Novel High Reproducible, Regenerative, Sensitive and Cheap Biosensor Developed by Using 3-Cyanopropyl Trimethoxysilane for PAK2 Detection

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The p21-activated kinases (PAKs) are a family of serine threonine kinases that are effectors for the small Rho GTPases, Cdc42 and Rac [1]. They consist of 6 members, which fall into 2 related subgroups of proteins: Group I, consisting of PAK 1, 2, and 3, and Group II, consisting of PAK 4, 5 and 6 [2]. A large body of research has demonstrated that PAKs are up-regulated in several human cancers, and that their overexpression is linked to tumour progression and resistance to therapy. Structural and biochemical studies have revealed the mechanisms involved in PAK signalling, and opened the way to the development of PAK-targeted therapies for cancer treatment [3].

In the this work, we described a novel immunosensor developed on modified ITO disposable electrodes. Anti-PAK2 was immobilized through covalent with 3-cyanopropyl trimethoxysilane which formed a self-assembled monolayers (SAMs) on modified ITO electrodes. Cyclic voltammetry (CV), square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS) techniques were employed to characterize the immobilization process and to detect. To achieve reproducible and repeatable biosensor system, all parameters such as SAMs concentration, antibody concentration and antibody incubation time were optimized. Analytical characteristics such as linear determination range, repeatability, reproducibility, regeneration and surface coverage of biosensors were determined. For expounding binding characterization of PAK-2 and anti- PAK-2 single frequency impedance method was utilized. Scanning electron microscopy was used for identifying the surface morphology and Kramers-Kronig transform was implemented on impedance datum. The biosensor has exhibited good repeatability and reproducibility. Linear range of developed biosensor was 0.05 pg – 2.5 pg/mL. To verify the availability of the biosensor, the human serum samples were experienced.

We are thankful for financial support from the Scientific and Technological Research Council of Turkey (TÜBİTAK, Project number: 113 Z 678).

Keywords: ITO (Indium Tin Oxide), PAK-2 , Biosensor, Single Frequency Technique

References

- 1.G.M.Bokoch, Biology of the p21-activated kinases, Annu. Rev Biochem (2003) 72 743-781.
- 2.C.K.Rane and A.Minden, P21 activated kinases: Structure, regulation, and functions, Small GTPases. (2014) 5.
- 3.Hong He, Graham S. Baldwin, Biochimica et Biophysica Acta (BBA) - Molecular Cell Research (2013) 1833 33-39.

Surface Enhanced Raman Scattering Based Immunoassay Versus Western Blotting

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Western blotting is a type of immunoassay in which antibodies are used to quantify target proteins. The proteins are separated by SDS-PAGE gel and the target protein is transferred onto a membrane such as Polyvinylidene difluoride, nitrocellulose or nylon. Washing procedures are applied using a solution containing the protein-specific antibody. Secondary antibodies, are used to detect the presence of the primary antibody on the membrane surface. The secondary antibody is linked to a reporter enzyme that can be bound to the primary antibody. Generally, chemiluminescence detection was performed to get high sensitivity. At this point, analytical challenge for target protein is not only high sensitivity but also rapid identification. Surface- enhanced Raman spectroscopy (SERS) has potential with high sensitivity, real-time response, high level of specificity, ability of qualitative and quantitative analyses, and utility in low-cost miniaturization system. Although western blotting dominates low content of protein analysis with high analytical performance, SERS can be an alternative with its promising features.

In this report, we present a Surface enhanced Raman probe (SERS) platform for the determination of prohibited substances such as erythropoietin (EPO) in urine matrix, using nanoparticles as substrate. The rod shaped gold nanoparticles were modified with antibody molecules as SERS probe. We developed both homogeneous and heterogenous SERS assays for detection and quantification of prohibited substances in urine. In heterogenous assay, after solid phase extraction (SPE) of prohibited substances, sandwich assay with the rod shaped gold nanoparticles was performed. In homogeneous assay, prohibited substances were extracted by using core shell-structured magnetic iron oxide gold nanoparticles, and sandwich assay was performed to quantify rEPO. To avoid nonspecific interactions, ethanolamine-alanine mixed solution was used to block active groups on the surface for 1 h. The selective binding between the target protein rEPO and antibody bound magnetic nanoparticle was also monitored by SDS-PAGE and Western blotting. A good linear correlation was obtained between logarithms of rEPO concentrations in urine and Raman intensities within the range of 10^{-1} pg mL⁻¹ – 10^3 pg mL⁻¹ rEPO concentrations. Detection limits which are smaller than 0.1 pg mL⁻¹ levels were achieved by the high extractive performance of nanoextraction techniques.

Keywords: Western Blotting, SERS, Erythropoietin, Sandwich Assay

Application of Photonics in Diagnosis of Invasive Ductal Carcinoma Tissues by FT-IR and Raman Spectroscopy

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Photonics is the science of light (photon) generation, detection, and manipulation through emission, transmission, modulation, signal processing, switching, amplification, and detection/sensing. Though covering all light's technical applications over the whole spectrum, most photonic applications are in the range of visible and near-infrared light. The term photonics developed as an outgrowth of the first practical semiconductor light emitters invented in the early 1960s and optical fibers developed in the 1970s.

In this study, it is aimed to diagnose and detect cancer cells in tissue samples of human breast. In order to carry out the study, different healthy and cancered tissues were collected from Ataturk University, Department of Pathology. Diagnosis of tissues was already achieved by histopathological tests.

Samples were deparafinized and 20 micron of each sample were located on a coverslip. Both healthy and cancered tissues exposure to Mid-Infrared light between wavenumber of 100-4000 cm^{-1} Obtained spectrum was evaluated on MATLAB software, PLS Toolbox package program. O-PLS and PARAFAC analysis were applied in order to separate cancer cells and healthy cells. Mapping of tissues was performed by Raman Spectroscopy including two-laser beam by filtering Ray-Leigh scattering.

In conclusion, it is claimed that this method make it enable to diagnose invasive ductal carcinoma in human breast tissue without any sample preparation, extraction or any other pre-treatment procedure. This easy and cheap method do not need any chemical for diagnosis of invasive ductal carcinoma tissues. Photonics studies exhibit a new perspective on qualitative determination of specific diseases.

Keywords: Photonics, FT-IR, Raman Spectroscopy, Invasive Ductal Carcinoma

References:

1. Chai Yeh, Applied Photonics, Academic Press inc. California, USA (2012).

Surface Chemometrics of Graphene-Based Materials with Principal Component Analysis (PCA) Using X-Ray Photoelectron Spectroscopy (XPS)

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XPS has been extensively used to characterize the surface chemistry of materials. It plays a unique role in giving access to qualitative, semi-quantitative/quantitative information as well as speciation and the presence of chemical functional groups on the surface of any material [1].

PCA is the analysis of variability in a particular set of data. It provides the most powerful graphical tools for understanding the relationships between the samples and variables. The first principal component accounts for as much of the variability in the data as possible and has a largest eigenvalue. Large image data sets obtained by XPS can be analyzed using PCA in order to extract the most significant information. The goal of PCA in an area scan of XPS is to find images which are correlated or anti-correlated and to visualize the pixels which are responsible for the correlations. Images are acquired as a function of binding energy in an images-to-spectra experiment. Small area spectra can be obtained from any part of the sample by plotting image pixel intensity for a single pixel or a group of pixels versus binding energy [2].

In the present study, graphene-based materials were synthesized *via* oxidation of graphite by Brodie Method. Then, chemical mapping has been produced (Figure 1) with PCA on the basis of spectral information. For this purpose, XPS area scan has been performed and then the data sets were subjected to PCA in order to present the compositional in homogeneities in the synthesized graphene based materials.

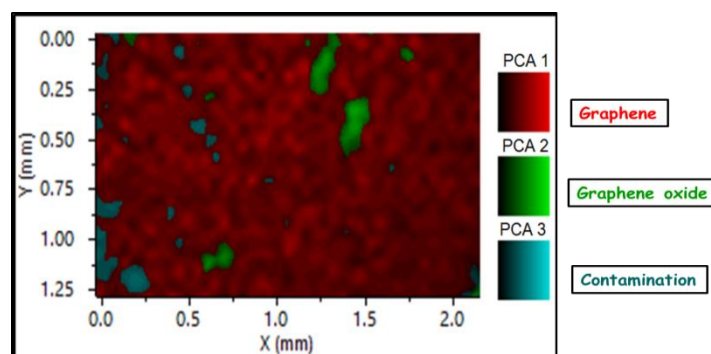


Figure 1. Chemical mapping of graphene-based material

Keywords: Surface Analysis Chemometrics, Chemical Mapping, XPS And PCA

References

1. Kateryna Artyushkova, Julia E. Fulghum. Journal of Electron Spectroscopy and Related Phenomena. (2001) 121 33-55.
2. Solène Béchu, Mireille Richard-Plouet, Vincent Fernandez, John Walton, Neal Fairley. Surface and Interface Analysis. (2016) 48 301-309.

Paper-Based Fluorescence Sensing of a Prohibited Substance in Sports

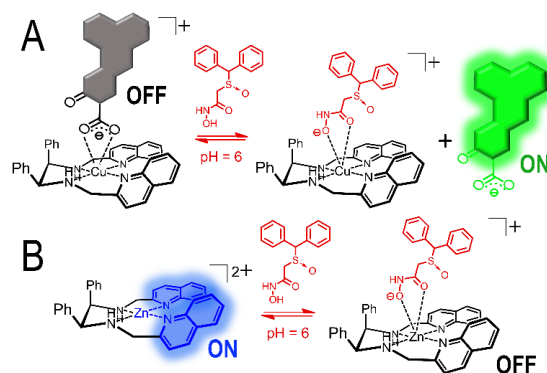
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Recognition of Lewis bases and anionic analytes in water containing matrix such as biological fluids is a challenge because water is an extremely competitive media in chemical sensing.¹ Metal–ligand interactions are a particularly powerful tool for the recognition of anionic or coordinating analytes in water containing samples because water is a relatively poor Lewis base^{1,2} and interferes less in this sensing strategy. Here we report two metal complexes of a fluorescent ligand (L), *meso*-1,2-diphenyl-*N,N'*-bis(quinoline-2-ylmethyl)-ethane-1,2-diamine for fluorescent sensing of adrafinil, which is a prohibited substances in sports, in urine samples. This ligand favours the coordination of d⁹ or d¹⁰ metal ions that can adopt square planar geometries or distorted tetrahedral geometries. When coordinated to a roughly planar ligand, these transition metals are coordinatively unsaturated and offer at least one coordination position for the binding of an analyte. Cu (II) complex of L shows fluorescent OFF state as Cu (II) quenched the emission of quinoline moieties. Therefore indicator displacement strategy with Coumaring343 indicator was employed in adrafinil sensing with Cu (II)-L. As expected, Zn (II) slightly enhanced the emission of L and in this case direct response from the Zn(II)-L sensor was used for sensing. The sensors are cross-reactive and they respond some other molecules with different level of responses. Qualitative, semi-quantitative and quantitative analysis of these responses were conducted by chemometric techniques: Linear Discriminant Analysis and Support Vector Machine. Fluorescent sensing of adrafinil in urine samples by these chemical sensors was carried out on paper based devices which are highly sensitive, user friendly, inexpensive and disposable³.



Keywords: Fluorescence Sensor, Adrafinil, Metal Complexes, Indicator Displacement Assay, Paper Based Sensing

Acknowledgement: M. G. C. is grateful for international postdoctoral fellowship from the Scientific and Technological Research Council of Turkey (TUBITAK).

References:

1. S. Kubik, Chemical Society Reviews (2010) 39 3648-3663.
2. V. Amendola, M. Bonizzoni, D. Esteban-Gómez, L. Fabbrizzi, M. Licchelli, F. Sanceno'n and A. Taglietti, Coordination Chemistry Reviews (2006) 250 1451–1470.
3. E. Carrilho, S. T. Phillips, S. J. Vella, A. W. Martinez and G. M. Whitesides, Analytical Chemistry (2009) 81 5990–5998.

Determination of Bismuth(III) in Environmental Samples by Ultrasound Assisted Emulsification Solid Floating Organic Drop Microextraction and Atomization Atomic Absorption Spectrometry

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Trace bismuth in environmental samples was determined by ultrasound assisted emulsification solidified floating organic drop microextraction for preconcentration prior to flame atomization atomic absorption spectrometry. By the help of the proposed method, bismuth analysis in environmental samples is possible in an ordinary flame atomic absorption spectrometry even at trace levels. The bismuth ion formed hydrophobic complex by dithizone that was extracted using a drop of 1-dodecanol. All significant parameters affecting the analytical performance were studied. Optimum pH value was found as 4. Optimum sample volume, dithizone concentration and extraction solvent volume were found as 7.5 mL, 0.15% (w/v) in dodecanol and 50 µL, respectively. In addition, optimum extraction time was obtained as 7 min, optimum extraction temperature was 45 °C and ideal extraction phase volume was 0.30 mL, respectively. Methanol was quite effective to use as diluent. Under the optimum conditions, the preconcentration factor was 25, the enhancement factor was 29, the limit of detection (3s) and precision were 7.5 ng/mL and 1.03% (n = 9, 100 ng/mL), the limit of quantification (10 s) was 25 ng/mL and linear working range was 30-650 ng/mL, respectively. The accuracy of the developed method was evaluated by analyzing a certified reference material. The optimized method was employed for the determination of Bi(III) in environmental samples.

Keywords: Environmental Samples; Green Chemistry; Heavy Metals; Bismuth.

A New Method for Simultaneous Determination of Al(III), Fe(III), Cu(II) and Pb(II) as Metal-Hematoxylin Chelates by DLLME-HPLC-VWD System

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Recently, there has been a great interest in the development of the miniaturized sample pretreatment techniques which aim a less time-consuming procedure with a reduction in the amounts of sample used and solvents spent [1]. Dispersive liquid-liquid microextraction (DLLME) which was reported by Rezaee et al. in 2006 has many advantages including short extraction time, simplicity of the operation, high recovery and enrichment factor, small amounts of solvents and low-cost when compared to other preconcentration procedures [2]. It has been used for the extraction and preconcentration of organic and inorganic compounds from different matrices prior to their chromatographic, spectroscopic and electrophoretic analysis [3,4].

In this study, DLLME coupled with high performance chromatography-variable wavelength detector (HPLC-VWD) was applied for the extraction and determination of aluminum, iron, copper, and lead in various water samples. In the proposed approach, hematoxylin was used as a chelating agent, carbon tetrachloride and methanol were chosen as the extracting and disperser solvents, respectively. Firstly, the influences of different experimental DLLME parameters such as extraction and disperser solvent type and their volumes, chelating agent concentration, salt addition, extraction and centrifugation times and pH were investigated and optimized. After preconcentration, the analytes were separated on a Bondapak C18 column by isocratic elution with methanol:THF:water (20:12:68, v/v/v) as mobile phase at a flow rate of 1 mL min⁻¹ and detected with a VWD at 575 nm. The enrichment factors and limits of detection (based on signal-to-noise ratio (S/N) of 3) for the target analytes were in the ranges of 284-327, and 10.7-53.8 ng L⁻¹, respectively. The relative standard deviations and relative recoveries for spiked water samples at 5 µg L⁻¹ of each metal varied from 1.7 to 5.4% and from 89.7 to 101.8%, respectively. In addition, the method was validated by a certified reference material of water (SRM 1643e). Finally, the proposed procedure was applied to the determination of investigated metals in tap water, bottled mineral water, lake water, and sea water with good results.

Keywords: DLLME-HPLC, Trace Metal Analysis, Water Sample.

References:

1. N.S. La Colla, C.E. Domini, J.E. Marcovecchio, S.E. Botte. J. Enviro. Manage. (2015) 151 44-55.
2. M. Rezaee, Y. Assadi, M.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani. J. Chromatogr. A (2006) 1116 1-9.
3. P. Vinas, N. Campillo, I. Lopez-Garcia, M. Hernandez-Cordoba. Anal. Bioanal. Chem. (2014) 406 2067-2099.
4. C. Xi, L.G. Lin, L. Ping, H.D. Mei, Z.X. Yan, L. Mao, J. Food Safety Quality (2015) 6 4598-4604.

The effects of Quercetin on Bone Quality in Healthy and STZ-induced Diabetic Rats: A Biomechanical and ICP-MS Study[‡]

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Type 1 diabetes mellitus (DM), characterized by hyperglycemia and bone loss, have been reported to be related with the increased risk of osteopenia/osteoporosis in humans (1,2). Quercetin, a naturally occurring flavonoid, has protective effects on β -cells in DM, is capable to decrease high blood glucose levels, and has been reported to be have beneficial effects on bone cells (1). Thus, the aim of the present study was to investigate the effects of QE on bone quality in healthy and STZ-induced diabetic rats. For this purpose, fifty-two, Wistar-Albino male rats (4-month; 288–396 g) were assigned randomly into four groups: sham (treated with saline), QE (treated with 50 mg/kg QE), diabetes (DM; received 45 mg/kg i.p. injection of STZ+treated with saline), and diabetes+QE (received 45 mg/kg i.p. injection of STZ+treated with 50 mg/kg QE). Saline or QE administrations were performed by gavage for 8 weeks. Blood glucose levels as well as body-weights were measured once weekly. Bone mineral composition (Ca^{+2} , P, PO_4^{-3} , Mg, Se, and Ca/P-ratio) was evaluated by using inductively coupled plasma mass spectrometry (ICP-MS) after microwave-assisted digestion. Three-point bending test was chosen for the mechanical analysis. Geometric features of bones were also evaluated by computerized tomography. Our findings showed that the QE lowered the hyperglycemic conditions and it averted the weight loss. Furthermore, our results also indicated that the deteriorative effects of DM on bone quality and strength in diabetic rats was partially prevented by QE administration via a possible mechanism of preventing collagen degradation. In addition to all, we found that QE has no any protective effects on mineral loss in diabetic rats. Moreover, QE caused a significant decrease in bone mineral content and bone integrity of healthy rats resulting with a partial reduction in bone quality. In conclusion, it can be suggested that the bone strength and quality is reduced in DM and QE treatment may partially inhibit this reduction. In addition, QE may have no protective effect on bone loss associated with DM and it might also cause a mineral imbalance in healthy subjects. Further detailed analysis should be performed to clarify the effects of QE on bone mineral and collagen integrity in diabetic and healthy conditions.

Keywords: Biomechanics, Collagen, Diabetes, Quercetin, Rat, Streptozotocin.

References:

1. Liang W, Luo Z, et al. Eur J Pharmacol (2011) 670 317–24.
2. Hamann C, Kirschner S, et al Nat Rev Endocrinol (2012) 8 5 297-305.

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Poly(hydroxyethyl methacrylate-co-methacryloylglutamic acid) Nanospheres for Adsorption of Cd²⁺ Ions From Aqueous Solutions

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Cadmium is a toxic heavy metal occurring in the environment naturally as well as a serious pollutant posing severe risks to human health emanating from industrial and agricultural sources [1]. Consequently, in recent years, scientific researches dealing with direct determination of Cd²⁺ are increasing day by day due to insufficient sensitivity and matrix effects. Therefore, separation and preconcentration of trace metals prior to their analysis are often required [2]. Highlights of this presentation will be the discussion of synthesis, characterization, and Cd²⁺ adsorption efficiency of the novel nano-sized sorbent to which Cd²⁺ binds directly without any activation.

In this study, poly(2-hydroxyethyl methacrylate-co-*N*-methacryloyl-(L)-glutamic acid) p(HEMA–MAGA) nanospheres have been synthesized, characterized, and used for the adsorption of Cd²⁺ ions from aqueous solutions. Nanospheres were prepared by surfactant free emulsion polymerization. The p(HEMA–MAGA) nanospheres were characterized by SEM, FTIR, zeta size, and elemental analysis. The specific surface area of nanospheres was found to be 1,779 m²/g. According to zeta size analysis results, average size of nanospheres is 147.3 nm with poly-dispersity index of 0.200. The goal of this study was to evaluate the adsorption performance of p(HEMA–MAGA) nanospheres for Cd²⁺ ions from aqueous solutions by a series of batch experiments. The Cd²⁺ concentration was determined by inductively coupled plasma-optical emission spectrometer. Equilibrium sorption experiments indicated a Cd²⁺ uptake capacity of 44.2 mg g⁻¹ at pH 4.0 at 25°C. The adsorption of Cd²⁺ ions increased with increasing pH and reached a plateau value at around pH 4.0. The data were successfully modeled with a Langmuir equation. A series of kinetics experiments was then carried out and a pseudo-second order equation was used to fit the experimental data. Desorption experiments which were carried out with nitric acid showed that the p(HEMA–MAGA) nanospheres could be reused without significant losses of their initial properties in consecutive adsorption and elution operations.

Keywords: Nanosphere, Cadmium, Adsorption, Heavy Metal, ICP-OES, Surface Science

References:

1. L. Järup & A. Åkesson, *Toxicol. Appl. Pharm.* (2009) 238 201-208.
2. Ç. Arpa, N. Bereli, E. Özdi, S. Bektaş, A. Denizli, *J. Appl. Polym. Sci.* (2010) 118 2208-2215.

Square Wave Voltammetric Behaviour and Quantitative Determination of β -N-oxalyl-L- α , β -diaminopropionic Acid (β -ODAP)

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Grass pea (*Lathyrus sativus* L., Mürdümük) has an amazing capability to survive under harsh environmental conditions. The presence of a neurotoxic free amino acid; β -ODAP (β -N-oxalyl-L- α , β -diaminopropionic acid) prevents the prevalent usage of grass pea seeds (*Lathyrus sativus* L.) as a food legume in human and animal diet[1].

Grass pea seeds with β -ODAP content lower than 0.2 % are presumed to be safe for human and animal consumption. Many breeding programs are in progress worldwide to develop genotypes combining high yield with high protein content and low or no neurotoxin (β -ODAP) [2]. Monitoring β -ODAP is very essential in such efforts. Therefore it is imperative to develop a fast, cheap and selective method to determine the neurotoxin, β -ODAP in seeds.

In this study the electrochemical behavior of ODAP is explored by square wave and cyclic voltammetric techniques, using glassy carbon electrode. ODAP exhibited two quasi reversible anodic peaks at about 147mV (Peak I) and 200 mV (Peak II) versus Ag/AgCl in 0.10 M phosphate buffer solution at pH 3.0. It is shown that ODAP can be easily electropolymerized on carbon electrode surface to form poly-ODAP by cyclic voltammetry, similar to its structural analog; glutamic acid.

Recently it was demonstrated that square-wave voltammetry is especially convenient for both kinetic characterization and quantitative determination of the redox couples strongly immobilized on the electrode surface. While the peak potentials as a function of the frequency have commonly been used to determine the kinetics of redox reactions from the dissolved state, the phenomenon of “quasireversible maximum” has emerged as a simple and viable method to determine kinetic parameters of surface-confined redox reactions [3].

Furthermore an adsorptive square wave voltammetric method was developed and validated for quantitative determination of ODAP in grass pea seed extracts.

Keywords: Square Wave Voltammetry, ODAP, Quasireversible Maximum, Electropolymerization, *Lathyrus Sativus* L.

References:

1. M. Van Moorhem, F. Lambein, L. Leybaert, Food Chem. Toxicol. (2011) 49, 550–555.
2. C. D. Hanbury, C. L. White, B. P. Mullan, K. H. M. Siddique, Anim. Feed Sci. Technol. (2000) 87,1-27.
3. R. Gulaboski, M. Lovrić, V. Mirceski, I. Bogeski, M. Hoth, Biophysical Chemistry (2008) 138 130–137.

Anodic Stripping Voltammetric Determination of Trace Amounts of Sb(III) Using Overoxidized Poly(Phenolred) Film Modified Glassy Carbon Electrode

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Antimony (Sb) is a toxic element and a global environmental contaminant that is found throughout the environment as a result of natural processes and human activities. In industry, antimony is used fabrication of fire retardants, glass and ceramics, batteries and polyethylene terephthalate (PET) bottles [1]. In view of its many uses, which are continually expanding and high toxicity, the development of sensitive and selective methods for the determination of antimony in various samples has become of increasing importance. Although spectroscopic techniques have been employed for Sb determination, electrochemical methods, particularly electrochemical stripping analysis, offer advantages of ease and speed of analysis, cost effectiveness and high sensitivity [2, 3].

We report here a simple and robust procedure to perform sensitive and selective anodic stripping voltammetric determination of Sb(III) in 0.1 mol L⁻¹ HCl media on overoxidized poly(phenolred) (PhRed_{ox}) film modified glassy carbon electrode (GCE). The PhRed_{ox}/GC electrode surface was characterized using cyclic voltammetry (CV), scanning electron microscopy (SEM), X-Ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS). Factors affecting the accumulation, reduction and stripping steps were investigated and an optimized procedure was then developed. Under optimized conditions, the calibration graph consisted of two linear segments of 3.6x10⁻¹⁰-1.0x10⁻⁸ mol L⁻¹ and 2.8x10⁻⁸-1.5x10⁻⁷ mol L⁻¹ with a detection limit of 6.2x10⁻¹¹ mol L⁻¹. The intra-day relative standard deviation (RSD) values at PPhRedox/GC for 2.0x10⁻⁹ and 2.0x10⁻⁸ mol L⁻¹ Sb³⁺ are 3.5 and 3.1%, respectively. The inter-day RSD values at PPhRedox/GC for 2.0x10⁻⁹ and 2.0x10⁻⁸ mol L⁻¹ Sb³⁺ are 4.3 and 3.9%, respectively. The proposed over-oxidized polymer film modified electrode was applied successfully for the analysis of antimony in different spiked water samples. Spiked recoveries for water samples were in the range of 93.0–103.0 %.

Keywords: Polymer Film Electrode, Antimony (III) Determination, Anodic Stripping Voltammetry

References

1. Kolliopoulos, A., Metters, J., Banks, C., Analytical Methods, (2013) 5 3490-3496.
2. Tanguy, V., Waeles M., Vandenhecke J., Riso R.D., Talanta (2010) 81 614–620.
3. Khoo, S.B., Zhu J., Analytica Chimica Acta (1998) 373 15-27.

Voltammetric and Chromatographic Determination of Boscalid in Tomato Juice

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The pesticides are used in agricultural production for food protection but, their residue in food alters the endocrine system. Boscalid is a broad spectrum fungicide for beans, berries and tomatoes. MRL values of Boscalid were established as 1 mg/kg for various types of food and therefore, sensitive and accurate analysis methods are required for BOS determination in food samples¹.

Present study describes electrochemical and chromatographic methods for Boscalid determination in tomato juice and puree samples. Boscalid is a pyridine carboxamide derivative which can give complexes with cobalt ions and become an electroactive complex². Electrochemical studies include indirect determination of Boscalid in the presence of Co(II) ions by AdCSV technique at a pencil lead electrode (PLE). After optimization of the experimental parameters, calibration graphs were drawn in in sub nanomolar levels by monitoring the reduction peak at -1.2 V. The catalytic character of the reduction process was established by mechanistic studies.

Chromatographic studies include the use of a green separation technique. In comparison to the other microextraction techniques, SPME is fast, simple and greener technique since no solvent is consumed during the process³. commercial (PDMS-DVB) and a lab made (PPy) solid phase microextraction (SPME) fibers. Experimental parameters such as pH, stirring rate and extraction time was optimized in tomato juice sample medium. The calibration graphs were drawn in ppb ranges. Overall results have demonstrated that Boscalid can be determined by both methods sensitively and selectively and the methods developed were applied to the real samples.

Keywords: Boscalid, Voltammetry, Gas Chromatography, Solid Phase Micro Extraction, Tomato Juice

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References:

1. EFSA Journal (2010) 8 1780.
2. S. Meghdadi, M. Amirnasr, M.H. Habibi, A. Amiri, V. Ghodsi, A. Rohani, R.W. Harrington, W. Clegg, Polyhedron (2008) 27 2771–2778
3. Solid Phase Microextraction-Theory and Practice. Wiley: New York, J. Pawliszyn, (1997).

Electrochemical Electrochemical DNA Biosensors for Medical Applications

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Biomolecule-sensitive sensors is already a well-established part of biomedical research field and some of biosensor companies have produced their point-of-care devices up to now. Besides this, newer biosensors called as “Nanobiosensors” uses to nanomaterials to design small-sized sensors with high sensitivity. Applications of biosensing strategies by using nanometer-sized DNA molecule in the absence or presence of nanomaterials have been reported in the last two decades and all aspects of this biosensor area are moving equally fast especially for biomedical field.

The studies related to the identification of DNA sequences are crucial for geneticists, pathologists,...etc. for the detection of genetic conditions underlying diseases [1,2]. Among them, electrochemical (nano)biosensors for application in medicine have been continuously designed as an alternative to other traditional and modern detection technologies [3-10].

Here, the present state of electrochemical DNA biosensors and their promising selected applications from the our lab are presented here.

Keywords: Electrochemical DNA Biosensor, DNA, Nanomaterial, Drug-DNA Interactions, Carbon Electrode.

References:

- 1- E. Palecek, M. Bartosik, Chem. Rev. (2012) 112 3427.
- 2- D.Ozkan-Ariksoysal, M. Ozsoz, Biosensors and Their applications in healthcare. Future Science Ltd Book chapter (2013) 8 113-126.
- 3- S.Campuzano, J. Wang , Electroanalysis (2011) 23 6 1289–1300.
- 4- D.A Giljohann, CA Mirkin. Nature(2009) 462 461.
- 5- A. Merkoci, Biosens. Bioelectron., (2010) 261164.
- 6- O. A. Loaiza, S. Campuzano, M. Pedrero, M. I. Pividori, P. Garcia and J. M. Pingarron, Anal. Chem., (2008) 80 8239.
- 7- D. Ozkan-Ariksoysal, B. Tezcanli, B. Kosova, M. Ozsoz, Anal. Chem. (2008) 80 588
- 8- S. Aydinlik, D. Ozkan-Ariksoysal, P. Kara, A. A. Sayiner, M. Ozsoz, Analytical Methods., (2011) 3 1607.
- 9- F. Lucarelli, G. Marrazza, A. P. F. Turner, M. Mascini, Biosensors & Bioelectronics., (2004) 19 515.
- 10- Y.U. Kayran, D.Ozkan-Ariksoysal, B.Tezcanli, B. Kosova, Mehmet Ozsoz, Electroanalysis, (2013) 25 12 2668 – 2676

A New Charge Transfer Complex of *p*-aminodiphenyldiamine with Maleic Anhydride

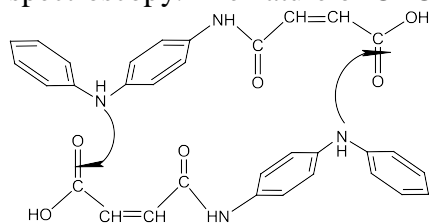
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The concept of "molecular association" has long been recognized as important in virtually all fields of chemistry. The concept is that of a relatively electron poor molecule, or acceptor, interacting in some way with an electron rich molecule, or donor. The literature also abounds with such terms as "molecular complexes", " π complexes", and "charge-transfer complexes (CTC)" which all refer to some sort of donor-acceptor interaction¹. The formation of molecular complexes of the charge-transfer plays important role of preparation of complexed molecules which have potential uses in many biological² and technological application fields³. The important role of CTC in material science⁴, drug action⁵, enzyme catalysis⁶, antibacterial⁷ and DNA binding⁸ are very attractive. The characterization of novel types of donor-acceptor complexes takes great attention to studies on many kinds of molecules design and preparation. Maleic anhydride (MA) is a highly electron acceptor molecule due to its low ionization potential and high electron affinity. *p*-aminodiphenyldiamine (PADPA) is an aromatic amine, which is used in pigment technology due to its oxidizing potential. Up to now, the charge transfer complex of MA and PADPA molecules has not been studied. Take into consideration finding changes in electronic levels of MA and PADPA molecules arising due to the electron transfer and determining the complex formation constant of CTC motivate us to design this study. CTC and amidization formed by the interaction between the electron donor of the PADPA and electron acceptor of MA has been identified by the IR, NMR and HRMS spectroscopy. The nature of CTC is characterized by SEM.



Amidization reaction is caused by the proton and charge transfer of the MA and PADPA molecules. The formation of complex within the MA–PADPA system and related constants—the complex formation constant ($K^{AD}=285.32 \text{ M}^{-1}$), the molar extinction coefficient ($\epsilon^{AD}=268 \text{ 810 M}^{-1} \text{ cm}$) and standard Gibbs free energy ($\Delta G^{\circ} = -3.35 \text{ kcal mol}^{-1}$)—were determined using the Benesi–Hildebrand equation by UV/Vis spectroscopy⁹.

Keywords: Charge Transfer Complex, *p*-aminodiphenyldiamine, Maleic Anhydride, NMR, Uv-Vis
Referenc:

1. Kurt, G. O.; University of Florida, USA: 1981, p 230.
2. Slifkin, M.; Academic Press Inc:1972, p 271.
3. Hunter, C. A.; Sanders, J. K. M., J. Am. Chem. Soc. (1990) 112, 5525.
4. Khan, I. M.; Ahmad, A., Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy (2010) 76 315.
5. Schwoerer, M.; Wolf, H. C.; Wiley-VCH: 2007, p 438.
6. Khan, I. M.; Ahmad, A., J. Mol. Struct. (2010) 977 189.
7. Mandal, R.; Lahiri, S. C., J. Indian Chem. Soc. (1999) 76 347.
8. Ungurenasu, C.; Airinei, A., J. Med. Chem. (2000) 43 3186.
9. Karaca, E.; Kaplan Can, H.; Bozkaya, U.; Özçiçek Pekmez, N., ChemPhysChem, n/a 2016.

Absorption of Chromium and its Toxicity in Human Health: A Physiological Approach

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Abstract

Chromium rank among the priority elements including mercury, arsenic, cadmium and lead that are of public health significance because of their high degree of toxicity. These elements can deactivate the enzymes and stop or alter metabolic processes due to strong affinity of their cations (M^{n+}) for sulfur found in proteins including enzymes. Even at low levels of exposure, these elements are known to induce cellular damage, inflammation, and cancers mainly in the kidney, liver, lung, prostate, and skin. The common cellular process of those elements are oxidative stress caused by reactive oxygen species (ROS), DNA damage, apoptosis and cell death. Among carcinogenic elements, only Cr(VI) directly interacts with DNA. It enters into cell by way of anion transporter and is reduced to Cr(III), (IV) and (V) by cellular reductants. In this presentation, absorption and toxicity of Cr were discussed taking into consideration its solubility in water as well as chemical species and way of intake into body.

Keywords: Toxic Elements; Cellular Damage; Carcinogenicity; Chromium.

Introduction

The absorption of metals from dietary sources occurs by a number of metal transporters to provide sufficient amounts of individual nutrient metals. Numerous studies have alluded to the fact that epigenetic dysregulation may play an important role in metal-induced carcinogenesis since carcinogenic metals typically tend to be fairly weak mutagens, and do not directly interact with DNA, except hexavalent chromium ^[1]. Cr(VI) entry into cell by way of anion transporter and is reduced to Cr(III), (IV) and (V) by cellular reductants and finally, attacks to DNA. Cr(III) is actually an essential human nutrient required to promote the insulin action for utilization of sugars, proteins and fats, and it is considered to be noncarcinogenic cells because it doesn't pass into cell ^[2]. Methylation is the most common and best understood epigenetic modification in DNA. The term 'epigenetics' refers to covalent modifications of the DNA or of the histones. These modifications can control gene expression and the pattern of modifications is altered in many cancers ^[3]. Increased metal levels in organism are associated with altered expression of nuclear factors like NF- κ B, activator protein-1 (AP-1), nuclear factor of activated T-cells (NFAT) and the tumor suppressor protein p53 ^[4]. Alterations of these nuclear factors result in dysregulation of cell proliferation, apoptosis and cell cycle progression, which ultimately leads to cancer ^[5].

Materials&Methods

Environmental pollution with various forms of Cr results from its numerous uses in the chemical industry, production of dyes, wood preservation, leather tanning, chrome plating, manufacturing of various alloys, and many other applications and products ^[6]. Due to the common usability of chromium and its toxicity, there is a great interest in determination of this element in food, beverage and biological matrices ^[7-11]. Hexavalent chromium compounds are well established human respiratory carcinogens and have also been shown to elevate other types of human cancers ^[12]. Hexavalent chromium, Cr(VI), is one of the few carcinogenic metals that can directly react with DNA, and induce mutations ^[13]. Chromium (VI) primarily exists as a

chromate anion (CrO_4^{2-}) under most physiological conditions. It resembles a sulphate (SO_4^{2-}) (Fig. 1) and phosphate (PO_4^{3-}) and is actively transported into all cells of the body by the oxyanion transporters [14]. Upon entry, Cr(VI) is reduced by cellular reductants such as GSH, ascorbate, and NADPH, to its lower oxidation states [15]. Reduction of Cr(VI) to lower oxidation states such as Cr(III) is mediated primarily by binding to low molecular weight thiols including GSH, antioxidants such as ascorbate and macromolecules such as proteins. This reduction can lead to binary [Cr(III)-ligand] and ternary [ligand-Cr(III)-ligand] complexes [e.g. GSH-Cr(III)-GSH]. Reduction of Cr(VI) can also lead to the formation of less stable intermediates such as Cr(V) and Cr(IV), as well as thiol radicals [16]. Noncellular in vitro studies indicate that Cr(VI) does not bind directly to DNA, whereas Cr(III) can bind directly to DNA [17]. These intermediate states of Cr are reactive and participated in the production of ROS, thereby causing several types of oxidative DNA damage, such as base modification, single-strand breaks, DNA–DNA inter-strand crosslinks, DNA–protein crosslinks, chromium-DNA adducts, and oxidative nucleotide changes, as well as chromosomal aberrations and lipid peroxidation [18]. These findings indicate that the key process involved in Cr-mediated carcinogenicity is the reduction of Cr(VI) to Cr(V), Cr(IV) and Cr(III) by cellular reductants.

The term genotoxicity is broadly used to describe genetic damage that can arise from both mutagenic and nonmutagenic processes. As similar to nickel, chromium also appears to have epigenetic effects. Cr(VI) is reported to induce epigenetic changes including microRNA, histone modification and DNA methylation in cells. Hexavalent chromium exposure can also decrease gene expression via post-translational histone modifications. Expression of genes involved in cell proliferation and apoptosis were also changed. On the other hand, Cr(III) is likely absorbed via pinocytosis or endocytosis thereby resulting in far less uptake into cells than Cr(VI). Cr(III) preferentially binds Cys, His, and negatively charged side chain COOH groups in glutation and Asp, all of which are rarely found in close contact with the duplex in DNA-binding proteins [19]. However, Cr(III) is considered to be noncarcinogenic cells because it doesn't pass into cell while Cr(VI) entry to cell by way of anion transporter and is reduced to Cr(III), (IV) and (V) by cellular reductants and finally, it attacks to DNA.

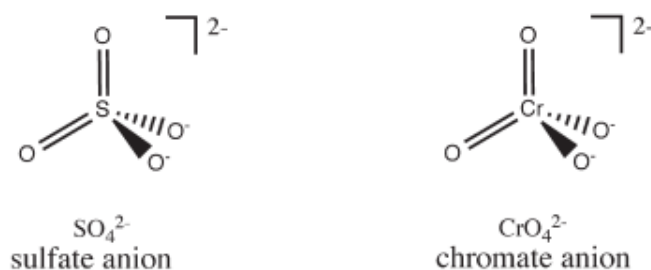


Figure 1. Structures of sulfate and chromate

Results and Discussion

Public health concerns are centered on the presence of hexavalent Cr that is classified as a known human carcinogen via inhalation. On the other hand, information about the carcinogenicity of ingested Cr(VI) is much more limited. The epidemiologic evidence for the oral route of hexavalent chromium exposure is not considered strong [14]. Further, extensive evidence of the carcinogenicity of hexavalent chromium in animals via ingestion does not exist. Taken together the studies on this subject, the considerations do not provide a basis for the characterization of hexavalent chromium as “carcinogenic to humans” via oral exposure because the “carcinogenic to humans” descriptor indicates strong evidence of human carcinogenicity [20]. Therefore, U.S. Environmental Protection Agency (USEPA) concluded that, based on the available information, the descriptor “likely to be carcinogenic to humans” is

the most appropriate descriptor for the carcinogenic potential of hexavalent chromium via ingestion ^[20]. Defence mechanisms against free radical-induced oxidative stress involve: (i) preventative mechanisms, (ii) repair mechanisms, (iii) physical defences, and (iv) antioxidant defences. It is known that there are various antioxidant defense mechanisms in the organism against ROS. These are numerous enzymatic (catalase (CAT), superoxide dismutase (SOD), glutathione reductase, glutathione peroxidase (GPx)), small antioxidant molecules (uric acid, glutathione, albumin, protein –SH groups, bilirubin) and certain vitamins (ascorbic acid (Vitamin C) and α -tocopherol (Vitamin E)) as well as carotenoids and flavonoids which have the capacity to neutralize free radicals acting all together. Under normal conditions, there is a balance between both the ROS activities and the intracellular levels of these antioxidants. This balance is essential for the survival of organisms and their health. Uptake of higher toxic metals disrupt this balance and cause to unwanted chain reactions. OH• as the most reactive ROS is capable for the oxidation of a variety of biomolecules, such as enzymes, proteins, DNA and lipids ^[21]. Accumulation of free radicals from ROS results in cell death via abnormal gene expression and lesions of cellular components including DNA, lipids, and proteins. Inhibition of DNA repair and DNA crosslinking with proteins via ROS generation is a major result of heavy metal-induced carcinogenesis.

Conclusion

The multiple industrial, domestic, agricultural, medical and technological applications have led to the wide distribution of toxic elements including arsenic, cadmium, lead, nickel and chromium in the environment. Due to strong affinity of metal cations (M^{n+}) for sulfur found in proteins including enzymes, metals can deactivate the enzyme and stops or alters metabolic processes. Among them, Cr(III) is considered to be noncarcinogenic cells because it doesn't pass into cell while Cr(VI) entry to cell by way of anion transporter and is reduced to Cr(III), (IV) and (V) by cellular reductants and finally, attacks to DNA. Briefly, the IARC (1997) has concluded that there is sufficient evidence in experimental animals for the carcinogenicity of the following chromium (VI) compounds: calcium chromate, zinc chromates, strontium chromate and lead chromates and that the evidence is limited for chromic acid and sodium dichromate ^[22]. The IARC (1997) has also concluded that the evidence for carcinogenicity of barium chromate and chromium (III) compounds is inadequate ^[22]. Cr(VI) poisoning is mainly associated with apoptosis, oxidative stress, and DNA damage response in addition to genomic interactions ^[23]. Thus, the food and beverages consumed by human should be examined for these priority toxic elements ^[24].

References:

1. Chervona Y, Costa M. *Free Radical Biol Med* (2012) 53 5 1041-1047.
2. Mulware SJ. *Biotech* (2013) 3 85–96.
3. Arita A, Costa M. *Metallomics* (2009) 1 222–228.
4. Reuter S, Gupta SC, Chaturvedi MM, Aggarwal BB. *Free Radic Biol Med* (2010) 49 11 1603–1616.
5. Elmore S. *Toxicol Pathol* (2007) 35: 495–516.
6. Welling R, Beaumont JJ, Petersen SJ, et al. *Occup Environ Med* (2015) 72 151–159.
7. Yaman M, Yaman IH. *Spectrosc Spectral Anal* (2014) 34 2 300-307.
8. Yaman M, Karaaslan NM, Yaman IH. *Bull Environ Contam Toxicol* (2014) 93 3 344-349.
9. Yaman M, Bal T, Yaman IH. *Food Add Contam: Part B* (2013) 6 4 301-306.
10. Yaman M. *Revue Roumaine De Chimie* (2003) 48 8 597-600.
11. Yaman B, Yaman M. *J Elem* (2016) 22(3): DOI:10.5601/jelem.2016.21.2.1117
12. Costa M, Klein CB. *Crit Rev Toxicol*. (2006) 36 155–163.
13. Chervona Y, Arita A, Costa M. *Metallomics* (2012) 4 7 619–627.

14. Zhitkovich A. *Chem Res Toxicol* (2011) 24 1617–1629.
15. Lee JC, Son YO, et al. *Free Radical Biol Med* (2012) 53 742–757.
16. O'Brien TJ, Ceryak S, Patierno SR. *Mutat Res-Fundam Mol Mech Mutag* (2003) 533 1-2 3-36.
17. Thompson CM, Proctor DM, Suh M, et al. *Crit Rev Toxicol* (2013) 43 3 244–274.
18. Ding M, Shi X. *Mol Cell Biochem* (2002) 234–235 293–300.
19. Macfie A, Hagan E, Zhitkovich A. *Chem Res Toxicol* (2010) 23 341–347.
20. EPA 2010, *U.S. Environmental Protection Agency Washington, DC*, EPA/635/R-10/004A.
21. Valko M, Leibfritz D, Moncol J, et al. *Inter J Biochem Cell Biol* (2007) 39 44–84.
22. IARC, 1997. International Agency for the Research on Cancer (IARC). Chromium, nickel and welding. Vol 49. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. IARC. 1997; Lyon.
23. Sasso AF, Schlosser PM. *Toxicol Appl Pharmacol* (2015) 287(3) 293-298.
24. Khlifi R, Olmedo P, Gil F, et al. *Sci Total Environ* (2013) 452 58-67

Monolithic Nano-Liquid Chromatography: Principles and Applications In Sample Analysis

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Abstract

Miniaturization in bioanalytical separation science progressed significantly. Herein, we report that the introduction of the general principle of monolithic nano-liquid chromatography. In addition, some selected applications dealing with various sample analysis will be illustrated, along with specific examples.

Key words: Nano-LC, monolith, proteomics, nanoparticles, chiral separation

Introduction

Microscale bioseparations in miniaturization chromatographic systems such as nano liquid chromatography (Nano-LC) have been one of the present trends in the separation science and technology. This system has been applied to the analyses of a wide number of biomolecules. As a one of new separation systems in separation science, Nano-LC offers to some advantages over conventional liquid chromatography such as low sample requirement, use of small amount of reagent, good efficiency, short analysis time, especially flow rate adjustment with flow splitter. In general, capillary columns (id between 10 and 100 μm) used in Nano-LC are either of fused silica or peek material currently employed in HPLC. Nano-LC applications are performed in packed, open tubular and monolithic capillary columns. The most common of them is monolithic columns. In this work, as an alternative approach for liquid chromatography based-monolithic stationary phases, the preparation and various sample application of HPMA-Cl based monolithic stationary phases by Nano-LC will be demonstrated.

Materials&Methods

Nano-LC experiments were performed on Ultimate 3000 Chromatography System with nano flow (Dionex Technologies, Munich, Germany). The system includes four parts with the following components (i) ultimate 3000 pump, (ii) ultimate 3000 flow manager with flow splitter, (iii) ultimate 3000 Autosampler, (iv) ultimate 3000 RS variable wavelength dedector. An Ultimate 3000 Chromatography System with ultimate 3000 pump (Dionex Technologies, Munich, Germany) was used for functionalization steps. The polyimide-coated fused-silica capillaries (id: 100 μm , od: 360 μm) were obtained from Polymicro Technologies (Phoenix AZ, USA). Ethylene dimethacrylate (EDMA, 99%), 3-chloro-2-hydroxypropyl methacrylate (HPMA-Cl, 99%), were purchased from Sigma-Aldrich Chemical (Milwaukee, WI, USA).

Results&Discussion

In Nano-LC, the incorporation of HPMA-Cl led to significant changes in solute retention and selectivity. In one approach, the monolithic columns were modified with well defined retentive ligands such as dodecylamine, boronic acid and that resulted in improving the

separation of standard proteins, small solutes such as alkylbenzenes. In a second approach, fumed silica nanoparticles constituted entirely the monolithic stationary phase responsible for solute retention and separation. The fumed silica nanoparticle (FSNPs) incorporated large surface area monoliths (see Fig. 1) proved useful in Nano-LC separations a wide range of small solutes including enantiomers.

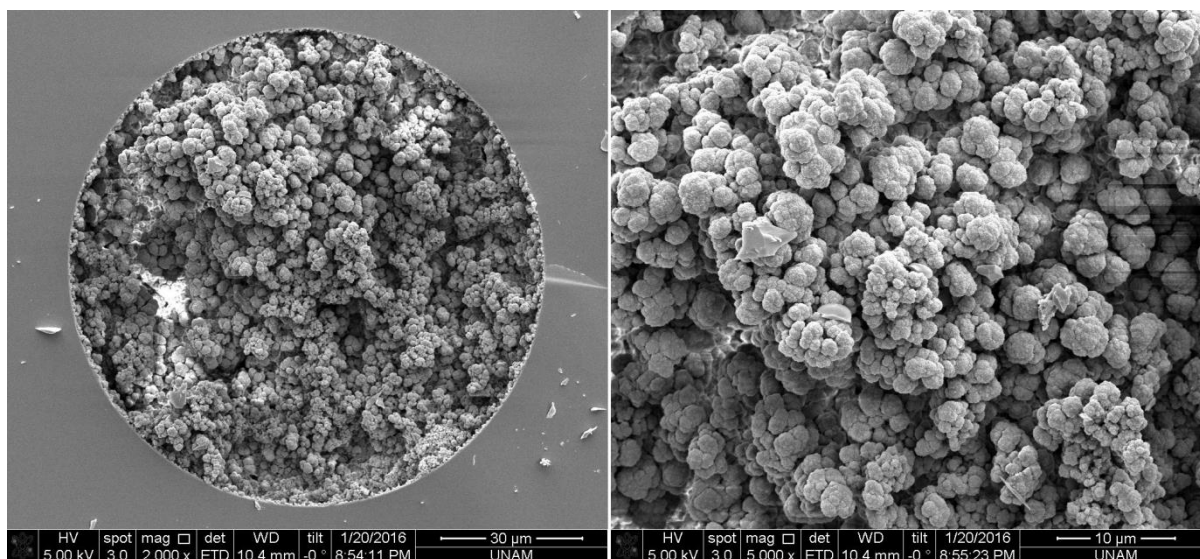


Fig.1. SEM photographs of FSNPs-Incorporated Capillary Monolithic Column with (A) Magnification 2000x; (B) 5000x.

With FSNPs, nonpolar and hydrophobic/affinity interactions were responsible for solute retention. Concerning Nano-LC with FSNPs based monoliths, the presence of FSNPs allowed many samples to separate to a greater extent than in the absence of FSNPs thus proving the superiority monolithic Nano-LC.

Conclusions

Monolithic Nano-LC based separation media are very promising for the separation of a wide range of compounds providing unique selectivity and high resolving power. The FSNPs may be used in the preparation of other Nano-LC based stationary phases such as chiral or ion-exchange and consequently broadening the usefulness of FSNPs in separation science.

References:

1. Aydoğan, C. J. Chromatogr. A (2015) 1392 63-68
2. Aydoğan, C; El Rassi, Z. J. Chromatogr. A (2016) 1445 55-61.

Method Development and Determination of Imidazolinone Herbicides in Sunflower and Soils by GC-MS

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At the present time, the number of macro and micro live pests that are damaging to agricultural products is about the approximate 65000 to 70000. Thereof the harms result are the loss of obtained product between 15% to 30%. The use of pesticides which is one of the essential inputs in modern agriculture brings with the disadvantages and the advantages in terms of human health and environmental pollution. Imidazolinones represent a relatively new class of herbicides that can be used either pre- or post-emergence for the control of a wide range of weeds in broadleaf and cereal crops, and in non-crop situations. In addition, the imidazolinone herbicides are used with imidazolinone tolerant crops (Clearfield® crops, for sunflower in the USA, Argentina and Turkey in 2003) [Tan et al., 2005]. Briefly, because of in modern crop protection compounds, the imidazolinone group herbicides is only used in agriculture. Imazamox, imazaquin, imazethapyr, imazapic and imazapyr are a representative member of the imidazolinone-family herbicides.

The aim of this study was to investigate the level of imidazolinone group herbicides (imazamox, imazaquin, imazethapyr, imazapic and imazapyr) in the Thrace Region, Turkey. Especially, imazamox which used as a herbicide in the production of sunflowers in the Thrace Region were intended to determine of residue levels in soil, different parts of plant and seed. Five herbicides were identified in sunflower samples using both solid-liquid extraction and results were determined by gas chromatography-mass spectrometry-single quadrupole instruments and EI ionization in the SIM mode (GC-MS-EI). The optimized conditions were found to be 1 ml per min⁻¹ flow rate in the mobile phase, 3 µl for injection volume using PTV solvent vent mode. Overall recoveries from sunflower plant and soil were high 45–98% for imazamox, 71–105% for imazaquin, 25–96% imazethapyr, 53–92% imazapyr and 40–83% for imazapic, respectively.

Keywords: Imidazoline Herbicides (Imazamox, Imazaquin, Imazethapyr, Imazapic, Imazapyr); GC-MS; Extraction; Sunflower; Soil.

References:

1. Tan, S., Evans, R.R., Dahmer, M.L., Singh, B.K., Shaner, D.L., Imidazolinone-tolerant crops: history, current status and future. *Pest Manag. Sci.* (2005) 61 246–257.

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SERS Based-rapid Detection Strategies of Group-A Beta-Hemolytic *Streptococcus*

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In food industry, environmental tests and in clinical diagnostics, the rapid detection of bacteria has great importance due to their serious medical conditions. Bacterial infection or contamination can be the reasons of death. There are several methods that are developed to detect bacteria however the fast and accurate detection of pathogens has still some challenges. Group A beta-hemolytic *Streptococcus pyogenes* is the main cause of acute pharyngitis¹ and patients are tested by either a throat culture or a rapid antigen detection². However, it takes 24-48 hours to obtain results and if there is any negative test results, there is a verification needed³. In this study, we have developed a new method to detect group A beta-hemolytic *Streptococcus* using modified gold nanoparticles. Antibody modified Fe₃O₄@Au nanoparticles are employed for capture probe of bacteria and antibody modified gold nanorod particles are used for Raman labeling of bacteria. After interacting between the capture probe with solutions of *Streptococcus* having different initial cell concentrations (15-1x10⁸ cfu/mL), SERS measurements are taken. Measured intense Raman peaks are used for quantitative detection of *Streptococcus* by using plotted calibration curve. Total detection time was around 1 hour which shows big advantage of this method compared with plate counting classical methods. This method is optimized as a fundamental for paper-based lateral flow immunoassay (LFIA). LFIA kits are prepared using different membranes and the presence of *Streptococcus* is tested by color change and SERS signal on the test line. The detection of *Streptococcus* by a paper-based test kit has been performed for the first time and it enables accurate and fast results.

Keywords: SERS Detection, Group A beta-Hemolytic *Streptococcus*, Lateral Flow Immunoassay, Nanoparticles

References:

1. Bisno, A.L., *Acute Pharyngitis*. New England Journal of Medicine, (2001) 344 3 205-211.
2. Bisno, A.L., et al., *Diagnosis and management of group A streptococcal pharyngitis: a practice guideline*. Infectious Diseases Society of America. Clin Infect Dis, (1997) 25 3 574-83.
3. Schlager, T.A., et al., *Optical immunoassay for rapid detection of group A beta-hemolytic streptococci. Should culture be replaced?* Arch Pediatr Adolesc Med, (1996) 150 3 245-8.

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The Effect of Ethionine Protonation on the Kinetics and the Mechanism of Bi(III) Ion Electroreduction

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Electroreduction of metal ions in aqueous solutions is highly dependent not only on the type and concentration of the supporting electrolyte, but also on the presence of the trace amounts of organic substances. Organic substances may inhibit, accelerate the electrode process or may not affect its course. The Bi(III) ion hydrolysis limits the pH range that allows investigating the electroreduction of these ions [1]. It was found that a change in the chloric (VII) acid/sodium chlorate (VII) ratio in the basic electrolyte, affects the structure of both the bismuth aqua ion and the molecule of the selected amino acid, and, consequently, the course of the electrode process.

Ethionine, which is an ethyl analogue of methionine, has a very destructive influence on the livers of living organisms and disrupts the activity of many enzymes. It is a strongly carcinogenic metabolite contributing to the development of most types of human cancer [2]. Ethionine, according to the cap-pair rule, catalyses the process of Bi(III) ion electroreduction. The applied electrochemical methods, such as DC polarography, SWV voltammetry and cyclic voltammetry (CV), as well as Electrochemical Impedance Spectroscopy, allowed us to determine kinetic parameters, indicating the extent of the catalytic effect of ethionine.

It was concluded that the presence of ethionine and the protonation of the catalysing substance have effects on the rate of the multi-step process of Bi (III) electroreduction in chlorates (VII). The mechanism of the catalytic effects of ethionine is associated with the formation of active Bi – ethionine complexes under specific conditions present on the electrode surface, when the Bi(III) ion hydration zone becomes partially degraded, and thus in the close proximity to the outer Helmholtz plane [3]. The catalytic activity of ethionine increases with increasing amounts of NaClO₄ in the basic electrolyte solution. Increased amounts of HClO₄ in chlorate (VII) solutions causes the decrease rate of the Bi (III) ion electroreduction process in the presence of ethionine. This confirms the assumption on the variety of active complexes mediating the passage of electrons. Probably, the arrangement of the adsorbed ethionine on the surface of the mercury electrode, due to a change in the degree of ethionine protonation in basic electrolyte solutions, plays a significant role in the formation of active Bi – ethionine complexes, which are the substrate in the process of electroreduction.

Keywords: Bi (III) Electroreduction, Ethionine, Catalytic Activity, Analytical Chemistry, Electrochemistry

References:

1. A. Ciszewski, M. Baraniak, Aktywność Chemiczna i Elektrochemiczna Pierwiastków w Środowisku Wody, Wyd. Politechniki Poznańskiej, Poznań (2006).
2. F. Yoshizawa, S. Mochizuki, M. Doi, I. Yamaoka, K. Sugahara, Biosci. Biotechn. Biochem. (2009) 73 1984 - 1988.
3. A. Nosal – Wiercińska Electroanalysis (2014) 26 1013 – 1023.

Use of Chemometric Approach for a Case Study on Western Turkish Olive Oil Assessed from Adulteration to Authentication

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Nowadays, addressing, classification, and geographical origin of olive oils are of great importance due to their variances in quality, and commercial concerns [1,2]. Quantification of sterols, fatty acids, triacylglycerol, trace elements contents and stable carbon isotope ratios composition of forty-nine virgin olive oils (VOOs) of six different regions of western part of Turkey (i.e. İzmir, Manisa, Aydın, Muğla, Bursa, and Edremit Bay) were performed through chromatographic methods. Variation among the trace elements within the olive oils were believed to be another important avenue were determined, employing an inductively coupled plasma mass spectrometry (ICP-MS). Prior to use of microwave-assisted digestion method, stable carbon isotope ratio profile of olive oil samples from different geographical locations were determined by elemental analyser isotope ratio mass spectrometry (EA-IRMS), quantification of sterol composition and fatty acid methyl esters (FAME) were determined by using gas chromatography (GC-FID) and determination of triacylglycerol was carried out using high performance liquid chromatography (HPLC) [3,4]. Selected data for above olive oil samples were compiled, and classified by statistical methods such as principal components analysis (PCA), and hierarchical cluster analysis (HCA) which were used to evaluate in respect to demonstrate whether significant differences might occur on the basis of principal constituents. As the results showed that incorporation of different types of analytical determination techniques improved ability of analysis to attempt for differentiation of geographical origin of Turkish virgin olive oils, hence, there is a remarkable potential for the adulteration of olive oils according to the quantitative data of FAME and TAG parameters. As a result, the data on parameters such as sterol, trace elements and stable carbon isotope ratios could be unequivocally employ to identify for authentication. Score Plot of PCA and dendrogram of HCA was shown in Figure 1.

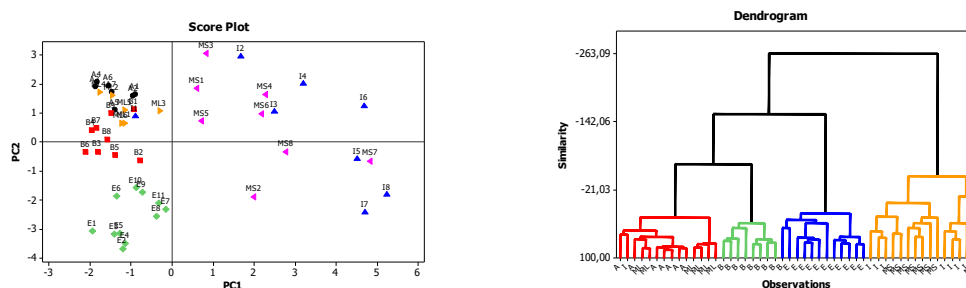


Figure 1. Score Plot of PCA and Dendrogram of HCA.

Keywords: Stable Carbon Isotope Ratios, Trace Elements, Sterol, FAME, TAG, PCA, HCA

References:

1. Spiros A. Drivelos, Contantinos A. Georgiou Trends in Analytical Chemistry (2012) 40 38-51.
2. Federica Camin and et al. Analytica Chimica Acta (2015) 853 384-390.
3. Ioannis Karabigas and et al. Food Research International (2013) 54 1950-1958
4. Ramon Aparicio and et al. Food Research International (2013) 54 2025-2038

Chemometric Approach for the Optimization of Controlled Released Tablets with Respect to Reference Product

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Medicines are usually delivered by different routes in to the human body. Among them, the oral route is by far the most favored way. The most common formulations are solid forms (tablets, capsules and powders). However, disadvantages linked to the administration by conventional dosage forms result not only from the brief duration of activity of medicines and the necessity of repeated intakes but also from the lack of tissular specificity of many pharmacological agents. It is, therefore, interesting to develop new pharmaceutical forms as controlled release (CR) systems. These systems are intended to dispatch or release active drugs at a constant rate directly into the pharmacologically active site. Thus it makes the patient compliance easier (Diarra et al., 2003).

Developing and optimizing a formulation of extended release (ER) tablet is a complex procedure that requires simultaneous determination of several factors. The traditional approach entails studying the influence of the corresponding factors by Changing One Single (or Separate) factor at a Time (COST), whilst keeping the others constant (Barmaplexis et al., 2009).

In this pharmaceutical development study, the optimum ratio of all ingredients in a compressed tablet is therefore, aimed to estimate through a chemometrical approach. The production of controlled released tablet was received great attention since the rate of dissolution of active substance within the body may cause some acute toxicity or even death. Due to the this fact that production of the wet granulated and compressed tablets with optimum concentration levels for each component and active ingredients were targeted during this project to avoid some non-compliance for patients. Three experimental parameters (amount of HPMC K100 M CR, Lactose Monohydrate and Avicel PH 102) to optimize formulation of Niacin 500 mg ER Tablet-Capsule were intended to study using the Fractional Factorial Design Methodology. In all experiments, the amounts of the API (Niacin) and stearic acid were kept constant. According to dissolution profile results it is possible to observe that there was a greater f2 value (f2: 80 and f2: 94) when HPMC K100 M CR amount was at the upper level. When HPMC K100 M CR and Lactose Monohydrate amounts were at the upper level the highest f2 value was obtained. As a result, the main factor effecting to the rate of dissolution was HPMC amount as extended release agent.

Keywords: Niacin, Controlled Release, Wet Granulation

References:

1. Barmaplexis, P., Kanazeb, F.I. and Georgarakisa, E. Journal of Pharmaceutical and Biomedical Analysis (2009) 49 1192–1202.
2. Diarra, M., Pourroy, G., Boymond, C., Muster, D. Biomaterials (2003) 24 1293–1300.

Comparison of Residential VOC Exposure in Different Towns of Çanakkale, Turkey

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Volatile Organic Compounds (VOCs) are including variety of compounds with different functional groups, such as aliphatics, aromatics, and carbonyls. Among them, some compounds are classified as carcinogenic (e.g. benzene) or probable carcinogen due to their adverse health effects. Indoor VOC levels were measured in homes ($n = 6$) of three different towns (*i.e.* rural, urban, and industrial) in Canakkale, Turkey. All indoor environments were selected randomly among the volunteer participants of a previous health survey of *Canakkale HealthAir* Study. Indoor VOC samples were collected once a month from the sampling sites by passive sampling principle throughout a year. VOC samples were collected on to Tenax TA-Carbograph1TD sorbent tubes and analyzed by Thermal Desorber-Gas Chromatography-Flame Ionization Detector. Concentrations of Benzene Toluene, and Xylenes in the passive samples were estimated according to the uptake rates given in ISO standard (ISO, 2003) for the sorbents used in this study. Total volatile organic compounds (TVOC) concentrations were quantified as toluene-equivalent. The highest levels of TVOC, benzene, toluene, and xylenes occurred in industrial, rural, and urban sites, in a descending order. Annual average TVOC levels were found to be higher than $100 \mu\text{g}/\text{m}^3$, while it was as high as $1000 \mu\text{g}/\text{m}^3$ in half of the sampling sites. Benzene levels did not exceed the limit value of 2008/50/EC, $5 \mu\text{g}/\text{m}^3$, in none of the sampling sites. In general, the highest levels for all air pollutants were found in sampling station 5, which was located at an industrial area. Thanks to the one-year round passive sampling of VOCs in this study, it was possible to estimate human exposure accurately in residential environments than grab sampling, taken at any time.

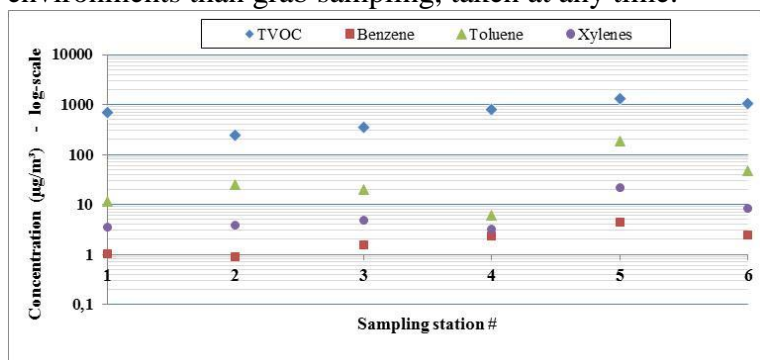


Figure 1. Annual average concentrations of TVOC, benzene, toluene, and xylenes at the sampling sites

Keywords: Indoor Air Pollution Exposure, Passive Sampling, Residential Air Quality, Volatile Organic Compounds.

References:

1. ISO (2003). ISO 16017-2: Indoor, ambient and workplace air-sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography - Part 2, ISO.

Acknowledgement: This study was financially supported by The Scientific and Technological Research Council of Turkey (TUBITAK). Project no: 112Y059.

Enhancing Electrochromic Performance of 2,5-di-(2-thienyl)-1H-pyrrole (SNS) Derivative via Schiff Base Metal Complexes Approach

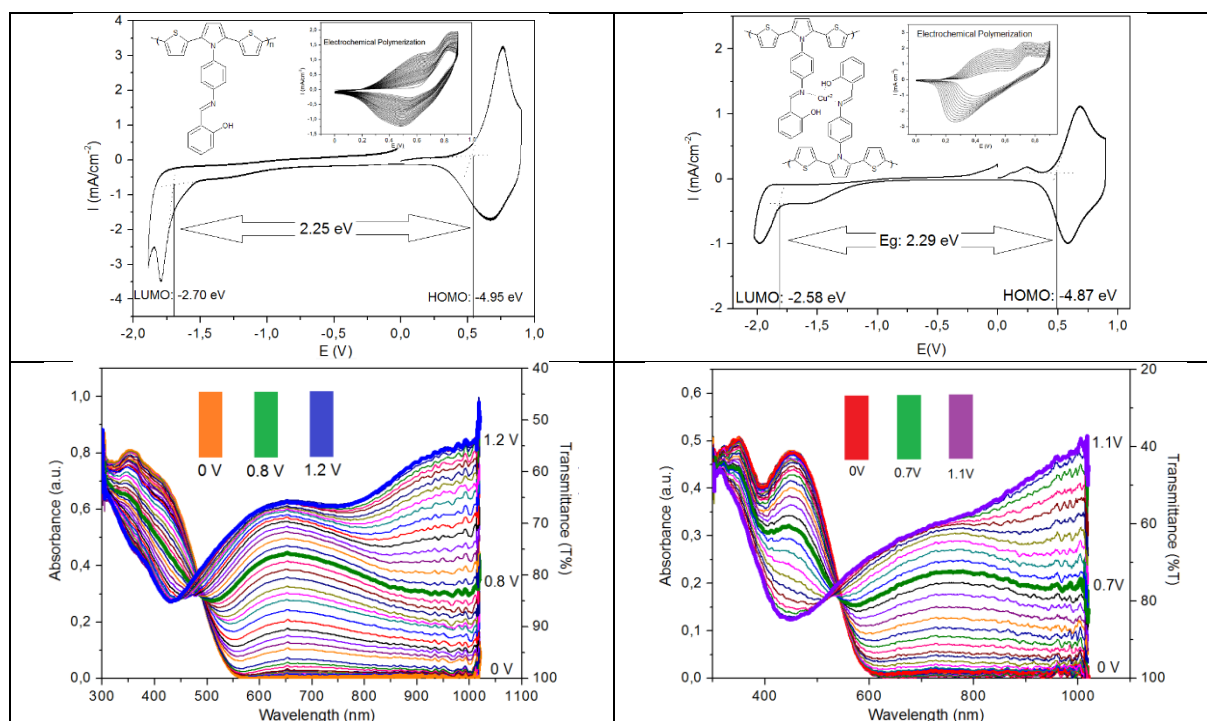
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2,5-di-(2-thienyl)-1H-pyrrole (SNS) derivatives are suitable to use in electrochromic materials due to their easy color tunability, a high contrast ability and a fast response time [1]. On the other hand, the Schiff base polymers containing imine ($-\text{CH}=\text{N}-$) moiety incorporated of nitrogen atoms into the conjugated system have another approach to form classes of materials with interesting electronic and optical properties [2]. Coordinating to various metal ion moieties on Schiff base derivatives, the materials have key roles both in biology as intermediates of many enzymatic reactions, and applications in chemistry, such as in asymmetric catalysis [3].



In this work, we synthesized a 2,5-dithienyl-1H-pyrrole based monomer containing imine subunit (AB53) and then its Cu^{+2} complex was prepared from the Schiff base derivative. Afterward, AB53 and its Cu^{+2} metal complexes directly polymerized on to ITO/glass surface via electrochemical process. The 50 nm bathochromic shift was observed in the neutral state UV-vis absorption spectrum after attaching the Cu^{+2} metal ion on the polymer structure. The results clearly show that the metal complexes approach has been improved the electrochromic performance of the AB53 as electrochromic Schiff base polymer. AB54 coordinating the Cu ion displays a high contrast ratio ($\Delta T\% = 57\%$ at 950 nm), a response time of about 1 s, high coloration efficiency ($316 \text{ cm}^2 \text{ C}^{-1}$) and retained its performance by 97.1% even after 5000 cycles.

References:

1. C.J. Yang, S.A. Jenekhe, *Conjugated Aromatic Polyimines. 2. Synthesis, Structure, and Properties of New Aromatic Polyazomethines*, *Macromolecules*, (1995) 28 1180-1196.
2. T. Kaliyappan, S. Rajagopan, P. Kannan, *New Polymeric Schiff Base and Its Metal Complexes*, *Journal of Applied Polymer Science*, (2004) 91 494 –500
3. P.E. Just, K.I. Chane-Ching, P.C. Lacaze, *Tetrahedron*, (2002) 58 3467–3472

Application of Paracetamol Derived Silver Nanoparticles in Reduction of Organic Dyes

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Chemical reduction process was used for the synthesis of silver nanoparticles. In this method paracetamol was used as a capping source without any stabilizing agent. Atomic Force Microscopy (AFM) confirmed that the synthesized nanoparticles have an average size of 15 ± 2 nm. Interaction of drug with nanoparticles was determined by Fourier transform infrared (FT-IR) Spectroscopy. While X-ray Diffractometry (XRD) showed that the synthesized nanoparticles have crystalline nature, face centered cubic (fcc) geometry and plane orientation with miller indices (111). The controlled shaped silver nanoparticles (Ag NPs) were applied for extremely-fast heterogeneous catalytic reduction of different dyes. The reduction of Eosin B was carried out within 4 minutes and followed first order rate kinetics having R^2 value 0.999. Similarly each paracetamol capped silver nanoparticles (para-Ag NPs) exhibited fast catalytic activity for the reduction of Methylene Blue (MB), Rose Bengal (RB) and Methyl Orange (MO) dyes individually as well as unanimously. The applied nanoparticles were easily recovered and recycled frequently with constant reduction efficiency. Reduction study of dyes follow first order rate kinetics when a graph is plotted between $\log(C/C_0)$ versus time (S).

Keywords: Chemical Reduction, Paracetamol Derived AgNPs, Kinetics, Catalytic Activity.

POSTER SESSION 1

Effects of Solvents, Salts and Sorbents Used to Analysis of Pesticide Residues in Milk by Dispersive Solid Phase Extraction & LC-MS/MS Method

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The aim of this study is to determine the effects of extraction conditions and clean up procedures to analyze the pesticide residues for milk by using LC-MS/MS. The chromatographic analysis was performed by using a mobile phase A of water: methanol with 0.5mM ammonium formate (95:5, v/v %) and mobile phase B of 100% methanol with 0.5mM ammonium formate with a Leapsil C18 column (2.7µm, 50x2.1 mm). A dispersive solid phase method was applied for the extraction and clean-up of pesticide analysis using a mixture of diatomaceous and C18. For this, different solutions such as acetonitrile (ACN) with 1.0% of formic acid (FA); acetonitrile with 1.0% of FA / tetrahydrofuran (THF) (75:25, v/v); ACN with 1.0 % of FA / THF (50:50, v/v); ACN with 1.0% of FA / THF (90:10, v/v); ACN / THF (75:25, v/v) and ACN were used and extraction efficiencies were confirmed. The best results were obtained from extraction of ACN with 1% of formic acid. Different salt types such as Na₂SO₄, MgSO₄ and NaCl were chosen as an extraction salts and extraction efficiencies were confirmed. However, different sorbent types such as PSA, diatomaceous and C18 have been researched and the main effects of these were established by using Minitab 17 software. According to the results, the developed method was applied for the analysis of multiclass pesticide residues in milk.

Keywords: Pesticides, LC-MS/MS, Dispersive SPE, Milk

References:

1. Anna Stachniuk, Emillia Fornal, Food Analytical Methods (2016) 9 1654-1665.
2. Efficchia G. Karageorgou, Victoria F.Samanidou, J.Sep.Sci (2011) 34 1893-1901.
3. Steven J. Lehotay, Journal of AOAC International (2007) 90485-520.
4. Martial Le Doux, Journal of Chromatography A (2011) 1218 1021-1036.

Development of an Analytical Method for the Determination of Valsartan in Commercial Drug and Sewage Sludge Samples by HPLC, and Evaluation of its Stability under Simulated Gastric System

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Angiotensin antagonists have been playing a major role in hypertension management for many years. Valsartan as a member of the angiotensin II type I receptor antagonists class is an effective, highly selective and orally active hypertensive drug. It is known that this active compound reduces blood pressure by blocking the angiotensin II type I receptor, thereby widening the blood vessels and restoring a normal blood flow rate (1,2). Hence, studies regarding the valsartan and its sensitive determination are of interest for many scientists. In this study, an analytical method was developed for determination of valsartan in commercial drug and sewage sludge samples by HPLC-UV using a single wavelength (250 nm). Under the optimum conditions, calibration plot was linear over a wide concentration range with a correlation coefficient of 0.9989. The limit of detection (LOD) and limit of quantitation (LOQ) were found to be 0.014 and 0.046 $\mu\text{g mL}^{-1}$, respectively. In addition, recovery experiment was performed to figure out the effectiveness of the developed method for the determination of valsartan in sewage sludge samples. The percentage recovery of valsartan from sewage sludge was found to be 99.8%. The effect of different environmental storage conditions on the stability of valsartan was examined for a period of 85 days, after which no degradation was observed. The post oral administration stability of the valsartan was also investigated by simulating gastric conditions for valsartan as active ingredient of many drugs. Results showed that the structure of valsartan was conserved over 3.5 hour period.

Keywords: Extraction, HPLC, Gastric Condition, Valsartan

References:

1. Markhan, A., Goa, K.L. *Drugs* (1997) 54 2 299-311.
2. Siddiqui, N., Husain, A., Chaudhry, L., Alam, M.S., Mitra, M., Bhasin, P.S. *Journal of Applied Pharmaceutical Science* (2011) 4 12-19.

Determination of Regional Intestinal Permeability of Valganciclovir and Metoprolol Using a Newly-Developed and Validated High Performance Liquid Chromatographic Method

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Absorption of orally administered drugs could vary at different segment of the small intestine such as duodenum, jejunum, and ileum [1,2]. The knowledge of the site of absorption of a drug and absorption characteristics in the intestine is especially important for the development of modified release formulations [3]. Since the small intestinal transit of drug formulations is about 3 - 4 h, significant part of the dose of drug in a modified release product can possibly reach the colon. This means that the absorption of the drug which is used for modified release formulations has to be classified as high permeability in the entire intestine. It is important to understand the absorption characteristics in the entire intestinal tract for BCS class II and III drugs, in order to identify and develop strategies for modified release formulations [4].

Valganciclovir (VGC, 2-[(2-amino-6-oxo-6,9-dihydro-3H-purin-9-yl)methoxy]-3-hydroxypropyl-(2S)-2-amino-3-methylbutanoate) is an orally administered prodrug of the standard anti-cytomegalovirus (CMV) drug ganciclovir.

The aim of this study was to determine segmental permeability and absorption characteristics of valganciclovir using a newly developed and validated reversed-phase liquid chromatographic method for the simultaneous determination of valganciclovir, metoprolol tartrate and phenol red in intestinal perfusion samples. In these studies, metoprolol tartrate was used as a reference standard to compare the permeability coefficient of diclofenac. Phenol red was used as a zero permeability marker for correction of permeability coefficient for water transport [2].

Keywords: Valganciclovir, Metoprolol Tartrate, Segmental Permeability, Intestinal Absorption,

Acknowledgments: This work was supported by TÜBİTAK (project 211T-007)

References:

1. Amidon GL, Lennernas H, Shah VP, Crison JR. Pharm. Res. (1995) 12 413-420.
2. Zakeri-Milani P, Valizadeh H, Azarmi Y, Jalali MB, Tajerzadeh H. DARU (2006) 14 102-108.
3. Nagare N, Damre A, Singh KS, Mallurwar SR, Iyer S, Naik A, Chintamaneni M. Indian Journal of Pharmaceutical Sciences (2010) 72 625-U315.
4. Lennernas H, Abrahamsson B. J Pharm Pharmacol (2005) 57 273-285.

Development and Validation of an HPLC Method for Determination of the Eplerenone in Rat Plasma

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Eplerenone (EP) is an antihypertensive agent in the pharmacological group of selective aldosterone receptor antagonists (SARAs). The chemical structure of EP, pregn-4-ene-7,21-dicarboxylic acid, 9,11 –epoxy-17-hydroxy-3-oxo, γ -lactone methyl ester (7 α , 11 α , 17 α) which is very similar to the spironolactone. EP is slightly soluble in water and its solubility is independent from pH [1, 2].

In the terms of biopharmaceutics, low water soluble active agents could not offer an effective therapy for the patients. To overcome bioavailability problems related to low solubility of drugs, there are some alternative ways like chemical and polymorphic modifications of drugs or designing appropriate pharmaceutical dosage forms. Designing novel dosage forms of low water soluble drugs is smart way to achieve an effective treatment.

To provide an effective treatment, colloidal drug carrier systems of EP were prepared in this study. Loading capacity and encapsulation efficiency of these carriers and in vitro drug release profiles and in vivo evaluation of formulations were highly depend on a reliable quantitative analytical method.

There are a few methods for the quantitative determination of EP [3-7]. These methods mostly include expensive instruments such as LC – MS, but one exception using high performance liquid chromatography (HPLC) with UV detection was found [7]. Whereas, to assess in vivo performance of EP formulations in rats, the method was not sufficient to provide specificity. Thus, a new specific method for EP detection was needed by using the simple extraction (liquid – liquid extraction) and detection (HPLC – UV) techniques.

To achieve a specific and simple quantification of EP in the rat plasma, a HPLC method with UV detection (241 nm) was developed and validated. To provide a calibration curve, EP spiked rat plasma samples were prepared. Then, spiked plasma was extracted with a dichloromethane and diethyl ether mixture (4:6). A C-18 column (50 mm x 4,6 mm, 2,7 μ m) was used for HPLC analysis. A mobile phase consisting acetonitrile:water (20:80, v/v) was applied at a flow rate of 1mL/min. The calibration curve was linear in the range of 50 – 5000 ng/mL.

References:

1. Delyani JA, Rocha R, Cook CS, Tobert DS, Levin S, Roniker B, Workman DL, Sing YL, Whelihan B, Cardiovascular Drug Reviews, (2001) 19 185 - 200.
2. Seferovic PM, Pelliccia F, Zivkovic I, Ristic A, Lalic N, Seferovic J, Simeunovic D, Milinkovic I, Rosano G., International Journal of Cardiology, (2015) 200 3-7.
3. V. P. Rane, K. R. Patil, J. N. Sangshetti, R. D. Yeole, D. B. Shinde, Acta Chromatographica, 2009. 21 4 619-629.
4. Zhang, J.Y., D.M. Fast, and A.P. Breau, J Pharm Biomed Anal, (2003) 31 1 103-15.
5. Zhang, J.Y., D.M., J Chromatogr B Analyt Technol Biomed Life Sci, (2003) 787 2 333-44.
6. Sonawane, S. and P. Gide, Journal of Liquid Chromatography & Related Technologies, (2011) 34 17 2020-2031.
7. Gide, P., S. Sonawane, and A. Chitnis, Journal of Pharmaceutical Analysis, (2012) 2 5 390-393.

Determination of Neurotransmitters in Cerebrospinal Fluid Samples by Using HPLC-FLD: Calculation of Uncertainty Budget

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Neurotransmitters are the primary chemical messengers that are synthesized in a neuron and released from synapses¹. Determination of neurotransmitters need continuous measurement and microdialysis sampling technique is a good technique for that purpose². However, the concentration of the neurotransmitters in the extracellular space is very low³ and microdialysis samples have also very small volumes. On the other hand, fluorescence detection give an opportunity for trace level analysis in complex matrices. Because it has higher sensitivity and selectivity. Therefore, a modified method was validated for the determination of well-known neurotransmitters like serotonin, noradrenalin and gamma- aminobutyric acid (GABA), glutamate and melatonin hormone with high performance liquid chromatography-fluorescence detection (HPLC-FLD) and uncertainty of the method was calculated. GABA and glutamate were determined by using derivatization step. Sensitivity, method detection limit, limit of quantification, linearity, recovery, interday and intraday precision values were calculated. Low detection limit values were obtained especially for the determination of GABA and glutamate. Uncertainty budget was done by using bottom-up approach. The critical stages of the method were evaluated. Calibration curves, stock solution and recovery were the critical stages for the analysis. The calculated percentage relative uncertainty values for the compounds changed between 10.1 and 16.7.

Keywords: Neurotransmitters, Microdialysis, HPLC-FLD, Uncertainty, Method Validation.

References:

1. Siegel A, Sapru HN (2006) Essential Neuroscience, Lippincott Williams & Wilkins, USA.
2. Chefer VI, Thompson AC, Zapata A, Shippenberg TS Overview of brain microdialysis. Current Protocols in Neuroscience (2009) John Wiley & Sons Inc., UK.
3. Shah AJ, de Biasi V, Taylor SG, Roberts C, Hemmati P, Munton R, West A, Routledge C, Camilleri P Journal of Chromatography B (1999) 735 133-140.

Simultaneous Determination of Troxerutin and Carbazochrome by High-Performance Liquid Chromatographic Method

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Flavonoids, such as troxerutin, are safe and effective agents for the treatment of chronic venous insufficiency. The fixed combination between troxerutin and carbazochrome has a good efficacy and safety profile in non-surgical patients with acute uncomplicated hemorrhoids. Therefore it is important to develop simultaneous analysis method of those drug substances.

In this study, a simple and selective HPLC method was developed for the analysis of troxerutin and carbazochrome in tablets. The method was based on separation by using a mobile phase (MeOH; %5'lik HAc), (99,5:0,5-V/V) and core-shell Pentafluorophenyl Propyl polar column. The mobile phase flow rate was 0.25mL/min. The substances were detected at 350 nm. The linearity ranges were found as 1,00-20,00 µg/mL for troxerutin and, 0,05-1,00 µg/mL for carbazochrome. The limits of detection and quantification were found to be 0,65 µg/mL and 1,00 µg/mL for troxerutin and ;0,05 µg/mL and 0,01 µg/mL for carbazochrome, respectively. The proposed method was successfully validated and can be applied for the determination of tablets.

Keywords: Troxerutin, Karbazokrom, HPLC, Simultaneous Analysis

References:

1. Basile M. , Gidaro S. Current Medical Research and Opinion (2001) 17.4 256-261
2. Hepsebah N. J. R., Nihitha, D. International Journal of Pharmacy and Pharmaceutical Sciences (2014) 1 0975-1491
3. Hu Xingjiang, Zheng Yunliang Journal of chromatography. B Analytical technologies in the biomedical and life sciences (2014) 1 951-952

Determination of Chondroitin Sulfate, Glucosamine and Hyaluronic Acid from Supplements for the Treatment of Osteoarthritis by High Performance Liquid Chromatography

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Glycosaminoglycan and amino sugar are widely used dietary supplements and injectable form for the treatment of osteoarthritis. Determination of these Polymeric molecules were important for quality control and stability analysis of supplements.

In this study, high performance liquid chromatography method has been developed for determination of chondroitin sulfate, glucosamine and hyaluronic acid. separation of molecules by using Phenomenex Polysep GFC-P-5000 column with deionized water based mobile phase. UV detector was set at 205 nm wavelength. The linear range was found 0,0275-0,88 mg/mL for chondroitin sulfate, 0,005-0,16 µg/mL for glucosamine and 0,02-0,64 mg/mL for hyaluronic acid. The developed method has been validated and successfully applied to preparats . This method is simple, reproducible and can be used safely routine analysis.

Keywords: Chondroitin Sulfate, Glucosamine, Hyaluronic Acid, HPLC-UV

References:

1. Ghada M. Haddad, Randa A. Abdel-Salam Journal of Chromatographic Science (2011) 50 307-315.
2. Ichiro Koshishi, Michinari Takenouchi Analytical Biochemistry (1998) 265 49-54.

Determination of Eugenol by HPLC with Electrochemical Detection in Some Plants

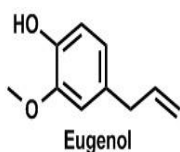
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Eugenol consuming in small amount gives the advantage of anti-microbial, anti-bacterial and anti-fungal properties, additional to this, eugenol antibacterial and antifungal activity is very helpful in treating many digestive problems such as diarrhea, gas, bloating, ulcers, and candida. Eugenol rich black paper and clove can increase the release of gastric acid, which help digest food and kill intestinal bacteria in the stomach. However, exceeding the limit of eugenol causes various harmful effects. Although Eugenol is nominated as SAFE to consume at some extent by FDA (Food and Drug Administration) but exceeding the limited amount very serious and fatal results can be seen. These limitations of eugenol make its quantitative analysis more considerable and of great interests [1, 2].



Electrochemical detection for HPLC is an extremely selective and sensitive detection technique. In this study, electrochemical properties of eugenol were observed on a modified carbon paste electrode by using cyclic voltammetry and determined the optimum conditions for the peak current and then an HPLC with electrochemical detection method was presented for the determination of eugenol. A modified carbon paste electrode was used as a working electrode. The electro-oxidation reaction mechanism of eugenol at the carbon paste electrode was determined. It was found that the oxidation peak current about 0.85 V can be used for quantitative determination of eugenol, with an ascertic acid, methanol, and acetonitrile system. Eugenol determined under optimum conditions obtained in clove, peppermint, sweet basil, cinnamon, black pepper, and bay leaf samples.

Keywords: Eugenol, HPLC, carbon paste electrode

References:

1. D. Afzali, S. Zarei, F. Fathirad, A. Mostafavi, Mater. Sci. Eng. (2014) 100 1-12.
2. G. Ziyatdinova, E. Ziganshina, H. Budnikov, Analytical Methods, (2013) 18 4750-4756.

Simultaneous Determination of Sildenafil and Tadalafil in Legal, Illicit/Counterfeit Drugs and Waste Water Samples by High Performance Liquid Chromatography

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Sildenafil and tadalafil are very popular chemicals which have been widely used to treat the male erectile dysfunction (1, 2). They are also used in the treatment of premature infants having severe respiratory failure and children with primary and post-surgical pulmonary hypertension or severe lung fibrosis (1,3). Hence, sensitive and accurate determination of these analytes in variety of matrices are very important. In this study, a sensitive analytical method was developed to determine sildenafil and tadalafil in legal, illicit/counterfeit drugs and waste water samples. Analytes were separated from each other in six minutes using 50 mM phosphate buffer at pH 6.0 and acetonitrile (35:65, v/v) at the flow rate of 1.0 mL/min. Limit of detection (LOD)/limit of quantitation (LOQ) values were found to be 28/92 ng/mL for sildenafil citrate and 39/129 ng/mL for tadalafil. Validated method was successfully applied to legal and illicit erectile dysfunction drugs samples consumed in İstanbul/Turkey and waste water samples. In order to calculate the recoveries of analytes from waste water samples, spiking experiment was performed and recoveries for sildenafil and tadalafil were calculated as 101.30 ± 3.43 and 102.68 ± 1.59 , respectively.

Keywords: HPLC, Sildenafil, Tadalafil, Drug, Waste water

References:

1. Strach, B., Wyska, E., Pocięcha, K., Krupa A., Jachowicz, R. Biomedical Chromatography (2015) 29 1559-1566.
2. Lee, J.H., Kim, H.J., Noh, E., Kim, J.Y., Cho, S.H., Do, J.A., Yoon, C.Y., Cho, S., Kim., W.S. Journal of Pharmaceutical and Biomedical Analysis (2015) 103 80-84.
3. Uthayathas, S., Karuppagounder, S.S., Thrash, B.M., Parameshwaran, K., Suppiramaniam, V., Dhanasekaran, M. Pharmacological Reports (2007) 59 150-163.

Development and Validation of a Simple and Rapid HPLC Method for the Determination of Iloperidone in Tablets

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Iloperidone (ILO) is an antipsychotic drug used in the acute treatment of schizophrenia in adults¹. In this study a new method was developed for determination of ILO in its tablets. The developed method was validated according to the ICH guideline² in terms of linearity, precision, accuracy, specificity, stability and robustness.

An Agilent 1290 Infinity Binary LC system (equipped with a binary pump, a degasser, an autosampler and a thermostatted column compartment) was employed for analyses. Separation was performed on an Zorbax Eclipse Plus C-18 (4.6 x 100 mm, 3.5 µm particle size) column using a mobile phase consisted of phosphate buffer (pH:3, 20 mM) and acetonitrile. Flow rate was 1 mL/min and column temperature was set at 35 °C. UV detection was performed at 274 nm and carbamazepine (CBZ) was used as internal standard.

Retention times of ILO and CBZ were 2.83 and 3.48 minutes respectively and total run time of the method was 10 minutes (Figure 1). The method was found to be linear in the concentration range of 0.5-100 µg/mL for ILO. Mean equation of the calibration curve was $y = 0.1576x - 0.1506$ ($R^2 = 0.9985$). The intra- and inter-day relative standard deviations were less than 3 % and mean recovery was found 102.78 %. All other validation parameters were within acceptable limits. The developed method was successfully applied for determination of ILO in its tablets.

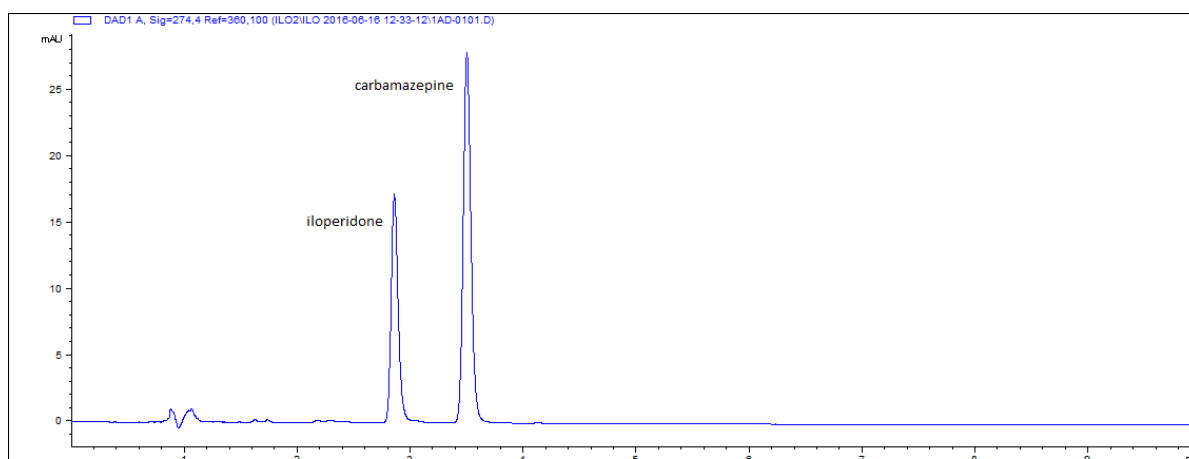


Figure 2. Chromatogram of 4 µg/mL ILO and 5 µg/mL CBZ (as internal standard).

Acknowledgments

The authors appreciate Research Council of Anadolu University for the support of the Project (Project No: 1302S023).

Keywords: Iloperidone, HPLC, Tablet Analysis.

References:

1. Crabtree, B.L., Montgomery, J., Clinical Therapeutics (2011) 33(3) 330-345.
2. ICH, Harmonized Tripartite Guideline, Validation of Analytical Procedures: Text and Methodology (2005), Geneva.

A Novel and Sensitive Chromatographic Method Based on HPLC for Simultaneous Determination of Abacavir and Lamivudine in Pharmaceutical Dosage Form

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Herein, we developed a facile, sensitive and reliable reversed-phase high performance liquid chromatography (RP-HPLC) method for simultaneous determination of abacavir (ABA) and lamivudine (LMV) in pharmaceutical dosage form. Chromatographic separations of ABA and LMV were successfully achieved on an Agilent Zorbax CN column with an isocratic mobile phase composed of a mixture of methanol: ammonium acetate (pH: 4.0; 0.015 M) (55:45, v/v) at a flow rate of 1.0 mL min⁻¹. The drugs were analyzed using a photodiode array detector set at a wavelength of 275 nm. The RP-HPLC method has been validated as per International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use guidelines to determine ABA and LMV in pharmaceutical sample. Under optimized conditions, RP-HPLC method exhibited the wide linear working regions in the range of 0.6-75.0 ppm for ABA and 0.3-75.0 ppm for LMV with the low detection limits of 24.0 ppb and 38.0 ppb, respectively. The proposed chromatographic method was successfully applied to the quantitative determination of the ABA and LMV in the laboratory-prepared mixtures with good recoveries. The fully-validated HPLC method could be promising analytical tool for routine simultaneous analysis of ABA and LMV in pharmaceutical or clinical samples.

Keywords: Abacavir, Lamivudine, HPLC, Determination, Validation

References:

1. Sweetman SC (2002) Martindale: The complete drug reference, 33rd Ed., Pharmaceutical Press, London.
2. W. Kromdijk, S.A. Pereira, H. Rosing, J.W. Mulder, J.H. Beijnen, A.D.R. Huitema, Journal of Chromatography B (2013) 919 43–51.
3. D.A. Kumar, G.S. Rao, J.V.L.N.S. Rao, E-Journal of Chemistry (2010) 7 180-184.
4. J.P. Vicente, M.V. Traver, I.C. Breva, S.C. Broch, J.E. Romero, Journal of Pharmaceutical and Biomedical Analysis (2014) 98 351–355.

Determination of Itraconazole from Caco-2 Cells Using High-Performance Liquid Chromatography

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The purpose of this study is to develop an accurate, precise, sensitive and selective HPLC method for determination of itraconazole from Caco-2 cells. As itraconazole was absorbed from the proximal part of the small intestine, controlled release dosage forms that are floating in the stomach were designed to increase the absorption. To investigate the permeability behaviour of itraconazole especially in the upper part of small intestine, Caco-2 cells were used (1). Before the experimental section, apical and basolateral area were submitted to Hank's Buffered Salt Solution (HBSS) (pH 5, 6 and 7.4) media. After 30 minutes of preincubation, all the media was removed. Prepared samples were added to the apical (pH 5, 6 and 7.4) and basolateral parts (pH 7.4), incubated for 2 h at 37°C, 50-60 rpm. After 2 h, samples were taken from the basolateral section and HPLC analysis of itraconazole were performed (2,3). Waters Symmetry C18 (250 x 4.6 mm (id), 5µm) column was used and isocratic elution was performed using Acetonitrile: H₂O (0.25% Na Acetate) (70:30) mobile phase with a flow rate of 1 mL/min. Measurements were done at 260 nm using DAD. Rt value of itraconazole was determined as 8.5 min. The slope and interception values of the calibration equation were 4091.6±0.0098 and -0.465 ±0.0028, respectively. For the accuracy test, three different concentrations (15 µg/mL, 75 µg/mL, 250µg/mL) of itraconazole were analyzed and recovery % values were determined as 75.92±1.09, 100.46±1.24 ve 99.90±1.15, respectively. LOD and LOQ values were 0.456 µg/mL ve 1.383 µg/mL, respectively. Consequently, in the permeability studies with both itraconazole powder and ideal formulation, the formulation at pH 5, which is the pH of the proximal region, showed the highest (two times of the itraconazole powder permeability) permeability value.

Keywords: Itraconazole, Caco-2 cells, HPLC, Validation

References:

1. Artursson P, Karlsson J. Biochem. Biophys. Res. Commun. (1991) 175 880-885.
2. Neuhoff, S., Ungell, A.L., Zamora, I., Artursson, P. Pharm. Res. (2003) 20 1141-1148.
3. Neuhoff, S., Ungell, A.L., Zamora, I., Artursson, P. Eur. J. Pharm. Sci. (2005) 25 211-220.

Microwave-Assisted Extraction Technique for the Determination of benzo(a)pyrene (BaP) by HPLC- Fluorescence Detection in Turkish Black Tea

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What Turkish people and the other people in the world commonly consumed is the black tea, which is a favourite drink in the world. Scientists have carried out a lot of researches about the effects of black tea on people's health, such as cancer and blood pressure[1]. However, researches show that there can be some toxic and carcinogenic contaminants like pesticide residues or polycyclic aromatic hydrocarbons (PAHs) in tea leaves [2]. Especially traditional tea is dried by using combustion gases obtained from burning wood, oil or coal and so causing tea leaves being contaminated by PAHs [1].

When compared with traditional extraction, it is shown that microwave-assisted extraction(MAE) uses smaller volumes of solvent and is faster, with having similar or better recoveries [3]. We demonstrate the applicability of MAE to extract benzo(a)pyrene (BaP) from tea samples.

Several extraction solvents, used frequently in the MAE studies, were investigated, including hexane/water, hexane/acetone, hexane/acetonitrile, dichloromethane (DCM), dichloromethane/acetonitrile. In our trials, the volume of solvent (5-10-15 mL) used for extractions as well as the MAE time (1-2-3-4 min) were optimized.

Tea samples were spiked (before being extracted) with known concentrations of BaP. The recoveries of BaP achieved ranged from 46.30 ± 0.75 to 103.83 ± 2.05 —%. Hexane/acetonitrile was chosen as the extraction solvent due to its high extraction efficiency. Approximately 1.0 g of tea was extracted twice by microwave (at the irradiation power of 180 W) with 10 mL of the selected solvent for 2 min. The extract was filtered and evaporated to dryness using a rotary evaporator, and the residue obtained was dissolved in 8 mL acetonitrile and transferred for HPLC analysis.

Keywords: Tea, BaP, Microwave-assisted Extraction, HPLC

References:

1. I. S. Grover, S. Singh, B. Pal. Environ Monit Assess (2013) 185 6291–6294.
2. L. Drabova, J. Pulkrabova, K. Kalachova, M. Tomaniova, V. Kocourek, J. Hajslova. Talanta 100 (2012) 207–216.
3. X. Li, N. Li, H. Luo, L. Lin, Z. Zou, Y. Jia, Y. Li, J. Agric. Food Chem. (2011) 59 5899–5905.

Ultrafiltration-Based Extraction and High - Performance Liquid Chromatographic Analysis of Ceftriaxone in Human Plasma and Perilymph Fluid Samples

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Ceftriaxone (CEF), a semisynthetic 3rd generation cephalosporin, is effective against a wide variety of Gram-positive and Gram-negative bacteria [1]. It is indicated in several infectious diseases. The administration of CEF may reduce the incidence of postoperative infections in patients undergoing surgical procedures [1, 2]. The usage of CEF in some clinical applications on infectious diseases (like labyrinthitis) of inner ear and meningitis is known, but the concentration of CEF in human plasma and perilymph fluid at the same time has not been investigated yet. The developed method in this study is the only reported method up to date for determination of CEF in plasma and perilymph fluid and it could be adapted for further clinical applications to investigate the concentration of CEF in different subjects. In this study, an ultrafiltration-based extraction technique was developed as an alternative to solid phase extraction of ceftriaxone prior to HPLC analysis. HPLC analysis was carried out on Nucleosil C18 100-3 (125 mm x 4.6 mm, 5 µm i.d.) column with a mixture of methanol:citrate buffer (30 mM, pH 3.0) (25:75, v/v) as the mobile phase using isocratic elution. The flow rate was 1.0 mL min⁻¹, injection volume was 20 µL, and UV detection was performed at 270 nm. The plasma and perilymph fluids of sensorineural hearing loss patients intravenously administered CEF were taken [3]. The developed ultrafiltration-based extraction technique was applied for determination of CEF in human plasma. Perilymph fluids, direct injected without any sample pretreatment, were analyzed. The extracted human plasma samples and perilymph fluids were analysed by HPLC. CEF level in human plasma samples and perilymph fluids were compared within each other.

Keywords: Ceftriaxone, Plasma, Perilymph Fluid, Clinical Application, HPLC.

References:

1. Cleeland R., & Squires E. Am. J. Med. (1984) 77 3-11.
2. Yuk J.H., Nightingale C.H. & Quintiliani R. Clin. Pharmacokinet. (1989) 17 223-235.
3. Conlin A.E. & Parnes L.S. Arch. Otolaryngol. (2007) 133 573-581.

Development of a High-Performance Liquid Chromatography Method Based on a Core-Shell Column Approach for the Determination of Clotrimazole

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Clotrimazole (CLO, Fig. 1), 1-[(2-chlorophenyl)diphenylmethyl]-1*H*-imidazole, is relatively non-toxic synthetic imidazole derivative with broad-spectrum of antimicrobial activity, first described in 1969. It is a well-established drug used in dermatology and gynaecology, available in the form of tablet, cream and solution formulations. Ointments containing CLO are widely used for the treatment of various systemic mycoses including candidiasis; the compound is highly effective, but can cause liver enzyme changes [1].

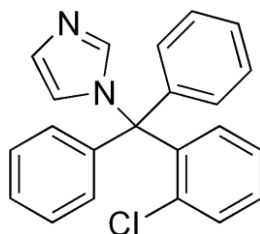


Figure1: Clotrimazole

Reversed-phase liquid chromatography (RPLC) is an essential analytical technique used in pharmaceutical analysis. The traditional packed columns still dominate the market, but in the last decade columns packed with sub-2 μm particles columns, short columns packed with nonporous or core-shell (superficially porous) particles are gaining popularity. Sub-2 μm particles columns require a dedicated instrumentation that can work at very high pressure (up to 1200–1300 bar), and therefore this technique has been called ultrahigh-performance liquid chromatography (UHPLC). The modern sub-3 μm core-shell particles columns can be used on conventional HPLC instrument, with a maximum pressure of 300 bar [2]. In this study a simple isocratic HPLC method with DAD detection for the determination of clotrimazole is developed using Agilent Poroshell 120 EC- C_{18} 2.1x100mm column with particle size 2.7 μm . The mobile phase consists of a mixture of acetonitrile and buffer at pH:7.0 (45:55). At a flow rate of 0.5 mL min^{-1} , detection at 220 nm, column set at 40°C total analysis time is less than 10 minutes.

Keywords: Clotrimazole, RP- HPLC, core-shell column, pharmaceuticals

References:

1. Renata Hájková, Hana Sklenářová, Ludmila Matysová, Petra Švecová, Petr Solich, Talanta (2007) 73 483-489.
2. Szabolcs Fekete, Erzsébet Oláh, Jenő Fekete, Journal of Chromatography A (2012) 1228 57-71.

Comparison of Three Different HPLC Analytical Columns for the Simultaneous Analysis of Methylprednisolone Aceponate and Benzyl Alcohol

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Methylprednisolone aceponate (MPA) is a nonhalogenated diester of 6 α -methylprednisolone which, based on its anti-inflammatory activity, has been classified as a potent glucocorticosteroid. MPA is a corticosteroid with two open-chain ester groups at position 17 and 21. It is therapeutically used for topical treatment of various forms of dermal eczema as well as of sunburn, psoriasis and atopic dermatitis. The introduction of 2 ester groups results in a molecule with increased lipophilicity, and enhanced penetration into skin [1].

Benzyl alcohol (BA) is prepared by the distillation of benzyl chloride with potassium or sodium carbonate. BA is a clear, colorless, oily liquid with a faint aromatic odor and a sharp, burning taste. It can oxidize slowly in air to benzaldehyde and benzoic acid. It does not react with water and can be stored in metal or glass containers. Usually methyl hydroxybenzoate and propyl hydroxybenzoate are used together since they have a synergistic effect. BA using as the preservative of lotion and cream form [2,3].

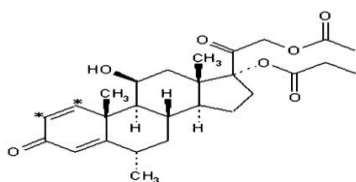


Figure1: Methylprednisolone Aceponate

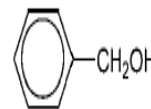


Figure2: Benzyl Alcohol

Best practices in method development and validation is equally important in the analysis of both active components and preservatives/excipients (inactive ingredients) used in the manufacturing of drug products. Preservatives are an important class of chemicals used to inhibit the growth of microorganisms harmful to industrial products [3].

Methylprednisolone aceponate which is a active ingredients use in eczema cream, benzyl alcohol was used as preservatives. Therefore simultaneous analysis of MPA and BA is important. In recent years, core-shell silica particles (solid core and porous shell or superficially porous) have been increasingly used for highly efficient separation with fast flow rate and relatively low back pressure. Core-shell column have a higher resolving power than the flat-C₁₈ column [4]. Three different columns were compared: ACE C₁₈ 4.0x250mm 5 μ m, Agilent Poroshell 120 EC-C₁₈ 2.1x100mm 2.7 μ m, Agilent Poroshell 120 Phenyl Hexyl 2.1x100mm 2.7 μ m.

Keywords: Methylprednisolone Aceponate, Benzyl Alcohol, HPLC, Core-Shell, Simultaneous Analysis

References:

1. Matthias Koitka, Joachim Höchel, Hille Gieschen, Hans-Hubert Borchert, Journal of Pharmaceutical and Biomedical Analysis (2010) 51 664-678.
2. George C Wood, Meera R Iyer, Arthur M Geller, Albert M Fleischner & Bhogi B Sheth, Journal of Liquid Chromatography & Related Technologies (2006) 46 1951-1961.
3. Ghulam A. Shabir, Journal of Liquid Chromatography & Related Technologies (2007) 69 2183-2190.
4. Richard Hayes, Adham Ahmed, Tony Edge, Haifei Zhang, Journal of Chromatography A (2014) 1357 36-52.

A Simple and Rapid Determination of Folic Acid in Certain Malt-based Beverages by Ultra-High Performance Liquid Chromatography

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Folic acid (FA) is a water soluble vitamin in B-group and it is vital for living organisms. FA deficiency causes some critical diseases including gigantocytic anemia and leukopenia, neural tube defects (NTDs), coronary heart disease, stroke, Alzheimer's disease in the elderly, psychosis, and certain forms of cancer such as pancreatic, colorectal and breast cancers [1-4]. Therefore, analysis of FA with a reliable analytical method is very important. In this study, an efficient and a rapid UHPLC-UV method is developed for FA analysis in malt-based beverages. The analysis was performed in an Eclipse Plus C18 column (2.1x50 mmx1.8 µm) with a guard column (2.1x5 mmx1.8 µm) using a solvent system of ACN: 0.1 % formic acid in water (10:90, v/v) by isocratic elution. Injection volume was 5 µl. The flow rates of the mobile phase were maintained at 0.2 mL min⁻¹ for 0.00–4.00 min and 0.5 mL min⁻¹ for 4.01–12.00 min. Methyl paraben was used as the internal standard (IS). The FA and IS signals were detected at 284 nm and 254 nm, respectively. Under these conditions, FA and IS were separated in 3.6 min and 11.4 min, respectively. The method was successfully validated in terms of precision, accuracy, linearity, limits of detection (LOD) and quantification (LOQ). The relative standard deviations for intra- and inter-day precision were less than 1.5%. The proposed method was successfully applied for the determination of FA in malt beers and alcohol free malt drinks.

Keywords: Folic acid, UHPLC, Malt-Based Beverages, Validation

References:

1. S., Zhao, H., Yuan, C., Xie, D., Xiao J. *Chromatogr. A* (2006) 1107 290–293.
2. V., Fajardo, E., Alonso-Aperte, G., Varela-Moreiras J. *Food Comp. Anal.* (2012) 28 155–163.
3. M., Edelmann, S., Kariluoto, L., Nyström, V., Piironen J. *Cereal Sci.* (2013) 58 37–44.
4. P., Pantuckova, L., Krivankova *Electrophoresis* (2010) 31 3391–3399.

Determine of Inulin, Fructose, Glucose and Sucrose in Roots of Chicory (*Cichorium Intybus*) using RP-HPLC-RID

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Chicory (*Cichorium intybus*) is cultivated for its roots which are the main source of inulin that is a beneficial effects on human health and used in the food industry to improve organoleptic characteristics, to balance the nutritional value, to replace fats and to enrich products with dietary fibers^{1,2,3,4}. The chicory roots are contains a small amounts of free monosaccharide (fructose, glucose and sucrose) and a lot amount of oligosaccharide (inulin)³. Inulin is consists of twenty two to fifty fructose molecules connected by β -(2→1) bonds and one glucose molecule at the end⁵. A newly developed high performance liquid chromatography method is carried out on an Inertsil-NH₂ column (4.6 x 250 mm) to measure simultaneously of free monosaccharide and inulin in roots of chicory using refractive index detector. The method ensures adequate sensitivity, quantitative recoveries, does not suffer from matrix interferences and shows good repeatability. The amount of inulin found after thermal treatment (80°C, 2 hours) measured as fructose after acidic hydrolysis (HCl 0.3 mol L⁻¹) was significantly lower compared with corresponding data obtained with a method based on direct analysis. The investigated concentration ranges of inulin from 29 samples were (89.1–167.5 g kg⁻¹), and of fructose, glucose and sucrose were (1.5–5.7, 0.09–1.65 and 3.7–9.6 g kg⁻¹, respectively), good linearity ($R^2 \geq 0.998$) was obtained. Analytical recoveries were 81.1–109.3%. An internal standard of rhamnose was used to quantify free monosaccharide. The limits of detection for Rhamnose (I.S), inulin, fructose, glucose and sucrose were 0.03, 0.23, 0.30, 0.40 and 0.18 g kg⁻¹, respectively with average RSDs 1.35% for repeatability and 5.2% for reproducibility.

Keywords: Chicory (*Cichorium intybus*), Monosaccharide, Oligosaccharide, RP-HPLC-RID.

References:

1. A. Bohm, I. Kaiser, A. Trebstein, T. Henle. European Food Research and Technology (2005) 220 466–471.
2. Michael Ernst, N. Jerry Chatterton, Philip A. Harrison. Scientia Horticulturae (1995) 63 251–261.
3. Nadezhda Petkova, Panteley Denev. International Scientific-Practical Conference "Food, Technologies & Health" (2015) Proceedings Book, Plovdiv.
4. Bao-Lam Huynh, Lachlan Palmer, Diane E. Mather, Hugh Wallwork, Robin D. Graham, Ross M. Welch, James C.R. Stangoulis. Journal of Cereal Science (2008) 48 369–378.
5. Pawel Glibowski, Adam Wasko. International Journal of Food Science and Technology (2008) 43 2075–2082.

A Validated Stability Indicating HPLC Method for Determination of A New Serotonergic Antidepressant Vortioxetine Active Pharmaceutical Ingredient and Its Pharmacuetical Dosage Forms

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An isocratic stability indicating reversed-phase liquid chromatographic determination was described for the determination of vortioxetine in bulk and its pharmaceutical formulations. Chromatographic quantitation of vortioxetine was developed on Waters Symmetry C₁₈, (100 x 4,6 mm, 3.5 µm) column using methanol and 0.05 M potassium dihydrogen phosphate (pH:3.0±0.5) (70:30, v/v) as mobile phase with flow rate of 1.3 mL·min⁻¹, loop of 20 µL, UV detection at 225.0 nm and column at 50°C temperature. The internal standard method using caffeine as the internal standard is used. The method was applied in the concentration ranges of 10.0 - 70.0 µg.mL⁻¹ (r: 0.9998), and the mean recovery value was 100.7 % .Besides stability tests were done through exposure of the analyte solutions to different conditions: acid, alkali hydrolysis, chemical oxidation and exposure to UV radiation. The performance of the method was validated according to the present ICH guidelines for specificity, limit of detection, limit of quantification, accuracy, and precision.

Keywords: Vortioxetine, Caffeine, Pharmaceutical Formulation, Stability Indicating, Validation, High Performance Liquid Chromatography

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References:

1. Bang-Andersen B, Ruhland T, Jorgensen M J Med Chem. (2011) 54 9 3206–3221.
2. Wesolowska A, Tatarczynska E, Nikiforuk A, Chojnacka-Wojcik E. Eur J Pharmacol (2007) 555 1 43–47

Micellar Liquid Chromatographic Determination of Penicillin-V in Pharmaceutical Formulations

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Penicillins are β -lactam antimicrobial agents used against various organisms by inhibiting of the peptidoglycan layer of bacterial cell walls. The peptidoglycan layer is important for cell wall structural integrity [1]. Penicillin-V (phenoxymethylpenicillin) comes under the group of small-spectrum β -lactam antibiotics. It kills a wide variety of bacteria that cause a wide variety of commonly occurring infections [2]. Many analytical techniques for determination of various types of penicillins in body fluids and pharmaceuticals have been published. Generally, spectrophotometric methods and high-performance liquid chromatography (HPLC) with different modes of detection, such as ultraviolet detection and mass spectrometry, belong to the most popular analytical methods for detection and quantification of penicillins. A technique known as micellar liquid chromatography (MLC) has been used as an alternative method to conventional liquid chromatography because of the large number of interactions of solutes with the mobile and stationary phases [3].

In this work, a rapid and simple micellar liquid chromatographic method for the separation of four penicillin antibiotics (methicillin, penicillin-V, amoxicillin, ampicillin) has been developed. Separation was achieved isocratically on a XTerra Shield RP18 column utilizing a mobile phase of 50 mM SDS-5% 1-butanol in a phosphate buffer (pH 3.5) at a flow rate of 1.0 mL min⁻¹ with UV detection at 200 nm. The method was applied to the determination of the penicillin-V in various pharmaceutical formulations.

Keywords: Penicillins, Micellar liquid chromatography, Urine, Pharmaceutical formulations.

References:

1. E.N. Evaggelopoulou, V.F. Samanidou Food Chemistry (2013) 136 1322-1329.
2. L. Svorc, J. Sochr, P. Tomcik, M. Rievaj, D. Bustin Electrochimica Acta (2012) 68 227-234.
3. P. Srisom, B. Liawruangrath, S. Liawruangrath Chromatographia (2007) 65 687-693.

Application of a Liquid Chromatographic Procedure for the Analysis of β -Lactam Antibiotics Using Sodium Dodecyl Sulphate /Butanol Mobile Phase

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The β -lactams are the most frequently utilized family of antibacterial compounds worldwide. They are used to treat respiratory tract infections that often result from the encroachment of sensitive bacteria. They are clinically used against Gram-positive and Gram-negative bacteria. Among several major classes of β -lactams, penicillins and cephalosporins are the most prominent [1].

High-performance liquid chromatography (HPLC) is currently the most widely used technique for analyzing antibiotics because it combines specificity with sensitivity, reproducibility and cost-effectiveness. Several HPLC methods have been reported for the determination of β -lactam group drugs in dosage forms, biological fluids and other matrices [2,3]. Micellar liquid chromatography (MLC), which uses a surfactant solution as the mobile phase and whose concentration is above the critical micellar concentration is an alternative to conventional HPLC [4].

The purpose of this study was to develop a new MLC method for the separation of six β -lactam antibiotics. Amoxicillin, ampicillin, methicillin, cephalexin, ceftriaxone and ceftazidime were analyzed using a XTerra Shield RP18 column and detected at 220 nm. These antibiotics were separated by an interpretive optimization procedure based on the accurate description of the retention and shape of the chromatographic peaks. The practical analytical utility of proposed method was demonstrated by the determination of cephalexin in pharmaceutical preparation.

Keywords: β -lactam, Penicillins, Cephalosporins, Micellar liquid chromatography

References:

1. European Centre for Disease Prevention and Control. Surveillance of Antimicrobial Consumption in Europe 2011; ECDC: Stockholm; 2014. Available at <http://www.ecdc.europa.eu/en/publications/Publications/antimicrobial-consumption-europe-surveillance-2011.pdf>.
2. F.J. Lara, M. Olmo-Iruela, C. Cruces-Blanco, C. Quesada-Molina, A.M. Garcí'a-Campanã (2012) 38 52-66.
3. B.C. McWhinney, S.C. Wallis, T. Hillister, J.A. Roberts, J. Lipman, J.P.J. Ungerer J. Chromatogr. B (2010) 878 2039-2043.
4. M. Rambla-Alegre, R. Marti-Centelles, J. Esteve-Romero, S. Carda-Broch J. Chromatogr. A (2011) 4972-4981.

Development of an Analytical Method for the Determination of Amoxicillin in Commercial Drugs and Wastewater Samples, and Assessing its Stability in Simulated Gastric Digestion

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Amoxicillin trihydrate is the most widely used β -lactam antibiotic for the treatment of bacterial infections including throat, skin, ear, nose and lower respiratory tract caused by susceptible microorganisms (1, 2). Absorption ability of this chemical is higher than other β -lactam antibiotics (3). On markets, capsules, tablets, suspensions and injectable solutions are available formulations for amoxicillin (4). Antibacterial effect and bacterial resistance have been improved by amoxicillin combination drugs (5). Due to importance of this chemical, sensitive and accurate determination method is very crucial for human health. In this study, a highly sensitive analytical HPLC-UV method was developed to determine amoxicillin in drugs and wastewater samples at a single wavelength. The calibration plot of the method was linear between 0.050 to 500 mg L⁻¹ with a correlation coefficient of 0.999. The limit of detection and limit of quantitation were found as 16 μ g L⁻¹ and 54 μ g L⁻¹, respectively. Recovery of amoxicillin from wastewater was also studied and % recovery was found to be 97.0 \pm 1.6%. In order to predict the *in vivo* behavior of the analyte, drug samples were subjected to simulated gastric conditions. Method developed was successfully applied to perform qualitative and quantitative determination of amoxicillin in tablet and suspension drug samples.

Keywords: HPLC, Amoxicillin, Simulated Gastric Juice, Wastewater, Commercial Drugs

References

1. Saptarini, N.Y., and Rusniyanti. International Research Journal of Pharmacy (2012), 3, 64-66.
2. Beg, S., Kohli, K., Swain, S., Hasnain, M.S. Journal of Liquid Chromatography & Related Technologies (2012), 35, 393-406.
3. Ashnagar, A., Naseri, N.G., E-Jornal of Chemistry (2007), 4, 536-45.
4. Samanidou, V.F., Evaggelopoulou, E.N., Papadoyannis, I.N. Journal of Separation Science (2006), 29, 1550-1560.
5. Matar, K.M. Chromatographia (2006), 64, 255-360.

Determination of Carcinogenic Benzo(a)pyrene (BaP) After Heat Treatment in Some Black Tea Grown in the Eastern Black Sea Region(Turkey)

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Tea commercialy grown and manufactured in the Eastern Black Sea Reagen of Turkey is the most consumed drink in Turkey after water [1]. Although tea consumption has many health benefits, leaves may contain some organic contaminants, such as pesticides and/or polycyclic aromatic hydrocarbons (PAHs). Exposure to PAHs through food consumption might cause a human health threat because some of them are carcinogenic and toxic [2].

Manufacturing processes of tea leaves and environmental pollution might be the main source of PAHs in tea product.[1-2]

As an indicator of the presence of other PAHs, benzo(a)pyrene (BaP) can be evaluated to be one of the most carcinogenic PAH. Therefore, the aim of this study is to develop a rapid, simple, and cost-efficient extraction technique for evaluating and screening BaP in tea.

In our study, extraction conditions, such as the solvent type, solvent volume and extraction time were optimized to obtain the best extraction performance. Approximately, one gram of tea samples was extracted shaking twice one after the other by hand with 10 mL of hexane/acetonitrile (7.5/2.5, v/v) for 1,2,3 and 4 minutes. The extract was then filtered through glass fiber into a separating funnel and after that, the extract was evaporated to dryness using a rotary evaporator, and the residue obtained was dissolved in 2 mL hexane and acetonitrile. This extract was dried with air, diluted to 8 mL by acetonitrile, centrifuged and transfered to HPLC analysis.

Tea samples were spiked with standard solutions of BaP. These standard solutions were added in tea before being extracted. Finally, the satisfactory recovery (97.76 ± 4.41 %) of BaP from tea samples was obtained when the samples were shaken twice by hand for one minute.

In tea the contamination for BaP is ranged from 1.27 to 1.91 $\mu\text{g kg}^{-1}$. This level for BaP is not classifiable as carcinogenic to humans by the International Agency for Research on Cancer.

Keywords: BaP, Dry Tea, HPLC.

References:

1. X. Li, N. Li, H. Luo, L. Lin, Z. Zou, Y. Jia, Y. Li, J. Agric. Food Chem. (2011) 59 5899–5905.
2. V.A.G. Londono, C.M. Reynoso, S.L. Resnik. Food Control (2015) 50 31-37.

Simultaneous Estimation of Irbesartan, and Hydrochlorothiazide in Their Binary Mixture by HPLC and UPLC

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Hypertension is an important problem that requires chronic treatment. Angiotensin-converting enzyme (ACE) inhibitors were primarily considered as antihypertensive drugs able to reduce significantly high blood pressures in hypertensive patients. Binary tablet formulations containing the angiotensin II receptor antagonist Irbesartan (IRB) and the diuretic hydrochlorothiazide (HCT) are used in the therapy to treat high blood pressure. The aim of this research is optimization and development of a simple, rapid, economical, sufficiently precise and accurate, reproducible, and fully validated HPLC and UPLC methods with good detection limits for estimation binary combination of IRB and HCT in bulk form and pharmaceutical preparations. The validation tests were also performed according to International Council on Harmonization (ICH) Guidelines and The United States Pharmacopeia (USP)), and the effect of acidic and basic additives were investigated on this regard.

The experiments were carried out on a reversed-phase Waters BEH C18 (50 mm × 2.1 mm I.D., 1.7 µm) UPLC column and Inertsil C8 (150 mm × 4.6 mm I.D., 5 µm) analytical HPLC column.

The UPLC system was operated under the gradient conditions at 40 °C using as mobile phase A of acetonitrile: B; NaClO₄ buffer (pH 3.2; 0.053 mM) at 0.6 mL.min⁻¹ flow rate was used to separate both compounds with a detection of 280 nm. The gradient program (T (min) / B%) is set as 0/5; 3/90; 3,5/5; 5/5. For HPLC study; an isocratic mobile phase with the flow rate of 0.9 mL.min⁻¹ that consisting of a mixture of methanol: water (68:32; v/v) containing with phosphoric acid (0.86 mL.L⁻¹) was used for the separation and analysis of IRB and HCT at 40 °C.

As a conclusion optimized HPLC and UPLC methods have been developed for separation of HCT, IS and IRB simultaneously that might serve as a versatile analytical tool suitable for the assay of this binary mixture and interest quality control and research laboratories. The proposed methods were successfully applied to determine both the quantity and uniformity of HCT and IRB from their pharmaceutical preparations without interferences.

Keywords: HPLC, UPLC, Validation, Irbesartan, Hydrochlorothiazide

Separation of Enantiomers of Butoxamine Using Polysaccharide Based Chiral Columns with Emphasis on Enantiomer Elution Order

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Butoxamine, (1S,2S)-1-(2,5-dimethoxyphenyl)-2-(tert-butylamino) propan-1-ol, is a β 2-selective agonist under preclinical study.

The purpose of this study was evaluation of six polysaccharide-based chiral columns (Lux Cellulose-1, Lux Cellulose-2, Lux Cellulose-3, Lux Cellulose-4, Lux Amylose-1, Lux Amylose-2) with the dimensions of 250 x 4.6 mm for separation of enantiomers of butoxamine.. Separations were performed with various polar organic and alcohol-hydrocarbon mobile phases. Especial attention was paid to the elution order of enantiomers as a function of the type of polysaccharide backbone and nature of polysaccharide derivative (benzoate or carbamate), as well as position of the substituent(s) on the phenylcarbamate moiety. Furthermore, the effect of polar modifier (2-propanol) content in the mobile phase and acidic and basic additives were investigated on this regard.

As a result of this study, the enantiomers of butoxamine were resolved on all studied chiral columns with using normal phase eluents. Elution order reversal for this compound was observed depending on the polysaccharide backbone (cellulose or amylose), type of derivative (carbamate or benzoate), nature and position of the substituent(s) on the phenyl moiety of polysaccharide derivative. No reversal of the elution order was observed with the addition of formic acid and diethylamine as additives to the mobile phase.

Keywords: HPLC, Enantiomer Elution Order, Chiral Separations, Butoxamine

Prediction of Retention Time in Reversed-Phase Liquid Chromatography as A Tool for Tryptophan and Its Major Metabolites Identification

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The use of retention data is of great help for metabolites identification in Metabolomics. In this context, quantitative structure-retention relationship (QSRR) models, based on metabolite molecular descriptors (MDs), are used more frequently lately [1]. In the present study, a 7-parameter alternative QSRR model was developed based on a dataset composed of tryptophan and its major metabolites belonging to three different ionizable groups: monoprotic and/or diprotic acids and bases as well as ampholytes. This model is differentiated from a common QSRR model by adding an extra variable which is the metabolite retention time measured under the same gradient conditions, but in two different chromatographic columns. Multiple linear regression (MLR) was applied to construct the linear QSRR models based on statistical significant molecular descriptors among a variety of theoretical molecular descriptors. The derived regression equations include structural descriptors as well as descriptors related to the pK values of solutes and they are formally given below

$$t_R(A) = a_1 MD_1 + a_2 MD_2 + \dots + a_n MD_n + b t_R(B)$$

where $t_R(A)$, $t_R(B)$ are the metabolites retention times measured under the same gradient conditions in two different reversed-phase columns, MD_1, \dots, MD_n are the statistically significant molecular descriptors and a_1, a_2, \dots, a_n, b are the adjustable parameters. The predictive capability of the developed QSRR models, which relate structural and chemical parameters of investigated compounds with their retention data obtained by two different chromatographic columns, is impressively improved in comparison to a classic QSRR model.

Keywords: Reversed Phase Liquid Chromatography, Retention Data Prediction, Quantitative Structure-Retention Relationships, Tryptophan And Its Metabolites

References:

1. G. M. Randazzo, D. Tonoli, S. Hambye, D. Guillarme, F. Jeanneret, A. Nurisso, L. Goracci, J. Boccard, S. Rudaz, *Analytica Chimica Acta* (2016) 916 8-16

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Solidified Floating Organic Drop Microextraction of Mercury from Water and Environmental Samples by Spectrophotometer and CVAAS

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Direct determination of mercury ions in water and environmental samples by using spectrophotometer and atomic absorption spectrometry is difficult because of low concentration of analyte ions than detection limit of instrument and matrix effects. Various separation and preconcentration procedures such as cloud point extraction, solid phase extraction, etc. are used for mercury determination [1,2].

A simple, rapid, sensitive and selective solidified floating organic drop microextraction (SFODME) method was developed for mercury(II). 1-undecanol was used as extraction solvent. Dithizone was used as complexing reagent. Various analytical parameters such as pH, amount of complexing reagent, volume of 1-undecanol, sample volume, centrifugation rate were optimized. Enrichment factor (EF), limit of detection (LOD) and RSD were found 100 and 0.32 $\mu\text{g L}^{-1}$, 3.5 %, respectively. Accuracy of the method was confirmed by analysis of certified reference materials. The SFODME method was applied to determination of Hg(II) in water and food samples after microwave digestion method by using spectrophotometer and cold vapor atomic absorption spectrometry (CVAAS).

References:

1. A. Niazi, T. Momeni-Isfahani and Z. Ahmari, Journal of Hazardous Materials, 2009, 165, 1200-1203.
2. N. Rajesh and M. Hari, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2008, 70, 1104-1108.

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Dual-Solidified Floating Organic Drop Microextraction Technique: A Novel Technique to Eliminate the Disadvantages of Conventional Solidified Floating Organic Drop Microextraction for Preconcentration of Cobalt Ions

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In this study, a new ultrasound assisted emulsification-dual-solidified floating organic drop microextraction (USAE-d-SFODME) technique, which eliminates the drawbacks of conventional SFODME, for preconcentration and FAAS determination of lead ions was developed for the first time. In this technique two SFODME steps are performed in sequence. In the first step conventional SFODME procedure was applied. For this purpose CR was used as a complexing agent and 1-dodecanol was used as an extraction solvent. After performing extraction CR-cobalt complexes were transferred into the 1-dodecanol phase. At this stage, instead of direct analysis of extraction phase, a second SFODME step was performed. For this purpose the extraction phase was treated with 1.0 M HNO₃ solution, and after applying ultrasound, cobalt species were back-extracted into the aqueous phase and determined by FAAS. Second extraction step provides the elimination of the drawbacks of the organic extraction solvent, 1-dodecanol. Several factors affecting the microextraction efficiency, such as type of extraction solvent, pH, complexing agent concentration, ultrasound extraction time, sample volume and equilibration temperature were investigated and optimized. Under optimized conditions, the preconcentration factor and the enrichment factor were obtained. The values for limit of detection (3s), the limit of quantification (10s) and the relative standard deviation (RSD) for 10 replicate measurements were calculated. The proposed method was successfully applied to the determination of lead in certified reference material and different water samples.

Keywords: Ultrasound Assisted Emulsification Dual Solidified Floating Organic Drop Microextraction, Cobalt, Preconcentration, Flame Atomic Absorption Spectrometer, Congo Red

References:

1. Y. Wang, J. Han, Y. Liu, L. Wang, L. Ni, X. Tang, Food Chem. (2016) 190 1130.
2. M. Falahnejad, H. Zavvar Mousavi, H. Shirkhanloo, A.M. Rashidi, Microchem. J. (2016) 125 236.
3. Ç. Arpa Şahin, İ. Durukan, Talanta (2011) 85 657.

Magnetic Dispersive Liquid Phase Microextraction on Fe₃O₄ Magnetic Nanoparticles for the Preconcentration of Mercury Assisted with Imidazolium Based Ionic Liquids Before Flow Injection Cold Vapour Atomic Absorption Spectrophotometric Determination.

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Mercury may cause negative effects such as cancer, permanent brain damages like other heavy metals while the contamination of biological and environmental samples. There is very little way to the excretion of mercury from the body, the effect is an increased accumulation of poisons [1]. The permitted (threshold) level of mercury in drinking water was set to be 1 ng/mL or 2 ng/mL [2, 3]. However, the concentration of mercury is commonly in the range of low ng/mL in environmental waters which indicate that sample pretreatment and sensitive detection techniques are essential for its quantitative analysis.

In this study a novel magnetic dispersive liquid liquid microextraction was developed on magnetic ferrous (III) oxide (Fe₃O₄) nanoparticles assisted with 1-butyl-3-methyl imidazolium hexafluorophosphate ionic liquid as an extractant for preconcentration of mercury spectrometric determination. For this, Fe₃O₄ nanoparticles was prepared using a simple procedure and characterisation studies was completed with X-Ray Diffraction, Transmission Electron Microscopy and Fourier Transform Infrared Spectroscopy. The metal complexes of mercury was prepared with 4-(2-pyridylazo)-2-resorcinol (PAR) and the extraction method was applied to aqueous media. The enriched mercury was analysed by atomic absorption spectrophotometer using of the flow injection cold vapour technique after preconcentration under optimum extraction conditions.

For the magnetic microextraction technique, enrichment factor and extraction recovery was calculated after applied optimum extraction parameters affecting the extraction efficiency as sample pH, effect of surfactant, amount of PAR, amount of ionic liquid and Fe₃O₄, volume of sample and co-existing ions. This study is supported by TUBITAK as a project number 214Z269.

Keywords: Magnetic Nanoparticle, Ionic Liquid, Mercury, DLLME

References:

1. K. Leopold, M. Foulkes, P.J. Worsfold Trends Anal. Chem. (2009) 28 426–435
2. Guidelines for Drinking-water Quality 3 ed., World Health Organization 2008.
3. National Primary Drinking Water Regulations 2009.

Determination of Trace Amount of Cadmium using Dispersive Liquid-Liquid Microextraction-Slotted Quartz Tube-Flame Atomic Absorption Spectrometry

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Determination of trace amount of cadmium at high accuracy and precision is very crucial due to its serious health effects (1, 2). This study was performed to develop an analytical method for cadmium using dispersive liquid-liquid extraction after complex formation using diphenylcarbazone. The parameters affecting the cadmium complex formation and its extraction output were varied in a stepwise manner to obtain optimum results. In the complex formation step, the pH and amount of the buffer solution together with the concentration of the ligand were optimized. The mixing period for the complex formation was also varied between 5 and 90 minutes to obtain the highest output. The DLLME method was comprehensively optimized based on the type and amount of extraction solvent, dispersive solvent and salt. The type and period of mixing needed for a more effective extraction was also investigated. In order to further improve the sensitivity of the analysis for cadmium, the flame atomic absorption spectrometry (FAAS) system was optimized. This included the flow rates of the sample inlet and the acetylene fuel gas. The limits of detection and quantitation (LOD and LOQ) for the FAAS system were 42 and 140 µg/L, respectively. This was improved upon using a slotted quartz tube (SQT) fitted to the FAAS system. The LOD and LOQ were lowered to 11.9 and 39.6 µg/L, respectively, after the height of the SQT and flow rates of both sample inlet and acetylene fuel gas were optimized. The LOD and LOQ of the optimized FAAS system after DLLME was 1.33 and 4.44 µg/L, respectively. Combining both optimized parameters of the DLLME and SQT-FAAS system gave 0.45 and 1.5 µg/L as LOD and LOQ, respectively.

Keywords: Cadmium, Microextraction, DLLME, SQT, FAAS

References:

1. Pérez-Outeiral, J., Millán, J., Garcia-Arrona, R. Journal of Spectroscopy (2014) Article ID 832398 4 pages.
2. Jiang, H., Hu, B., Microchimica Acta (2008) 161 101–107.

Optimization of a Closed Batch Vessel Hydride Generation Atomic Absorption Spectrometry Method for the Determination of Lead in Drinking and Waste Water Samples at Trace Levels

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Lead is one of the poisonous metal which can be absorbed into the human body as inorganic lead accumulated in soft tissues, bones and teeth (1). Lead poisoning causes hyperactivity, developmental delays, liver and kidney damage, hearing loss, anemia and in extreme cases, death for children (2). Concentration of lead in many environmental samples falls below the detection limit of most conventional analytical methods. The maximum allowable limit for lead in drinking water is 15 $\mu\text{g L}^{-1}$ and 10 $\mu\text{g L}^{-1}$ according to the United States Environmental Protection Agency and the World Health Organization, respectively (USEPA 2014; Etchie et al. 2013). Hence, development of an analytical method giving precise and accurate results to meet the desired concentration guidelines is very important. In this study, the optimization of parameters in batch type hydride generation atomic absorption spectrometry system for the determination of lead at trace levels was performed. The parameters which affect the production, transport and atomization of plumbane were varied to obtain optimum results. Chemical parameters including the concentrations of reagents affecting the generation of the lead hydride were optimized to obtain high hydride generation efficiency. Other parameters such as atomization temperature, reaction period, pump speed, pump period, flow rates of reducing agent and carrier gas were also optimized to obtain lower detection limits. The method developed gave a linear Pb concentration range from 2.0 to 40 $\mu\text{g L}^{-1}$ ($r^2=0.9995$) under the optimum conditions. The limit of detection was calculated as 0.56 $\mu\text{g L}^{-1}$. Accuracy of the method was also checked through the analysis of certified reference materials.

Keywords: Lead, HGAAS, Optimization, Water

References:

1. Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton D.J., Heavy Metals Toxicity and the Environment (2014) NIH Public Access.
2. United States Environmental Protection Agency, Human Health and Lead. Available at: <http://www.epa.gov/superfund/lead/health.htm>, (2015) Accessed on June 2016.
3. United States Environmental Protection Agency, Drinking Water Contaminants. Available at: <http://water.epa.gov/drink/contaminants/index.cfm>, (2015) Accessed on June 2016.
4. Etchie, A.T., Etchie, T.O., Adewuyi, G.O., Krishnamurthi, K., Saravanadevi, S., Wate, S.R., Bulletin of World Health Organization (2013) 91 553-561.

Ultra-Trace Determination of Arsenic and Selenium in Foods and Vegetables by Hydride Generation Atomic Absorption Spectrometry

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In human body, approximately thirty elements play a key role in physiological activities and are recognized as essential elements [1]. However, essential elements are toxic at high concentrations. The toxicity of arsenic differs markedly between individuals and populations, which might be related to the metabolism (methylation) of inorganic arsenic (As), as well as the selenium (Se) nutritional status [2]. Therefore a simple and ultrasensitive detection technique is required to determination of this elements.

In the work, a new and simple ultrasonic assisted extraction procedure was developed for the determination of arsenic and selenium in foods and vegetables by hydride generation atomic absorption spectrometry. Some factors such as Tween 60 concentration, ligand concentration, pH, extraction time, and sample volume were investigated and optimized in details. At optimal conditions, the linear range was in the range of 4.5-250 for As, and 15-400 ng L⁻¹ for Se and the relative standard deviation (RSD) was 3.8% for As, and 3.3% for Se. The relative recoveries of As and Se spiked at 20–150 ng L⁻¹ in the selected samples were in the range of between 94.1.2 and 104.8%. The sensitivity improvement factor for As and Se was 185 and 140, respectively. The validity and accuracy was evaluated by analyzing of two certified reference material (CRMs) and spike recovery experiments. The method was successfully applied to the determination of As and Se in the samples. Finally, the method was demonstrated to be rapid and sensitive for extraction and determination of As and Se in the selected samples with good results.

Keywords: Arsenic, Selenium, Hydride Generation-Atomic Absorption Spectrometry, Extraction, Foods, Vegetables.

Referances:

1. Tu, H., & He, Y. Analytical Letters. (2015) 48 10 1629-1637.
2. Yoshida, N., Inaoka, T., Sultana, N., Ahmad, S. A., Mabuchi, A., Shimizu, H., & Watanabe, C. Environmental research (2015) 140 300-307.

Determination of Macro and Micro Element Concentrations in Hardaliye Beverages Using Flame Atomic Absorption Spectrometer after Ultrasound-Assisted Extraction, Microwave-Assisted Extraction and Wet Extraction Procedures

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Abstract

In the presented study, the concentration of macro and micro elements in hardaliye samples produced in Turkey and collected from homemade and Turkish supermarkets was determined by flame atomic absorption spectrometer after microwave-assisted extraction (MAE), wet extraction (WE) and ultrasound-assisted extraction procedures (UAE). However, there is limited work present an ultrasound-assisted extraction in the determination of trace elements in beverage samples. Classical time-consuming and hazardous procedures for sample preparation have been compared by ultrasound-assisted extraction. The parameters effecting UAE experimental conditions such as ultrasound amplitude, sonication time, sample amount, extractant type and volume were studied. Optimal experimental conditions for metal extractions from UAE procedure were as follow: 2-min sonication time, % 30 amplitude, 3 mL sample volume, % 5 (v/v) HNO₃ extraction solution, and 1 mL of extractant volume for Ca, Cu, Mg, Mn, Na and Zn in hardaliye samples. The results in the hardaliye samples (minimum-maximum in mg L⁻¹) from UAE procedure were Ca 33-63, Cu 0.049-0.27, Mg 3.9-14.4, Mn 1.0-3.2, Na 32-58, and Zn 0.39-1.1. The UAE procedure was found to be fast, accurate, and simple, fewer contaminants and lower concentrated reagent consumption in comparison with the other used conventional extraction procedures.

Keywords: Hardaliye, Macro and Micro Elements, Flame Atomic Absorption Spectrometer, Microwave-Assisted Extraction, Wet Extraction, Ultrasound-Assisted Extraction

Introduction

Hardaliye is an indigenous traditional beverage of the Trakya region of Turkey, where It has been produced and consumed for centuries [1,2]. It is also known as a grape-based, fermented, non-alcoholic beverage, produced by lactic acid fermentation. Traditionally, hardaliye is made of grape, fermented with *L. paracasei subsp. paracasei* and *Lactobacillus casei subs. Pseudoplatantum*, which grows in lactic acid bacteria (LAB) [3]. Due to the LAB, it has been non-dairy probiotic beverages [4]. The pH of hardaliye samples in the literature have been reported in the range of 3.21-3.97 [1,4]. There are four main steps in the hardaliye production which are preparation of raw material is an important stage, pressing, fermentation, and storage [3, 4]. In the preparation step, washed red grapes (Papaz karası, Alfars or Cardinal) or grape juice and crushed black mustard seed are pressed until the rupture of their crusts. Pressed grapes, 0.2 % pressed mustard seeds, cherry leaves and/or 0.1 % benzoic acid is mixed with a wooden (or plastic) barrels. Then, the mixture is allowed to ferment for 5-10 days at room temperature in closed barrels. After the fermentation step, the mixture filtered, and the final product of hardaliye is stored in a suitable container at 4 °C [1,5]. Atomic spectrometric techniques like the flame, electrothermal atomic absorption spectrometry and high-resolution continuous source atomic absorption spectrometer (F-AAS, ET-AAS, HR-CS-AAS), as well as inductively coupled plasma optical emission and mass spectrometer (ICP-OES and ICP-MS),

have been frequently used for trace element determination in fruit juice samples [5-9]. However, the determination of metals in such samples by using atomic spectrometric technique is difficult due to its matrix and low-level metal concentration in the sample [7]. Because this, different sample-preparation procedures like: microwave-assisted and wet extractions are usually used. The aim of this study was to determine the trace element contents in home-made and commercial fermented drink hardaliye samples to assess the risk for Turkey consumer by using FAAS, after microwave-assisted extraction, wet extraction, and ultrasound-assisted extraction procedures. In addition, the advantages and disadvantages of the acid-based ultrasound-assisted extraction procedure were evaluated.

Materials&Methods

Determination of Ca, Cd, Cr, Cu, Mg, Mn, Na, Pb, Zn in the hardaliye samples was made with a Perkin-Elmer AAnalyst 800 Atomic Absorption Spectrometer. The ultrasound-assisted extraction was carried out using a 900 W, 20-25 kHz XO-900D ultrasonic cell crushing/disruptor-homogeniser. Microwave MarsXpress closed vessel sample preparation system. A Stuart Block heating digester was used. HNO₃ (65 %, v/v), HCl (37 %, v/v) and H₂O₂ (35 % v/v) purchased from Merck (Darmstadt, Germany) were used for the sample extraction. Ca, Cr, Cu, Mn, Pb and Zn stock standard solutions (1000 g L⁻¹) were supplied by Fluka, while Na and Mg stock standard solutions (1000 g L⁻¹) were from Merck. Cd stock standard solution (1000 g L⁻¹) was also purchased from Inorganic Ventures.

The analyses of different commercial and homemade hardaliye samples were purchased from the local market or village (Trakya, Turkey). The samples were stored at the refrigerator in the original packing (glass bottle) and rinsed thoroughly before analysis. The following optimum sample preparation procedures were tested:

Wet extraction (WAE) and Ultrasound-assisted extraction (UAE): These procedures were performed according to Bentlin et al [10]. *Microwave-assisted extraction (MAE):* This procedure was performed according to Husakova et al. [11].

Results&Discussion

Effect of Sonication Time: A % 30 sonication amplitude of the probe fixed, 3 mL of the samples was placed in a tube, 1 mL of the extraction solution (either % 1 HCl or % 5 HNO₃) was added, and the extraction time varied between 1 to 15 minute and the extraction was performed. Metal concentration was not changed with increasing sonication time, 1 min being sufficient for the metal investigated (Fig 1 (a) and (b)). Higher sonication times was not chosen due to the detrimental effect by longer times on the titanium tip [12].

Effect of Sonication Amplitude: The influence of Sonication amplitude in the range of 15-45 % was investigated by using 1 min as sonication time and applying the same procedure above (Fig 2 (a) and (b)). Extraction efficiency fixed when the amplitude was larger than 30 % for the six elements. For further experiments, the sonication amplitude of the probe was set at 30 %. Because an increase in signification intensity will provide for an increase in the chemical reactions. In addition, higher sonication amplitude generated effective cavitation in the liquid medium extraction takes place [13].

Effect of Sample Volume: 1-9 mL of hardaliye samples were subjected UAE procedure extraction with, 1 min sonication time and 30 % amplitude. Figure 3 (a) and (b) shows that the sample volume of Ca, Cu, Mg, Mn, and Na remains constant up to sample volume 3 mL.

Effect of Extractant Type, Concentration and Volume: Metal extraction can be promoted by adding to the acidic strong reagents such as HCl and HNO₃. The influence of acidic reagent type on metal extraction was studied for Ca, Cu, Mg, Mn, Na and Zn in the concentration range of 0.1-30 % (v/v). In HCl extraction, slightly change in the extraction efficiency observed

between 0.1 and 30 % (v/v) except for Mn and Zn. For a nitric acid extractant, maximum extraction is observed for Cu, Mg, Mn, Na and Zn for a 0.1-30 % (v/v).

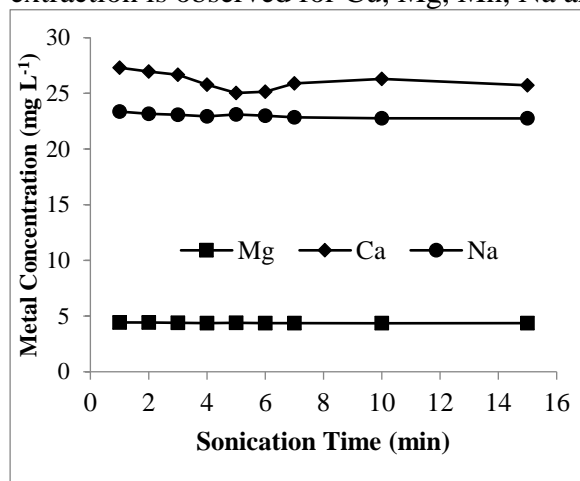


Fig 1a. Effect of sonication time for macro (Ca, Mg, Na) element extraction

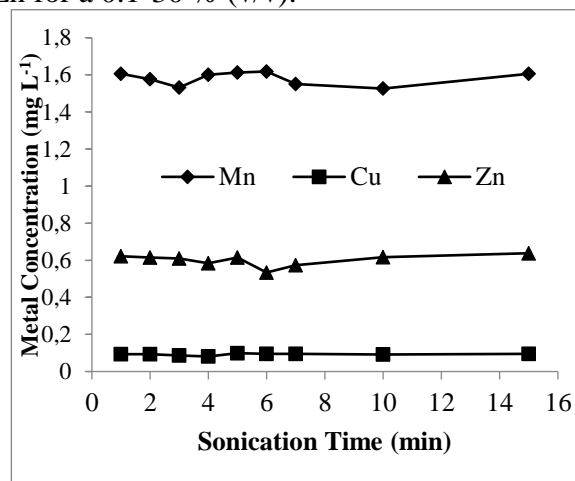


Fig 1b. Effect of sonication time for micro (Cu, Mn, Zn) element extraction

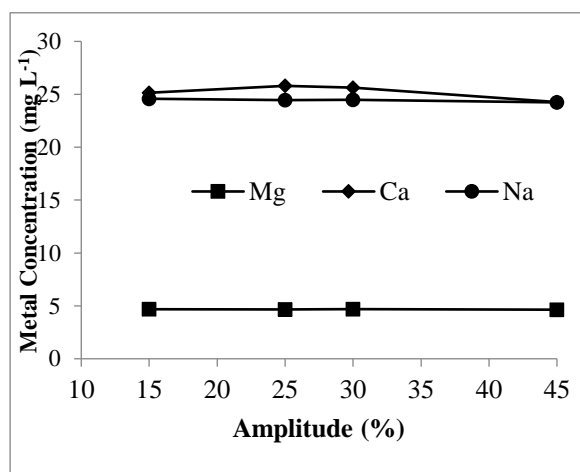


Fig 2a. Effect of amplitude percentage for macro (Ca, Mg, Na) element extraction

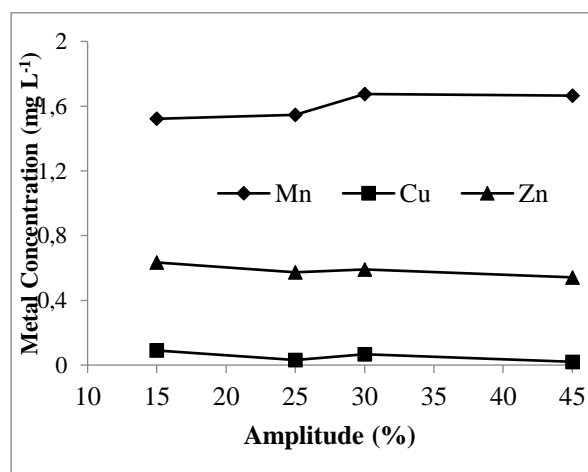


Fig 2b. Effect of amplitude percentage for micro (Cu, Mn, Zn) element extraction

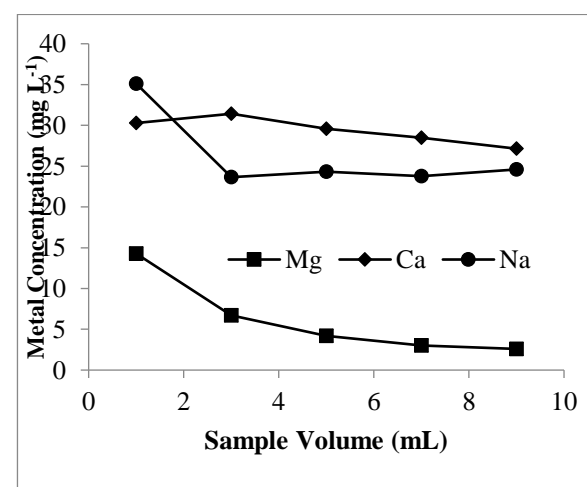


Fig 3a. Effect of sample volume for macro

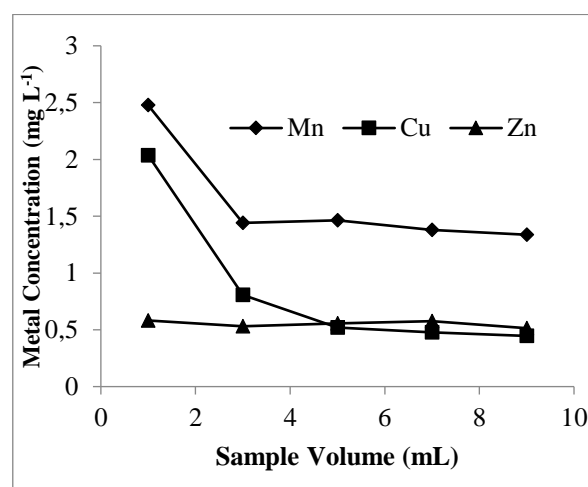


Fig 3b. Effect of sample volume for micro

(Ca, Mg, Na) element extraction

(Cu, Mn, Zn) element extraction

In contrast, an increasing Ca extraction occurs in the range of 0.1-5 % (v/v). A 5 % (v/v) nitric acid concentration was chosen for subsequent extraction experiment since it has not damaged the tip of the probe. The concentrated reagent may be penetrated the titanium probe. The effect of extractant volume was also studied in the 1-5 mL range.

Comparison of UAE Procedure with the Microwave-Assisted Extraction and Wet Extraction Procedures: The UAE procedure was compared with the conventional extraction procedures such as microwave-assisted extraction and wet extraction procedures. Ten samples were subjected to extraction and eight replicates were performed. Both extraction procedures one can say that good agreements for studied elements were found using UAE procedure. There was no certified hardaliye beverage available with respect to studied elements. Thus, matrix interference, precision, and accuracy were examined by analyte recovery tests. These experiments were carried out using 0.25, 0.50, 1.00, and 2.00 spiked samples due to matrix effects in the hardaliye samples. The results obtained for the spiked hardaliye samples recoveries were around 100 % and low standard deviation (precision). The comparison of Ca, Cu, Mg, Mn, Na and Zn concentrations in hardaliye samples with fruit juice and drinking water samples are shown in Table 6. In Our experiments, a significant increase in the Mn contents was verified, comparing to the fruit juice and drinking water samples. One of the major influential factors is the preparation of hardaliye samples by using non-standard processes. In addition, fermentation process also effects the metal concentration. However, the analysis of macro element contents was not exceeded the acceptable limit for drinking water and fruit juices according to USEPA and WHO standard [14,15].

Conclusion

Ultrasound-assisted extraction procedure for the determination of in the analysis of Ca, Cu, Mg, Mn, Na and Zn elements in hardaliye samples by using FAAS is useful for analysis of metal, and it can be considered as an alternative to other sample preparation procedures such as microwave-assisted extraction and wet extraction. This procedure avoids the use of high concentration and volume of extractant and time-consuming extraction of the hardaliye samples. In addition, this procedure described offers a simple, rapid, efficient and sensitive sample preparation procedure for the direct determination of macro and micro element in hardaliye samples by FAAS.

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References:

1. M. Arici, F. Coskun. Food Microbiology (2001) 18 417–421.
2. FC. Prado, JL. Parada, A. Pandey, C.R. Soccol Food Research International (2008) 41 111–123.
3. F. Altay, F. Karbancıoglu-Güler, et al. Int J Food Microbiol (2013) 167 44–56.
4. S. Güven, M. Aksoy (2009) Some modifications in hardaliye production. II. Traditional Foods Symposium Abstract Book. Van, Turkey.
5. A. Dehelean, D.A. Magdas The Scientific World Journal (2013) 2013 1-6.
6. A.B. Williams, O.O. Ayejuyo, A.F. Ogunyale Environ Monit Assess (2009) 156 303–306.
7. A. Szymczycha-Madeja, M. Welna Food Chemistry (2013) 141 3466–3472.
8. F.J.A. Paula, R.P.F. Guine, L.C. Lopes, et al. Czech Journal of Food Sciences (2015) 33 384–391.
9. H. Çiftçi, Ç. Er, Ö. Yalçinkaya, et al. Int J Environ Anal Chem (2014) 94 579–593.
10. F.R. Bentlin, C.M. dos Santos, et al. Analytica Chimica Acta (2012) 710 33– 39.
11. L. Husakova, I. Urbanova, et al. Food Chemistry (2011) 129 1287-1296.
12. D. Garcia-Casillas, S. Garcia-Salgado, M. A. Quijano Analytical Methods (2014) 6 8403-8412.
13. A.V. Filgueiras, I. Lavilla, C. Bendicho Fresenius J Anal Chem (2001) 369 451–456.
14. <http://www.cdph.ca.gov/certlic/drinkingwater>
15. WHO, Guidelines for Drinking Water Quality, World Health Organization, Switzerland, 2008.

Determination of Iron and Lead in Raw and Refined Canola Oil by FI-FAAS Use of a New Extraction System Based on Emulsion Breaking

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Depending on the purpose of the analysis, pretreatment of oil sample can be difficult. In the oil analysis, even when appropriate spectrometric techniques are used, viscous oily organic materials cause some problems. Additionally, in the pretreatment of oil samples, different procedures used: such as dilution of organic solvent, transfer to the aqueous solution of analyte and emulsification method. Emulsification method can be ensured, transfer to the aqueous solution of the analyte by acidic surfactant solution, after oil in water emulsion [1].

Canola is an important plant as a source of vegetable oil in the world, its planting area, and yields have been increasing steadily. It is considered an important source of the healthiest edible oil, due to it is one of a kind of fatty acid profile that occurs of the low-level of saturated fat, moderate level of polyunsaturated fat and high level of mono-unsaturated fat [2,3].

In this work, a new extraction system by emulsion breaking has been developed for the determination of iron and lead in raw and refined canola oil before it's the determination by using flow injection flame atomic absorption spectrometry (FI-FAAS). The optimization of the procedure was performed by investigating the influence of different parameters that could affect the extraction efficiency such as the sample volume, the concentrations of surfactant, emulsion breaking time and temperature for extraction. In addition, the flow injection conditions affecting the analytical performance of the method was also investigated.

Keywords: Canola, Emulsion, FI-FAAS, Extraction, Metal

References:

1. J.L. Burguera, M. Burguera Talanta (2011) 83 691-699.
2. Y.M. Gao, B.L. Ma Journal of Plant Nutrition (2015) 38 473-483.
3. D. Bakircioglu, N. Topraksever, Y.B. Kurtulus Food Chemistry (2014) 151 219-224

Preconcentration and Determination of Pb^{2+} and Zn^{2+} Metal Ions Using Cloud Point Extraction and Ultrasonic Nebulizer Combined Inductively Coupled Plasma Optic Emission Spectrometry

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Environmental pollution has increased in conjunction with developing technology and industrialization nowadays. These pollutions not only the life of the human but also effect the life of all living creatures negatively. Urbanization, industrial development and heavy traffic conditions cause the pollution of the waters with heavy metals [1,3].

In this work Pb^{2+} and Zn^{2+} ions in natural water samples were separated and preconcentrated from the sample with developed cloud point extraction method by ultrasonic nebulizer inductively coupled plasma optic emission spectrometry (USN-ICP-OES). 1,5-diphenylthiocarbazone (dithizone) was used as complexing agent and (1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol (Triton X-114) was used as surfactant. Phase separation was observed at pH=7 and surfactant rich phase was diluted with 2 ml 2 M HNO_3 . Ligand concentration, surfactant concentration, pH, ionic strength, interferences, equilibration temperature and time parameters were optimized. Under optimized conditions enrichment factor were calculated for Pb^{2+} as 9.6 and for Zn^{2+} as 9.2 ; limit of detection were calculated for Pb^{2+} 0.012 and for Zn^{2+} 0.02 ng mL⁻¹. The method was successfully applied to the analysis of natural water samples.

Keywords: Cloud Point Extraction, Dithizone, Ultrasonic Nebulizer, ICP-OES, Heavy Metal Analysis, Natural Water Pollution

References:

1. E. Melek, M. Tuzen, M. Soylak Analytica Chimica Acta 578 2 (2006) 213–219.
2. E. L. Silva, P. S. Roldan, M. F. Gine Journal of Hazardous Materials 171 1-3 (2009) 1133-1138.
3. L. Zhao, S Zhong, K. Fang, Z. Qian, J. Chen Journal of Hazardous Materials 239-240 (2012) 206-212.

Adsorption and Preconcentration of Ni(II), Cd(II) and Pb(II) Ions by Silica Gel Functionalized with Pyromellitic dianhydride

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Solid phase extraction (SPE) is one of the widely used preconcentration technique and based on the transfer of analytes from liquid phase to solid support material [1,2].

In this study, pyromellitic dianhydride bonded silica gel (PMDA-SG) was synthesized. Column solid phase extraction of Ni(II), Cd(II) and Pb(II) ions using the modified silica gel was investigated. The effective factors such as pH of sample solution, type and concentration of eluent solution, flow rate and volume of sample solution, and presence of matrix ions in sample solution were studied by using solid phase extraction method. According to the results, the optimum conditions were found to be pH 7.0, 1 M HNO₃ eluent and 5 mL/min. flow rate. Atomic absorption spectrometry was used for the determination the metal levels. This method was applied to certified reference materials and a variety of water samples. In addition, the batch method was studied to investigate the adsorption of Ni(II), Cd(II), and Pb(II) ions. For this purpose at pH 5.5, effect of contact time and initial metal concentration were examined, and their adsorption equilibrium and kinetics were analyzed.

Keywords: Solid Phase Extraction, Preconcentration, Modified Silica Gel, Pyromellitic Dianhydride (PMDA)

References:

1. Yu. A. ZOLOTOV, N.M. KUZMIN (1990) Preconcentration of Trace Elements, Netherland.
2. M. Imarnoglu, D. Perez-Quintanilla, I. Sierra, Micropor. Mesopor. Mat. (2016) 229 90-97.

Column Solid Phase Extraction of Ni(II) and Cu(II) Using Salicylaldehyde Modified Polyamine Polyurea Resin For Their Determination by FAAS in Waters

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Heavy metals that are toxic at high concentrations accumulate and harm directly to aquatic living organisms and to indirectly human beings [1]. Hence their determination in waters is very important to monitoring their levels. Flame atomic absorption spectrometry is widely used due to ease of usage and cheapness for the determination of metal levels in several samples. But in many case, a separation and preconcentration of analytes are required prior to the measurement, especially in case of low level of the analytes and matrix of samples. Column solid phase extraction (SPE) is commonly preferred technique for its leading properties such as uncomplicated nature, low cost, high recovery, selectivity and enrichment factor [2,3]. The success of SPE is also closely associated with the kind and features of the used solid phase as sorbent [4]. The chelating resins have been preferred as solid phase in various SPE processes due to having the characteristics expected from a good sorbent like chemical stability, large surface area, high selectivity and high enrichment factor [5]. In this study, an extraction-preconcentration process was developed for Ni(II) and Cu(II) ions by using a salicylaldehyde modified polyamine polyurea resin as solid phase. Determination of these ions was carried out with flame atomic absorption spectrometer. The process was optimized based on analytical parameters such as pH, eluent type, concentration, flow rate and volume, sample volume, flow rate of sample solution and matrix ions. The accuracy and precision of the method was validated by using a standard reference material, trace element fortified water sample (TMDA-54.4). The optimized solid phase extraction method was used for determination of Ni(II) and Cu(II) levels in various environmental water samples.

Keywords: SPE, Preconcentration, Ni(II), Cu(II), Resin, Environmental Waters

References:

1. E. Vereda Alonso, M.D.M. Guerrero, P. Colorado Cueto, J. Barreno Benítez, J.M. Cano Pavón, A. García De Torres, Talanta. (2016) 153 228–239.
2. R.M. Peña Crecente, C.G. Lovera, J.B. García, C.H. Latorre, S.G. Martín, Food Chem. (2016) 190 263–269.
3. Z.A. Alothman, E. Yilmaz, M. Habila, M. Soylak, Ecotoxicol. Environ. Saf. (2015) 112 74–79.
4. X. Zhu, Y. Cui, X. Chang, H. Wang, Talanta. 146 (2016) 358–363.
5. S. Kagaya, T. Kajiwarra, M. Gemmei-Ide, W. Kamichatani, Y. Inoue, Talanta. (2016) 147 342–350.

A New Procedure for Determination of Nickel in Some Cosmetics Samples After Dispersive Liquid–Liquid Microextraction by FAAS

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Metallic nickel and compounds are used in manifold industrial and commercial applications such as stainless steel and other nickel alloys, electroplating, foundries, catalysts, batteries, electronics, ceramics, pigments, and coinage. The main exposure route for nickel in the general population is food with an average daily nickel intake of about 0.1–0.3 mg. In contrast, Ni(II) uptake by inhalation is below 0.8 µg day⁻¹ for non-smoking urban residents [1-2].

A new, dispersive liquid–liquid microextraction (DLLME) procedure has been optimized for the preconcentration of trace amounts of Ni(II) as a prior step to its determination by flame atomic absorption spectrometry (FAAS). It is based on the microextraction of nickel, where appropriate amounts of the extraction solvent (CHCl₃), disperser solvent (ethanol) and the chelating agent which named as 2-methyl-5-[(E)-(5-methylisoxazol-3-yl)diazenyl]quinolin-8-ol (MMD) were firstly synthesized/characterized and used. Various parameters that affect the extraction procedure such as pH, centrifugation rate and time, the chelating agent (MMD) concentration and sampling volume on the recovery of Ni(II) were investigated. The limit of detection (3s/b) obtained under optimal conditions was 1.00 µg L⁻¹. The relative standard deviation for certified reference material determinations was 1.2 %. The accuracy of the method was verified by the determination of Ni(II) in certified reference material of wastewater, (BRC-CRM403). The proposed procedure was successfully applied to the determination of Ni(II) in some cosmetics samples.

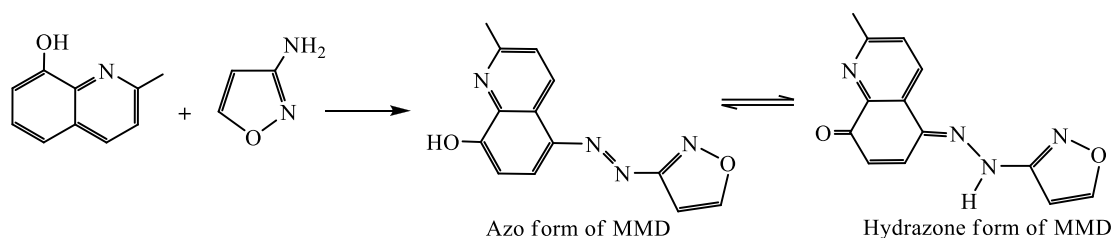


Figure 1. The reaction scheme of the chelating agent (MMD).

Keywords: Cadmium, Nickel, Microextraction, Chelating reagent, Food and Make-up product, FAAS

References:

1. Sereshti H., Khojeh V., Samadi S. *Talanta* (2011) 83 885–890.
2. Schaumlöffe D. *Journal of Trace Elements in Medicine and Biology* (2012) 26 1–6.

Fast Solid Phase Extraction of Trace Copper and Lead from Water, Food and Street Dust Samples by Ionic Liquid Coated Carbon Nanospheres

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Solid phase extraction is one of the most widely used sample pretreatment techniques mainly due to the variety of different materials employed as sorbents. The new materials as adsorbent in sample preparation are required to obtain more selective materials with higher adsorption capacity. The solid phase extractants are distinguished by fast kinetic properties, as well as by the simplicity of their preparation. Nanoscale carbon-based materials, such as fullerenes, nanodiamond, carbon nanofiber, carbon nanotubes, and graphene/graphene oxide have attracted great interest as powerful solid phase extraction materials because of their attractive physical and chemical properties. Due to the ultrahigh specific areas and increasing surface activities they show high adsorption speed and capacity. As an important member of the carbon family, carbon nanospheres (CNSs) have attracted considerable attention. Ionic liquids (ILs) are salts formed by organic cations and inorganic or organic anions. ILs have many unique physicochemical properties, such as low vapor pressure, good thermal stability, high conductivity, wide range of viscosities and miscibility with water and organic solvents. The use as adsorbent of IL modified materials significantly affects the enrichment factor, extraction efficiency and selectivity, since the prepared material combines the advantages of IL and solid support [1-3].

In this work, CNSs, a new kind of IL (1,8-naphthalene monoimide bearing imidazolium salt) and IL coated carbon nanospheres were synthesized and characterized. The IL coated CNSs were used as an adsorbent for the solid phase extraction of copper and lead from various samples. The determination of analytes was made by FAAS. Various parameters were optimized. The pH was found to be 6. The preconcentration factor and adsorption capacity of the method were found to be 300-fold and 60 mg g⁻¹ for copper and 300-fold and 50.3 mg g⁻¹ for lead, respectively. The copper and lead were easily adsorbed and desorbed from the adsorbent without vortexing/shaking. The accuracy of the developed method was confirmed by analyzing certified reference materials and by spiking sea water, wastewater, street dust and spice samples.

Keywords: Ionic Liquid, Carbon Nanospheres, Solid Phase Extraction, Fast Kinetic

References:

1. Ş. Tokaloğlu, E. Yavuz, H.Şahan, S.G. Çolak, K. Ocakoğlu, M. Kaçer, Ş. Patat Talanta (2016) 159 222–230
2. B.H. Fumes, M.R. Silva, F.N. Andrade, C.E.D. Nazario, F.M. Lancas TrAC Trends in Analytical Chemistry (2015) 71 9–25.
3. L. Vidal, M.-L. Riekkola, A. Canals, Analytica Chimica Acta (2012) 715 19-41.

Vortex-Assisted Solid Phase Extraction of Lead by Highly Porous Zirconium Metal–Organic Framework

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Recently, hetero-structured nanocomposites have received attention due to their new physicochemical properties compared with their single component analogues. Among various nanomaterials, metal-organic frameworks (MOFs), which are a new type of porous crystalline materials that are fabricated by linking metal ions or clusters and organic molecules by strong bonds, have attracted significant attention due to their larger specific surface areas, easy separation, higher porosity, diversity of structures and functions. They can contain many different functional groups which make them useful for a variety of applications such as gas separation and storage, catalysis, energy storage, sensors, pollutant removal and biomedicine. MOFs are especially useful adsorbents for the removal of hazardous materials [1-2].

In this study, a porous zirconium metal–organic framework (MOF-545) adsorbent was synthesized and characterized. The MOF-545 was used for the first time as an effective adsorbent for the separation/preconcentration of the lead ions in various samples prior to detection. The pH, amount of adsorbent, adsorption and elution contact times, centrifugation rate and time, eluent type, volume and concentration, sample volume, and interfering ions were examined. Optimum pH was found to be 7. A vortexing time of 15 min was selected as contact time. Only ten milligrams of MOF-545 was enough for adsorption. The centrifuge speed and time were found to be 4000 rpm and 5 min, respectively. The eluent was 2 mL of 1 mol L⁻¹ HCl. The preconcentration factor of the method was found to be 88.

Keywords: Porous Zirconium Metal–Organic Framework, Lead, Solid Phase Extraction, FAAS

References:

1. X. Zhao, S. Liu, Z. Tang, H. Niu, Y. Cai, W. Meng, F. Wu, J. P. Giesy Scientific Reports (2015) 5 11849-11859.
2. Z. Wang, J. Wang, M. Li, K. Sun, C.-jun Liu Scientific Reports (2014) 4 5939-5945.

Quantification of Selected Essential and Toxic Elements in Royal Jelly Samples from Bulgaria by ICP-OES and ETAAS

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The reliable characterization of major and trace elements content in Bulgarian Royal Jellies could be accepted as a possibility to detect adulterations of this relatively expensive product. Although Royal Jelly (RJ) is important product from a commercial point of view, there are relatively limited researches in this area. Analysis of RJs from different geographical regions is important from both view point –to define essential elements content, which ensures health benefits and to confirm potential absence of toxic elements which could have hard adverse effects on humans.

The purpose of the present study was to quantify a number of major and trace chemical elements in various RJ samples from Bulgaria. The analyses are focused on the determination of essential elements like K, P, Ca, Mg, Na, Fe, Zn and toxic elements such as As, Pb, Cd, Co and Ni. Results obtained will be discussed in the light of suggestion that RJ is a form of lactation on the insect level and shows homeostatic adjustments of chemical elements content.

Keywords: Royal Jelly, Essential Elements, Toxic Elements, ICP-OES, ETAAS

Traditional Bulgarian Wines – Characterization and Identification

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Wine is relatively “easy” for adulteration product and “difficult” for authenticity and origin certification. The chemical composition of wine depends on many factors, some of which are related to the specific production area. This complex picture makes the choice of methodological approach for wine identification and confirmation of its authenticity and origin quite problematic. The efforts are focused to choose suitable descriptors, which allow obtaining of maximum reliable identification. In respect of mineral content it is proven: highest number of elements determination is not quite effective. Contrariwise the ratios Mg/Rb, K/Rb, Ca/Sr give much more reliable information about geographical origin. The purpose of the present work is to choose the most suitable descriptors for chemical elements (including identification of elements, concentration ratios of element and isotope ratios) for identification of varietal and geographical origin of Bulgarian wines. In order to investigate elements migration in the system soil-grape-wine experiments were carried out with model wines with definite varietal origin and definite production technology. Elements, which were determined in wine samples, were also determined in soil extracts from Rhizosphere area in order to obtain information about the bioavailable fraction of elements which pass on from soil to grape vine. The same elements were quantified in vine leaves in order to separate the influence of aerosol from the soil phytoavailability on chemical elements content. In addition desired elements were determined in each technological step through winemaking process. By this way there were defined the changes of elements’ concentrations during the winemaking process and influence of different clarifying procedures and agents on additional redistribution of elements from initial must to final wine product.

Keywords: Wine, Origin, Identification, ICP-MS

Multi-element Determination of Trace Metals in Un-digested Honey Samples by ICP-MS

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Honey as a naturally-produced liquid from the nectar of plants by honey bees, *Apis Mellifera*, consists of carbohydrate-based components, water, proteins, organic acids, and vitamins.

Although mineral content of honey is only around 0.1%, the concentrations of metals vary considerably. As elemental composition is associated with the geographic origin where melliferous flora grows it has been used in authentication. On the other hand, the mineral content has been used as a quality assessment. Finally, the metal content of honey has been utilized in environmental monitoring. Consequently, the reliable determination of trace elements in honey is important in terms of nutrition, toxicology, quality control, and environmental monitoring.

Trace element determination in honey mostly requires previous digestion of sample prior to analysis using sensitive instruments. The thermal treatment and aqueous dilution procedures lead to deterioration in method detection limit and precision also to increased cost and environmental waste.

This study describes simple and fast analysis of honey samples omitting thermal treatment procedure by ICP-MS using aerosol dilution approach.

Keywords: Honey, Trace Elements, Aerosol Dilution, ICP-MS.

References:

1. Döker, S., Aydemir, O., Uslu, M. *Analytical Letters* (2014) 47 2080–2094.
2. Fernandez-Torres, R., Perez-Bernal, J. L., Bello-Lopez, M. A., Callejon-Mocho, M., Jimenez-Sanchez, J. C., Guiraum-Perez, A. *Talanta* (2005) 65 686–691.
3. Fodor, P., Molnar, E. *Mikrochim. Acta.* (1993) 112 113–118.

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Atmospheric Dry Deposition of Heavy Metals in Çankırı, Turkey

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Airborne particles carry various organic and inorganic pollutants and have been of considerable environmental interest due to their impacts on environment and human health. It affects also materials, soil, plants, aquatic life and visibility. As volcanic activities and storms are major sources of natural atmospheric particles, fossil fuels, urban waste and other industrial activities constitute anthropogenic sources.

Wet and dry deposition is considered to be one of main process removing pollutants from the atmosphere. Despite public concerns, knowledge of metal deposition from the atmosphere through atmospheric particles remains scarce.

This study deals with the analysis of atmospheric particles collected through dry deposition in Çankırı city center. Analysis is based on the extraction of heavy metals from particulate matter and elemental determination using inductively coupled plasma mass spectrometry (ICP-MS).

Keywords: Airborne Particles, Dry Deposition, Heavy Metals, ICP-MS.

References:

1. Yatin, M., Tuncel, S., Aras, N.K., Olmez, I., Aygun, S., Tuncel, G. Atmos. Environ. (2000) 34 1305–1318.
2. Kim, K.H., Lee, J.H., Jang, M.S. Environ. Pollut. (2002) 118 41– 51.

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Selenium Enrichment in *Petroselinum crispum*

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Selenium is an essential element for animals and human. It has anticancer and antioxidant properties. Low Se content of water and soil in European Countries and Turkey leads to health problems arising from low Se levels in human and animals. The productions of Se-enriched vegetables such as garlic, broccoli, cabbage and the sales of Se-supplements have become widespread to eliminate Se deficiency in humans.

Parsley (*Petroselinum crispum*) is widely used in Asian, European and American cuisine and a good candidate to produce a Se-rich food. It may be consumed either raw or cooked.

The present study consists of growing of plants in pots and enrichment via foliar application of selenium. Efficiency of diverse forms of Se, selenite and selenate, will be assessed in assimilation of selenium in parsley. Se content will be determined after acidic digestion of samples followed by ICP-MS analysis.

Keywords: *Petroselinum Crispum*, Selenium Enrichment, ICP-MS.

References:

1. Clark, L.C., Combs, GF. Jr., Turnbull, B.W., Slate, E.H., Chalker, D.K., Chow, J. JAMA (1996) 276 1957-1963.
2. Thiry, C., Ruttens, A., De Temmerman, L., Schneider, Y-J, Pussemier, L. Food Chemistry (2012) 130 767–784.
3. Pedrero, Z., Madrid, Y. Analytica Chimica Acta (2009) 634 135–152.
4. SCF, Scientific Committee on Food. (2000). SCF/CS/NUT/UPPLEV/25Final, p. 1–18.

Acknowledgements

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Assessment of Toxic Trace Element Concentrations in Ground Water Samples Collected from Çankırı, Turkey

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Water quality is an essential requirement to the environment and human health. Ground water consists of elements present at ultra-trace to high ppm levels in dissolved state depending on the geological environment. Drinking of water with toxic metals at high levels or for long term may cause various health effects to the human and other livings. Ground water pollution is an important problem in worldwide since it is consumed by human and animals and used in agriculture. Soil erosion, the reach of industrial and municipal waste into the underground and other activities contaminate the water.

In this study 22 samples were collected in various villages of Çankırı where most of them are used for drinking by animals and human beings. The element levels were determined by ICPMS. The results showed that some element concentrations were higher than the drinking water quality standards given by World Health Organization (WHO). ICP-MS multi-element fingerprinting should find a more routine use to for assessment of water quality and temporal variations in element levels especially for toxic ones.

Keywords: Ground Water, Toxic Trace Elements, ICP-MS.

References:

1. Stetzenbach, K.J., Amano, M., Kreamer, D.K., Hodge, V.F. Ground Water, (1994) 32 976-985.
2. Rasheed, M.A., Rao, P.L.S., Radha, B.A., Lakshmi, M., Dayal, A.M. Journal of Environmental Protection and Ecology, (2011) 12 425-433.

Acknowledgements

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The Levels of Co, Cr, Ni and Zn in the Soil Formed on Different Geological Materials between Çanakkale and Çan District (Turkey)

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The soil is a dynamic system that undergoes gradual changes in response to changes in environmental factors. Soil formation is the process by which a thin surface layer of soil develops on weathered rock material [1]. Weathering can be chemically defined as the process of dissolution, hydration, oxidation, reduction and carbonation. Chemical weathering brings about the destruction of parent materials and to the passing of the elements from the minerals into solutions [2]. The aim of this study is to determine the content of Co, Cr, Ni and Zn in the soil formed on various geological materials between Çanakkale and Çan district (Turkey). For this purpose eleven samples in total were taken from the soil surface (0-20 cm depth) formed on the igneous rocks. Geological facies range from altered andezite to kaolinite. These are; andesite-kaolinited tuff, andesite (andesite together basalt), andesited tuff (fertric and zeolite), basalt, kaolinite formed by alteration of rhyolite and andesite, alteration with iron, kaolinite mine (kaolinited tuff), andesited agglomera, over coal (kaolinited alteration), andesited tuff, serpentinized ophiolite. The total trace metal contents of soil samples were determined through using the *aqua regia* digestion (HCl/HNO₃, volume ratio of 1/3) procedure [3]. The concentrations of trace metals were determined by means of a flame atomic absorption spectrometer (Analytic Jena Model novAA-350) equipped with a hollow cathode lamp. Data accuracy was assessed by a certified reference material (NIM-GBW07425, soil) and considering all metals, recoveries were found to be satisfactory. The results indicated that the highest levels of Co, Cr and Ni were determined as 143 mg kg⁻¹, 1289.8 mg kg⁻¹ and 944.6 mg kg⁻¹ on the serpentinized ophiolite, respectively. In other sampling parts, Co was found between 14.3 and 61.2 mg kg⁻¹, Cr is found between 25.5 and 131.5 mg kg⁻¹ and lastly Ni was found between 3.0 and 34.5 mg kg⁻¹. The highest Zn values formed on andesite. The soil forming on the andesite-basalt togetherness and the kaolinited tuff was found as 81 mg kg⁻¹ and 77 mg kg⁻¹ for Zn.

Keywords: Geological Materials, Soil, Co, Cr, Ni, Zn

References:

1. Alloway, B. J. Heavy Metals in Soils (1990) Blackie Academic and Professional, Glasgow.
2. Kabata-Pendias, A. Trace Elements in Soils and Plants (2011) CRC Press, Boca Raton, Florida.
3. Tuzen, M., Sari, H., Soylak, M. Analytical Letters (2004) 37 9 1925–1936.

Assessment of Multi-Elemental Composition in Different Types of Linden (*Tilia* sp.) Samples

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Growing interest on the complementary and alternative medicine raises the concerns related with exposure to contaminants such as heavy metals. Contamination of the herbal materials with toxic metals can be attributed to many sources. Environmental pollution contributes to the problem mostly during the cultivation/growth (e.g. emissions from industry, vehicles, contaminated water sources and soil); however, various manufacturing processes (e.g. grinding) also lead to contamination of the products. Presence of potentially toxic metals necessitates use of versatile analytical methods. In multi-element analysis, inductively coupled plasma mass spectrometry (ICP-MS) has become a method-of-choice with its low limit of detection and wide linear dynamic range.

The aim of our study was to simultaneously determine total concentrations of 29 toxic, essential and some other elements in different types of commercially available linden samples. A systematical sampling was followed (n=60), i.e. 5 different types (tea bags, packed flowers, unpacked flowers, packed leaves, unpacked leaves), each consisting of 12 samples were collected. Samples were homogenized using an agate mortar and pestle, and then digested in HNO₃ and H₂O₂ with microwave digestion system. ICP-MS was used for determination of following elements (and isotopes): lithium(⁷Li), beryllium(⁹Be), sodium(²³Na), magnesium(²⁶Mg), aluminum(²⁷Al), potassium(³⁹K), calcium(⁴³Ca), vanadium(⁵¹V), chromium(⁵²Cr), manganese(⁵⁵Mn), iron(⁵⁷Fe), cobalt(⁵⁹Co), nickel(⁶⁰Ni), copper(⁶³Cu), zinc(⁶⁶Zn), gallium(⁶⁹Ga), arsenic(⁷⁵As), selenium (⁷⁸Se), rubidium(⁸⁵Rb), strontium(⁸⁸Sr), silver(¹⁰⁷Ag), cadmium(¹¹¹Cd), tin(¹¹⁸Sn), antimony(¹²¹Sb), tellurium(¹²⁵Te), barium(¹³⁷Ba), mercury(²⁰²Hg), thallium(²⁰⁵Tl) and lead(²⁰⁸Pb).

The results have shown that concentrations of some elements (e.g. Li, Al, K, V, Cr, Fe, As, Ag, Cd, Sb, Te, Hg, Pb) - mostly in tea bags- were statistically different as compared with other sample types. It is essential to note that while some elements may be beneficial, excessive use of herbal products may result in an increase of total concentration of toxic elements exposed. Current findings highlight the importance of safe use and verification of manufacturing steps.

Keywords: ICP-MS, Multi-Element Analysis, *Tilia* Sp., Flower and Leaf Samples, Tea Bags

References:

1. European Medicines Agency (EMA), Committee on Herbal Medicinal Products (HMPC) Assessment Report on *Tilia cordata* Miller, *Tilia platyphyllos* Scop., *Tilia x vulgaris* Heyne or their mixtures, flos. (13 September 2011) EMA/HMPC/337067/2011
2. Pytlakowska K, Kita A, Janoska P, Polowniak M, Kozik V. Food Chem. (2012) 135 494-501.
3. Tokaloğlu Ş. Food Chem. (2012) 134 2504-2508.

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Determination of Toxic Trace Elements (Al, Ni, As, Cd, Pb) in Samples of *Salvia fruticosa* Mill. Collected from Hatay and Antalya, Turkey

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The use of natural products and particularly herbal materials for treating diseases has probably been as early as the history of human being. Globally, many herbal materials such as *Salvia* species are in common use. It is essential that use of herbal materials must meet the criteria of both safety and efficacy. For necessary protection of the patient/consumer, quality should be controlled as strictly and systematically as possible. *Salvia fruticosa* Mill. is a naturally grown species in Mediterranean region, used mainly as infusion or decoction for mucosal inflammations and infections especially of the mouth and throat as well as for some digestive disorders.

In this study, samples of *S. fruticosa* (n=10) were collected from Hatay and Antalya, Turkey. ICP-MS was used for simultaneous determination of some toxic trace elements (Al, Ni, As, Cd, Pb). The results showed that Pb levels were not generally above recommendations of World Health Organization. However, for most of the samples a regional impact may appear especially with regard to Al. Therefore, ICP-MS multi-element fingerprinting should find more routine use in the evaluation of herbal material quality.

Keywords: *Salvia Fruticosa* Mill., Toxic Trace Elements, ICP-MS.

References:

1. World Health Organization (2007). WHO guidelines for assessing quality of herbal medicines with reference to contaminants and residues.
2. European Medicines Agency (2015). Assessment report on *Salvia fruticosa* Mill., folium.

Acknowledgements

This study was partially supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK) projects-112T365 and 214O244. Çankırı Karatekin University is also acknowledged, project no: FF060515B31.

Heavy Metal Analysis by Flow Injection System

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Heavy metals determination of ultra trace concentration in environmental and food samples is important. Some heavy metals such as Cd(II) ions have toxic properties even at trace levels.

Flame atomic absorption spectrometry (FAAS) is one of the most extensively used techniques for the determination of various elements with significant precision and accuracy. However, there are many difficulties in trace determination of heavy metals in environmental samples due to insufficient sensitivity. Metals can be determined at trace levels by addition of preconcentration and Flow Injection Analysis (FIA) systems to the analytical process.

FIA systems allow inexpensive automation of chemical analysis [1]. Moreover, it works in a closed system with a significant reduction of airborne contamination and a fairly high sampling frequency [2]. In FIA experiments, a known sample volume is injected into a flowing stream solution. FIA systems consist of pumps, an injection valve, a mini column, and a detector [3]. Several flow injection analyses applications have been described in the literature [4].

In this study, as a preconcentration adsorbent, we used composite polymers such as chitosan, pumice-chitosan, and carbonnanotube-chitosan beads. Optimization of adsorption and desorption studies were done by batch studies. Highest adsorption and desorption values were obtained by using pumice-chitosan beads. Adsorption capacities for Cd(II) ions were calculated as 0.41 mg g⁻¹ respectively. Cd(II) ions were eluted from the column via 0.1 M EDTA and determination of Cd(II) ions were done by using flame AAS. The optimum experimental conditions (loading time, eluent concentration, flow rate, effect of pH,) were also investigated.

Keywords: FIA, Cadmium, Preconcentration, Heavy Metals

References:

1. J. Ruzicka, E.H. Hansen, Flow Injection Analysis, second ed., (1988) Wiley, New York.
2. P.C. Rudner, A.G. Torres, J.M.C. Pavoin, F.S. Rojas, Talanta (1998) 46 1095
3. Trojanowicz, M. *Flow Injection Analysis Instrumentation and Applications*; World Scientific: Singapore (2000).
4. Z. Fang, G.Tao, Fresenius J. Anal. Chem., (1996) 355 376-580

Element Analysis of Animal Feed by Inductively Coupled Plasma Mass Spectrometer after microwave digestion extraction

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Abstract

In this study, 100 pieces in a variety of animal feeds like beef cattle feed, small ruminant feed, poultry feed, mixed feed and feed ingredients were randomly collected from different feed mills and feed sales shop located in Kocaeli, Sakarya, and Yalova provinces. The elements of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Se, Sn, and Zn were examined in animal feeds and feed additives by using inductively coupled plasma mass spectrometer (ICP-MS). Microwave digestion procedure was used to digest the sample matrices and the consequent digests were subjected to the by inductively coupled plasma mass spectrometer (ICP-MS). The digestion of animal feed samples was carried out with concentrated nitric acid and hydrogen peroxide (3:1) with the help of microwave heating. The concentrations of macro and micro element in animal feed samples were found to be 47-64, 2.8-6.9, 0.039-0.067, 0.156-0.38, 0.035-1.3, 14-22, 40-85, 1.9-4.1, 0.047-0.18, 224-357, 42, 92 mg kg⁻¹ for aluminum, barium, cadmium, cobalt, chromium, copper, manganese, nickel, lead, selenium, zinc and 0.028-7.2, 0.33-0.36, 23-48, 1.8-4.6, 1.4-4.4, 0.27-0.43 g/100g for calcium, iron, potassium, magnesium, sodium and phosphor. High macro element accumulation levels in the samples were found in small cattle feed and micro accumulation levels were determined in mixed feed samples.

Keywords: Animal Feed, Element, ICP-MS, Risk Assessment, Livestock Feed

Introduction

Heavy metal pollution caused by industrialization is a serious problem for the whole world. Metals have proven to accumulate in soil, water, and air. When animals eat contaminated feed, harmful substance (such as; pesticide, heavy metal, and aflatoxin) are taken into the human body from milk, meat and egg products. Animal foods are an important part of human diet world wide because they contain healthy food protein. Thus, the animal feeds that are eaten are essential determinants of the healthy and quality of human diet [1]. However, all elements present in different types of animal feeds at elevated level can cause several adverse health problems to animal [2]. For example, some elements such as Cd, Pb, Zn and Cu in the poultry feeds are both important due to their essential function and toxic due to the deleterious effect on poultry which may accumulate particularly in the liver and kidney [2]. That's why animal feeds should be kept under control for human health [3]. Trace element contaminant in animal feed causes a hazard to both animal health and human food safety [4].

The management of animal feed safety risks using a risk management framework begins with identifying and quantifying the presence of hazards. For animal feed, insufficient information exists about the presence of heavy metal in feed ingredients, premixes, and finished the feed. That's why macro and micro elements must be restricted in the diet at the adequate levels in order to achieve the best response and to offer protection for the consumers. For the safety of both, dietary maximum tolerable levels of these elements have been provided which is serving as guidelines to control the quality of different types of animal feeds.

Many atomic spectroscopic techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace spectrometry (GFAAS), inductively coupled plasma optical emission or mass spectrometry (ICP-OES or ICP-MS) have been widely used for the quantitative analysis of macro and micro elements concentration in different types of animal feed products. [5, 6, 7, 8]. One of the most important advantages of the ICP-MS is more sensitive, higher selectivity and accuracy in complicated matrices than ICP-OES and FAAS spectrometry. Moreover, it has a much larger dynamic range and greater multi-element capability than graphite furnace atomic absorption spectrometry (GF-AAS).

The elemental analysis of animal feed products typically requires acid digestion for the reduction of matrix interference and sample decomposition prior to the determination by atomic spectrometric techniques. Conventional wet digestion methods performed by using hot plate requires high boiling point acid mixtures and long reaction times. In dry digestion methods also required high boiling points and longer reaction times. After dry and wet digestion methods, filtration is required which cause sample loss and contamination [9]. The possible advantages of microwave digestion extraction method is as follow: simplicity, reduce the risk of sample contamination, reagent use, losses from evaporation and sample preparation times [10, 11]. Additionally, the elevated temperature increases the oxidizing power of mineral acid and provides the higher decomposition of matrix components [9].

In the current study, different types of animal feeds were determined by ICP-MS technique after microwave digestion procedure.

Materials&Methods

Instruments and apparatus: An Agilent 7700 ICP-MS measurement was performed for simultaneous multi-element detection of the macro, micro and toxic element. Aqueous solutions were introduced to the nebulizer spray chamber by an ASX-500 autosampler which was also used to reduce detection time and sample volume. A MARSXpress microwave digestion system (CEM Corporation, Matthews, North Carolina) was used for digestion of animal feed samples. A Waring 1200 blender was used for homogenization of samples.

Reagents: All solutions were prepared with analytical reagent ultra-pure grade. Argon and helium purity was higher than 99.999 %. Water was purified with the multi-stage process from an ELGA system. To optimize the performance (torch alignment, RF power, and nebulizer flow rate, suitable ion lens voltage for maximal signal) of ICP-MS before use, capable of covering a wide range of masses ($1 \mu\text{g L}^{-1}$ of Ce, Co, Li, Mg, Tl and Y in a matrix of 2% HNO_3 (w/v)) was purchased from Agilent Technologies (Santa Monica, CA, USA). Suprapur[®] HNO_3 65%, H_2O_2 %30, and a stock standard solution containing 1000 mg/L of each element was purchased from Merck (Darmstadt, Germany). The multi-element calibration solutions were prepared at different levels (range from 0,5 $\mu\text{g/L}$ to 2000 $\mu\text{g/L}$) from 1000 mg/L single element ICP-MS certipur standard, traceable to SRM from NIST, were purchased from Merck KGaA (Germany).

Sampling: A total of 68 feed samples was collected from feed mills and from their outlets in three different areas (Kocaeli, Sakarya, and Yalova) Turkey. The feed samples divided into five groups: poultry, beef cattle, small ruminant, mixed feed, and feed additive. For the beef cattle feed samples, 17 feed materials were the collection. For the poultry feed samples, 5 feed materials were the collection. For the small ruminant feed samples, 4 feed materials were the collection. For the mixed feed, 29 sample materials were the collection. For feed additive materials, the total of 13 sample was the collection. Choice of groups is settled on the typical animal species feed on commercial feed. A subsample of 500 g of each sample taken was ground to particle sizes lower than 1mm. Then, homogenized materials were packed in polyethylene bags and stored away from light at +4 °C until analysis.

Sample treatment: The total concentrations of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Se, Sn and Zn elements were determined by using after microwave digestion system. 1 g animal feed, mixed feed, and feed additive samples were transferred to teflon bomb and 6 mL of %65 HNO₃ and 2 mL of %30 H₂O₂ were added. After digestion, the final volume was made up 50 mL in a volumetric flask with ultrapure water. The final solutions were analyzed for studied elements by inductively coupled plasma mass spectrometer [12].

Results&Discussion

The concentrations of macro and micro elements were determined in animal feeds and feed additives after microwave digestion followed by ICP-MS measurements. The results of all analyzed animal feed and feed additives samples for Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Se, Sn, and Zn are shown in Table 1 and 2.

Table 1. Micro element concentrations (mg kg⁻¹) of animal feeds and feed additives.

Element	Feed additives (n=13)	Beef cattle (n=17)	Small ruminant (n=4)	Poultry (n=5)	Mixed (n=29)
Al	61±16	55±10	48±2	47±4	64±14
As	nd	nd	nd	nd	nd
Ba	2.8±0.9	3.7±1.1	6.9±0.1	3.2±0.7	4.6±1.9
Cd	0.044±0.017	0.042±0.005	0.039±0.005	0.067±0.004	0.063±0.047
Co	0.16±0.05	0.15±0.05	0.18±0.05	0.38±0.09	0.22±0.08
Cr	0.37±0.12	0.35±0.08	0.35±0.02	1.3±0.4	0.48±0.16
Cu	21±6	15±4	14±3	22±4	17±6
Fe*	0.36±0.08	0.35±0.05	0.33±0.02	0.35±0.04	0.34±0.06
Hg	nd	nd	nd	nd	nd
Mn	40±7	75±14	85±2	43±10	49±16
Ni	4.1±1.8	2.8±0.5	2.6±0.1	1.9±0.3	2.7±0.8
Pb	0.050±0.013	0.085±0.005	0.18±0.03	0.060±0.009	0.047±0.013
Se	224±29	357±29	252±11	281±22	225±42
Sn	nd	nd	nd	nd	nd
Zn	49±12	42±7	45±4	92±6	61±15

nd: below the limit of detection

*g/100g

Table 2. Macro element concentrations (g/100g) of animal feeds and feed additives.

Element	Feed additives (n=13)	Beef cattle (n=17)	Small ruminant (n=4)	Poultry (n=5)	Mixed (n=29)
Ca	0.028±0.006	0.070±0.014	7.2±0.2	0.070±0.007	0.11±0.04
K	48±9	28±5	23±1	25±7	27±5
Mg	4.6±1.1	3.3±0.3	3.7±0.5	1.8±0.2	3.1±0.9
Na	nd.	3.3±0.8	4.4±0.3	1.4±0.1	2.4±1.2
P	0.43±0.12	0.31±0.04	0.37±0.02	0.27±0.05	0.29±0.06

nd: below the limit of detection

In the most analyzed animal feed and feed additive samples, the amount of the analyzed elements was found to be good agreement with the maximum tolerable level of National Research Council (NRC), The European Commission Regulation (EU) and Turkish Animal Feed Codex (TAFC) [13, 14, 15, 16]. Great variation for Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, and Zn was observed among the animal feed and feed additives samples. Animal feeds and feed additives are made from a variety of agricultural crops.

Additionally, they have complicated compositions, which introduce great discussions for feed analysis. Animal feed and feed additives generally contain lipid, protein as well as supplemental vitamins, minerals and antibiotics. The cellulose, protein, ash and moisture content (%) of animal feed and feed additive is given in Table 3. Limits of detection calculating to the 3 s criterion were 16.5, 51.9, 4.8, 10.3, 4.3, 8.5, 12.3, 36.7, 12.3, 0.97, 79.7, 46.4, 0.40, 199.8, 3.8, 129.6, 78.0, 578.4, 752. 5 µg L⁻¹ for Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn, Ca, Fe, K, Mg, Na, and P, respectively.

Table 3. Cellulose, protein, ash and moisture content (%) of animal feeds and feed additives.

	Cellulose (%)	Protein (%)	Ash (%)	Moisture (%)
Feed additives (n=13)	14±9	41±6	7.1±0.7	8.8±1.4
beef cattle (n=17)	12±5	17±3	10±3	10±1
Small ruminant (n=4)	14±1	17±4	13±2	10±1
Poultry (n=5)	2.4±0.3	21±3	6.8±3.5	8.6±1.1
Mixed feed (n=29)	11±4	17±3	7.9±1.9	8.6±1.7

Conclusion

Quantitative analysis of macro and micro elements in animal feed products like beef cattle feed, small ruminant feed, poultry feed, mixed feed and feed additives by using inductively coupled plasma mass spectroscopy technology after microwave digestion was demonstrated in this work. Microwave digestion procedure for the determination of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Se, Sn and Zn in animal feeds and feed additive samples by using ICP-MS is useful, simple and sensitive for routine analysis and it can be considered excellent sample preparation procedure.

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References:

1. T.G. Kazi, A.Q. Shah, H.I. Afridi, N.A. Shah, M.B. Arain *Ecotox Environ Safe* (2013) 87 120–123.
2. S.A. Mahesar, S.T.H. Sherazi, A. Niaz, et al. *Food Chem Toxicol* (2010) 48 2357–2360.
3. Ö. Dağışan, N. Özen *Akdeniz Univ. Ziraat Fakültesi. Dergisi.* (2011) 24 9-13.
4. S.Y. Dai, B. Jones, K.M. Lee, et al. *Journal of Regulatory Science* (2016) 1 21-32.
5. M.T. Vidal, M.C. Pascual-Mart, A. Salvador, C. Llabata *Microchem J* (2002) 72 221–228.
6. C.P. Bosnak, W.K. Barnes *Atomic Spectroscopy* (1998) 19 40-42.
7. W. Li, P. Simmons, D. Shrader, T.J. Herrman, S.Y. Dai *Talanta* (2013) 112 43–48.
8. P. Atkins, L. Ernyei, W. Driscoll, R. Obenauf, R. Thomas *Spectroscopy* (2011) 26 46-56.
9. Z. Yang, X. Hou, B.T. Jones, D.C. Sane, et al. *Microchemical Journal* (2002) 72 49–54.
10. H.M.S. Kingston *Atomic spectroscopy* (1998) 19 27-31.
11. D. Bakircioglu, Y.B. Kurtulus, G. Ucar *Food and Chemical Toxicology* (2011) 49 202-207.
12. D. Mendil, Z. Demirci, M. Tuzen, M. Soylak *Food and Chemical Toxicology* (2010) 48 865-870.
13. EU Directive (2015) Commission regulation 2015/186 of 6 February 2015 amending Annex I to Directive 2002/32/EC of the European Parliament and of the Council as regards maximum levels for arsenic, fluorine, lead, mercury, endosulfan and Ambrosia seeds (Text with EEA relevance)
14. NRC, 1980. *Mineral Tolerance of Domestic Animals*. National Academy Press, Washington, DC.
15. NRC, 1994. *Nutrient Requirements of Poultry*, ninth rev. ed. National Academy Press, Washington, DC.
16. TAFC, Turkish food codex Notification on food additives. 2014/14 regarding undesirable substances in animal feed.

Determination of Heavy Metals using Magnetic Solid-phase Extraction for Water samples

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Heavy metal pollution occurs globally in water. Rising demands for clean water with extremely low levels of heavy metals make it greatly important to develop various efficient technologies for heavy metal removal. Recent research indicated that humic acid (HA) has high affinity to Fe₃O₄ nanoparticles, and sorption of HA on the Fe₃O₄ nanoparticles enhanced the stability of nano dispersions by preventing their aggregation [1]. Humic acid is generally characterized by a dark brown to black color. It is an odorless, colloidal poly dispersed substance, and assumed to be hydrophilic and acidic in nature [2]. The capacity to bind metal ions is one of the most important physicochemical properties of humic substances (HS). This property is mainly attributed to the large content of oxygenated reactive functional groups of HS, which include carboxylic, phenolic, alcoholic, and enolic hydroxyl groups, and carbonyl functionalities of various types [3].

The aim of this work is to find the removal percentage of copper and cadmium ions from water samples using synthesized Fe₃O₄/HA/Ag multifunctional composite structure. For the synthesis of the structure co-precipitation process was used in a basic medium. Synthesis was made in air atmosphere and particles were dried in 60 °C. Characterization of particles was made with Scanning Electron Microscope (SEM) combined with EDX mode. Zeta Potential and Dynamic Light Scattering (DLS) analysis was made to support SEM image and to find the mean diameter of the particles. Heavy metal adsorption was carried out using Atomic Absorption Spectrometer (AAS). The concentration of magnetic adsorbent was fixed at 20 mg particle/25 mL solution. Unless otherwise specified, the adsorption experiments were performed in aqueous solution at pH 9. Solution concentration ranged between 0.5 to 2 ppm. As a result removal percentage of copper and cadmium was found 92% and 97%, respectively.

Keywords: Adsorption, Heavy Metals, Humic Acid, Nanoparticles.

References:

1. Vrana B. G.A. Mills, et.al.; Trends Anal. Chem. (2005) 24 845.
2. J. Liu, Z. Zhao and G. Jiang; Environ. Sci. Technol. (2008) 42 6949-6954
3. F.N. Crespilho, V. Zucolotto, J.R. Siqueira, C.J.L. Constantino, F.C. Nart, O.N. Oliveira Jr., Environ. Sci. Technol. (2005) 39 5385–5389.

Sulfur Determination in Some Nuts and Dried Fruits Sold in Turkey By High Resolution Graphite Furnace Molecular Absorption Spectrometry

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This work describes the determination of S in some nuts and dried fruits using a High Resolution Continuum Source Electrothermal Atomic Absorption Spectrometer (HR-CS ET AAS). The two rotational molecular of CS at 257.959 nm and 258.056 nm were simultaneously evaluated. Sulfur was determined in a W coated graphite tube/platform at the two wavelengths mentioned above using thiourea as a calibrant, Pd/citric acid as a matrix modifier and applying a pyrolysis temperature of 800 °C and a molecule forming (vaporization) temperature of 2200 °C.

The calibration curve prepared from thiourea was linear up to 2500 ng of S. The limit of detection and characteristic mass of the method were 21.6 ng and 7.4 ng of S, respectively. The accuracy of the method was tested by analyzing certified reference spinach, milk powder, tea samples applying linear calibration technique prepared from thiourea aqueous standard. The results were in good agreement with the certified values.

Keywords: Sulfur, Nuts, Dried Fruits, Molecular Absorption, High-Resolution Continuum Source Electrothermal Atomic Absorption Spectrometer

Fabrication of Fe₃O₄ Embedded Polymer for Removal of As(V) Ions

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Polymers have been widely used in metal removal studies due to have high removal capacity via many different functional groups [1]. They are also thermal stable and environmentally safe materials. Nano/micro particle-polymer hybrid materials have been recently used for the removal of toxic metals from wastewater. Fe₃O₄ is one of the used particles due to small size, high surface area, easy separation and reusability features of these nanoparticles [2]. Hybrid materials are useful in multiple fields via high physical, chemical and mechanical properties [3].

Acrylamide as a monomer and triazine compound as a copolymer agent was used in the present study. Fe₃O₄ particles were synthesized and added to the polymerization media. The polymerization was carried out by photo initiation radical polymerization method. After synthesis, the obtained acrylamide-triazine polymer was washed with double distilled water and vacuum drying at 25°C. The As(V) metal ion solutions were prepared by using ICP standard solution with double distilled deionized water. The experiments were carried out by adding 0.25 g Fe₃O₄ embedded polymer with rotary shaker. The heavy metal concentrations in treated solutions were analyzed in ICP-OES.

According to the results, the removal percentage was 100% at pH 2.5 under the conditions of contact time 150 min, agitation rate 150 rpm, temperature 25°C, initial As(V) ion concentration 2.5 mg/L, and polymer dosage 0.25 g.

Keywords: Polymer, Fe₃O₄, arsenic, acrylamide, triazine

References:

1. M.A. Barakat Arabian Journal of Chemistry (2011) 4 361–377.
2. Pragnesh N. Dave, Lakhani V. Chopda Journal of Nanotechnology (2014) 398569
3. Babak Samiey, Chil-Hung Cheng, Jiangning Wu Materials (2014) 7 673-726.

Application of Alginate-*Ficus Carica* L. Biocomposite for the Adsorption of Lead Ions from Aqueous Solutions

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Lead is a well-known highly toxic metal considered as a priority pollutant [1]. Among the heavy metals, lead is one of the major pollution sources which [are](#) discharged into the environment from metal finishing, ceramics, pulp, lead smelters, electroplating, mining and battery manufacturing industries [2]. The presence of high levels of lead in the environment may cause long-term health risks to humans and ecosystems. Therefore, it is necessary to remove the lead ions before they are released into the environment.

Fig (*Ficus carica* L.) is among the oldest fruits and is known to manhood from ancient times. *F. carica* L. (common fig), belonging to the Moraceae family, is a deciduous tree native to South-western Asia and the Eastern Mediterranean [3]. Figs are an important traditional crop in Turkey, due to the wide adaptability to the soil and climatic conditions [4].

Natural zeolites have been also known by their high ion-exchange capacity, relatively high specific surface areas and, more importantly, their relatively low prices [5]. The adsorptive properties of alginate based on the presence of carboxylic acid and hydroxyl functional groups that have a high affinity towards heavy metals. On the other hand, it is highly porous and allows an extended use of the surface [6].

In this study, fig leaves and zeolite were encapsulated into alginate beads to prepare a biocomposite for adsorption/biosorption of Pb(II) ions from aqueous solutions. Effects of various parameters on the adsorption process such as pH, temperature, initial lead concentration and contact time have been investigated. Under optimum conditions the amount of adsorbed lead per gram of adsorbent (q_e) was found to be approximately 10mg/g. The obtained results have suggested that the prepared biosorbent is suitable for the removal of Pb(II) ions from aqueous solutions.

Keywords: adsorption, lead, biosorbent, fig leaf, alginate

References:

1. Mondal MK Journal of Environmental Management (2009) 90 11 3266-3271.
2. Isaac RA, Gil L, Cooperman AN, Hulme K, Eddy B, Ruiz M, Jacobson K, Larson C, Pancorbo OC Environmental Science and Technology (1997) 31 3198–3203.
3. Ugulu I, Unver MC, Dogan Y. Oxidation Communications (2016) 39 765–775.
4. Aksoy U, Can HZ, Hepaksoy S, Sahin N (2001) Incir Yetistiriciligi. Turkiye Tarımsal Arastırma Projesi Yayinlari, Izmir.
5. Chmielewská E, Sabová L, Peterlik H, Wu A, Brazilian Journal of Chemical Engineering (2011) 28 1 63-71.
6. Navarro AE, Musaev H, Serrano K, Masud ME. J Earth Sci Clim Change (2014) 5 8 223-228.

Transport of Heavy Metals through a Novel Liquid Membrane System: MDLM

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Heavy metal ions such as Pb^{2+} , Cd^{2+} , Cr^{6+} , Hg^{2+} , Cu^{2+} , etc., are discharged into the environment from metal finishing, ceramics, pulp, lead smelters, electroplating, mining and battery manufacturing industries [1]. Water pollution caused by these heavy metal ions is extremely unsafe to the human beings, as they can penetrate into the human body through the food chain and thus cause cancer, central nervous system damage, lung damage, damage to the brain and eventually leads to death [2]. Therefore, the removal of toxic heavy metal contaminants from aqueous waste streams is currently one of the most important environmental issues being investigated.

Numerous technologies have been studied for years to remove heavy metal ions which include chemical precipitation, ion-exchange, adsorption, electro coagulation, extraction and membrane separation. Solvent extraction process is one of the techniques for separation and purification is widely used in recovery and separation of metal ions from aqueous solutions.

In this study, a new method which is more practical and more effective than other techniques is applied. This method resembles bulk liquid membrane system but shows a little difference. Actually it can be called as Multi Dropped Liquid Membrane System (MDLM). The advantages of this technique are as follows: simple construction, lack of moving parts, lightweight and portable, flexible in operation, high membrane capacity, high separation factor than mixer-settler. And this new method reduces operation time, risk of contamination, amounts of reagents used, generated waste. Because of these attractive advantages, the current experimental studies can be a great alternative and economical process in order to remove the heavy metal ions caused by heavy metal industries.

The system has been applied for transport of U^{6+} , Th^{4+} , Zn^{2+} , Mo^{6+} , Cr^{6+} , Pb^{2+} , Cu^{2+} , Cd^{2+} and Fe^{3+} ions from aqueous solutions and successful results have been obtained. Suitable donor, extractant, acceptor solutions and working conditions have been determined for each metal ion. The MDLM system that used in the current experimental studies can be a great alternative and economical process in order to remove the heavy metal ions caused by heavy metal industries.

Keywords: Liquid Membrane, Extraction, Heavy Metals, Transport, MDLM

References:

1. Isaac RA, Gil L, Cooperman AN, Hulme K, Eddy B, Ruiz M, Jacobson K, Larson C, Pancorbo OC Environmental Science and Technology (1997) 31 3198–3203.
2. Xiong L, Chen C, Chen Q, Ni J Journal of Hazardous Materials (2011) 189 741-748

Investigation of Platinum (IV) Adsorption by Polyamine Polymer

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In this study, adsorption of Pt (IV) ions from containing chloride solutions by 1,3,5-triazine pentaethylenhexamine (TAPEHA) polymer was investigated. The effective factors on the batch adsorption of Pt (IV) such as of acidity of aqueous phase, contact time, initial concentration and temperature were investigated and optimized. Concentration of Pt (IV) remaining in the solution after adsorption was measured using flame atomic absorption spectrometer and the adsorbed amount of Pt per gram of the polymer was calculated from difference of initial concentration and the final equilibrium concentration.

Adsorption of Pt (IV) was found to be maximal at 0.1M hydronium concentration and Pt (IV) adsorption was decreased by increasing of hydronium concentration. It was found to be increasing of temperature was caused to decrease in adsorption of Pt (IV). The contact time was found to be effective for adsorption of Pt, increasing of the time increases the adsorption of Pt (IV) until equilibrium condition occurs and the time to reach equilibrium was found to be 24 hours. Increasing of the initial concentration of Pt (IV) ions enhanced the adsorption until it reaches a saturation capacity of TAPEHA polymer. Pt (IV) adsorption kinetics was examined using kinetic models such as intra-particle diffusion model, pseudo first and second order equation and adsorption of Pt (IV) was found to be compatible with pseudo second order kinetic model. The equilibrium of Pt (IV) was investigated by using Langmuir and Freundlich equations. Adsorption isotherm of Pt (IV) is presented in Fig.1. Adsorption of Pt (IV) was found to be compatible with Langmuir equation providing an adsorption capacity of TAPEHA 909.1 mg/g for Pt (IV).

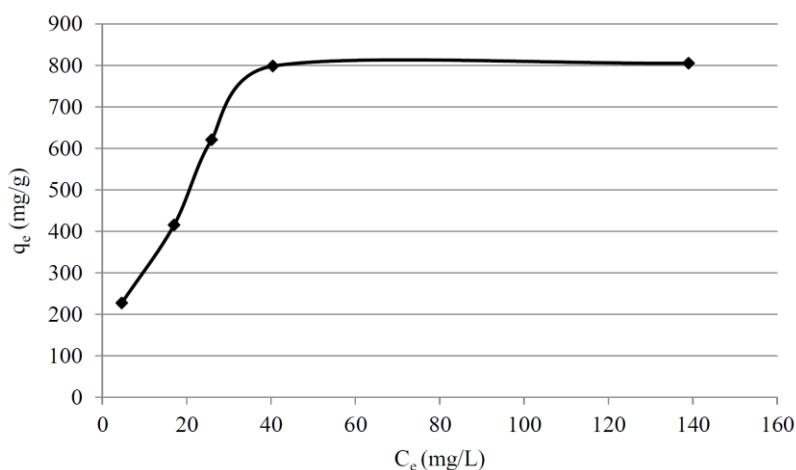


Fig.1. Adsorption isotherm of Pt (IV) by polyamine polymer

Keywords: Adsorption, Platinum, Triazine-Polyamine Polymer, Chelating Resin

Removal of Cu(II) Ions from Aqueous Solution by Hazelnut Husk Activated Carbon Prepared with Potassium Acetate

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Hazelnut husk, an agricultural waste, was converted to activated carbon (AC) material by chemical activation using potassium acetate. The AC was characterized by FT-IR, SEM, N₂ adsorption-desorption experiments, C,H,N elemental analysis, and determination of moisture, ash and point of zero charge. Cu(II) adsorption ability of the AC from aqueous phase was tested batch-wise. Optimum pH and contact time were found to be 5.0 and 240 min, respectively. Adsorption equilibrium data were described well by Langmuir equation providing 105 mg g⁻¹ Cu(II) adsorption capacity. Pseudo second order model successfully described the kinetic of Cu(II) adsorption. A complete desorption of Cu(II) was achieved using 0.5 M nitric acid. In conclusion, hazelnut husk activated carbon produced by potassium acetate activation method is very useful and efficient sorbent material for removal of Cu(II) from aqueous solution.

Keywords: Agricultural Waste, Hazelnut Husk, Activated Carbon, Adsorption, Removal, Heavy Metal, Copper

References:

1. M. Imamoglu, H. Sahin, S. Aydın, F. Tosunoglu, H. Yilmaz, S.Z. Yildiz, Desalination and Water Treatment, (2016) 57 4587– 4596.
2. M. Imamoglu, G. Simsek, Desalination and Water Treatment, (2015) 54 1747– 1753.
3. M. Imamoglu, Journal of Dispersion Science and Technology, (2013) 34 1183– 1187.
4. B. Acevedo, C. Barriocanal, RSC Advances (2015) 5 95247– 95255.

Removal Of Arsenic (III) Ions From Aqueous Systems Using Modified Pumice Stone

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Arsenic is a naturally occurring element in the earth's crust, and is found throughout the environment [1]. Arsenic contamination in natural water is a serious problem in many parts of the world due to its toxicity and carcinogenicity. [2]. Arsenic can occur in the environment in several oxidation states but in natural waters it is mostly found in inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. While As(V) is the major arsenic species in surface water, As(III) is the dominant arsenic in groundwater since it is favored under reducing conditions. As(III) is more toxic to biological systems than As(V) [3].

Arsenic exposure via drinking water on a chronic basis can cause various types of skin lesions, skin and other cancers, cardiovascular, respiratory, and neurological disorders. The World Health Organization (WHO) set the limit of 10 µg/L arsenic in drinking water. Therefore, a water treatment process is necessary to remove arsenic from drinking waters in order to reduce its concentration. Various treatment methods have been studied for removal of arsenic water like precipitation-coagulation, membrane separation, ion exchange, and adsorption. Adsorption techniques are generally considered to be promising method for removing heavy metals from wastewater and water supplies.

In this study, various adsorbents were used to remove as As(III) ions from aqueous media. For this, pumice was used as sorbents and after some modifications to remove As(III) ions. Adsorption studies were carried out using a batch method and adsorption parameters such as contact time, pH, temperature, As(III) concentration were researched to have the maximum adsorption. As(III) amount in the beginning and As(III) amount left in the solution after treatment the un adsorbed were determined by using hydride generation atomic absorption spectrophotometer (HG-AAS) with air-acetylene flame. Maximum adsorption was observed on pumice which modified with $\text{FeCl}_3 + \text{NaOH}$ and after two hours of treatment the adsorption capacity was found 4.7 mg g^{-1} .

Keywords: Arsenic, Adsorption, Atomic Absorption Spectroscopy, Pumice

References:

1. Baskan B., Pala A. Desalination, (2010) 254 42–48.
2. Gulbas G., et al., Environmental Progress and Sustainable Energy (2012) 31 3 443-448
3. Zeng L., Water Research, (2003) 37 4351–4358

Synthesis of Polymeric Materials Including Antibiotic and Their Applications as Potential Adsorbent for Mercury Removal

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Mercury is a serious environmental pollutant because of its toxic effects on all living organisms. Mercury and its compounds cause serious diseases such as leukemia [1-2]. Mercury compounds can be present as a result of anthropogenic activities in various environmental samples. They are usually present in natural waters at trace levels [3]. The lakes, rivers in vicinity of the industrial areas are the important indicators for mercury pollution. Adsorption is used as a common method for removal of several species including toxic metals and organic matters in aqueous [4,5]. Adsorption is not only a removal method; it is also used for enrichment and pre-concentration of target species. It is mostly preferred due to simplicity, selectivity, the availability of different adsorbents, efficiency and practical use. If a selective adsorbent is chosen for target species, an effective removal can be performed easily [6].

A new material containing Tetracycline (T) grafted polyacryl amide (PAA) was synthesized and its adsorption properties were examined for the removal of mercury(II) ions from aqueous media. The new developed adsorbent was characterized by FTIR and PZC analysis. Selective adsorption of Hg(II) ions from aqueous solution as a function of ion concentration, pH, ionic strength, temperature, and reusability of adsorbent was investigated in detail. The adsorption data were analyzed by using the Langmuir, Freundlich and Dubinin-Radushkevich (DR) models. The adsorption mechanism followed an endothermic and spontaneous process with increased disorderliness at adsorbate/adsorbent interface. The new developed material is a potential adsorbent for effective removal of mercury (II) ions. The maximum adsorption capacity of adsorbent was calculated as 0.136 mol kg⁻¹ based on Langmuir model.

Keywords: Polymer, Adsorption, Antibiotic, Mercury

References:

1. M. Yoshida, A. Satoh, A. Shimada, Y. Sumi, C. Tohyama, Toxicology (1999) 139 1–2 129-138.
2. H.İ. Ulusoy, R.Gürkan, S. Ulusoy, Talanta (2012) 88 516-523.
3. M. Saber-Tehrani, H. Hashemi-Moghaddam, M.H. Givianrad, P. Abroomand-Azar, Anal. Bioanal. Chem. (2006) 386 5 1407-1415.
4. J.L. Manzoori, M.H. Sorouaddin, A.M. Hajishabani, J. Anal. Atom. Spectrom. (1998) 13 305-317.
5. M.S. Hosseini, H. Hashemi-Moghaddam, Talanta (2005) 67 555-563.
6. K.G. Gupta, Adv. Colloid Interface (2011) 162 1-2 39–58

New Nanocomposite Development and Application of Membrane Technique for Removal of Heavy Metals from Waste Waters

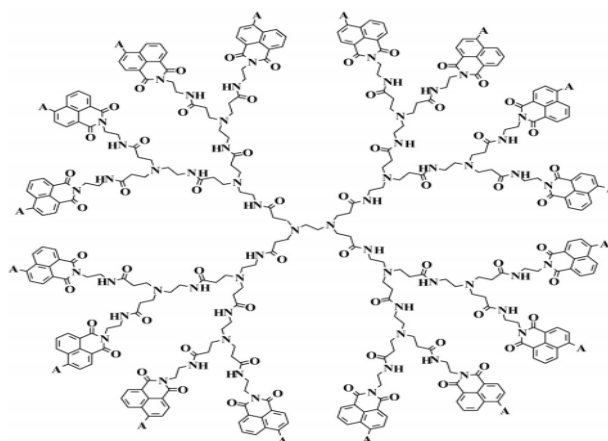
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Dendrimers are new polymer architectures of a well definite structure. They are perfectly branched three-dimensional macromolecules of unique structure and properties [1,2]. Being a new form of organization of the polymeric materials, namely a combination of the properties of low- and high-molecular weight substances, those macromolecules have been attracting greater and greater attention. Polyamidoamine (PAMAM) is a commercial class of dendrimers finding application in various areas [3,4]. And by binding various functional groups to the ends of large number owned by the dendrimer molecule it can be made more active.

In this study; firstly 4-N,N-dimethylaminoethoxy-1,8-naphthalimide labeled (G2-NH₂) PAMAM dendrimer, which has ethylenediamine core, was synthesized and characterized with such spectroscopic methods; secondly it was immobilized onto a membrane surface and finally complexing properties of new nanocomposite with Cu(II) ion was investigated with ICP-MS in various waste waters.



Keywords: Dendrimer, Membrane, Nanocomposite, Spectroscopic Methods, Heavy Metal

References:

- [1] Caminade A-M, Majoral J-P. Prog Polym Sci (2005) 30 491-505.
- [2] Astruc D, Boisselier E, Ornelas C. Chem Rev (2010) 110 1857-959.
- [3] Newkome GR, Shreiner CD. Polymer (2008) 49 1-173.
- [4] Grabchev I, Qian X, Bojinov V, Xiao Y, Zhang W. Polymer (2002) 43 5731-6.

Removal of Copper Using Low-Cost Adsorbents: Application to Industrial Wastewater

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Industrialization, over the past few decades, has led to enormous increase in the use of heavy metals especially in the aquatic environment. When heavy metals such as nickel, cadmium especially copper reach body by the food chain they can accumulate in the tissues and can cause serious health problems such as gastrointestinal irritation, central nervous system irritation followed by depression, hepatic and renal damage, and possible necrotic changes in the kidney and liver. Therefore, prior to its discharge to the environment it is necessary to treat with a chemical processes metal-contaminated wastewater. Copper is one of the most important heavy metal that used in industry. Waste sources of copper include plating baths, mining wastes, fertilizer industry, pigments and paints, etc. [1]. In case of excessive intake of copper by human leads to vigorous widespread capillary damage, corrosion and mucosal irritation [1,2]. There are many heavy metal clean-up technologies such as reverse osmosis, cover precipitation, ion exchange, extraction, etc. [3-7]. Adsorption, among numerous clean-up techniques for water treatment, is one of the alternatives for such cases and is an effective separation and purification technique used in industry especially in wastewater treatments. Cost that an important parameter is vital for comparing the adsorbent materials. For these reasons, there is increasing research interest in using alternative low-cost adsorbents.

The sorption of Cu(II) onto clay and astragalus for removal of copper from aqueous solution has been investigated in this study. Various parameters effects on adsorption capacities such as pH, adsorbent dose, and stirring time were investigated using batch experiments. Equilibrium isotherms have been evaluated and equilibrium data agreed well with Langmuir isotherm and Freundlich isotherm models. Clay and astragalus adsorption capacity for Cu(II) were determined with the Langmuir model. Clay was shown to be a promising sorbent for Cu(II) removal from aqueous solutions. Characterization of the surface modification was performed with FTIR measurements. FTIR spectra showed that chemisorption takes place at surface of the adsorbent.

Keywords: Copper, clay, astragalus, industrial waste-water, Langmuir isotherm model

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References

1. Ince M., Atom. Spectrosc. (2014) 35, 223-233.
2. Canizares P., de Lucas A., Pérez A., Camarillo R., J. Membr. Sci. (2005) 253, 149-163.
3. Ozaki H., Sharma K., Saktaywin W., Desalination (2002) 144, 287-294.
4. Marder L., Sulzbach G.O., Bernardes A.M., Ferreira J.Z., J. Electrochem. Soc. (2003) 14, 610-615.
5. Trivunac K., Stevanovic S., Chemosphere (2006) 64, 486-491.
6. Kumano M., Yabutani T., Motonaka J., Mishima Y., Int. J. Mod. Phys. B (2006) 20, 4051-4056.
7. Ince M., Kaplan Ince O., Yonten V., Karaaslan N.M., Atom. Spectrosc. (2016) 37 125-130.

Comparison of Natural Adsorbent Performance for Removal of Toxic Metal From Aqueous Medium

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Heavy metals, such as copper (Cu), lead (Pb), and cadmium (Cd) are major toxic pollutants to the environment and for human health because they tend to accumulate in the tissues of living organisms and are non-biodegradable [1-6]. When they accumulate in the body, they can cause severe damages such as malfunction of the body's organisms, pathological states, and serious behavioral, developmental and learning problems, particularly in children [7,8]. If these metals move into the ecosystem, they can be adsorbed by marine animals and enter the human food chain, resulting in high health risks to the consumer. For these reasons, removing heavy metals from aqueous solutions by accurate and economical techniques is of great importance. Water pollution because of inorganic contaminants is a serious problem due to acute toxicities and carcinogenic nature of pollutants. Recently, much attention has been focused on using natural and low-cost adsorbents especially food residues, for removing toxic metal ions [8,9].

Batch experiments for removal of copper from aqueous medium using several natural adsorbents were investigated in this study. Various parameters effects on adsorption capacities such as pH, adsorbent dose, and stirring time were investigated. Maximum adsorption capacities for chestnut shell, tea waste and banana peel were found as 2.3 mg g⁻¹, 3.9 mg g⁻¹ and 2.0 mg g⁻¹, respectively. Characterization of the surface modification was performed with FTIR measurements. FTIR spectra showed that chemisorption takes place at surface of the adsorbents.

Keywords: Natural adsorbents, heavy metals, batch experiment, FTIR

This study was a part of the project supported by Tunceli University Scientific Investigations Project Unit (TUNIBAP- MFTUB014-01).

References

1. Langmuir I., J. Am. Chem. Soc. (1918) 40, 1361-1403.
2. Freundlich H. M. F., J. Phys. Chem. (1906) 57, 385-470.
3. Coen N., Mothersill C., Kadhim M., and Wright E.G., J. Pathol. (2001) 195, 293-299.
4. Giller K.E., Witter E., and McGrath S.P., Soil Biol. Biochem. (2009) 41, 2031-2037.
5. Kocaoba S., Orhan Y., and Akyüz T., Desalination (2007) 214, 1-10.
6. Ince M., Atom. Spectrosc. (2014) 35, 223-233.
7. Zuorro A., and Lavecchia R., Am. J. Applied Sci. (2010) 7, 153-159.
8. Manahan S.E., Environ. Chem. In: Complexation by humic substances, 6th ed. USA: CRC Press, 1994:80/2 (Chapter 3).
9. Ince M., Kaplan Ince O., Yonten V., Karaaslan N.M., Atom. Spectrosc. (2016) 37 125-130.

Effective Removal of Pb(II) Ions from Aqueous Solutions by a Plant Based Magnetic Biosorbent in Fixed-Bed Column

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Abstract

This study was designed for the development of immobilized and magnetic biosorbent system for the removal of lead (II) ions from aqueous medium. For this purpose, chitosan immobilized magnetic olive pomace biosorbent system was prepared. Column performance of biosorbent system was investigated and biosorbent amount and flow rate were optimized. The biosorbent demonstrated strong removal performance towards lead (II) ions in continuous mode. Desorption studies revealed that the biosorbent may be regenerated using 10 mM EDTA solution with about 98% recovery and reused in twenty biosorption–desorption cycles. Biosorption performance of the investigated biosorbent system was also be tested in wastewater conditions. Consequently, a new and effective biosorbent was obtained from biological waste source and used for the removal of toxic lead (II) ions from aqueous medium.

Keywords: Biosorption, Heavy Metal, Lead (II), Magnetic Biosorbent, Regeneration, Wastewater

Introduction

Growth in human population and industrial activities such as mining, refining ores, fertilization, tanning, electroplating, plastic manufacturing, textile, storage batteries and metallurgical process may cause heavy metals accumulation in nature. They are highly important pollutants because of their persistent, non-degradable nature and accumulation potential in food chain. Lead is among and highly toxic metal pollutant. The main sources of lead pollution in nature are human industrial activities such as fertilization, electroplating, mining, refining ores, tanning, plastic manufacturing, textile, storage batteries and metallurgical processes [1]. Muscle weakness, anemia, sterility, vascular degeneration, headache, kidney, and brain damages are some negative effects on human body exposing to lead [2]. Biosorption is a promising alternative to traditional water treatment methods. Simple operation, selectivity, and reusability are the most important advantages of this process. Biosorbents can be stored and used in later times since the biomass is not living [3]. The advantages of magnetic-based biosorbents such as ease of separation with the aid of magnetic field, effective biosorption ability and great mechanical properties make them attractive in the biosorption studies [4].

Therefore, in this work, chitosan immobilized magnetic olive pomace biosorbent (CIMOP) was used for the removal of lead (II) ions from aqueous media. The effects of bed height and flow rate were investigated using fixed-bed column. Desorption characteristics of the biosorbent were also tested to evaluate reusability potential.

Materials&Methods

Olive pomace was obtained from olive production process and washed several times with deionized water. Then it was dried in an oven at 60°C for 24h and ground and sieved to 212 μ m of maximum particle size. Magnetic biosorbent was prepared as follows: 0.4 g chitosan, 0.4 g olive pomace and 0.4 mL acetic acid were added into 40 mL of 0.1 mol/L sodium

acetate solution under ultrasonic stirring for 15 min. Then, 1.5 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1.75 g FeCl_3 were mixed and put into 100 mL 0.1 mol/L sodium acetate solution. These two phases were mixed and heated to 55°C in incubator shaker (Gerhardt Thermoshake). This mixture was added into 40 mL of 6 mol/L NaOH solution and stirred in incubator shaker for 1h at 55°C . The resulting magnetic biosorbent was washed with deionized water. Afterwards, the biosorbent was dried, milled in a analytical mill (IKA A11) and sieved to select particle size less than 300 μm . The powdered biosorbent was stored in a glass bottle for further use [5]. Lead (II) stock solution (1000 mg/L) was prepared by dissolving 1.5985 g anhydrous $\text{Pb}(\text{NO}_3)_2$ (%100) into 1 L deionized water. Other concentrations were prepared by diluting a proper volume of this stock solution.

Glass columns with 9 mm internal diameter were used in the column studies. CIMOP was packed in glass columns and 25 mL lead (II) solution was passed through the columns. Biosorbent amount and flow rate were optimized using 100 mg/L lead (II) solution. Desorption performance of CIMOP was examined using 25 mL of 10 mmol/L EDTA solution as regeneration agent. Biosorption performance of CIMOP in dynamic flow mode was also tested in real wastewater obtained from the wastewater treatment plant in organized industrial area of Eskişehir (Turkey). After the biosorption process residual lead(II) concentrations were determined by an Flame Atomic Absorption Spectrophotometer (FAAS) at a 283.3 nm wavelength. All of the experiments were performed at least in triplicate and the average values were used in the calculations.

Results&Discussion

The magnetic properties of the prepared magnetic biosorbent was characterized by vibrating sample magnetometer (VSM) with field between -6 and $+6$ kG. CIMOP showed S shaped narrow hysteresis loops. Biosorbent showed S shaped narrow hysteresis loops (Fig. 1), representing that CIMOP is showing ferromagnetism [6].

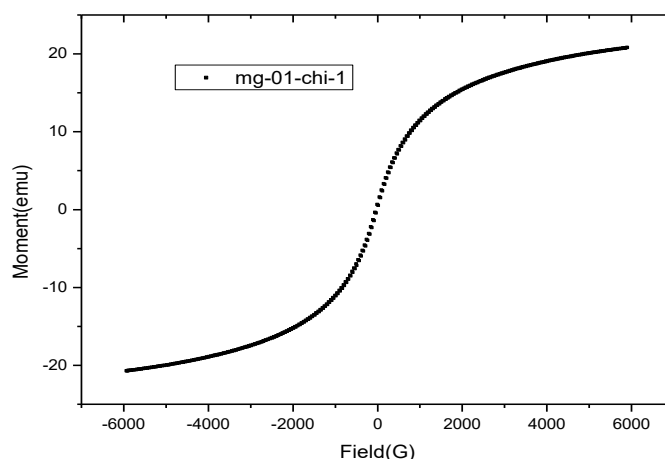


Fig. 1. Magnetic hysteresis loop for CIMOP at room temperature.

The effect of bed depth on the lead (II) biosorption by CIMOP was investigated and result are presented in Fig. 2 a. The removal of lead (II) ions depends on bed depth and bed depth is also depend on biosorbent amount of CIMOP that packed in the column. Initial metal ion concentration and flow rate were kept constant at 100 mg/L and 1 mL/min. Biosorbent amounts are varied from 0.2 g to 1.0 g. With an increase in the biosorbent amount up to 0.6 g, biosorption yield increased from 50.11% to 97.19%. The biosorption yield did not change noticeable with a further increase up to 1.0 g ($p > 0.05$). This may be ascribed to the better availability of free active sites and surface area by increasing amount of CIMOP [7].

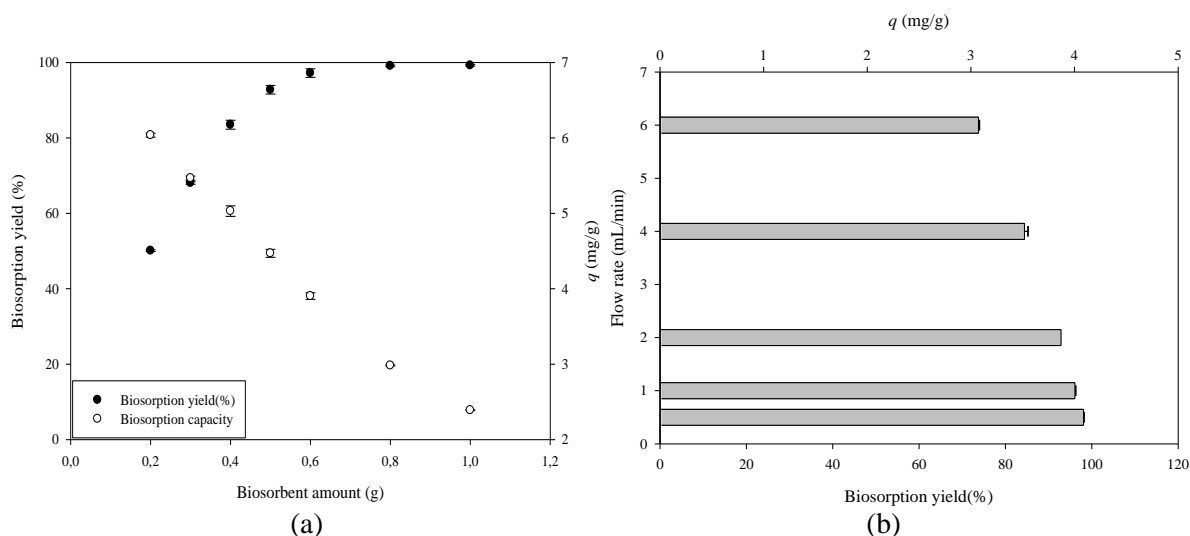


Fig. 2. Effect of biosorbent amount on the biosorption yield and biosorption capacity of CIMOP (a), Effect of flow rate on the biosorption yield and biosorption capacity of CIMOP (b).

The influence of flow rate on biosorption yield and capacity of lead (II) was evaluated by varying flow rates as 0.50, 1.0, 2.0 and 4.0 mL/min, while the initial lead (II) concentration and CIMOP amount were kept constant at 100 mg/L and 0.6 g, respectively. The results illustrated in Fig. 2b it indicates that, as flow rate increases, biosorption yield and capacity decreased. At a lower flow rate lead (II) and biosorbent interaction is longer to biosorption of lead (II) onto available free active sites around or inside the CIMOP. Lead (II) have also longer time to diffuse into the pores of CIMOP through intra-particle diffusion when flow rate is lower [8]. The biosorption yield and capacity of CIMOP increased from 73.68 to 95.86% and from 3.08 to 4.00 mg lead (II)/g CIMOP when the flow rate decreased from 6.0 to 1.0 mL/min. The biosorption efficiency did not change with a further decrease ($p > 0.05$). As a result, the maximum lead (II) biosorption was observed at a flow rate of 1.0 mL/min.

The stability and reusability potential of the biosorbent was tested in 20 consecutive biosorption–desorption cycles keeping the initial metal ion concentration, biosorbent amount and flow rate constant. Column was regenerated by 10 mM EDTA and the results are represented in Fig. 3. After 20 cycles, recovery yield was remained at 97.94%. These results indicated that suggested biosorbent has potential to be used more than 20 times in column operations.

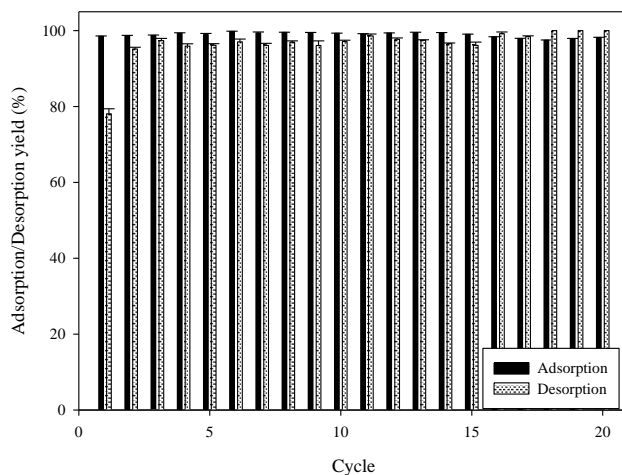


Fig. 3. Consecutive biosorption-desorption cycles of CIMOP

Conclusion

In current investigation, dynamic flow mode biosorption potential of CIMOP was investigated for removal from aqueous solutions. The biosorptive percentage of lead (II) was investigated to be dependent on initial biosorbent amount and flow rate. The highest biosorption efficiency (97.19%) was attained with 1 mL/min flow rate and 0.6 g sorbent amount. During sequential 20 biosorption-adsorption cycles, biosorptive performance of biomaterial was maintained at about 98%. Results demonstrate that this new biosorbent could be a good alternative for uptake of lead (II) from contaminated media.

References:

1. T. Bahadir, G. Bakan, L. Altas, H. Buyukgungor, *Enzyme and Microbial Technology* (2007) 41 1-2 98-102
2. T. Akar, Y. Y. Balk, O. Tuna, S. T. Akar, *Ecological Engineering* (2013) 61 A 251-257
3. S.T. Akar, Y. Y. Balk, O. Tuna, T. Akar, *Carbohydrate Polymers* (2013) 94 1 400-408
4. P. Janoš, M. Kormunda, F. Novák, O. Životský, J. Fuitová, V. Pilařová, *Reactive and Functional Polymers* (2013) 73 1 46-52
5. J. Tong, L. Chen, *Analytical Letters* (2013) 46 8 1183-1197
6. R. Tholkappiyan, K. Vishista, *Applied Surface Science* (2015) 351 1016-1024
7. S. T. Akar, F. Sayin, D. Yilmazer, T. Akar, *CLEAN – Soil, Air, Water* (2016) 44 2 202-210
8. P. D. Sahaa, S. Chowdhurya, M. Mondala, K. Sinhaa (2012) 47 1 112-123

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Synthesis of Polyaniline-Derived Polymers, Characterization and Investigation of Adsorption Properties

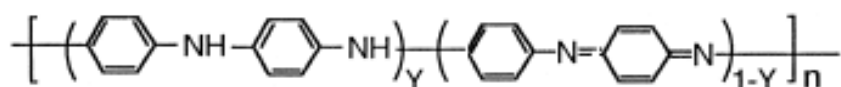
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Polyaniline is a conductive polymer that offers good stability in the presence of air and moisture media. It can be synthesized by oxidation of aniline following a head-to-tail coupling mechanism with chemically and electrochemically reaction. The polymer includes the following repeating units of:



Disulfide compounds have been applied as new organic /polymer cathode material lithium batteries. The theoretical capacity and energy density of those materials more than obtained from conventional batteries such as intercalation compounds and conductive polymers. A number of compounds having -SH group in the molecules are regarded as an energy storage material. So it can be reversed based on the energy exchange process, because the cleavage and recombination of S-S bonds is expected to be as follows.

In the present paper, polymeric materials such as poly [bis-(2-aminophenyl) disulfide] and poly[1,2-bis(o-aminophenylthio)ethane] were synthesized by chemical synthesis. These polymers were characterized by scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), elemental analysis of C, H, N and S, and thermogravimetric analysis (TGA), raman spectroscopy. The electrical conductivity of these synthesized polymers will be examined. These polymers will be used in adsorption of several precious metals.

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Keywords: polyaniline, polymer, characterization, adsorption

References:

1. F.R. Diaz, C.O. Sanchez, M.A. del Valle, L. Ugalde, L. Gargallo Synthetic Metals (1999)105 161-169.
2. K. Naoi, S. Suematsu, M. Komiyama, N. Ogihara Electrochimica Acta (2002) 47 1091-1096.
3. Y.G. Lee, K. S. Ryu, S. Lee, J.K. Park, S. H.Chang Polymer Bulletin (2002) 48 415-421.

The Adsorption Kinetics, Equilibrium and Thermodynamic of Acid Blue 93 on Green Bioadsorbent

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Acid blue 93 is known as Cotton Blue or Methyl blue as shown in Figure 1.

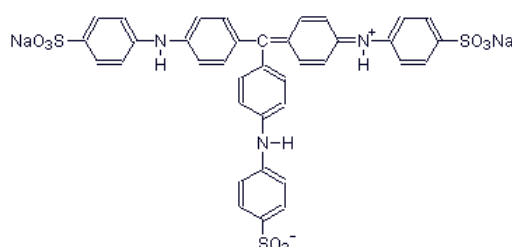


Figure 1: Chemical structure of Acid Blue 93

The adsorption of Acid Blue 93 (AB 93) was investigated on green bioadsorbent (GBA). Green bioadsorbent was prepared with clay (bentonite) and a waste seaweed by solution method. Bentonite (Reşadiye-Türkiye) was chemically modified by cetyl trimethyl ammonium bromide (CTAB). The adsorption of acid dye on the green bioadsorbent GBA/modified bentonite (MB) bioadsorbent was studied at four different temperatures, (25°C, 35°C, 45°C, 55°C) and at four different concentrations (5×10^{-5} - 2.5×10^{-4} M). The AB 93 acid dye adsorption onto the bioadsorbent was investigated in a batch adsorption process¹. Freundlich, Langmuir and Temkin adsorption isotherm models were applied to the experimental data. The adsorption kinetics of dye on GBA/MB bioadsorbents were calculated by pseudo first order, pseudo second order kinetic models. The various thermodynamic parameters such as enthalpy of sorption (ΔH°), free energy change (ΔG°), and entropy change (ΔS°) were estimated. The negative value of free energy change (ΔG°) shows the randomness at the solid liquid interface during the adsorption of dyes onto adsorbent. Bioadsorbent was determined by the Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The maximum adsorption uptake of bioadsorbent was 98 %.

Keywords: Seaweed, Green Bioadsorbent, Modified Bentonite, Kinetic Model, Isotherm.

References:

1. Y. Wu, Y. Wang, J. Wang, S. Xu, L. Yu, C. Philippe, T. Wintgens, Journal of the Taiwan Institute of Chemical Engineers (2016) 66 191-199.

A Novel Bio-nanocomposite from Organic and Inorganic Materials

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There is an increasing demand of producing novel materials that are durable, applicable and cheap. New materials are formed by mixing two or more different – commonly organic / inorganic- materials with different physical and chemical properties and known as composites. Bio-Nanocomposites are prepared by adding an inorganic filler components into biopolymer matrix. One of the most important key point of preparing nanocomposite systems is homogeneous distribution with less agglomeration, which could be achieved successfully by having strong interfacial attractions between the surfaces of the organic and the inorganic surfaces [1-2].

In our studies, non-toxic, biodegradable bio-nanocomposites were prepared via simple solution method under ultrasonic irradiation. Natural amino polysaccharide biopolymer chitosan and Gelatine mixture were used as the organic matrix to create a stable environment for dispersed ZnO nanoparticles. In order to get stronger structure SiO₂ was added to the structure. Because of the ultrasonic irradiation on the surface of SiO₂, there are OH radicals created in which caused to extra ordinary chemical conditions during the preparation step. By addition of metal salts into the biopolymer solution during the ultrasonic irradiation, the radical formation on the silica surface plays an important role on metals or metaloxides formation even in nanoscale.

Keywords: Chitosan, Gelatine, Bio-Nanocomposite, Ultrasonic, Dispersion.

References:

1. Jong-Whan Rhim, Hwan-Man Park, Chang-Sik Ha, Progress in Polymer Science (2013) 38 1629–1652.
2. A. Sorrentino, G. Gorrasi, V. Vittoria., Trends in Food Science & Technology (2007) 18 84–95.

Removal of Azo Dyes from Aqueous Solutions by Using Eggshell Membrane

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In this study, egg shell membrane was used as an adsorbent for removal of reactive black 5 dye from aqueous solutions. Structural characterization of egg shell membrane was done by FTIR and SEM analysis. The experiments were carried out by batch system and operation variables such as pH, incubation time, temperature, and dye concentration were optimized. The pH of the adsorption medium had important effect on the adsorption of the dye on eggshell membrane and maximum adsorption was observed at pH 2.0. Maximum adsorption capacity of eggshell membrane for reactive black 5 was found as 247 mg/g. Equilibrium isotherm for the adsorption of dye was analyzed by Freundlich and Langmuir isotherms. The Langmuir isotherm was fitted the isotherm data better than the Freundlich model. The thermodynamic parameters, Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also evaluated. The adsorption kinetics was represented by pseudo-second-order kinetic model. Moreover, desorption experiments revealed that the egg shell membrane can be reused effectively for seven consecutive adsorption-desorption cycles without any loss of its original capacity.

Keywords: Eggshell Membrane, Reactive Black 5, Adsorption, Desorption, Characterization.

References:

1. S.Ziane, K. Marouf-Khelifa, H. Benmekki, J. Schott, A.Khelifa, Desalination and Water Treatment, (2015) 56 695–708.
2. B. Chládková, E. Evgenidou, L. Kvítek, A. Panáček, R. Zbořil, P. Kovář, D. Environ Sci Pollut Res (2015) 22 16514–16524.
3. G.M. Ratnamala, Shetty K. Vidya, G. Srinikethan Desalination and Water Treatment (2016) 57 11361–11374.

Removal of Methylene Blue from Aqueous Solution with Acorn Based Magnetic Activated Carbon

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Methylene blue is one of the most common components of cationic paint. The use of methylene blue leads to several problems in terms of human health and the aquatic environment. Activated carbon is one of the mostly commonly used adsorbents. Recently, the use of activated carbons enriched with iron has become an alternative method of enriching activated carbons. In this study, the prepared activated carbons was gained magnetic property by means of ZnCl_2 activation of acorn shells. This is a cheap and widely-used form of coprecipitation. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (3.9 gram, 14 mmol) and FeCl_3 (7.8 gram, 14 mmol) solutions are added to a 400 ml beaker and heated to 70°C. 3.3 g of activated carbons are weighed and added to the mixture. 100 mL from the 5M NaOH solution is added to the mixture, and the iron oxide is precipitated. The composite material is washed with distilled deionized water and filtered using blue band filter paper. The magnetic composite obtained is dried in the oven for 2 hours at 80°C. The magnetic characteristic is determined through pretesting using a neodymium magnet. The structural and chemical characteristics of the synthesized magnetic activated carbons are characterized by using XRD, SEM, FT-IR techniques. The surface areas of the activated carbons and magnetic activated carbon sorbents are also measured by using BET method. In the second step of this study, the synthesized material was used as novel adsorbent for the removal of the methylene blue from water and waste water. The methylene blue concentration in the solution was determined using a UV-VIS spectrophotometer. The effects of pH, temperature, the adsorbent amount, contact time, etc. are examined in the dyestuff adsorption trials. It is concluded that magnetic activated carbons are a suitable adsorbent for the removal of the dyestuff from water and waste water.

Keywords: Acorn, Magnetic Activated Carbon, Methylene Blue, Removal

References:

1. Emily K. Faulconer, Natalia V. Hoogesteijn von Reitzenstein, David W. Mazyck Journal of Hazardous Materials (2012) 199-200 9-14.
2. Hui Denga, Jianjiang Lua, Guoxue Li, Genlin Zhanga, Xugen Wanga Chemical Engineering Journal (2011) 172 326– 334.

Removal of Congo Red from Aqueous Solution Using Crosslinked Poly(N-vinylpyrrolidone)

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The dyes one of the important classes of synthetic organic pigments utilize in manufactured coloured productions. Synthetic dyes are widely used in many fields of advanced technology as textile, paper, leather tanning, food processing, plastics, cosmetics, rubber, printing and dye manufacturing industries [1]. Industrial effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid. These problematic wastewaters have to be treated to accord with discharge limit before discharge not only for their high chemical and biological oxygen demand but also for suspended solids of toxic properties to aquatic life and reduce in light penetration [1]. Congo red (CR) one of important anionic dyes that found in the wastewater have higher solubility in the water about 1 g/30 mL and was widely used in textiles, paper, rubber and plastic industries [3-4]. Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods; adsorption process is one of the effective techniques that have been successfully employed for dyes removal from wastewater. The adsorption has benefits as water treatment and waste management to removal of dyes from waste water by using low cost alternative adsorbent [1-2].

The present work aims to removal of Congo red (CR) from aqueous solution with cross-linked poly(N-vinylpyrrolidone) can be used by batch adsorption techniques at 25°C. Several sorption parameters such as pH, initial dye concentrations and amount of adsorbent were studied. The effects of these factors in adsorption process were determined by Response Surface Methodology (RSM) based on Box-Behnken design (BBD). The significance of the effects was checked by Analysis of Variance (ANOVA) and the optimum values of selected variables were found. The results revealed that cross-linked poly(N-vinylpyrrolidone) can be used as an efficient adsorbent for removal of CR.

Keywords: Adsorption, Box-Behnken design (BBD), Congo red (CR), Response Surface Methodology (RSM).

References:

1. Liua Y., Wanga J., Zhenga Y., Wanga A, Chemical Engineering Journal (2012) 184 248-255.
2. Yagub M.T., Kanti S.T., Afroze S., Ang H.M., Advances in Colloid and Interface Science (2014) 209 172-184.
3. Ekici S., Isikver Y., Sahiner N., Saraydin D., Adsorption Science&Technology, (2003) 21 651-659.
4. Patil K., Shrivastava V.S., International Journal of ChemTech Research, (2010) 2 842-850.

Optimization of Methylene Blue Removal on a New Hybrid Material by Box-Behnken Design

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Dyes are widely used as coloring agents in a variety of industries, such as textiles, cosmetics, pulp mills, leather, dye synthesis, printing, foods, and plastics. Dyes in effluents from industry are the important sources of water pollution. Amount of organic dyes in water is considered very important because, besides having possible harmful effects, the color in water is aesthetically unpleasant¹. Many studies have been developed for dye removal from aquatic environments, including physical, chemical, and even biological approaches. Studies include the use of coagulants, oxidizing agents, ultra-filtration, electrochemical and adsorption techniques. Among these approaches, absorption is regarded as an easy and economic process. Various materials, such as commercial active carbon, natural materials, biosorbents, and wastes from agriculture have been used for such processes². In the last few years, organic-inorganic hybrid materials have been used as adsorbents due to their mechanical attributes, thermal stability, and high specificity².

In this study, a synthesized and characterized novel organic-inorganic hybrid material³, Al(OBu^s)₃-GPTS-NaOSiMe₃-Hydrolyzate (Al-GPTS-NaOSiMe₃-H), was used for removal of methylene blue dye. Removal of methylene blue dye by a new adsorbent were carried out using batch method considering parameters of pH, adsorbent quantity, initial dye concentration. In order to determine the optimum experiment conditions of the adsorption process, Box-Behnken design were applied which different levels of multiple factors can investigate simultaneously and one factor can be examined at different levels of the other factor or factors, and provide a large amount of useful information from a reduced number of experiments.

$$R(\%) = 36.65 + 12.900 \text{ pH} - 0.0194 \text{ Co (mg/L)} + 110.65 \text{ m (g)} - 0.9142 \text{ pH} \cdot \text{pH (uncoded)}$$

$$R(\%) = 91.36 + 7.718 \text{ pH} - 0.972 \text{ Co (mg/L)} + 9.958 \text{ m (g)} - 14.63 \text{ pH} \cdot \text{pH (coded)}$$

The aforecited coded and uncoded equations describes how the experimental variables and their interactions influence the adsorption. The positive values of these effects reveal that the increase of these parameters increased R%. Conversely, negative values of the effects decreased the response. According to equations, pH and amount of adsorbent had a positive effect on methylene blue adsorption, and in view of these terms optimum R% value has found 94,89. All results shows that synthesized hybrid material Al-GPTS-NaOSiMe₃-H can be used effectively for removing methylene blue dye from aqueous solutions effectively.

Keywords: Adsorption, Box-Behnken Design, Dye Removal, Hybrid Material, Methylene Blue

References:

1. Wenga C-H., Lin Y.T., Tzeng T-W., Journal of Hazardous Materials (2009) 170 417–424.
2. Yang S., Chen S., Chang Y., Cao A., Liu Y., Wang H., Journal of Colloid and Interface Science (2011) 359 24–29.
3. Kayan A., Journal Inorganic Organometric Polymer (2015) 25 1345–1352.

Continuous Biosorption of Reactive Yellow 2 from Contaminated Real Wastewater by *Thamnidium elegans* Cells

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Abstract

Thamnidium elegans (*T. elegans*) has successfully been evaluated as a biosorbent for decolorization of Reactive Yellow 2 (RY2) from contaminated real wastewater in continuous systems. The biosorbent demonstrated 98% decolorization yield in continuous mode. The Langmuir isotherm model showed better correlation coefficients and maximum monolayer biosorption capacity calculated from this model were found to be 3.30×10^{-4} mol/g (287.84 mg/g). The findings obtained from dynamic flow system also indicated that the suggested biosorbent may be a potential alternative for the continuous mode decolorization of wastewater in large scale. Even after 10 repeated cycles of regeneration, the original biosorption capacity was constant and recovery yield of dye was maintained at around 95%. The breakthrough point emerged around 300 min and reached to exhaustion after 600 min. Overall, these features indicated that *T.elegans* is an effective and promising alternative for the treatment of synthetic dyes from real wastewaters.

Keywords: Biosorption, Dye, Reactive Yellow 2, Real Wastewater, Regeneration, *Thamnidium Elegans*

Introduction

Synthetic dyes in aquatic media are highly visible even at small concentrations. They have been widely used in various industries such as paint, plastic, paper, printing and textile. These dyes may cause toxic effect to nature when they are discharged into aquatic media. Skin and eye irritation, rhinitis, dermatitis, asthma and allergic conjunctivitis are some symptoms related to dye exposure [1]. Therefore, environmentally friendly and economical treatment methods are required for the removal of synthetic dyes from industrial effluents.

Biosorption is an alternative biotechnological treatment technique that may be used for the decolorization of synthetic dyes in water sources since they are not easily biodegradable. Biosorption has received increasing attention because of its environmental friendly, selectivity, rate of uptake, toxicant affinity, recovery, small quantity of sludge and low cost features. Biosorption, is based on the possible interactions between pollutants and biosorbents [2]. It has a great potential to remove organic and inorganic pollutants from contaminated wastewaters, even at small amounts. Different types of biosorbents such as bacteria, fungi, algae, plants and biologic wastes have been used under various experimental conditions. Although a large number of decolorization studies have been carried out with synthetic dye solutions, the current biosorption applications are still insufficient to cover the problem of the pollutant removal from industrial real wastewaters [3,4]. The goal of the present study was to suggest an efficient biomaterial to treat the real industrial wastewater.

Materials&Methods

Reactive Yellow 2 (RY2), was used as a model synthetic dye. Biosorption experiments were performed using real wastewater obtained from the wastewater treatment plant in

organized industrial area of Eskişehir (Turkey). The chemical composition of the wastewater was presented in Table 1 and chemical oxygen demand (COD) was measured as 828.0 mg/L.

Table 1. Chemical composition of wastewater

Constituents	C (mg/L)	Constituents	C (mg/L)
Calcium (Ca ⁺)	162.46	Chloride (Cl ⁻)	87.55
Magnesium (Mg ⁺)	44.01	Sulfate (SO ₄ ²⁻)	381.75
Sodium (Na ⁺)	863.50	Nitrate (NO ₃ ²⁻)	1306.35
Potassium (K ⁺)	21.19	Fluoride (F ⁻)	0.58
Zinc (Zn ²⁺)	0.02	Bromide (Br ⁻)	0.35
Cobalt (Co ²⁺)	0.03	Phosphate (PO ₄ ²⁻)	2.13
Copper (Cu ²⁺)	0.10	Manganese (Mn ²⁺)	0.15
Cadmium (Cd ²⁺)	-	Nickel (Ni ²⁺)	-
Chromium (Total)	-	Nitrite (NO ₂ ⁻)	-
Iron (Total)	-	Sulfite (SO ₃ ²⁻)	-

T. elegans was grown at 297 K for 7 days on potato dextrose agar medium in order to prepare the mycelium suspension. A liquid growth medium proposed by Wang [5] was used for biosorbent production. After seven days, the resulting biosorbent separated from its medium, washed and dried at 333 K. Dried biosorbent was milled in a analytical mill (IKA A11) and sieved to lower than 212 µm particle size. Prepared biosorbent was stored in order to use in biosorption process.

The continuous biosorption studies were performed by placing *T.elegans* into the glass columns (9 mm internal diameter). 25 mL of dye was added into columns and passed the packed bed at various bed height and flow rates. In order to investigate reuse potential of the biosorbent, desorption characteristics were investigated. Breakthrough study was also carried out to test the biosorption performance of the biosorbent in continuous flow conditions. The residual dye concentrations in the solutions were determined by an UV/vis spectrophotometer at λ_{max}: 396 nm.

Results&Discussion

The decolorization ability of *T. elegans* was evaluated for real wastewater [2,6]. Biosorption experiments were conducted at different biosorbent amount (30-80 mg) and flow rates (0.25-2 mL/min). pH was adjusted to 2.0 to reach optimum removal efficiency [7].

In order to determine the optimum bed height to maximize the biosorption efficiency, the biosorbent amount was increased from 30 to 80 mg at flow rates of 1.00 mL/min and the results are presented in Fig. 1a. The biosorption yield of *T. elegans* increased from 56.27% to 93.03% when the biosorbent amount increased from 30 to 40 mg. The biosorption yield did not noticeable change with a further increase up to 80 mg (*p* > 0.05). An increase in the biosorbent amount caused an increase in bed height. This may be ascribed to the greater availability of free active sites and surface area of biosorbent by increasing amount of *T.elegans* [2]. Thus, dye solutions longer interact with biosorbent in the column. Therefore, the optimum *T. elegans* amount was chosen as 40 mg.

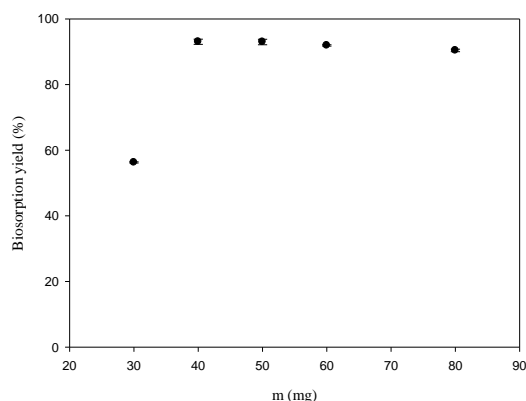


Fig. 1 (a)

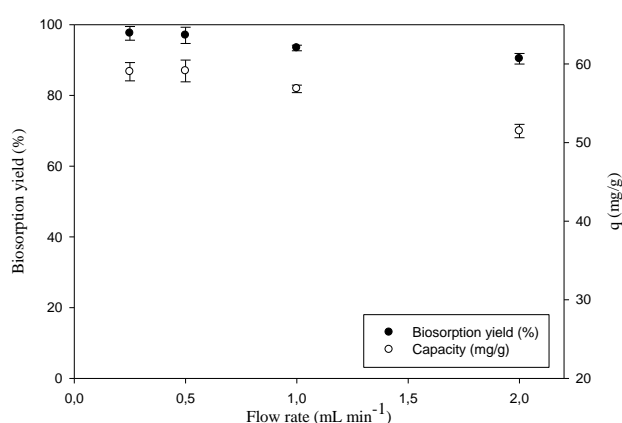


Fig. 1 (b)

Fig. 1. Effect of biosorbent amount on the biosorption yield of RY2 (a), Effect of flow rate on the biosorption yield and biosorption capacity of *T. elegans* (b).

The influence of flow rate on the biosorption yield of RY2 was evaluated by varying flow rate from 0.25 to 2 mL/min and the results are presented in Fig. 1b. Initial dye concentration and biosorbent amount were kept constant at 100 mg/L and 40 mg, respectively. Biosorption yield was lower at higher flow rates. At a lower flow rate RY2 and biosorbent interact longer to biosorp RY2 onto available free active sites of biosorbent. RY2 have also longer time to diffuse into the pores of *T. elegans* through intra-particle diffusion when flow rate is lower [8]. In contrast, biosorption yield of RY2 decreased at high flow rates due to inadequate time for the interaction between biosorbent and dye molecules. The biosorption yield of *T. elegans* increased from 90.36% to 96.98% when the flow rate decreased from 2.0 to 0.5 mL/min. The biosorption efficiency did not change with a further decrease ($p > 0.05$). As a result, the maximum RY2 biosorption was observed at a flow rate of 0.5 mL/min.

Desorption characteristics of the biosorbent were investigated to examine the interaction type between biosorbent and dye solution and to test the reuse potential of biosorbent. Desorption of sorbate was carried out by adding 0.01 M KOH solution into the packed bed glass columns at room temperature. Initial dye concentration, biosorbent amount and flow rate were set to 100 mg/L, 40 mg and 0.5 mL/min, respectively. Fig 2 (a) indicated consecutive biosorption-desorption cycles of *T. elegans* biosorbent. Even after 10 repeated cycles of regeneration, the original biosorption capacity was retained and biosorption yield of dye was maintained at 94.52%. These findings strongly indicated that *T. elegans* cells have great potential on industrial practical applications for decolorizing reactive dyes.

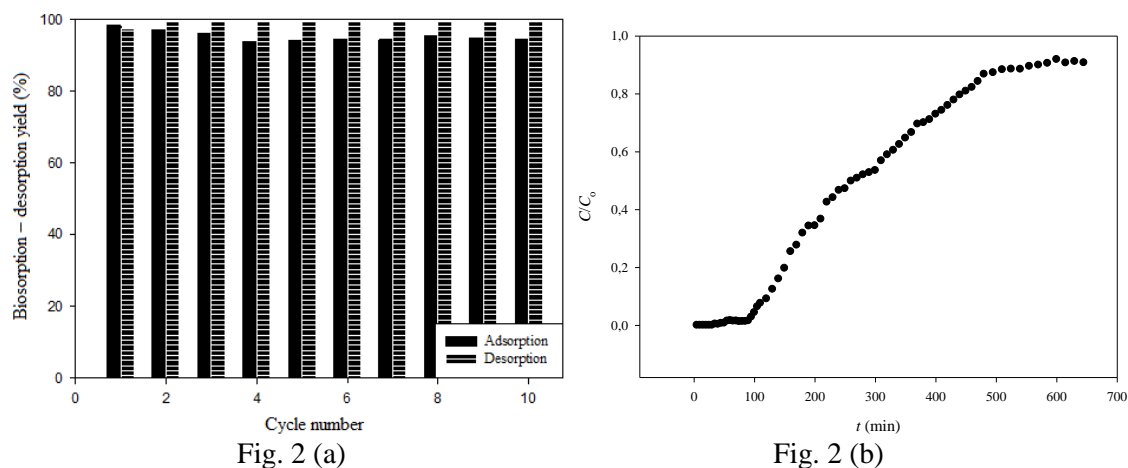


Fig. 2. Consecutive biosorption-desorption cycles of *T. elegans* biomass (a), Breakthrough curve for RY2 biosorption process (b).

In order to examine the breakthrough behaviour of *T. elegans* (Fig. 2b), 100 mg L RY2 solution was passed through the column packed with 0.2 g of the biosorbent at a flow rate of 0.5 mL/min. The breakthrough point emerged around 300 min and reached to exhaustion after 600 min. These data showed that *T. elegans* can be successfully used in column applications for the decolorization of RY2 containing solutions.

To analyze the biosorption equilibrium, three isotherm models (Langmuir, Freundlich, and Dubinin–Radushkevich) were used. The Langmuir isotherm model showed better correlation coefficients and maximum monolayer biosorption capacity calculated from this model were found to be 3.30×10^{-4} mol/g (287.84 mg/g).

Conclusion

Our results indicated that the biosorbent prepared from *T. elegans* was successfully used for the treatment of the real wastewater and it exhibited great biosorption efficiency in dynamic flow mode. Bed height of column and flow rate were optimized and best biosorptive performance attained at 96.98% with 40 mg biosorbent and 0.5 mL/min flow rate. The experiments showed that biosorption reusability of biomass kept of 10 consecutive cycles. According to breakthrough results *T. elegans* can be effectively used in column applications. Overall this suggested biosorbent has potential alternative for the wastewater decolorization in continuous system.

References:

1. R. M. Christie (2007) Environmental aspects of textile dyeing, Cornwall.
2. S. T. Akar, F. Sayin, D. Yilmazer, T. Akar, CLEAN – Soil, Air, Water (2016) 44 2 202-210
3. T. Akar, S. Arslan, S. T. Akar, Ecological Engineering (2013) 58 363-370
4. K. Chojnacka, Environment International (2010) 36 3 299-307
5. D. Wang, M. Li, D. Wei, Y. Cai, Y. Zhang, L. Xing, Journal of Eukaryotic Microbiology (2007) 54 1 110-117.
6. T. Akar, A. Kulcu, S. T. Akar, Chemical Engineering Journal 221 461-468
7. S. W. Won, Y. Yun, Dyes and Pigments (2008) 76 2 502-507
8. P. D. Sahaa, S. Chowdhury, M. Mondala, K. Sinhaa (2012) 47 1 112-123

Acknowledgements: This work was supported by the commission of Scientific Research Projects of Eskişehir Osmangazi University (ESOGU) with project number 201519D07.

Preparation of Polyaniline Coated Hydrogel for Removal of Remazol Black B

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Abstract

In this study, a hydrogel was prepared by crosslinking copolymerization of 3-Sulfopropyl methacrylate potassium salt with ethylene glycole dimethacrylate (EGDMA) in aqueous solution, using $K_2S_2O_8$ as a radical initiator at 80 °C. The obtained gel was interacted with 3 M HCl to obtain sulfonic acid containing sorbent. The sulfonic acid groups on the surface of the gel brushes were neutralized with excess of aniline, and the adsorbed aniline was polymerized by oxidizing with ammonium persulfate to give self-doped polyaniline. The sorption capacity of the reactive black dye was found about 0.120 g / g sorbent.

Keywords:Hydrogel, Polyaniline, Dye removal.

Introduction

Dyes usually have synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade [1]. Reactive dyes are barely eliminated under aerobic conditions and probably decompose into carcinogenic aromatic amines under anaerobic conditions [2]. Therefore, colour removal from wastewater is a major environmental problem. Adsorption techniques employing solid adsorbents are effective methods for water decontamination. Most commercial systems currently use activated carbons and organic resins as adsorbents to remove dye in wastewater because of their excellent adsorption abilities [3,4].

Interestingly, polymerization of aniline in the presence of polyacids such as, poly(4-styrene sulfonic acid) [5] and polyacrylic acid [6] has been reported to give doped and flexible PANI chains. This can be ascribed to template effect of the polyacids.

In this study, a new PANI coated hydrogel was prepared and characterized. PANI coated sorbent was used for removal of ramazol black B from water.

EXPERIMENTAL

Materials&Methods

Materials

3-Sulfopropyl methacrylate potassium salt (Aldrich), Ethyleneglycole dimethacrylate (EGDMA), Remazol Black B (Aldrich), Aniline /Aldrich) and all the other chemicals, solvents utilized were analytical grade commercial products.

Preparation of the hydrogel

3-Sulfopropyl methacrylate potassium salt (10 g, 41 mmol) and 0.896 g (4.52 mmol) EGDMA were placed in a flask attached to a reflux condenser and a nitrogen inlet. An appropriate amount of water was added to the flask, to obtain a total monomer concentration of 20%. Then, 0.20 g (7.40 mmol) $K_2S_2O_8$ was added to the solution and nitrogen was flushed

through the solution. The mixture was stirred until gelation proceeded at 80°C. The formed gel was washed with excess water and acetone respectively. The product was dried under vacuum at room temperature for 24 h. The yield was 10 g.

Polymerization of aniline on the hydrogel

The obtained hydrogel (3.0 g dry weight) was placed in a flask (100 mL) containing distilled aniline (10.0 mL). The mixture was stirred for 24 h. Then, aniline sorbed gel was filtered, and washed sequentially with excess of ethanol and ether respectively. 3.0 g of sorbed aniline on the gel was polymerized in aqueous solution of ammonium persulfate (7 g or 0.03 moles in 100 mL). The reaction mixture was shaken at room temperature for 24 h. After this period, the dark green product was filtered, and washed as described above.

Extraction of dyes

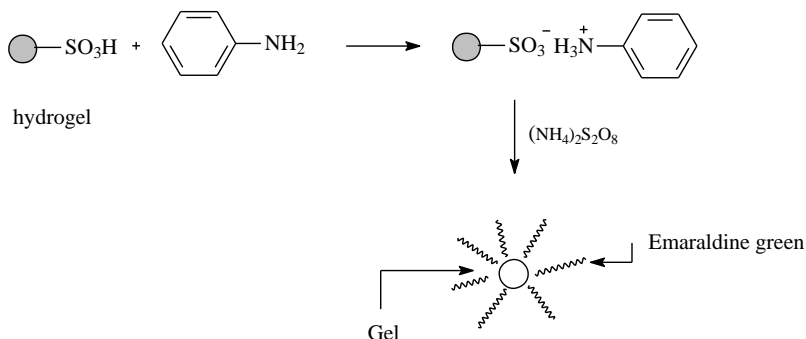
Dye capacities of the sorbent were determined by mixing weighed amount of polymer sample (0.1g) with 10 mL aqueous dye solution ($2.016 \cdot 10^{-3}$ M– $1.01 \cdot 10^{-4}$ M). In these experiments Reactive Black 5 was used. The mixture was stirred for 24 h and then filtered. Dye sorption capacity of the resin was assigned by colorimetric analysis of residual dye contents.

Kinetics of the dye sorption

Batch kinetic experiments were performed using diluted dye solutions ($4 \cdot 10^{-3}$ M) to estimate the efficiency of the sorbent for trace dye. For this purpose, sorbent (0.1 g) was wetted with distilled water (1.5 mL) and added to a solution of dye (90 mL). The mixtures were stirred with a magnetic stirring bar and aliquots of the solution (4 mL) were taken at appropriate time intervals for the analysis of the residual dye contents by the method as described above.

Results&Discussion

In this study, copolymerization of 3-Sulfopropyl methacrylate potassium salt with EGDMA in aqueous solutions (20%) with $K_2S_2O_8$ initiator at 80°C gives transparent hydrogels in high yields. Hydrogel sample was soaked into excess aniline to obtain anilinium salt. To remove free aniline contaminants, the samples were washed with ethanol and ether. The anilinium salt containing gel was directly polymerized in water by using ammonium persulfate as oxidant to give polyaniline (PANI) layers. It was observed that, polymerization of aniline takes place at room temperature. An immediate dark green colorization on the sorbent was observed, but the aqueous phase was almost clear, indicating formation of Emeraldine Green solely on the sorbent (Scheme 1).



Scheme1.Preparation of the PANI coated hydrogel

Extraction of Dyes

Dye extraction experiments were carried out simply by contacting wetted sorbent samples with aqueous dye solutions at room temperature. Capacities were assigned by colorimetric analysis of residual dye contents. Dye sorption capacities are given in Table 1.

Table 1. Dye sorption capacities of the sorbent

Dye Concentration, M	Capacities (mg/g)
0.000101	6.510
0.000202	13.657
0.000504	33.642
0.001008	62.442
0.002016	121.250

According to the Table 1, adsorption of dye on the sorbent was found to be concentration dependent. The sorption capacity of dye increases with increase in initial concentration.

Dye sorption kinetics of the sorbent

This material is able to remove the anionic dyes completely even from highly diluted aqueous dye solutions which are highly important. Here batch kinetic sorption experiments was performed with highly diluted dye solution ($4 \cdot 10^{-3}$ M) to investigate the efficiency of the sorbent in the presence of trace quantities of dyes. The concentration–time plot in Fig. 1 shows that the dye concentration falls to zero within about 60 minutes of contact time for remazol black B.

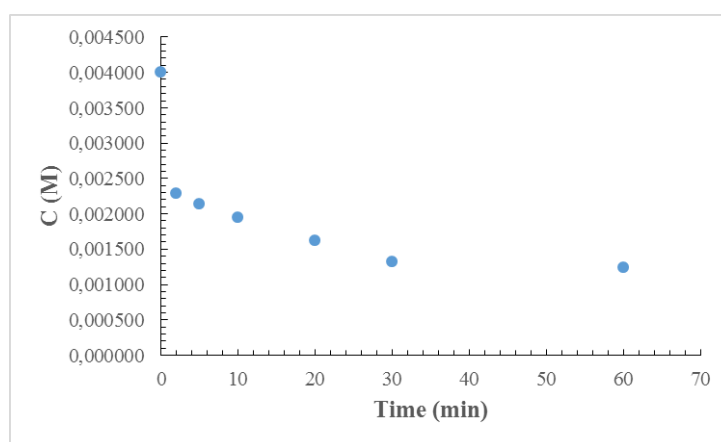


Figure 1. Dye sorption kinetics.

The kinetics of sorption is an important aspect of the process control of removal of pollutants. As shown in Fig. 1, there was a rapid uptake kinetics and adsorption equilibrium, which would be attained within about 60 min.

Conclusion

In this work, 3-Sulfopropyl methacrylate potassium salt hydrogel was synthesized and interacted with HCl to obtain sulfonic acid functions. This hydrogel was employed as solid acid dopant for generation polyaniline shell layer. The resulting PANI coated sorbent was used as solid support for removal of Remazol Black B successively. The polymeric sorbent was regenerated by using KOH in ethanol/water solution. Dye loaded sorbent can also be regenerated without losing its initial adsorption capacity.

Acknowledgments

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References:

1. Seshadri, S., Bishop, P. L., and Agha, A. M., Waste Management (1994) 14 127-137.
2. Peterson, D., (1990) in Colorants and Auxiliaries: Organic Chemistry and Application Properties, Vol 1, J. Shore, Ed. Manchester, England: Society of Dyers and Colourists
3. JJM. Orfao, A.I.M. Silva, J.C.V. Pereira, S.A. Barata, I.M. Fonseca, P.C.C. Faria. J. of Colloid and Interface Sci. (2006) 296 480-489.
4. A.A. Attia, W.E. Rashwan, S.A. Khedr. Dyes and Pigments (2006) 69 128–136.
5. C. W. Kuo, T.C. Wen, Eur Polym J (2008) 44 3393-3401.
6. B. Gupta, R. Prakash, J Appl Polym Sci (2009) 114 874-882.

New and Effective Material for Removal of Murexide Dye from Aqueous Solution

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Synthesis of tin chelate compound was performed by using simple and inexpensive schiff base ligands. Synthesized material was used for murexide dye removal from aqueous solution. Murexide is also called ammonium purpurate or MX. It can damage the eye and skin, also cause respiratory tract irritation to mucous membranes, and upper respiratory tract. During the use of murexide, a considerable amount of this dye goes with wastewater to environment and cause environmental damage as giving water undesirable color and reduce sunlight penetration [1].

In this study, metal schiff base chelate compound was synthesized and used for murexide removal from aqueous solutions. Firstly, (E)-2-((p-tolylimino)metil)fenol (TIMPH) ligand was synthesized with p-toluidine and salicylaldehyde. Secondly, TIMP-metal complex compound was synthesized from the reactions of TIMPH with BuSnCl_3 . This compound was characterized by Fourier transform infrared (FT-IR), nuclear magnetic resonance ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$), elemental analysis and mass spectroscopies [2]. Then, dye removal optimization was performed by studying effect of time, pH, amount of dye and dye concentration e.g. on novel formed of Schiff base tin chelate compound. From the results we obtained very high recovery percentages with low pH values, at low amount of dye in a short time.

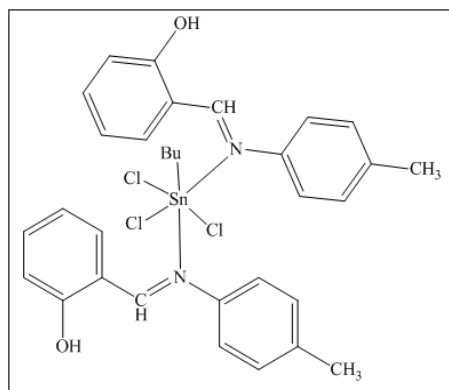


Figure 1. Butyltrichlorobis(TIMP)tin(IV) (Schiff base tin chelate compound)

Keywords: Tinchelate Compounds, Murexide, Removal Dye.

References:

1. S. Davoodi, F. Marahel, Mehrorang Ghaedi, Mostafa Roosta, Arash Hekmati Jah, Desalination and Water Treatment, Tin oxide nanoparticles loaded on activated carbon as adsorbent for removal of Murexide, (2014) 52 7282–7292.
2. Y. Begüm Canan, 2016, Organokalayşelat Bileşiklerinin Sentezi, Karakterizasyonu ve Uygulamaları, Yüksek Lisans Tezi, Kocaeli.

Removal of bisphenol-A from aqueous solution via poly(DVB-MATrp) microbeads

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Bisphenol-A (BPA), the common name for 2,2-bis(4- hydroxyphenyl) propane, is a chemical used as a monomer in the manufacturing of polycarbonate, epoxy resins, acrylic resins and polysulphones(1). It is found in many products such as feeding bottles, food containers, plastic water bottles and their caps, eye glasses, CD's, DVD's, electronic devices, dental sealants and composite filling materials(2). Bisphenol A is a moderately water-soluble compound (300 mg L⁻¹ at room temperature) and it dissociates in an alkaline environment (3). Many compounds, for example organochlorine pesticides, alkylphenols, polychlorobiphenyls, organotin compounds, and bisphenol A and its derivatives, have recently been shown to have effects on humans similar to those of estrogens(3).According to the European Food Safety Authority, BPA amount of a human body can tolerate daily is 0.05 mg per kilogram of body weight(2).A variety of treatment methods such as adsorption, biochemical, electrochemical, photochemical reactions and ozonization have been used by researchers to remove BPA from different aquatic environment(1).

In this study, poly(divinylbenzene N-methacryloyl-amido-L-tryptophan methyl ester) microbeads (average diameter=120–150 µm) were synthesized and used for removal of bisphenol-A (BPA)from aqueous solutions. The microbeads were characterized by scanning electron microscopy, infrared spectroscopy and elemental analysis techniques. To evaluate the efficiency of poly(DVB-MATrp) beads for adsorption of BPA from aqueous medium, the effects of pH, initial concentration, contact time and temperature were analyzed. The maximum BPA adsorption capacity of the poly(DVB-MATrp) microbeads was determined as 141.7 mg/g at pH 7.0, 35 °C.

Keywords : Adsorption, Bisphenol-A, poly(DVB-MATrp) Microbeads

References:

1. Bilgen Osman, Elif Tümay Özer, Ali Kara, Emel Yeşilova, Necati Beşirli, J. Porous Mater (2015) 22 37–46
2. Serap Akyüz, Ayşen Yarat, Edibe Egil, MÜSBED (2011) 1 3 190-195
3. I. Rykowska and W. Wasiak, Acta Chromatographica, (2006) NO. 16

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Development of a Versatile Material for Effective Removal of Bisphenol A

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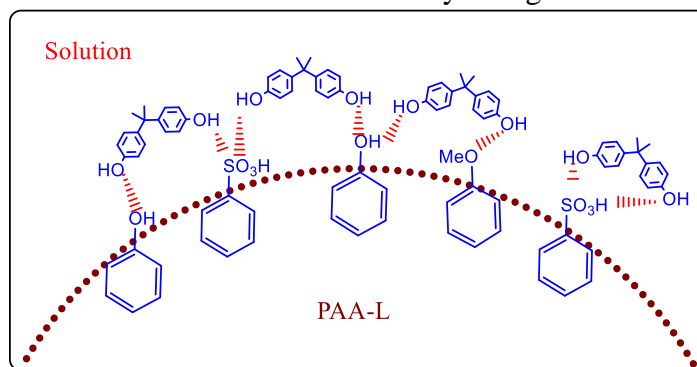
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Polycarbonates, polyesters, and epoxy polymers are mostly used in the industry due to their good properties such as lightness, durability, and high melting point [1, 2]. Bisphenol A (BPA) is one of the most used additive chemicals during polymerization of polycarbonates. Polymers including BPA are extensively used in the various industries such as packing for food and drug, medical equipment, lens, dye. [3].

A composite material containing polyacrylamide amide (PAA) and lignin (L) was developed and characterized for effective Bisphenol A (BPA) removal. Fundamentals of the proposed approach are based on adsorption of BPA molecules on PAA-L composite. Characterization of material was carried out by FTIR and PZC analysis. Adsorption of BPA ions from aqueous solution as a function of BPA concentration, pH, ionic strength, temperature, and reusability of adsorbent was investigated in detail. The adsorption data were analyzed by using the Langmuir, Freundlich and Dubinin-Radushkevich (DR) models. As a result of this analysis, r^2 values were found as 0.991, 0.984, and 0.873, respectively. Maximum adsorption capacity obtained from Langmuir models was calculated as 55.358 mg g⁻¹. Freundlich heterogeneity was found as 0.637 while EDr value obtained from DR model as 12.219. Experimental results showed that the adsorption of BPA is based on chemical binding, exothermic and spontaneous process. Reusability of PAA-L adsorbent was verified by recovery experiments for a lot of times and was not observed any change or deterioration on the material.



Keywords: Bisphenol A, Removal, Adsorption, HPLC

References:

1. M. Yoshida, A. Satoh, A. Shimada, Y. Sumi, C. Tohyama, Toxicology (1999) 139 1–2 129-138.
2. L.N. Vandenberg, R. Hauser, M. Marcus, N. Olea, W.V. Welshons, Human exposure to bisphenol A (BPA), Reprod. Toxicol, (2007) 24 139-177.
3. C.A. Staples, P.B. Dorn, G.M. Klecka, S.T. O'Block, L.R. Harris, A review of the environmental fate, effects, and exposures of bisphenol A, Chemosphere, (1998) 36 2149-2173.

Decolorization Potential of Immobilized *Mucor Plumbeus* in Dynamic Flow Treatment

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Abstract

This study focused on the development of an efficient and new immobilized sorbent for the continuous mode treatment of dye contaminated solutions. Methyl violet (MV) is chosen as model dye. *Mucor plumbeus* cells were passively immobilized onto with Sepiolite to prepare a new sorbent system. The effects of flow rate and sorbent dosage on the decolorization process were investigated. The highest sorption yield 97.99% was obtained with 0.5 ml min⁻¹ flow rate. Breakthrough behavior of the immobilized system was also examined. It exhibited good sorption performance up to 270 min. Result indicated that the suggested sorbent system can be a good alternative for the dynamic flow mode treatment of cationic dye contamination.

Introduction

Synthetic dyes are recalcitrant organic pollutants found in industrial effluents. Dyes have complex molecular structures that contain various functional groups. This chemical structure of dye often serves them stable molecules against sunlight, oxidizing agent and microbial attack. On the other hand traditional water treatment processes usually involve some disadvantages such as high operating and maintaining costs, incomplete dye removal, generation of dye bearing sludge or other waste products that require safe disposal [1]. Biosorption process is a potential alternative to traditional treatment techniques for the decolorization. After the biosorption process treated water can be re-used in industry. Thus, it reduced damage to the environment. Biosorption is also an environmentally friendly process [2].

Numerous studies on the sorption of organic and inorganic water pollutants in batch systems have been reported in the literature. However dynamic flow mode sorption applications are more useful in real and large scale wastewater treatment. This type of treatment is simple to operate, attains a high yield and it can be easily scaled up from a laboratory-scale procedure. A large volume of polluted water can be continuously treated using a known quantity of sorbent material packed in the column [3].

The present work aims to investigate the sorption potential of *M. plumbeus*-Sepiolite as a new and alternative sorbent system for the removal of MV dye from aqueous solutions in a packed bed column. The study includes an evaluation of the effects of key process parameters flow rate and sorbent amount. Breakthrough behaviour of the proposed system was also examined.

Materials&Methods

M.plumbeus strain was maintained at 4°C on potato dextrose agar (PDA) slants. In order to prepare mycelium suspension, cells were grown on PDA slants for 7 day at 26°C. Prewighted (1g) powdered sepiolite was transferred to 250 mL erlenmeyer flasks containing 100 mL of liquid growth medium[4] before autoclaving at 121°C at least 20 min. Spore suspension of *M.plumbeus* was added to each flask under aseptic conditions. Growth was allowed to proceed for 7 days at 26°C on a shaker operating at 120 rpm. Cylindrical fixed bed columns were used in sorption experiments. Tygon tubing was used for the connections between dye solutions and columns. Dye solution at pH ~8.0 were fed into the columns by a peristaltic pump. While the sorbent dosage loaded in columns was varied from 0.4 to 6.0 gL⁻¹, flow rate was screened in the range of 0.5 to 6.0 mL min⁻¹. In order to investigate the breakthrough profile of immobilized sorbent, 100 mgL⁻¹ dye solution was fed at 0.5 mL min⁻¹ into the column containing 0.5 g of sorbent dye concentrations in the solutions were determined using UV visible spectrophotometer (Shimadzu 2550-UV) at 580 nm After this period, immobilized biomass was separated from growth medium by filtration, washed with distilled water. Dried at 60°C, ground using a laboratory mill and sieved to 212 µm particle size.

Results&Discussion

The initial stage of continuous experiments in column, the effect of flow rate on the sorption of MV onto immobilized sorbent was investigated and results were given in Fig.1. When the flow rate was decreased from 6.0 to 0.5 mL min⁻¹ the percentage decolorization yield of immobilized sorbent increased from 64.69 to 97.90%.

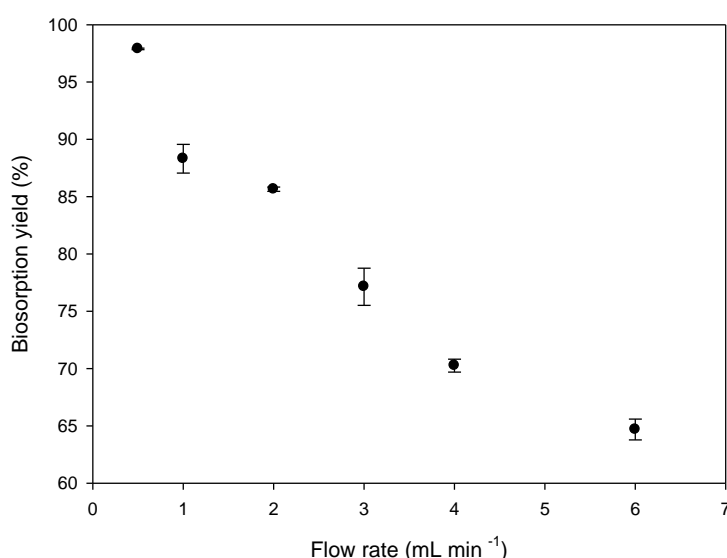


Fig 1. The effect of flow rate on the MV removal process.

A decreasing dye removal trend with increasing flow rate may be explained by the diffusion limitations of dye molecules into the sorbent pores and insufficient residence time of the dye solutions in the column [5] therefore 0.5 mL min⁻¹ was chosen as optimum flow rate for further studies.

On the other hand as illustrated in Fig. 2 an increase in the sorbent amount filled in the column from 0,01 to 0,02 g caused an increase in dye removal yield up to 97.90% Further increase in the sorbent dosage up to 0.1 g resulted no significant change in the sorption yield. This trend may be attributed to saturation of dye binding sites of immobilized sorbent.

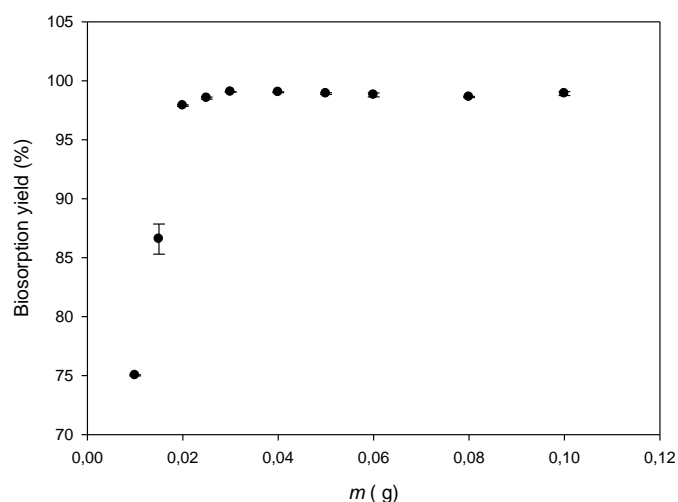


Fig.2. the effect of 0.01 immobilized sorbent amount on the MV removal process.

The breakthrough profile of immobilized sorbent material is presented in Fig.3.

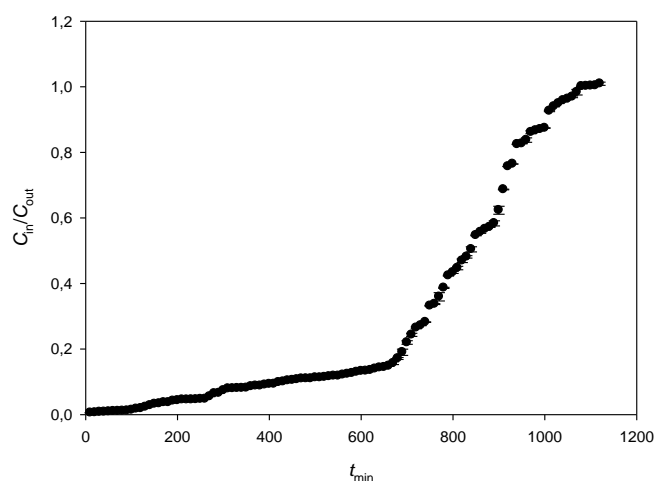


Fig.3. Breakthrough profile of immobilized sorbent.

As can be seen from Fig.3 before the breakthrough point 270 min. the dye concentration in the effluent was too low the sorption column reached exhaustion after 1040 min. This results showed that the suggested sorbent material can be used in continuous type of treatment for the removal of MV dye.

Conclusion

The study reports on the potential of *M.plumbeus* cells immobilized onto sepiolite for the removal of MV dye from contaminated solutions in batch and dynamic flow mode operations. Results indicated that flow rate and sorbent amount parameters significantly affects the dye removal yield of sorbent material. The suggested immobilized sorbent can be evaluated as a good alternative for decolorization purpose when the dynamic flow mode conditions were optimized.

Keywords: Methyl Violet, Biosorption, Immobilization, Column

References:

1. G.Crini, Bioresource Technology (2006) 97 1061-1085.
2. K. Chojnacka, Environment International (2010) 36 299-307.
3. D. Charumathi, N. Das, Desalination (2012) 285 22-30.
4. S.F. Arantes, J. R Hanson, D. J Mobbs. Phytochemistry (1999) 52 631-634.
5. T.Akar, S.Arslan, S. Tunalı Akar, Ecological Engineering (2013) 58 363-370.

Methyl Violet Biosorption by Fungi-Mineral Composite: Batch Mode Optimization

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Abstract

The potential use of fungi- mineral composite for the removal of Methyl violet (MV) dye from aqueous solutions was investigated in batch mode. Decolorization conditions were investigated as functions of initial pH and sorbent amount. Result indicated that decolorization process is highly dependent on solution pH. Good biosorption yields were observed about neutral pH values. Up to 89.15% decolorization performance was achieved with 1.2 g L⁻¹ of sorbent material. Our results suggest that the proposed fungi-mineral composite may be useful for decolorization of MV contaminated solutions.

Introduction

Synthetic dyes are common water pollutants. Many of them are toxic even at trace levels. The effluents containing dyes cause serious and irreversible environmental and biological damage. Therefore, adequate treatment of dye containing effluents prior to discharge into aquatic media is of great importance for human health and environment. Traditional methods such as reverse osmosis, ion exchange and Fenton reactions etc. have been extensively used for the treatment of colored effluents [1]. The biosorption has considerable amount of attention as an alternative process to traditional water treatment methods. The potential important advantages of the biosorption process over traditional techniques include low operation cost, small quantity of sewage sludge to be dispose and simple operation [2].

The use of immobilized cells in the biosorption applications has received increasing interest in recent years because their several advantages. Good mechanical strength, chemical stability and high regeneration ability are some important advantages of the immobilized sorbent materials. Therefore, some attempts have been made to prepare the new and efficient immobilized sorbents for the removal of organic and inorganic pollutants from contaminated aquatic media [2]. In addition to biotechnological applications, immobilization technique is also used in different fields such as food industry, biosensor applications and pharmaceutical studies [3]. The goal of this study was to investigate the possible use of a *Mucor plumbeus*-Sepiolite (*M.plumbeus*-Sepiolite) composite sorbent for decolorization of (MV) contaminated solutions in batch mode. In this context pH and sorbent dosage critical parameters, affecting the decolorization process were optimized.

Materials and Methods

M.plumbeus was passively immobilized on sepiolite in growth media. Biomass was produced in the liquid medium with the composition (per liter) of sepiolite (1g), glucose (30 g), KH₂PO₄ (2 g), MgSO₄ (2 g), (NH₄)₂C₄H₄O₆ (2 g), Yeast extract (1 g), CaCl₂ (0.1 g), NaCl

(1 g), $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ (0.1 g) and trace element solution (2 mL) [4]. The pH of the liquid growth medium was adjusted to 5.5 before autoclaving at 121 °C for at least 20 min and adding trace element solution. Erlenmeyer flasks containing the growth media (100 mL) were inoculated with mycelium suspension (1 mL) of *M. plumbeus*, under sterile conditions and shaken at 26 °C and 120 rpm for 7 days in a rotary shaker. After growth period, the produced immobilized sorbent was separated from growth media by filtration and washed repeatedly with deionized water, dried at 60°C, ground using a laboratory mill and sieved to 212 μm particle size. 25 mL of 100 mgL^{-1} dye solutions were placed in beakers. An accurate weight of biosorbent sample was added to flask and stirred at 200 rpm on a multipoint magnetic stirrer. At the end of the each experiment the biosorption mixture was centrifuged at 4500 rpm for 5 min and supernatant was collected for quantitative dye analysis. In order to determine the optimum pH and sorbent dosage, initial pH of the sorption medium was varied from 3.0 to 10.0 and sorbent amount was screened between 0.4-4.0 g L^{-1} .

Results and Discussion

The pH of the sorption medium affects the ionization state of the sorbent functional groups like carboxyl, amino, sulphoxide and hydroxyl etc. the effect of initial pH of the sorption medium on the decolorization process is given in Fig.1.

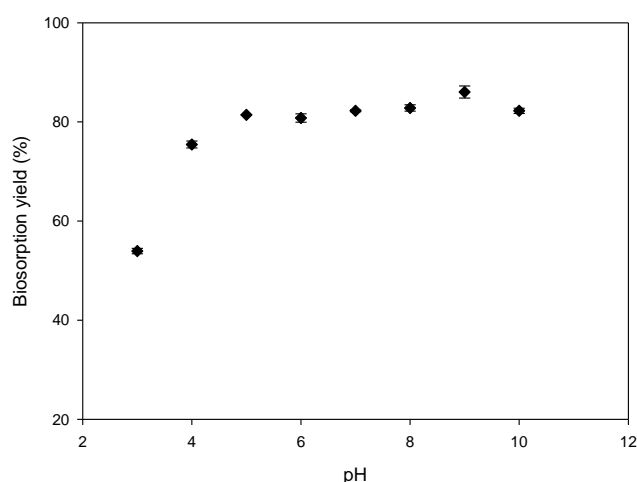


Fig 1. Effect of initial pH of the solution on the MV sorption process

As can be seen from this figure, the sorption yield of the composite material increased from 53.95 to 81.42% when the initial pH was increased from 3.0 to 5.0. Thereafter, the sorption yield was kept from 5.0 to 10.0. the low decolorization performance of immobilized sorbent at the high acidic pH value can be attributed to electrostatic repulsive forces between cationic dye molecules and protonated sorbent surface. At higher pH value the immobilized sorbent negatively charged as a result of deprotonation and this attraction forces stimulate the binding of dye molecules to the sorbent surface [5]. The further decolorization studies were carried out at the pH value about 7.0. The biosorption yields against the composite sorbent dosage were depicted in Fig.2. Along with the increase of immobilized sorbent dosage from 0.4 to 1.2 g L^{-1} , the dye removal yield increased from 59.08 to 89.15%. this trend may be explained by the greater surface area and large number of vacant sorption sites of immobilized sorbent [6].

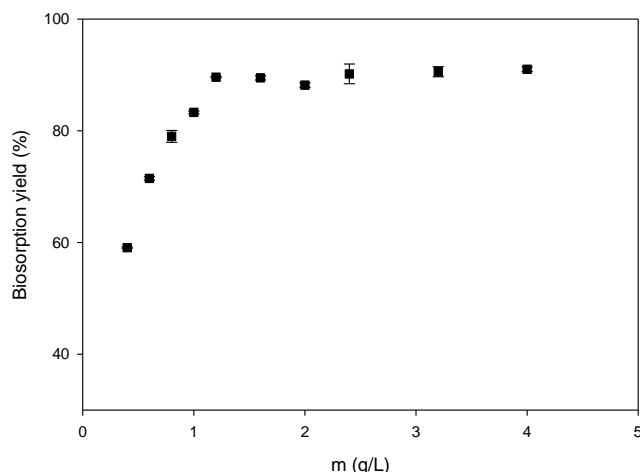


Fig 2. Effect of biosorbent dosage of composite sorbent on the MV sorption process

After the sorbent dosage of 1.2 g L^{-1} the biosorption yield has no changed. Therefore, 1.2 g L^{-1} was selected as optimum sorbent dosage for batch mode MV removal process.

Conclusion

This study was indicated that initial pH and biosorbent dosage are played important role in the sorption of MV dye onto suggested sorbent material. Findings indicated that the prepared fungi mineral-composite can effectively used for the removal of MV from aqueous solutions by adjusting the pH and sorbent dosage parameters to optimum values.

Keywords: Cationic Dye, Sorption, Composite, *Mucor Plumbeus*, Alunite

References:

1. G.Crini, Bioresource Technology (2006) 97 1061-1085.
2. T. Akar, Z. Kaynak, S.Tunali Akar, Journal of Hazardous Materials (2009) 163 1134-1141.
3. N. Tewari, P. Vasudevan, B.K. Guha, Bioresource Technology (2012) 123 290-295.
4. S. F.Arantes, J. R. Hanson, D. J Mobbs, Phytochemistry (2012) 52 631-634.
5. T. Akar, B. Anilan, A.Gorgulu, S. Tunali Akar, Journal of Hazardous Materials (2009) 168 1302-1309.
6. T.Akar, Z. Kaynak, S. Tunali Akar, Journal of Hazardous Materials (2009) 163 1134-1141.

Preparation of Molecularly Imprinted Microparticle-Embedded Cryogel for The Selective Recognition of Tetracycline from Aqueous Medium

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Due to the good activity against acute diseases caused by bacteria, tetracyclines (TCs), are commonly used to cure several infectious diseases for prevention and treatment of farm animals. Following administration, TCs are poorly absorbed by the digestive system with mostly excreted unmetabolized, and a portion of them still remains biologically active in animal waste. In previous studies, a fact that exposure of TCs residue in soil and water environment could result in a significant ecological concern has been proved. Because of broad-spectrum antimicrobial activity and low cost, the wide applications of TCs have led to fairly concerns with regard to unsafe residue in animal-production foods such as milk, meat, egg, cheese, and honey, which could be directly toxic. Therefore, it is of great necessity to development efficient and inexpensive methods for the selective removal of such compounds from the environment [1]. Molecularly imprinted polymers (MIPs), possessing tailor-made recognition sites, exhibit the ability of specifically rebinding to a target molecule in preference to analogous compounds. Owing to the high specificity and selectivity, as well as favourable thermal, mechanical and chemical stability, MIPs have been widely used as artificial receptors in solid phase extraction, chromatography separation, chemical sensors, catalysis, and many other applications. Due to the high porosity, high permeability, soft, flexibility, and high flow velocity cryogels are widely used as new materials. Cryogels permit the free passage of microparticles and nanoparticles without blockage because of the pore size within the range of 10–100 µm. For increasing the surface area a particle embedding become a new approach in separation processes [2].

The main purpose of this study is to prepare poly(hydroxyethyl methacrylate)(PHEMA) cryogel embedded with tetracycline-imprinted microparticles. Firstly, the imprinted microparticles were synthesized via emulsion polymerization and characterized by using FTIR, X-ray photoelectron spectroscopy (XPS), zeta potential and size analyzes. PHEMA cryogel-embedded with microparticles were characterized scanning electron microscopy (SEM) and swelling test. To evaluate the efficiency of the cryogel system, the effect of various experimental parameters such as pH (2.0-8.0), initial concentration (5-85 mg/L), contact time (1-300 min), and temperature (4-23 °C) were determined. The maximum adsorption of tetracycline from aqueous solution was obtained at pH 5.0. Selectivity studies were conducted by using ciprofloxacin and amoxicillin. The adsorption process obeyed pseudo-second-order kinetic model. All the isotherm data can be fitted Freundlich isotherm model with high correlation coefficients for all studied temperatures.

Keywords: Tetracycline, Removal, Molecular Imprinting, Cryogel, Embedded

References:

1. J Daia, J Pana, L Xua, X Li, Z Zhouc, R Zhanga, Y Yana. Journal of Hazardous Materials (2012) 205-206 179–188.
2. A Göçenoğlu Sarıkaya, B Osman, A Kara. Desalination and Water Treatment 2015 1–10.

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POSTER SESSION 2

Fluorimetric Determination of Carbendazim After Preconcentration with Magnetite-Molecularly Imprinted Polymer

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Carbendazim is a systemic benzimidazole fungicide which has been widely used to control various kinds of diseases in agricultural processes. It is also a metabolite of two other fungicides; benomyl and thiophanate methyl (1). However, the usage of benomyl is now restricted in many countries carbendazim is still being used all over the World (2). Trace levels of carbendazim gives serious damages to endocrine system and shows mutagenic and teratogenic effects on animals.(3) It is indicated that in the literature that carbendazim is embryotoxic and phytotoxic and it also shows negative effects on the male mammalian reproductive system (4). Therefore, quantitative determination of trace levels of carbendazim is very important.

In this study, magnetite-molecularly imprinted polymer has been used for the first time as selective adsorbent before the fluorimetric determination of carbendazim. Limit of detection (LOD) and limit of quantification (LOQ) of the method were found to be 2.3 and 7.8 µg/L, respectively. Proposed method has been successfully applied to determine carbendazim residues in apple and orange, where the recoveries of the spiked samples were found to be in the range of 95.7-103%. Characterization of the adsorbent and the effects of some potential interferents were also evaluated. With the reasonably high capacity and reusability of the novel adsorbent, dynamic calibration range, rapidity, simplicity, cost-effectiveness and with suitable LOD and LOQ values, the proposed method appears to be one of the ideal methods which can be used for the determination of carbendazim.

Keywords: Carbendazim, Magnetite, Molecularly Imprinted Polymer, Fluorimetric Determination

References:

- 1.G. M. Patel, J. V. Rohit, R. K. Singhal and S. K. Kailasa, *Sensor Actuat B-Chem* (2015) 206 684–691.
- 2.M. E. Wisniewski and C. L. Wilson, *HortScience* (1992) 27 94–98.
- 3.Z. Wang, Y. Wang, F. Gong, J. Zhang, Q. Hong and S. Li, *Chemosphere* (2010) 81 639–644.
- 4.R. Panadés, A. Ibarz and S. Esplugas, *Water Res* (2000) 34 2951–2954.

Synthesis of Molecularly Imprinted Polymers (MIPs) for Selective Determination of 2,4-D Acid

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Molecular imprinting has become a universal tool for the preparation of artificial and robust recognition materials useful for diagnostics, industry and environmental analysis. Molecular imprinting polymers (MIPs) are easily obtained by copolymerization of suitable functional monomers and cross-linkers in presence of the desired molecule.

The aim of this study is to synthesize 2,4-D acid imprinted polymers, determination of its performance such as recovery of 2,4-D acid from polymer, rebinding of 2,4-D acid on polymer and its determination by spectrometric methods. Two different approaches were investigated. First one is bulk polymerization; by simply adding methacrylic acid monomer (MAA), etilen glycol dimethacrylate (EDMA) cross linking agent, 2,2'-azobis(isobutyronitrile) (AIBN) initiator and 2,4-dichlorophenoxyacetic acid (2,4-D) template molecule; a polymer that can bind 2,4-D selectively was acquired. The second one is suspension polymerization; there are two phases in this approach one is water the other one is chloroform. Water phase contains PVA and organic phase contains MAA, EDMA, AIBN and 2,4-D which the polymerization occurs. The monomer:template ratios were used as 4:1.

The extraction of 2,4-D from polymer was performed by soxhlet extraction with methanol. It gives very close results such as 94-100% respectively. Measurements were carried out with spectrophotometer at 284nm. The maximum rebinding capacity of 2,4-D suspension polymerized extracted polymer in methanol-water 1/1 was found 45.8 mg/g. For the non-imprinted polymer (NIP) it was found as 6.37 mg/g. The maximum rebinding capacity of 2,4-D bulk polymerized extracted polymer in methanol-water 1/1 was found 34.81 mg/g. For non-imprinted polymer (NIP) it was found as 22.37 mg/g.

In this study the novel 2,4-D acid imprinted polymer was examined as extraction material for separation and pre-concentration purposes. The MI-SPE of the 2,4-D was carried out using the polymer we have synthesized the binding yield of 94% was obtained. After selective separation of 2,4-D acid spectrometric measurements can be easily carried out without any interference.

Keywords: Suspension Polymerization, MIP, 2,4-D Acid,

References:

1. Giuseppe Cirillo, Manuela Curcio, Ortensia Ilaria Parisi, Francesco Puoci, Francesca Iemma, Umile Gianfranco Spizzirri, Donatella Restuccia, Nevio Picci, Food Chemistry (2011) 125 1058–1063
2. A. Prieto, S. Schrader, C. Bauer, M. Möder, Analytica Chimica Acta (2011) 685 146–152
3. Wassim Hadj Ali, Delphine Derrien, Florent Alix, Céline Pérollier, Olivier Lépine, Sami Bayouth, Florence Chapuis-Hugon, Valérie Pichon, Journal of Chromatography A (2010) 1217 6668–6673

Synthesis, Characterization, Spectroscopic Properties: Schiff Base Derivative Bearing Zinc(II) Phthalocyanine

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These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated. Several metal complexes of Schiff bases containing nitrogen, oxygen and sulfur donor atoms have been synthesized and studied [1]. The presence of nitrogen and oxygen donor atoms in the complexes makes these compounds effective and stereospecific catalysts for oxidation, reduction hydrolysis and they also show biological activity and other transformations of organic and inorganic chemistry [2]. It is well known that some drugs have higher activity when administered as metal complexes than as free ligands [3]. Metallo phthalocyanines (MPcs) are organometallic macrocycles that typically comprise the usually planar organic ligand and a metal ion or metalloid within the central cavity of the ring. MPcs have attracted considerable attention in solar cells, photo dynamic therapy, gas sensors, liquid crystal, and electrochromic displays because of their remarkable optical, and electrical properties, the conjugated system, as well as chemical, and thermal stability [4]. The aim of the present research is to produce new synthetic compound combining two functional materials (phthalocyanines and 4-[(1E)-(5-bromo-2-hydroxyphenyl)methylene]amino}-N-(5-methyl-1,3,4-thiadiazol-2-yl)benzene as a bioactive compound) and investigated its spectroscopic properties. Thus, novel 4-[(1E)-(5-bromo-2-hydroxyphenyl)methylene]amino}-N-(5-methyl-1,3,4-thiadiazol-2-yl)benzene,(E)- -(((4-bromo-3',4'-dicyano-[1,1'-biphenyl]-2-yl)methylene)amino)-N-(5-methyl-1,3,4-thiadiazol-2-yl)benzenesulfonamide compound and new peripherally tetra-substituted zinc(II) Pc complex and were synthesized and characterized by various spectroscopic techniques. in this study (Figure 1).

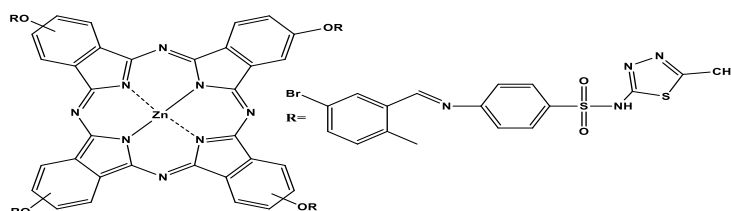


Fig. 1. Chemical structure of novel phthalocyanine

Keywords: Phthalocyanine, Sulfapyridine, Sulfamethizole, Zinc, Spectroscopy

References:

1. O. Güngör and P. Gürkan. *Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy* (2010) 77 304.
2. R. Ramesh and M. Sivagamasundari. *Synthesis Reactivity in Inorganic and Metal-Organic Chemistry* (2003) 33 899.
3. A. M. A. Omya, M. H. K. Mostafa, M. A. Gehad and M. R. Ramadan. *Spectroscopy Letters*, (2003) 36 71.
4. C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines: Properties and Applications*, vols. 1e4, VCH Publishers, New York, 1989, 1993, 1996.

A New Fluorimetric Detection for the Determination Ag(I) Species in Some Food Samples

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The widespread use of silver compounds and silver-containing procedures in industry, medicine, jewellery, cloud seeding and in the disinfection of drinking water has resulted in an increasing silver content of environmental samples. Silver impregnated filters are used in water disinfection, while silver concentrations up to 200 µg L⁻¹ are permitted for antimicrobial activities for human health [1]. A new turn-on fluorimetry procedure for the determination of silver by fluorimetry system has been described. [2-((E)-{[3',6'-bis(diethylamino)-3-okso spiro[isindol-1,9'-xantene]-2(3H)-yl]imino}methyl) cyclopenta-2,4-dien-1-yl](cyclopenta-2,4-dien-1-yl)-iron (DKMS) fluorescent reagent (Fig. 1), after synthesis/characterized was firstly used. Ag(I) was complexed with the fluorescent reagent and directly made measurements using fluorimetry without any separation/preconcentration. Best determinations conditions were established by testing different the reagent quantities, acidity and pH of sample, effect of temperature and interfering ions. The detection limit of the method was 1.00 µg L⁻¹ while the relative standard deviation was 0.1 % for 0.1 mg L⁻¹ Ag(I) concentration. The developed method has been applied successfully to the determination of silver in burn cream, some food and water samples. The results of analysis of the certified reference material (3101a and INCT-TL-1) are in good agreement with the certified value.

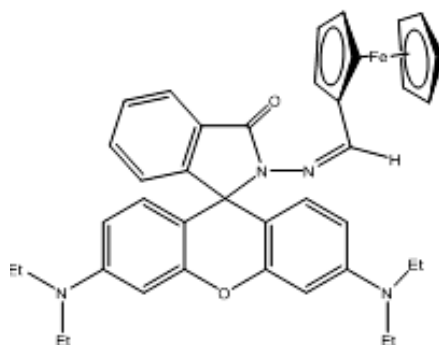


Figure 1. Chemical structure of the DKMS reagent

Keywords: Fluorescence Reagent, Direct Determination, Silver Ions, Food Samples, Water Samples

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References:

1. J. Liu, Z. Cao, Y. Lu, Functional Nucleic Acid Sensors, Chem. Rev (2009) 109 1948-1998.

Determination of Peroxynitrite Anion Scavenging Activity of Biothiols

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Abstract

In this study, a novel fluorometric method for the determination of peroxynitrite anion (ONOO⁻) scavenging (PAS) activity of biothiols, which can mostly trap peroxynitrite *in vivo*, is described. This assay is based on the conversion of gentisic acid probe to its non-fluorescent oxidation products with ONOO⁻. The attenuation of fluorescence intensity (FI) of the probe upon peroxynitrite attack is diminished with antioxidants, the difference in FI being related to PAS activity of antioxidants. IC₅₀ (50% inhibitive concentration) values of biothiols and tissue homogenates were estimated, in comparison with the reference Pyrogallol Red (PR) bleaching method.

Keywords: Peroxynitrite anion, scavenging activity, biothiols, pyrogallol red bleaching method.

Introduction

Peroxynitrite anion (ONOO⁻) is an effective oxidant known to be crucial in the macrophage killing of various pathogens.¹ It plays a significant role in neurodegenerative diseases, cardiovascular disorders and inflammation.² ONOO⁻ can react with various biomolecules including thiols and amino acids.³ Toxicity of ONOO⁻ is due to its ability to directly oxidize ($E^0_{\text{ONOO}^-}=1.40$ V) the sulfhydryl group of cysteine and glutathione (GSH),⁴ and even the sulfur atom of methionine.⁵

Tyrosine can be used as the detector molecule for ONOO⁻. This method also requires multifaceted HPLC equipment for determining the remaining tyrosine and its ONOO⁻ oxidation products (such as 3-nitrotyrosine and 3-hydroxytyrosine).⁶ *In vivo* tyrosine is the primary target for ONOO⁻ damage. Its main reactive group is the OH group at position 1, but it has a low PAS activity because of the sizable substituent at position 4.⁷ Dihydrodichlorofluorescein (DCFH) and dihydrorhodamine-123 (DHR) have been used for the determination of PAS activity.⁸

Materials & Methods

Synthesis of ONOO⁻ was achieved by utilizing the autoxidation of hydroxylamine in alkaline medium.⁸ The formation of ONOO⁻ was demonstrable spectrophotometrically at 302 nm and its concentration was determined by using the molar absorption coefficient ($\epsilon_{302} = 1670 \text{ M}^{-1}\text{cm}^{-1}$) in accordance with Beer's law.⁹

The spectrofluorometric proposed assay (*Gentisic acid assay*) is based on the attenuation of fluorescence intensity of gentisic acid probe by ONOO⁻. The kinetic competition between scavenger and probe was started by addition of ONOO⁻ to reaction mixture containing phosphate buffer, gentisic acid probe and scavenger solution.

The fluorescence intensity of gentisic acid at 450 nm ($\lambda_{\text{ex}} = 267$ nm) was measured initially (I_0) and after peroxynitrite attack with (I_2) or without (I_1) scavenger ($I_0 > I_2 > I_1$). The inhibition ratio % was calculated by using Eq. (1).

$$\text{Inhibition ratio (\%)} = 100 [(I_2 - I_1)/(I_0 - I_1)] \quad (1)$$

The spectrophotometric reference method¹⁰ (*PR bleaching assay*) is based on the bleaching of PR dye by ONOO^- . The loss of absorbance due to oxidation of PR was monitored at 540 nm ($\epsilon = 2.04 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).¹¹ the absorbance was diminished at 540 nm due to oxidation of PR. The inhibition ratio % was calculated according to Eq. (2) by using absorbances measured initially (A_0) and after peroxynitrite attack with (A_2) or without (A_1) the scavenger ($A_0 > A_2 > A_1$).

$$\text{Inhibition ratio (\%)} = 100 [(A_2 - A_1)/(A_0 - A_1)] \quad (2)$$

Results & Discussion

PAS activity of biothiols measured by the fluorometric and PR bleaching methods are listed in Table 1. It demonstrates that the IC_{50} values found with fluorometric assay were lower than those found with PR bleaching assay. Biothiols were found as effective scavengers by the fluorometric gentisic acid assay.

The Spearman's rank correlation test was employed for comparative IC_{50} values found with gentisic acid assay and PR bleaching assay. The interrater Spearman's rank correlation (consisting of eight peroxynitrite scavengers) was high and statistically significant ($r = 0.9762$, $p < 0.001$).

Even though PR is the best among dyes (Carminic acid, Gallein, Evans Blue, Alizarin Red S etc.) which can be used for determination of PAS activity,⁶ its sensitivity is low because it is based on measurement of absorbance. For this reason we used a novel fluorometric probe in order to improve the sensitivity. In general, fluorometric probes are more sensitive than that absorptimetric ones. The highest PAS activities in the gentisic acid assay were observed for cysteamine > cysteine > GSH > homocysteine > NAC > cystine > methionine > homocystine > GSSG in this order in accordance with PR bleaching assay.

L-cysteine was previously reported as an efficient ONOO^- scavenger ($\text{IC}_{50} = 25 \text{ } \mu\text{M}$) through competitive oxidation of free sulfhydryls.¹² Peroxynitrite-mediated oxidation of biothiols can occur through one-electron oxidation reactions.¹³ Peroxynitrite possibly oxidizes a variety of thiols by forming the corresponding thiyl anion radicals as intermediary products.¹⁴

Table 1. PAS activity of biothiols measured by the fluorometric and in comparison to the spectrophotometric methods (IC₅₀ values were calculated with respect to Eq.s (1) and (2), N=4 or 5 data points)

ONOO ⁻ scavengers	Gentisic acid assay	PR bleaching assay
	[M]	[M]
Glutathione (GSH)	4.00x10 ⁻⁵	3.02x10 ⁻³
N-acetyl-cysteine (NAC)	7.83 x10 ⁻⁵	8.30x10 ⁻³
Cysteine	1.45 x10 ⁻⁵	2.20x10 ⁻³
Homocysteine	4.38 x10 ⁻⁵	5.70x10 ⁻³
Cysteamine	8.90 x10 ⁻⁶	2.00x10 ⁻³
Methionine	3.05 x10 ⁻⁴	3.50x10 ⁻²
GSSG	6.70 x10 ⁻⁴	9.58 x10 ⁻²
Cystine	2.42 x10 ⁻⁴	7.00x10 ⁻²
Homocystine	3.60x10 ⁻⁴	-

The ONOO⁻ scavenging activity values evaluated with the gentisic acid assay and reference PR bleaching assay are comparatively displayed in a bar diagram (Fig. 1). PAS activity of liver tissue homogenate was found to be higher than that of kidney and heart homogenates with respect to both methods, probably because liver is the central organ for enzymatic and non-enzymatic antioxidative defenses of detoxification in the organism.

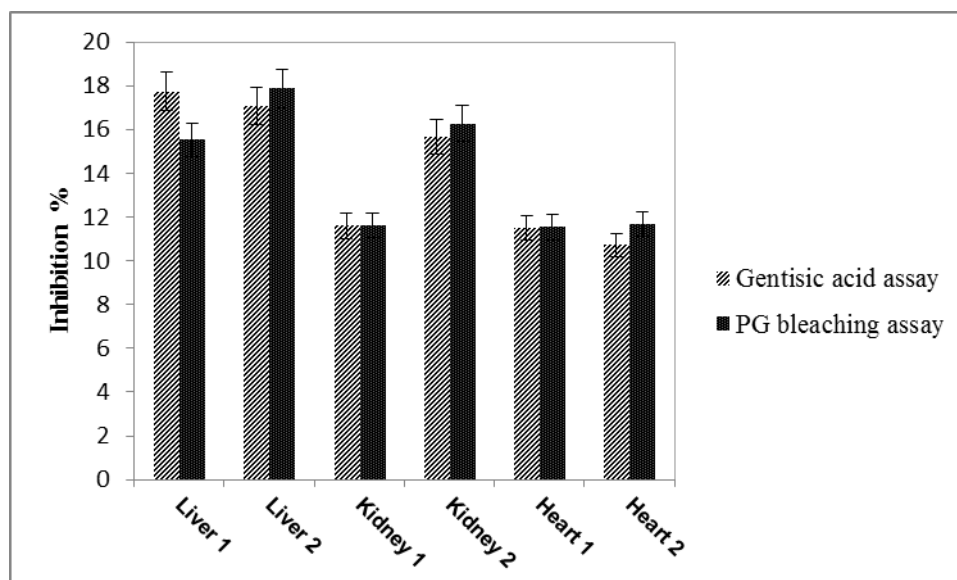


Fig. 1 The peroxynitrite scavenging activity of some tissue homogenates calculated with the gentisic acid assay in comparison to PR bleaching assay.

Conclusion

A spectrofluorometric analytical method based on gentisic acid probe was developed for determination of peroxynitrite anion scavenging activity of biothiols. Gentisic acid is more sensitive and sufficiently selective redox probe for peroxynitrite than pyrogallol red probe. These results are revealed that biothiols are good peroxynitrite scavengers and PAS activity of liver tissue homogenate was found to be higher than that of kidney and heart homogenates.

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References:

1. T.D. Oury, L. Tatro, A.J. Ghio, and C.A. Piantadosi, *Free Radic. Res.*, (1995) 23, 537-547.
2. C. Ducrocq, B. Blanchard, B. Pignatelli, and H. Ohshima, *Cell. Mol. Life Sci.*, (1999) 55, 1068-1077.
3. B. Alvarez, and R. Radi, *Amino Acids*, (2003) 25, 295-311.
4. L. Zhu, C. Gunn, and J.S. Beckman, *Arch. Biochem. Biophys.*, (1992) 298, 452-457.
5. L.B. Valdez, S. Alvarez, S.L. Arnaiz, F. Schöpfer, M.C. Carreras, J.J. Poderoso, and A. Boveris, *Free Radic. Biol. Med.*, (2000) 29, 349-356.
6. G. Gilbert, A. Balavoine, and Y.V. Geletii, *Nitric Oxide*, (1999) 3, 40-54.
7. C.G.M. Heijnen, G.R.M.M. Haenen, J.A.J.M. Vekemans, and A. Bast, *Environ. Toxicol. Pharmacol.*, (2001) 10, 199-206.
8. X.-F. Yang, X.-Q. Guo, and Y.-B. Zhao, *Talanta*, (2002) 57, 883-890.
9. M.N. Hughes, and H.G. Nicklin, *J. Chem. Soc. A.*, (1968) 450-452.
10. V.B. Bhat, and K.M. Madyastha, *Biochem. Biophys. Res. Commun.*, (2001) 285, 262-266.
11. R.G. Brannan, and E. Mah, *Meat Science*, (2007) 77, 540-546.
12. N.W. Kooy, J.A. Royall, and H. Ischropoulos, *Free Radic. Res.*, (1997) 27, 245-254.
13. C. Quijano, B. Alvarez, R.M. Gatti, O. Augusto, and R. Radi, *Biochem J.*, (1997) 322, 167-173.
14. H. Karoui, N. Hogg, C. Fréjaville, P. Tordo, and B. Kalyanaraman, *J. Biol. Chem.*, (1996) 271, 6000-6009.

Effect of Cu(II) ion on the Fluorescence Properties of the (G2-NH₂) PAMAM Dendrimer Periphery Modified 4-N,N-dimethylaminoethoxy-1,8-Naphthalimide

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Dendrimers are new category of branched polymers with perfect three-dimensional structure. They can be defined by three components as central core, interior dendritic structure and exterior surface with different functional groups [1-3].

One of the new classes of commercial dendrimers is poly(amidoamine) (PAMAM) initially synthesized and investigated by Tomalia et al [4].

They are highly branched macromolecules with different functional groups in the dendrimer core periphery. The design and modification of PAMAM dendrimers with fluorescent units can lead to interesting new properties. The fluorescent and functional properties of dendrimers showed that they could act as sensors for different metal cations.

When PAMAM dendrimer from second generation has been used as ligand the metal ions coordinate first with the dendrimer core and after they react with the 1,8-naphthalimide units in the dendrimer periphery [5].

In this study; firstly 4-N,N-dimethylaminoethoxy-1,8-naphthalimide labeled (G2-NH₂) PAMAM dendrimer, which has ethylenediamine core, was synthesized and characterized with UV-Vis, FT-IR, ¹³C-NMR, ¹H-NMR, MALDI-TOF and SEM analysis and in the presence of Cu²⁺ cation, the fluorescence intensity of the dendrimer enhances several orders which reveals that the new dendrimer can be used as a sensitive detector for the Cu(II) cation.

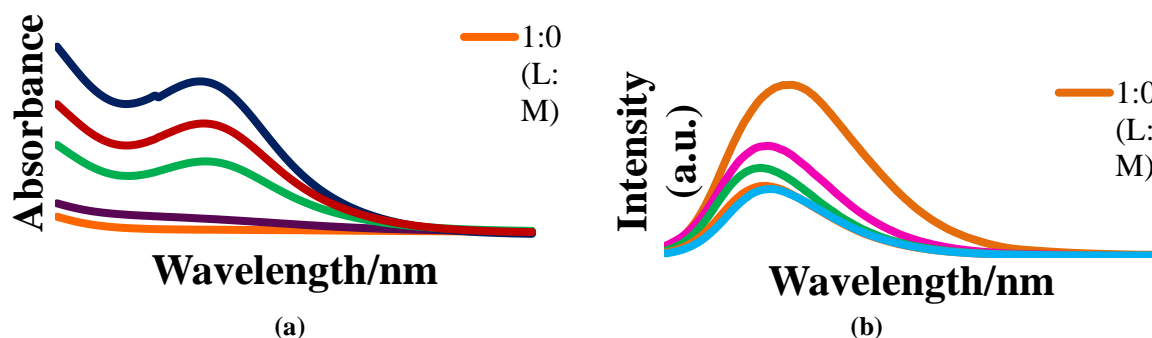


Figure 1 : (a) UV-Vis Spectra and (b) Fluorescence Spectra for various PAMAM dendrimer ($c=2 \times 10^{-6}$ M) and Cu²⁺ ratio at pH=3.

Keywords: PAMAM, Dendrimer, Fluorescence, Spectroscopic Methods, Cu(II) Cation.

References:

1. G.R. Newkome, C.D. Shreiner, Polymer 49 (2008) 1.
2. V. Balzani, P. Ceroni, M. Maestriand, Ch. Saudan, Top. Curr. Chem. 228 (2003) 159.
3. B. Adhikari, S. Majumbar, Prog. Polym. Sci. 29 (2004) 699.
4. D.A. Tomalia, H. Baker, J.R. Dewald, M. Hall, G. Kallos, S. Martin, Polym J. 17 (1985) 117.
5. I. Grabchev, J.P. Soumillion, B. Muls, G. Ivanova, J. Photochem. Photobiol. Sci. 3 (2004) 1032.

A Simple and Rapid Dispersive Liquid-Liquid Microextraction of Uranium and Spectrophotometric Determination of Its in Water Samples

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The direct determination of uranium in water samples by using spectrophotometer is not possible due to its low sensitivity and matrix effects of some cations, anions and transition metal ions (1, 2).

A rapid and simple dual dispersive liquid-liquid microextraction (DDLL-ME) method was used for the extraction of uranium. The main objective of this study is to disperse extracting solvent by using air-agitated syringe system overcome on the matrix effect and to avoid the dispersion by using heat, hazardous dispersive organic solvents. The DDLL-ME consist of two dispersive liquid-liquid step with chloroform as extraction solvent. The uranium form complexes with 4-(2-thiazolylazo) resorcinol in aqueous phase and extracting into extracting solvent after the first dispersive liquid-liquid processes. The uranium was back-extracted into the acidic aqueous phase in the second dispersive liquid-liquid process step and finally determined by spectrophotometric detection technique. Various analytical parameters such as pH, volume of extraction solvent, amount of chelating reagent, sample volume were studied and optimized. Enhancement factor and limit of detection were achieved to be 45 and 0.69 ng L⁻¹. The accuracy of the procedure was checked by an analyzing a certified reference material (TM-28.3). The optimized method was applied to various water samples.

Acknowledgment

Naeemullah is grateful to the Scientific and Technological Research Council of Turkey (TUBITAK) for awarding him “2216 Research Fellowship Program for Foreign Citizens” and providing financial support.

References

- 1.Q. un Nisa, A. Ali, M.H. Khan, J. Radioanal. Nucl. Chem. (2013) 295 2203-2214.
- 2.E. Bagda, M. Tuzen, J. Radioanal. Nucl. Chem. (2015) 306 385-392.

Serum Selenium(Se) Levels and Related Antioxidant Enzyme Glutathione Peroxidase(GPx) Activity in Obstructive Sleep Apnea Syndrome (OSAS) Patients

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Macronutrients are micronutrients chemical elements essential to life in large quantities. Selenium(Se) is an essential micronutrient at low concentration but toxic at high concentration with a relatively small difference between these levels. Human body uses selenium to produce glutathione peroxidase, which works with vitamin E to protect cell membranes from damage caused by dangerous, naturally occurring substances known as free radicals produced by oxidative metabolism[2]. Metabolic syndrome has become a major global disease. Four major cardiovascular disease risk factors, i.e., visceral obesity, dyslipidemia, hyperglycemia, and hypertension, have been studied separately, but the association of these factors has recently become the focus of research[1].

Obstructive sleep apnea syndrome (OSAS) is a disorder that affects the respiratory system and upper airway during sleep (apnea, hypopnea). Continuous apnea/hypopnea in OSAS results with cardiovascular and cerebrovascular morbidity and is emerged as an independent risk factor for mortality[3]. In this syndrome, as a cause of cardiovascular risk, increased oxidative stress and reduced antioxidant defense of the body is involved. In this study, we aimed to determine the levels of selenium (Se) element with related antioxidants of glutathione peroxidase (GPx) enzymes in OSAS patients and these levels were compared with control groups.

Our study consists of 38 OSAS patients and 27 control individuals. Serum samples were taken after polysomnographic examination. Serum Se(IV) concentration from patients and healthy control were measured by GFAAS. Antioxidant enzyme activities of GPx were determined using enzyme-mediated immuno-sorbent (ELISA) detection. Results are given as mean \pm SD and data were compared using student-t test, $p < 0.05$ were regarded as significant. Serum Se(IV) levels in patients with OSAS were significantly lower than control individuals ($p < 0.0001$). GPx activity in OSAS patients were lower than controls ($p < 0.01$). Our results suggested that OSAS patients have lower Se(IV) levels and decreased GPx activities compared to healthy controls. It is clear that in OSAS patients the antioxidant capacity is reduced following by increased oxidative stress. In conclusion, supporting of Se(IV) can increase the activities of antioxidant enzymes in OSAS patients.

Keywords: GFAAS, Se (IV), GPx.

References:

1. Čuparigova F., Stafilov T., Chemical Sciences Journal, 46 (2011) 1-7.
2. Mutakin, Meilianac A., et al., Journal of Trace El. in Medicine and Biology, 27(2013) 112-116.
3. Mancuso M., et al., Sleep Medicine, 13 (2012) 632–636.

Serum Mangan (Mn) Levels and Superoxide Dismutase (SOD) Enzymes Activity in Obstructive Sleep Apnea Syndrome (OSAS) Patients

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Trace elements are essential nutrients with regulatory, immunologic, and antioxidant functions resulting from their action as essential components or cofactors of enzymes throughout metabolism. They play a part in the synthesis and structural stabilization of both proteins and nucleic acids. Therefore, imbalances in the optimum levels of trace elements may adversely affect biological processes, and are associated with many diseases. Trace elements like manganese (Mn), copper (Cu), zinc (Zn) etc. have been studied in many diseases, including autoimmune diseases, cardiovascular, hypertension and psychiatric disorders[1,2].

Obstructive sleep apnea syndrome (OSAS) is a disorder that affects the respiratory system and upper airway during sleep (apnea, hypopnea). Continuous apnea/hypopnea in OSAS results with cardiovascular and cerebrovascular morbidity and is emerged as an independent risk factor for mortality[3]. In this syndrome, as a cause of cardiovascular risk, increased oxidative stress and reduced antioxidant defense of the body is involved. In this study, we aimed to determine the levels of manganese (Mn) element with related antioxidants of superoxide dismutase enzymes in OSAS patients and these levels were compared with control groups.

Our study consists of 38 OSAS patients and 27 control individuals. Serum samples were taken after polysomnographic examination. Serum Mn (II) concentration from patients and healthy control were measured by GFAAS. Antioxidant enzyme activities of SOD were determined using enzyme-mediated immuno-sorbent (ELISA) detection. Results are given as mean \pm SD and data were compared using student-t test, $p < 0.05$ were regarded as significant. Serum and Mn(II) levels in patients with OSAS were significantly lower than control individuals ($p < 0.0001$). Serum SOD activity in OSAS group were lower than control subjects but there was no significance ($p > 0.05$).

Our results suggested that OSAS patients have lower Mn(II) levels and decreased SOD activities compared to healthy controls. It is clear that in OSAS patients the antioxidant capacity is reduced following by increased oxidative stress. In conclusion, supporting of Mn(II) can increase the activities of antioxidant enzymes in OSAS patients.

Keywords: GFAAS, Mn (II), SOD, Antioxidant,

References:

1. Hossain I., et al., German Journal of Psychiatry, (2007) 41-45.
2. Yerlikaya H., Toker A., Arbaş A., Indian J. Med. Res., 137 (2013) 339-345.
3. Mancuso M., et al., Sleep Medicine, 13 (2012) 632-636.

Simultaneous Determination of Rosuvastatin Calcium and Ezetimibe by Derivative UV-VIS Spectrophotometry

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Rosuvastatin (RSV) is an HMG Co-A inhibitor and Ezetimibe (EZT) is an intestinal cholesterol absorption inhibitor. RSV is used to treat hypercholesterolemia in patients with type 2 diabetes mellitus, but many of these patients fail to achieve the target LDL-C level. Recent reports have suggested that a synergistic effect can be obtained by concomitant administration of the cholesterol absorption inhibitor EZT and a statin group drug (1).

Simultaneous determination of multicomponent mixtures could be performed by derivative uv-vis spectrophotometry under the Lambert-Beer law compatible conditions. Concentration of the species could be calculated by using standard calibration curves and absorbance measurement results of the mixture (2-3). The aim of the study is develop a zero cross derivative uv-vis spectroscopic method for the simultaneous determination of RSV and EZT.

The mixture of EZT (15 mcg/mL) and RSV (15 mcg/mL) prepared in a volumetric flask with Methanol:Water (60:40 v/v) and the uv-vis spectrum recorded against to blank solvent at Shimadzu UV-2550 spectrophotometer. Data processing performed with UVProbe 2.42 software.

The first derivative amplitudes at 236 and 228 nm were selected for the determination of EZT and RSV respectively. The linearity ranges were determined between 1,0 – 20,0 mcg/mL ($R^2:0,9972$) and 2,5 – 40 mcg/L ($R^2:0,9983$) RSV and EZT respectively. The amount of RSV and EZT in mixture solvent calculated from calibration curves.

The proposed method give good results for the determination of the EZE and RSV in the mixture solutions of them and the method will apply to estimation of these drugs in combine tablet formulations in the next step of our study

Acknowledgement

This study is a part of master thesis of Volkan Demir and it is supported by Marmara Üniversitesi Bilimsel Araştırma Projeleri Birimi (Project code: SAG-C-YLP-080715-0325)

Keywords: Ezetimibe, Rosuvastatin calcium, Derivative, UV-VIS Spectrophotometry

References:

1. http://www.accessdata.fda.gov/drugsatfda_docs/label/2005/21366slr0051bl.pdf [Accessed: 22/06/2016]
2. Gupta A, Mishra P, Shah K. E-Journal of Chemistry, 6(1), 89-92, 2009.
3. Dinç E, Palabıyık İ.M, Üstündağ Ö, Yurtsever F, Onur F. J of Pharm Biomed Anal, 28:3–4 (2002) 591–600.

A New Atomic Absorption-Based Method Development for Indirect Determination of Histamine in Fish Samples, Dairy Products, and Alcoholic Beverages by Flame AAS

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Histamine is known as a biogenic amine, which is low molecular mass and possesses biological activity for its complex physiological role in human body [1]. The compound is essential in humans owing to its important role in functioning of physiological processes, such as neurotransmission, allergic reactions, microcirculation regulation [2]. For all these reasons, a simple, inexpensive and rapid analytical method is now required for the accurate and reliable monitoring of histamine in the related samples all over the world.

A new and sensitive analytical method for the indirect determination of histamine in fish samples, dairy products, and alcoholic beverages by flame atomic absorption spectrometry (FAAS) was developed. The method is based on the complex formation of histamine with Fe(III) and 2',4',5',7'-tetrabromofluorescein (eosin) at pH 4.5, and then extraction into the micellar phase of polyethylene glycol dodecyl ether (Brij 35). In this study, ultrasonic assisted cloud point extraction (UA-CPE) procedure was used for separation/preconcentration of histamine from the related sample matrices. The optimal conditions were established, and a good preconcentration was achieved using 25 $\mu\text{mol L}^{-1}$ Fe(III), 5 $\mu\text{mol L}^{-1}$ eosin, 10 mmol L^{-1} Brij 35 and 0.7 % (w/v) Na_2SO_4 , pH 4.5 citrate buffer, equilibrium temperature of 45 °C, incubation time of 20 min and ultrasonic effect of 40 kHz at 300 watt. At optimal conditions, a detection limit of 0.25 $\mu\text{g L}^{-1}$ with a sensitivity improvement of 143-fold in linear working range of 0.8–170 $\mu\text{g L}^{-1}$ was obtained. The proposed method was evaluated for the analysis of some food samples and received a good recovery with the standard addition assay. In addition, the validity of the method was tested by intra- and inter-day precision studies and recovery experiments, obtaining satisfactory results. To our knowledge, this method is also the first study for indirect determination of histamine in the selected samples using UA-CPE coupled to FAAS.

Keyword: Eosin, Fe(III), Indirect Determination, Histamine, Food, Preconcentration, Atomic-Based Method

Reference:

1. J. Švarc-Gajić, Z. Stojanović, Food Chem. (2011) 12 1172.
2. M. Previati, A. Raspadori, L. Bertolaso, A. Parmeggiani, D. Bindini, C. Vitali, I. Lanzoni, E. Corbaccia, M. Saviano, F. Fagioli, G. Blo, J Chromatogr. B (2002) 780 331.

Indirect Determination of The Flavor Enhancer Maltol in Foods and Beverages by Ultrasonic Assisted Extraction Coupled to Flame Atomic Absorption Spectrometry

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Contamination of food and beverage samples with food dyes, food additives and flavor enhancer has motivated the development of determination and extraction methods. One of the chemical species, which is used as a potent flavor enhancer in foods and beverages, is maltol (3-hydroxy-2-methyl-4H-pyran-4-one) [1]. Therefore, it is important to develop simple, low cost, and sensitive methods for the accurate and reliable determination of maltol in food products.

In the current research, a simple ultrasonic assisted extraction procedure was recommended and combined with flame atomic absorption spectrometry (FAAS) for the indirect determination of flavor enhancer maltol in selected food and beverages. Under ultrasonic power, the extraction process is based on the charge transfer complexation of 3-Hydroxy-2-methyl-4-pyrone (maltol) with Cu(II) ions in presence of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, BCP), which is selective neutral ligand for Cu(I) ions, and sodium dodecyl sulphate (SDS) at pH 6.5, and then extraction of ion-associate complex into the micellar phase of nonionic surfactant, polyethylene glycol sorbitan monooleate (Tween 80). All factors affecting the complex formation and extraction conditions were extensively evaluated and optimized. This procedure were carried out with the optimum conditions: pH 6.5; frequency 45 kHz; temperature 65 °C; complexing concentration, BCP, 40 $\mu\text{mol L}^{-1}$; SDS concentration 15 $\mu\text{mol L}^{-1}$; sample volume 25 mL; Tween 80 concentration 0.09 mmol L^{-1} ; solvent type and volume, THF and 1.0 mL. For the indirect determination of maltol using FAAS, the signal changes of Cu(II) was investigated in detail depending on maltol concentration. Under optimum conditions, the analytical parameters of the proposed procedure was found as follows; linear working range, 4-230 $\mu\text{g L}^{-1}$; the limit of detection (LOD), 1.24 $\mu\text{g L}^{-1}$; sensitivity enhancement factor, 150; and relative standard deviation (RSD %), 2.6 %. The proposed procedure was validated by intra- and inter-day precision studies using standard addition method, was obtained with the recoveries in the range of 92.1–107.8 %. As the last, the proposed method was successfully applied to the indirect determination of maltol in foods and beverages.

Keyword: Flavor Enhancer, Maltol, Ultrasonic Assisted Extraction, Indirect Determination, Foods, Foods/Beverages

References

1. Alonso MS, Zamora LL, Calatayud JM. *Analytica chimica acta* (2001) 438 1 157-163.

A Novel Colorimetric Sensor Based Schiff Base for Mercury(II) Ion

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In recent years, heavy metal ions has emerged as an attractive goal in the field of chemical sensors due to the high level contamination of environment [1]. As extremely toxic metal mercury ion which has high affinity for thiol groups in proteins and enzymes, can enter human cell easily. It cause several diseases such as minimata disease, nerve disorder and perforation of stomach [2]

In literature, several analytical methods such as AAS, ICP-MS, electrochemical determination...etc, have been proposed for the determination of mercury ions. Recently, great attention has been also paid to improvement of optical chemosensors for the detection of mercury ion. The optical chemosensor has more advantages in comparison with other reported methods with regard to simple pretreatment procedure, low cost, high selectivity and sensitivity, fast response time.

The aim of this study is to reveal the high selective colorimetric response of 1-((4-(3-(2,5-dimethylphenyl)-3-methylcyclobutyl)thiazol-2-yl)imino)methyl)naphthalen-2-ol ligand towards mercury (II) ions. Result show that the presence of Hg^{+2} , the color of proposed chemosensor changed from yellow to orange-color.

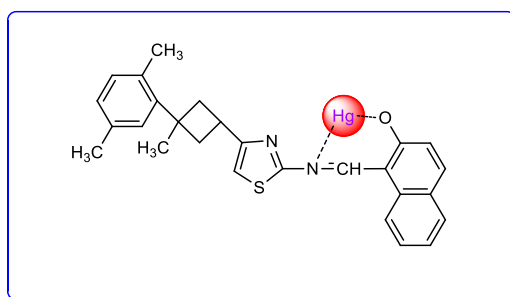


Fig.1. Structure of 1-(((4-(3-(2,5-dimethylphenyl)-3-methylcyclobutyl)thiazol-2-yl)imino)methyl)naphthalen-2-ol with Hg^{+2} ion.

Keywords: Colorimetric Sensor, Mercury (II) Ions, Schiff Base

References

1. Y. Liao, Q. Li, N. Wang, S. Shao, Development of a new electrochemical sensor for determination of Hg(II) based on Bis(indolyl)methane/Mesoporous carbon nanofiber/Nafion/glassy carbon electrode, *Sensors Actuators B Chem.* 215 (2015) 592–597. doi:10.1016/j.snb.2015.04.006
2. S. Chemate, N. Sekar, A new rhodamine based OFF–ON fluorescent chemosensors for selective detection of Hg^{2+} and Al^{3+} in aqueous media, *Sensors Actuators B Chem.* 220 (2015) 1196–1204. doi:10.1016/j.snb.2015.06.061

A Simple and Efficient Ultrasonic-Assisted Extraction Procedure Combined with UV-Vis Spectrophotometry for Preconcentration and Determination of Folic Acid (Vitamin B₉) in Various Sample Matrices

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The water-soluble vitamins include the Vitamin B₉ (folic acid, FA), which is essential in very small amounts for the normal functioning of the body [1]. The FA is a generic term referring to the mono- to poly-glutamate derivatives of pteric acid that occur naturally in many foods, and have the important biological tasks such as amino acid interconversions, synthesis and repair and functioning of DNA on human metabolism [2].

A simple and efficient ultrasonic assisted extraction (UAE) procedure for preconcentration of (2S)-2-[(4-[(2-amino-4-hydroxypteridin-yl)methyl]amino)phenyl]formamido]pentanedioic acid (folic acid) in vegetables, pharmaceuticals and foods prior to the determination at 540 nm using UV-Vis spectrophotometry has been proposed. The method is based on hydrophobic ternary complex formation of folic acid with silver ions in the presence of cetyl trimethyl ammonium bromide (CTAB) as sensitivity enhancer counter ion at pH 7.0, and then extraction into micellar phase of polyethylene glycol monoalkyl ether (Genapol X-080). The matrix effect on the preconcentration and determination of folic acid was investigated, and it was observed that the proposed method was highly selective against possible matrix concomitants. Under optimized conditions, the calibration graph was obtained in the range of 0.6–180 $\mu\text{g L}^{-1}$ with a detection limit of 0.19 $\mu\text{g L}^{-1}$ and quantification limit of 0.63 $\mu\text{g L}^{-1}$. The applicability was evaluated using samples fortified at different concentration levels, and the higher recoveries than 94.1 % was obtained. The precision as the percent relative standard deviation, RSD % were in range of 2.5-3.8 % (10 and 40 $\mu\text{g L}^{-1}$, n: 5). The proposed method was validated by analysis of the two standard reference materials (SRMs) and various real samples, and the satisfactory results were obtained.

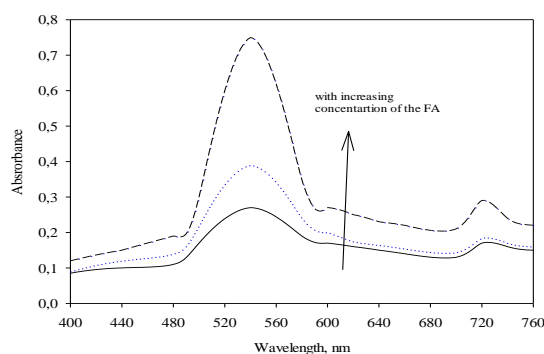


Figure 1. The absorption spectra of micellar system against analyte blank in presence of folic acid at levels of 5 and 30 $\mu\text{g L}^{-1}$.

Keywords: Folic Acid, Vegetables, Silver, Ultrasonic-Assisted Extraction, UV Spectrophotometry.

Reference:

1. Vaze VD, Srivastava AK. *Electrochimica Acta* (2007) 53(4) 1713-1721.
2. Jamali T, Karimi-Maleh H, Khalilzadeh MA. *LWT-Food Science and Technology* (2014) 57(2) 679-685.

A New Green Extraction Procedure of Selenium in Water, Food and Vegetable Samples, and Its Spectrophotometric Determination

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Selenium (Se) are essential for certain physiological reactions, including thyroid hormone metabolism, antioxidant defense systems and immune functions. But, its excessive intake is harmful to human health. (Stosnach, 2010). Therefore, a new, simple and reliable analytical method for the highly sensitive determination of trace Se in real samples need to be established for the assessment of human exposure.

In the present investigation, a simple and efficient ultrasonic assisted extraction (UAE) procedure was developed for preconcentration of selenite, Se(IV) from sample matrix prior to analysis by spectrophotometry at 620 nm. The method is based on pH sensitive charge transfer complexation between 7-hydroxy-3H-phenoxazin-3-one 10-oxide (resazurin) and triiodide, I_3^- , which is produced by reaction of Se(IV) with excess KI in presence of cetylpyridinium chloride (CPC) at pH 5.0, and then extraction of the formed complex into micellar phase of polyethylene glycol monoalkyl ether (Genapol X-080). The process offers good sensitivity, ease of use and short analysis time. At optimal conditions, the calibration graph was linear in the range of 2.5–120 $\mu\text{g L}^{-1}$ with a preconcentration factor of 100. The validity was evaluated by analysis of two certified reference materials (CRMs) and recovery test. Finally, the method was successfully applied to determination of selenium in water, vegetable and food samples.

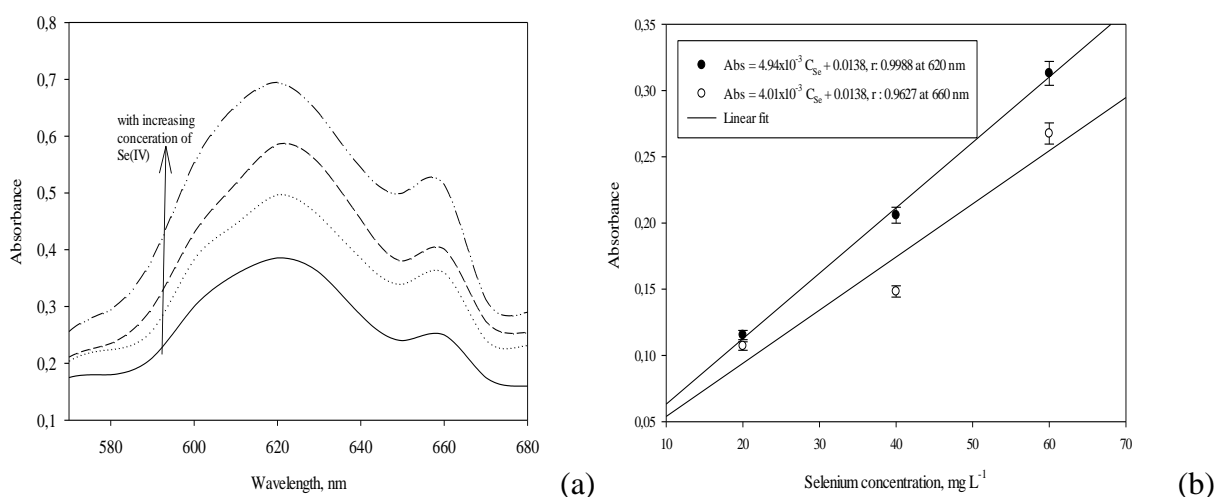


Figure 1 (a) The absorption spectra of charge transfer complex as a function of absorption wavelength, nm in absence and presence of Se(IV) at levels of 20, 40 and 60 $\mu\text{g L}^{-1}$ (b) Linearity relationship of analytical signal corrected against blank with increasing selenium concentration for three replicate measurements at peak maximum.

Keywords: Selenium Determination, Resazurin, Ultrasound Assisted Extraction, Foods, Vegetables, Spectrophotometry

References:

1. Stosnach H Spectrochimica Acta Part B: Atomic Spectroscopy (2010) 65 9 859-863.

Application of PCA-PCR Models to Spectrophotometric Data for Quantitative Analysis of a Caffeine and Methamizol in a Pharmaceutical Product

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Drug pharmaceutical preparations for the therapy of pain of weaker genesis contain the different components, usually acetylsalicylic acid and paracetamol with caffeine, codeine, derivatives of pyrazolones, barbiturates, vitamins, phenacetine, pentazocine which can improve the pharmacological value of these preparations. Concerning the different mechanism of action, they sometimes act as synergists which lead to a better efficiency. Since each component in the multicomponent preparation is in the fewer amounts than in the mono component of each one, the main metabolic organs are less loaded since any components engages the different subsystem of metabolism[1].

The quality control of dosage form preparations of drug requires reliable and quick analytical methods. UV/VIS spectrophotometry is by far the instrumental technique of choice of industrial laboratories, owing mainly to simplicity, often demanding low cost equipment. Simultaneous quantitative analysis of pharmaceuticals containing multi-active compounds is difficult to perform by classical spectrophotometric method due to overlapping spectra [2]. In recent years, multivariate chemometric methods seem to be the techniques showing a best performance in terms of complex mixture solution [3].

A multivariate calibration-prediction techniques, principal component principal regression models were applied to the spectrometric multicomponent analysis of the drug containing caffeine and methamizol without any separation step. The selection of variables was studied. A series of synthetic solution containing different concentrations of MET and CAF were used to check the prediction ability of the PCA-PCR. The results obtained in this investigation strongly encourage us to apply these techniques for a routine analysis and quality control of the drug.

Keywords: PCA-PCR, Caffeine, Methamizol, Chemometry

References

- 1.J.T. Franeta, D. Agbaba, S. Eric, S. Pavkov, M. Aleksic, S. Vladimirov, *Il Farmaco* (2002) 57 709-712.
- 2.M. R. Khoshayand H. Abdollahi, M. Shariatpanahi, A.Saadatfard, A. Mohammadi, *Spectrochimica Acta Part A* (2008) 70 491-495.
- 3.G. Ragno, G. Ioele, A. Risali, *Anal. Chim. Acta* (2004) 512 173-178.

Simultaneous Determination of Codeine and Acetaminophen in Pharmaceutical Preparation by ICA-ANN Methods

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Codeine is a morphine (morphine 3-methyl ether), consisting of morphine by methylation of the phenolic OH group[1]. Morphine be methylated in a way that reduces the impact of its analgesic and addictive activity significantly, but it does not weaken over the antitussive activity. Codeine, opium (opium) are contained in the natural rate of about 0.5% is obtained by extraction from opium or poppy capsule or with morphine methylation is carried out by semi-synthesis. Codeine use is subject to control, according to the legislation in Turkey but some preparations containing codeine "drug" does not count [2]. Worked in the chemical structures of these two substances are shown in Figure 1.

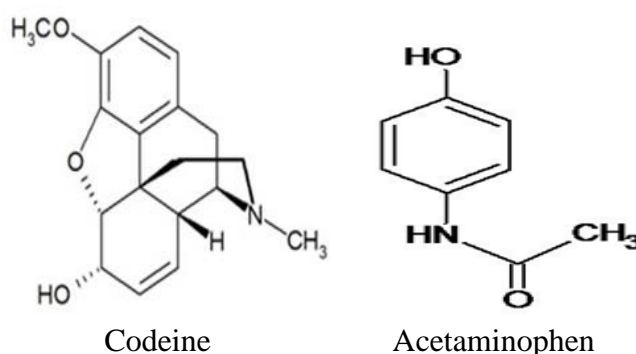


Figure.1 Structures of the two studied compounds

For the validation of this chemometric method, a calibration set of 15 binary mixtures containing compounds in the working range of 5-25 µg/mL for COD and 8-40 µg/mL for ACE was prepared in % 96 Ethanol. Calibration sets 200-300 nm range absorption spectra were recorded. The chemometric calibrations were constructed by using the relationship between the calibration set and its corresponding absorption data obtained in the range 220-280 nm. The synthetic mixtures of two drugs were used for the validity of the calibrations. Means recoveries (percent) and relative standard deviation of ICA-ANN methods were found to be 100.03% / 1.02% and 100.11% / 1.29 % for COD and ACE respectively.

In the next step, the ICA-ANN method was applied to the simultaneous determination of COD and ACE in commercial pharmaceutical preparations and successful results were obtained.

Keywords: Codeine, Acetaminophen, ICA-ANN, Pharmaceutical.

References

- [1] The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals, 13th Ed. Whitehouse Station, NJ 2001
- [2] T. Değim, C. Akay, K. Büyükaşar, S. Cevheroğlu, J. Pharm. Biomed. Anal. (2001) 26 15-21.

A Simple and Green Procedure for Preconcentration of Acrylamide from Thermally Processed Foods Prior to Its Spectrophotometric Detection

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Acrylamide (AA) is a low-molecular-weight vinylic compound. It is a colorless and odorless crystalline substance and it is highly water soluble, easily reactive in air, and rapidly polymerizable [1]. The AA can be especially formed in high temperatures heating of carbohydrate-rich foods. According to the research, neural destructions was observed in people exposed to this chemical [2]. The AA is also estimated to be a human carcinogen. According to Food and Agriculture Organization of the United Nations and World Health Organization, daily intake of the AA from the food can be in the range of 0.3–0.8 $\mu\text{g kg}^{-1}$ [3]. The excess of this value can cause toxic properties. In conclusion, we can say that the AA creates a risk for human health only in the cases of long term exposure to it [4]. Thus, the determination of trace the AA residues in foods needs the development of new, cost-effective, simple, and powerful analytical methods in terms of control the quality attributes.

In the current study, a simple ultrasonic assisted extraction procedure was recommended and combined with spectrophotometry for the determination of the AA in processed food samples. Under ultrasonic power, the extraction process is based on the charge transfer complexation of prop-2-enamide (acrylamide) with Sn(IV) ions in presence of phenyl safranin and potassium fluoride (KF) at pH 5.0, and then extraction of ion-associate complex into the micellar phase of nonionic surfactant, (1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol (Triton X-114). This procedure were carried out with the optimum conditions: pH 5.0; frequency 40 kHz; temperature 45 °C; ultrasonic time 20 min; complexing concentration, phenyl safranin, 15 $\mu\text{mol L}^{-1}$; KF concentration 50 $\mu\text{mol L}^{-1}$; sample volume 10 mL; Triton x-114 concentration 0.23 mmol L^{-1} ; solvent type and volume, methanol and 0.5 mL. Under optimum conditions, the analytical parameters of the proposed procedure was found as follows; linear working range, 10-180 $\mu\text{g L}^{-1}$; the limit of detection (LOD), 6.7 $\mu\text{g L}^{-1}$; sensitivity enhancement factor, 90; and relative standard deviation (RSD %), 2.2 %. The proposed procedure was validated by intra- and inter-day precision studies using standard addition method. As the last, the proposed method was successfully applied to the determination of acrylamide in processed food samples such as chips, crackers and cereal-based baby.

Keywords: Acrylamide, Processed Foods , Food Safety, Preconcentration, Spectrophotometry

References:

1. Claus A, Reinhold C, Andreas S. Journal of Cereal Science (2008) 47:118-133.
2. Friedman, M. Levin, C.E. Journal of Agricultural and Food Chemistry (2008) 56:6113-6140.
3. International Agency for Research on Cancer (IARC). Acrylamide, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Some Industrials Chemicals, International Agency for Research on Cancer, Lyon, France (1994) 389–433.
4. FAO/WHO Health implications of acrylamide in food. Report of a joint FAO/WHO consultation. (2002). WHO, Geneva.

Method Development and Validation of Derivative Spectrophotometric Method for the Quantitative Determination of Nebivolol in Dosage Forms

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Three simple, accurate, and rapid spectrophotometric methods are proposed for the determination of nebivolol in dosage forms. The firstly method is direct UV spectrophotometry. In this method, absorbance values of standard and sample solutions in methanol were measured at 280.779 nm. As a result of experiments that performed in 15.0-90.0 µg/mL working range, calibration curve was plotted and the coefficient of correlation was calculated as 0.9991. The second applied method in this study is first derivative UV spectrophotometry. Solutions of Standard and samples' derivative absorbance values were measured at 227.450 , 271.111 and 291.677 nm's. Measured first derivative absorbance values, by plotting against the concentration, the working graphs were obtained. According to the data which is obtained, the correlation coefficient's being approximate to 1 points out that the sensibility of the method is higher. In scope of this project, the third method is second derivative UV spectrophotometry. This method was applied to the standard and sample solutions containing nebivolol and second derivative absorbance values of these solutions were measured at 289.801 and 294.044 nm. Linear working range was 15.0-90.0 µg/mL. Calibration graphs of 246.5 and 284.4 nm's' coefficients of correlation were 0.9988 and 0.9996, respectively. With these spectrophotometric methods which is applied, successful results were obtained for preparations containing Nebivolol.

Keywords: Antihypertensive, Nebivolol, Direct UV Spectrophotometry, Derivative UV Spectrophotometry, Second Derivative UV Spectrophotometry

References:

1. VAN NUIJS, ALN ; TARCOMNICU, I ; SIMONS, W ; BERVOETS, L; BLUST, R; JORENS, PG ; NEELS, H ; COVACI, A ; Analytical and Bioanalytical Chemistry (2010) 398 5 2211-2222
2. DHANDAPANI,B. THIRUMOORTHY, N. PRAKASH,DJ. ; E-Journal of Chemistry (2010) 7 2 341-348
3. MEYYANATHAN,SN. BİRAJDAR,AS. SURESH,B. ;Indian Journal of Pharmaceutical Education and Research (2010) 44 (2) 156-159

Bivariate and Multivariate Calibration Approaches for the Spectrophotometric Multicomponent Analysis of Rosuvastatin and Amlodipine in a Solid Dosage Form

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In this study, a novel and simple spectrophotometric method was developed for the multicomponent quantitative estimation of rosuvastatin and amlodipine in tablets.

Standard solutions of rosuvastatin and amlodipine were prepared in the working range of 4.0-28.0 µg/mL. Absorbance spectra of the sample solutions were recorded between 200-450 nm as illustrated in Figure 1. Conventional spectrophotometric approach was unable to analyze these two drugs in their combination due to their overlapping spectra. Bivariate and multivariate calibration techniques were applied for simultaneous determination of rosuvastatin and amlodipine [2-3].

In order to construct the bivariate calibration method, 22 different regression equations were computed using known concentrations and absorbance values in different wavelengths between 224 and 371 nm. The slope values were used to create the sensitivity matrices. Determinant of the sensitivity matrices were calculated for each wavelength pair and illustrated in Figure 1. Optimal wavelength pair was chosen using Kaiser's technique and an equation set was constructed using this wavelength pair in order to apply bivariate calibration approach. Multivariate calibration technique was applied by using all 22 regression equations.

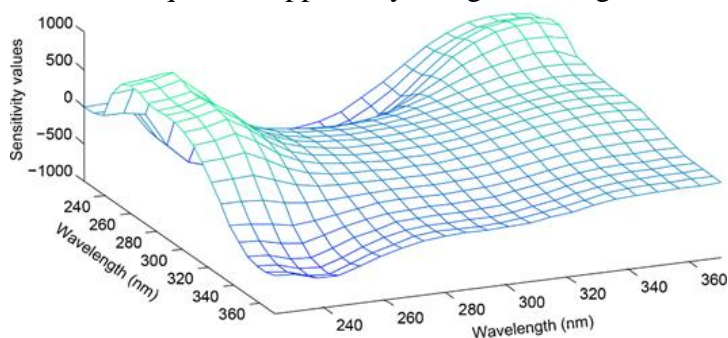


Figure 1. Wavelength pairs and corresponding sensitivity values

Validation studies were performed by analyzing various synthetic mixtures, standard addition samples and intra- and inter-day samples. After proving validity and applicability of the proposed methods, they were applied to the analysis of real tablet samples and successful assay results were obtained.

Keywords: Rosuvastatin, Amlodipine, Spectrophotometry, Bivariate Calibration, Multivariate Calibration

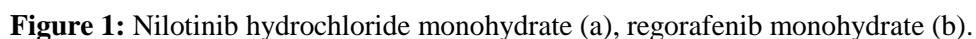
References:

1. Üstündağ, Ö., Dinç, E., Die Pharmazie (2003) 58 623-628.
2. Dinç, E., Baleanu, D. Revista de Chimie (2013) 64 233-237.

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In this study, a simple, rapid and accurate spectrophotometric method was developed for the simultaneous determination of two tyrosine kinase inhibitors. The method is based on the first derivation of ratio spectra. This method has been successfully applied to the binary mixtures. The linear range was 1-20 $\mu\text{g/mL}$ for both drugs. The drugs in the mixture analyzed in methanol at 212 and 247 nm wavelengths for regorafenib and nilotinib respectively.



References:

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Two Rapid Spectrophotometric Method for Determination of Silodosin in Human Plasma

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Silodosin (SLD), 1-(3-hydroxypropyl)-5-[(2R)-({2-[2-[2-(2,2,2-trifluoroethoxy) phenoxy] ethyl} amino) propyl]indoline-7-carboxamide, selective antagonist of α -1-adrenoreceptors and a class of medications called alpha-blockers used for symptomatic treatment of benign prostatic hyperplasia (Figure 1).

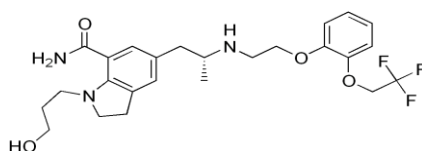


Figure 1. Chemical structure of silodosin

Several analytical methods were presented for determination of SLD in previous studies [1-2]. It wasn't observed a first derivative spectrophotometric method in literature. The aim of our study was to develop two (UV and first-derivative) spectrophotometric method for determination of SLD in the samples from human plasma. It's also intended to achieve the extraction procedure which has high recovery percentage with low plasma volumes.

A standard stock solution (1 mg/mL) of SLD was prepared and the standard working solutions (5- 50 μ g/mL, for both methods) were prepared by dilution of the stock solution. Measurements were carried out at 270 and 281 nm wavelength for UV spectrophotometric and first-derivative spectrophotometric method, respectively.

LOQ and LOD values were calculated to be 5 μ g/mL and 3 μ g/mL, respectively. The mean recovery value of the extraction procedure was statistically calculated and it was founded as 96.8%. The methods were validated according to ICH guideline. According to the results of this study, the spectrophotometric methods for determination of silodosin have particularly advantageous in terms of rapid, simple and cheap method for rapid determination of silodosin in quality control studies.

Keywords: Silodosin, Spectrophotometry, Human Plasma

References:

1. Xia Zhao, Yuwang Liu, Junyu Xu, Dan Zhang, Ying Zhou, Jingkai Gu, Yimin Cui. Journal of Chromatography B (2009) 877 3724–3728.
2. Shaik, J.F., Saladi, S.K., Sait, S., Journal of Chromatographic Science (2013) 52 7 1–8.

Spectrophotometric Determination of 2,3-Dihydroxybenzoic Acid and Catechol

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There are different biologically important aromatic vic-diols (containing adjacent hydroxyl substituents) such as catechols, epinephrine and dopamine. Additionally, 2,3-dihydroxy benzoic acid (2,3-DHBA) is one of the most important indicators of hydroxyl radical damage in the human body. These DHBA derivatives can be determined selectively among other diols as described by Barnum¹. In the present study, salicylic acid was decomposed to DHBAs (namely 2,3- ; 2,4- ; 2,5-DHBA) and catechol, using hydroxyl radicals produced by the Fenton reaction (between Fe(II)-EDTA complex and H₂O₂). After this operation an aliquot was withdrawn and nitrated using sodium nitrite in weakly acidic medium and then sodium molybdate (VI) was added. After the mixture was let to stand at room temperature, NaOH solution was added to produce a red complex according to proposed reaction below and the absorbance was read at 510 nm.

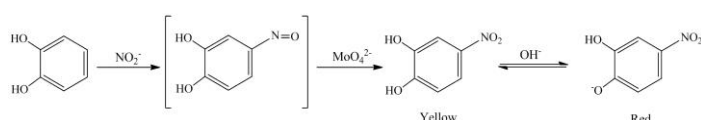


Figure 1. Spectrophotometric determination of vic-diols

On the other hand, selective vic-diol determination was applied to all mentioned DHBAs and catechol standard solutions. While 2,3-DHBA and catechol caused an absorption at 510 nm, none of the other DHBA isomers absorbed at this wavelength (Figure 2).

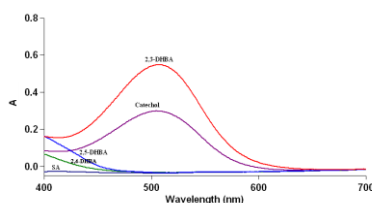


Figure 2. Absorbance spectra of DHBAs and catechol according to proposed

The residual salicylic acid, generated DHBA and catechol after Fenton reaction were measured using HPLC (slightly modified from Singh et al.²); the contents of 2,3-DHBA and catechol were determined and compared with spectrophotometric results. The Fenton reaction was repeated in the presence of antioxidants and because of the radical scavenger effects of antioxidants, the amounts of generated DHBA and catechol decreased.

Keywords: 2,3-Dihydroxybenzoic Acid, Catechol, Salicylic Acid, HPLC

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References:

1. D.W. Barnum, *Analytica Chimica Acta* (1977) 89 157-166.
2. D.P. Singh, R. Govindarajan, A. Khare, A.K.S. Rawat, *Journal of Chromatographic Science* (2007) 45 701-705.

Magnetic Solid Phase Extraction Using Fe₃O₄/Reduced Graphene Oxide Aerogel Prior to Spectrophotometric Determination of Rhodamine B

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Dyes and pigments are widely used as coloring agents. The total dye consumption in the textile industry worldwide is more than 10.000 ton/year. The release of colored waste water from these industries may present an eco-toxic hazard [1]. Rhodamine B, a red dye, is used as a colorant in textile, plastic, leather, dyeing, paper, and printing industries. However, it is harmful to humans and animals, causing irritation to the skin, eyes, and respiratory tract. Because of the fact that the Rhodamine B is present at low levels in the environment samples and sample matrices are very complex, direct analysis is difficult and therefore, it is necessary to develop a separation/ pre-concentration method [2]. Among these methods, magnetic solid phase extraction is an important technique that uses a magnetic material as a solid adsorbent. The adsorbents are dispersed in the solution and can be simply isolated from the sample solution with an external magnet. The method has the advantages of high extraction efficiency, simple separation and good reusability [3]. Aerogels are three-dimensional networks consisting of interpenetrating micropores and mesopores. Among them, RGO-based aerogels have attracted significant attention due to their peculiar properties, including low density, high surface area, and large open pores [4].

In this study, Fe₃O₄/reduced graphene oxide aerogel was synthesized and characterized. It was used for the first time as an adsorbent for the solid phase extraction of Rhodamine B. The determination of Rhodamine B was carried out at a wavelength of 554 nm by spectrophotometry. The parameters affecting quantitative recovery of Rhodamine B such as pH, amount of adsorbent, contact time for adsorption and elution, elution type, volume and concentration were investigated. The optimum solution pH and adsorbent amount were found to be 2 and 75 mg, respectively. Vortexing was used for adsorption and ultrasonication was used for elution process. The contact times for adsorption and elution were 2 min. and 10 min., respectively. Elution was made by 1 mL ethanol.

Keywords: Fe₃O₄/Reduced Graphene Oxide, Magnetic Solid Phase Extraction, Rhodamine B, Spectrophotometry

References:

1. K. R. Shoueira, A. A. Sarhan, A. M. Attab, M. A. Akl Environmental Nanotechnology, Monitoring & Management (2016) 5 62-73.
2. J. Chen, X. Zhu Food Chemistry (2016) 200 10-15.
3. Q. Zhou, M. Lei, J. Li, K. Zhao, Y. Liu Journal of Chromatography A (2016) 1441 1–7.
4. W. Liu, Y. Wang, Z. Li Chemical Communications (2014) 50 10311-10314.

Using A New Surfactant Enhanced Kinetic Spectrophotometry to Determine Trace Amounts of Bisphenol A in Food Samples

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Bisphenol A (BPA) is a chemical monomer used in the production of polycarbonate and epoxy-phenolic resins. Polycarbonate (PC) is widely used in the manufacture of food containers (e.g., milk, water and infant bottles) and epoxy resins are used as an interior protective lining for food and beverage cans. As a result of these food contact uses, trace amounts of bisphenol A can potentially leach out into the water or food and consumers may be exposed to bisphenol A through the diet (1-6).

In this sense, due to possible toxic effect of bisphenol A on human health, a new kinetic spectrophotometric method for the determination of bisphenol A in food samples for fixed time method of 5 min at 447 and 476 nm was established. The method is based on selective and rapid reduction of $\text{Mn(III)(C}_2\text{O}_4)_2^-$ and/or $\text{Mn(III)(P}_2\text{O}_7)^-$ with trace amounts of bisphenol A in presence of CPC as both counter ion and sensitivity enhancer at pH 5.5 and 6.5 respectively. The influences of pH, concentration of reactants, reaction time, reaction temperature, and interfering ions on absorbance change, ΔA were evaluated in detail, and the optimum reaction conditions were established based on analysis results. The results, which were provided by optimal reaction conditions, show that there is a good linear relationship between the absorption change of each ternary complex and the concentration of bisphenol A in range of 5-200 $\mu\text{g L}^{-1}$ with a detection limit of 1.46 $\mu\text{g L}^{-1}$ and 2-120 $\mu\text{g L}^{-1}$ with a detection limit of 0.58 $\mu\text{g L}^{-1}$. The method was used in the determination of bisphenol A in the selected food samples, the relative standard deviations were in range of 3.20-4.70 % and 2.85-4.35% (25, 100 $\mu\text{g L}^{-1}$, n:5) respectively and the recoveries were quantitative in range of 96.8-99.5% and 97.2-101.3% (25, 100 $\mu\text{g L}^{-1}$, n: 5) with satisfactory results.

Key Words: Bisphenol A; Mn(III)-Oxalate, Mn(III)-Pirofosfat; Food Samples; Fixed Time Method; Kinetic Spectrophotometry

References

1. A.Ballesteros-Gomez; S. Rubio; D.Perez-Bendito, j. Chrom A, (2009) 1216 449-469.
2. A. Gonzalez-Casado, N. Navas, M. del Olmo and J.L. Vilchez, *J. Chromatogr. Sci.*, (1998) 36 565-570.
3. T. Yoshida, M. Horie, Y. Hoshino and H. Nakazawa, *Food Addit. Contam.*, (2001) 18 69-75.
4. C. Nerin, M.R. Philo, J. Salafranca and L. Castle, *J. Chromatogr. A*, (2002) 963 375-380.
5. R. Braunrath and M. Cichna, *J. Chromatogr. A*, (2005) 1062 189-98.
6. R. Braunrath, D. Podlipna, S. Padlesak and M. Cichna-Markl, *J. Agric. Food Chem.*, (2005) 53 8911-7.

Separation of Aldosterone Hormone via Molecular Imprinted Magnetic Nanoparticles and Determination by UV Spectrophotometry

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In this study, molecular imprinted magnetic nanoparticles (MIP-MNPs) were synthesized and used for the selective determination of aldosterone hormone. Magnetic nanoparticles were synthesized by co-precipitation of Fe^{2+} and Fe^{3+} in alkaline medium¹. Subsequently, functional monomer dopamine and template molecule aldosterone were polymerized via self-oxidative polymerization in alkaline medium to imprint thin polymer films on the surface of the magnetic nanoparticles². The synthesized nanoparticles were characterized by FT-IR, XPS, TEM and VSM analysis. The selectivity of the MIP-MNPs to aldosterone was verified by direct adsorption of hormone in the presence other hormones. Aldosterone was determined by UV-VIS spectrometry at 280 nm after removal from MIP-MNPs. It was observed that the MIP-MNPs indicated excellent selectivity. The maximum Langmuir adsorption capacity for aldosterone was 22.9 mg g^{-1} . The MIP-MNPs maintained its adsorption capacity up to thirteen adsorption-desorption cycles without significant loss. The accuracy and precision of the method were checked by determining aldosterone in the spiked water samples. The recoveries were above 95% (Table 1).

Table 1. Recovery of aldosterone in water after extracted from MIP-MNPs ($n = 3$).

Added aldosterone, mg/mL	Found aldosterone, mg/mL	Recovery, %	RSD, %
0.5	0.49 ± 0.03	98	6.1
1.0	0.98 ± 0.05	98	5.1
2.0	1.98 ± 0.08	99	4.0

Keywords: Self-Oxidative Polymerization, Aldosterone, Molecular Imprinted, Magnetic Nanoparticle.

References:

1. R. Gao, X. Mu, Y. Hao, L. Zhang, J. Zhang, Y. Tang, J. Mater. Chem. B (2014) 2 1733-1741.
2. Y. S. Li, X. Y. Meng, Y. Zhou, Y. Y. Zhang, X. M. Meng, L. Yang, P. Hu, S. Y. Lu, H. L. Ren, Z. S. Liu, X. R. Wang, Biosens. Bioelectron (2015) 66 559-564.

Determination of BSA by Glutathione-Modified Silver Nanoparticles in the Presence of Metal Ions

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Abstract

A colorimetric method for the determination of bovine serum albumin (BSA) using glutathione-modified silver nanoparticles in the presence of some metal ions is reported. Silver nanoparticles were prepared by NaBH₄ reduction of silver nitrate and stabilized with using glutathione (GSH). The modified nanoparticles and formed complexes between GSH modified silver nanoparticles-metal ion-BSA were analyzed by ultraviolet-visible (UV-Vis) spectroscopy. Nine metal ions were used for complex formation: Ag⁺, Cd²⁺, Co²⁺, Cu²⁺, Fe³⁺, Hg²⁺, Ni²⁺, Pb²⁺ and Zn²⁺. Absorption changes were measured to see formed complexes. The shifted absorption peaks obtained in the presence of Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions. These peaks were intensified depending on the BSA concentrations. The obtained linear determination ranges for BSA were 5-200 µg/mL, 10-400 µg/mL, 50-500 µg/mL, 100-500 µg/mL in the presence of Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions, respectively. IR spectroscopy and atomic force microscope were also used for characterization of modified nanoparticles and complexes.

Keywords: BSA, GSH, Silver Nanoparticle, Modification, Metal Ions

Introduction

BSA is a soluble protein in the circulatory system and serves as a depot protein [1]. It participates in many enzymatic reactions and also used as blocking agent [2]. One of the major role of this protein is maintaining the osmotic pressure and pH of blood [3]. It is able to reversibly bind to endogenous and exogenous substances [4]. BSA also has unusual ligand-binding properties [5]. There have been many methods reported to determine BSA in the literature. Yu et al. [6] used resonance rayleigh scattering (RRS) method for the determination of BSA. 3-(4'-methylphenyl)-5-(4'-methyl-2'-sulfophenylazo) rhodamine molecule associated with BSA in the presence of sodium dodecylsulphonate microemulsion. Hence, the RRS intensity had linear relationship with concentration of BSA. Suznjevic et al. [7] have reported determination of BSA by anodic stripping voltammetry with a rotating glassy carbon electrode in the presence of Hg(II) and Cu(II) ions. The method based on binding affinity of BSA towards to Hg(II) and Cu(II) and measurement of dissolution currents of metal ions. Jinghua et al. [2] have reported flow injection chemiluminescence sensor for the determination of BSA using molecularly imprinted polymeric microspheres. The polymer was synthesized using methacrylic acid (monomer) and ethylene glycol dimethacrylate (cross-linker) in the BSA template molecule. BSA was adsorbed on the polymer and then reacting with potassium permanganate and hydrochloric acid to obtain chemiluminescence signal. Lee et al. [8] have reported a fluorimetric method for the determination of BSA based on its enhancement effect of Nile Blue fluorescence via formed complex. Shrivastava and Dash [9] has reported colorimetric determination of BSA by un-modified silver nanoparticles. The described method based on interaction of BSA and silver nanoparticles and measurement of changed absorption properties.

GSH is an intercellular tripeptide consisting of γ -glutamic acid-cysteine-glycine amino acids [10]. It is a nonprotein thiol in mammalian cells and able to detoxification of the cell via binding to toxins such as heavy metals [11]. GSH was used as modification agent for silver nanoparticles in this study due to the high affinity of -SH groups toward silver nanoparticles. Silver nanoparticles have unique surface chemistry. At nanometer dimensions the electron cloud can oscillate on the particle surfaces and this oscillation known as surface plasmon resonance (SPR). Silver nanoparticles exhibit SPR bands and ultraviolet–visible spectroscopy (UV-vis) an effective monitoring method.

In this study, we have investigated a new methodology for the determination of BSA in aqueous solutions by using GSH modified silver nanoparticles (AgGSH) in the presence of various metal ions. The method based on AgGSH nanoparticles-metal ion-BSA cooperative metal–ligand interactions. The linear determination concentration ranges obtained in the presence of Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} ions.

Materials&Methods

All of the used chemicals were of analytical grade. All the solutions were prepared with double distilled deionized water (Millipore 18Mcm^{-1} resistance). Silver nitrate (AgNO_3), sodium borohydride (NaBH_4) and studied metal ion salts, $\text{CoCl}_2\cdot\text{H}_2\text{O}$, $\text{Cd}(\text{CH}_3\text{COO})_2$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, HgCl_2 , FeCl_3 , $\text{Ni}(\text{NO}_3)\cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{Pb}(\text{NO}_3)_2$ was purchased from Merck Chemicals. GSH was purchased from Fluka and BSA purchased from Sigma-Aldrich. All used glass wares were washed with dilute nitric acid and ethanol to avoid contamination of metal and organic substances, respectively. FTIR spectra of samples were measured with Perkin Elmer spectrometer. UV-Vis absorption spectra were obtained by UV-Vis spectrophotometry (Shimadzu UV-Vis 160A) in a 1 cm quartz cuvette by measuring the full absorption spectrum of mixtures in the range of 200–800 nm. The morphology of the synthesized and modified nanoparticles were characterized by atomic force microscopy (AFM) using a NTMDT Integra instrument.

Glutathione-modified silver nanoparticles were synthesized according to the published methods [10-12]. NaBH_4 (0.01 g) was added to a concentrated aqueous solution of AgNO_3 (100 mL, 1×10^{-4} M) at room temperature in order to reduce silver ions. After stirring for 5 min to provide a homogeneous nucleation, an aqueous solution of GSH (2 mL, 1×10^{-3} M) was added to stabilize the silver nanoparticles. After aging the silver colloidal solution for 2 h, AgGSH nanoparticles were obtained and stored in the dark.

Results&Discussion

Figure 1 shows the absorption spectra of AgGSH, AgGSH-BSA, BSA, AgGSH- Cd^{2+} -BSA, AgGSH- Cu^{2+} -BSA, AgGSH- Ni^{2+} -BSA, AgGSH- Zn^{2+} -BSA. The AgGSH absorption spectrum has a peak at around 395 nm. This absorption peak was little decreased with the addition of BSA to the solution due to nanoparticles-BSA interaction. BSA does not show significant absorption peaks. A board peak was observed in the AgGSH- Ni^{2+} -BSA spectrum due to aggregation of nanoparticles via formed complexes. The absorption spectra of AgGSH- Cd^{2+} -BSA and AgGSH- Zn^{2+} -BSA showed a red shift to 410 and 404 nm, respectively. In the case of the AgGSH- Cu^{2+} -BSA complex, the absorption intensity increased and shifted to 403 nm. According to the results, BSA interacted with both of the nanoparticles and metal ions.

A linear relationship exists between the absorbance of the solution and the BSA concentration, at 412, 410, 403, 404 nm for AgGSH- Ni^{2+} -BSA, AgGSH- Cd^{2+} -BSA, AgGSH- Zn^{2+} -BSA, AgGSH- Cu^{2+} -BSA, respectively (Figure 2). The obtained determination ranges are

50-500 $\mu\text{g/mL}$ for AgGSH- Ni^{2+} -BSA, 5-200 $\mu\text{g/mL}$ for AgGSH- Cd^{2+} -BSA, 100-500 $\mu\text{g/mL}$ for AgGSH- Zn^{2+} -BSA and 10-400 $\mu\text{g/mL}$ for AgGSH- Cu^{2+} -BSA. The linear equations for each case were shown in Figure 2.

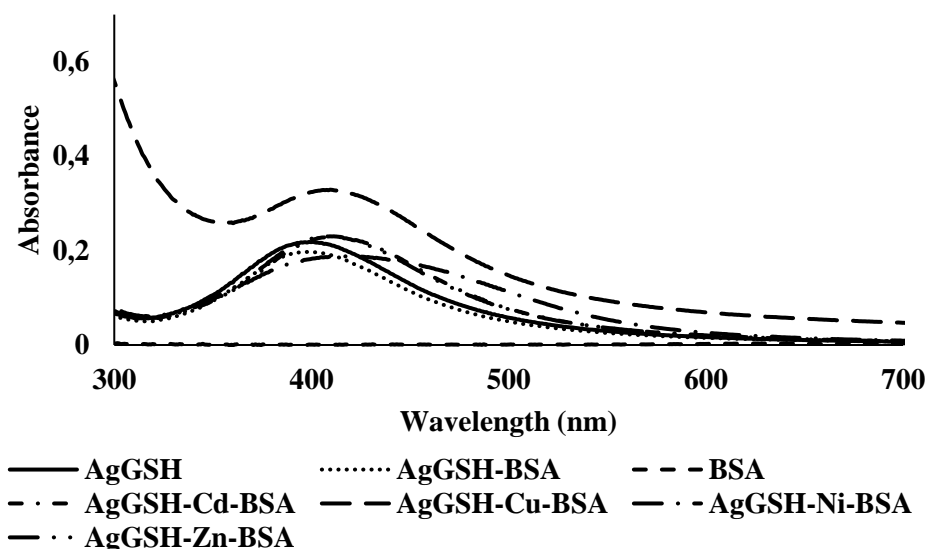


Figure 1. Absorption spectra of AgGSH, AgGSH-BSA, BSA, AgGSH- Cd^{2+} -BSA, AgGSH- Cu^{2+} -BSA, AgGSH- Ni^{2+} -BSA, AgGSH- Zn^{2+} -BSA

FTIR analyses (not shown here) were also provided the AgGSH-BSA and AgGSH-metal ion-BSA interactions. The amide I and II peaks, which observed at 1643 and 1532 cm^{-1} , were appeared in the range of 1643 - 1585 cm^{-1} in the AgGSH-metal ion-BSA spectra, respectively. Also, the carboxylate vibration peak of AgGSH (1408 cm^{-1}) was shifted to 1413 - 1417 cm^{-1} region in the AgGSH-metal ion-BSA spectrum. The shifted peaks indicating that these groups were participated to the complex formation.

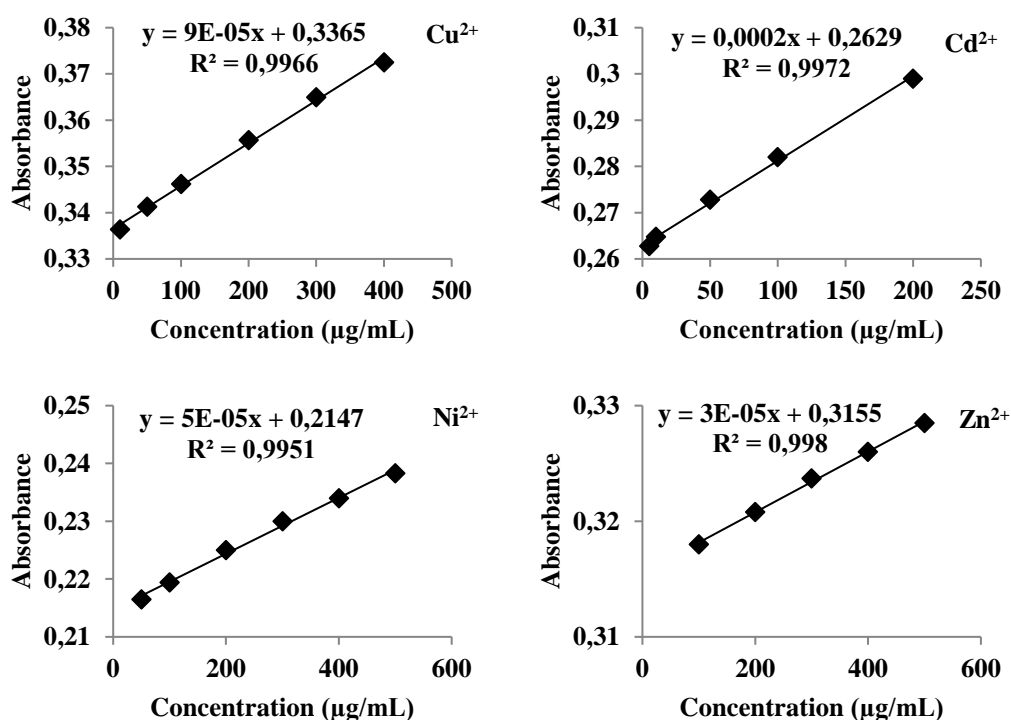


Figure 2. Calibration curves of AgGSH-metal ion-BSA complexes

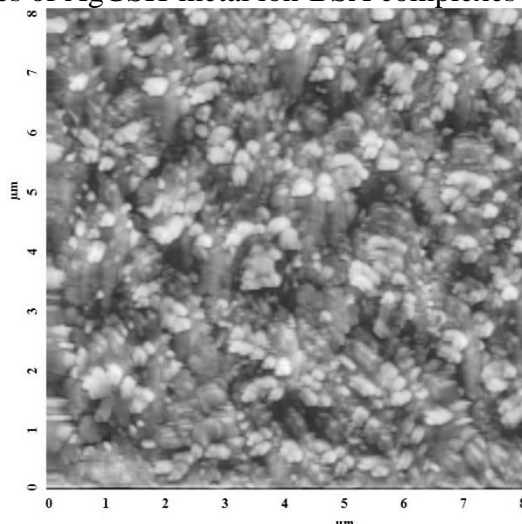


Figure 3. AFM topographical image of AgGSH nanoparticles

Figure 3 shows 2D-topographic AFM image of the assembly of aggregated silver nanoparticles. The particle aggregation is observed due to interaction with the other particles via charged groups.

Conclusion

We have demonstrated a BSA determination method based on glutathione-modified silver nanoparticles, metal ions and BSA complex formation. Best results obtained in the presence of copper ions. The absorption band of AgGSH was increased (except in the presence of Ni^{2+}) and shifted from 395 nm to 403-412 nm region via formed complexes. In the presence of Ni^{2+} , more aggregation observed due to strong AgGSH- Ni^{2+} complexes. The determination ranges varies between 5-500 $\mu\text{g/mL}$ concentrations of BSA. The FTIR results verified the occurred complex formation.

Acknowledgments

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References:

1. Li Li, Fenfen Zhang, Yaping Ding, Yaping Wang, Lulu Zhang J Fluoresc (2009) 19 437–441.
2. Yu Jinghua, Wan Fuwei, Zhang Congcong, Yan Mei, Zhang Xiaona, Wang Shaowei, Biosensors and Bioelectronics (2010) 26 632–637.
3. Yuping Zhang, Shuyun Shi, Xiaorui Sun, Xiang Xiong, Mijun Peng Journal of Inorganic Biochemistry (2011) 105 1529–1537.
4. Reza Khodarahmi, Seyyed Arash Karimi, Mohammad Reza Ashrafi Kooshk, Seyyed Abolghasem Ghadami, Sirous Ghobadi, Mojtaba Amani Spectrochimica Acta Part A (2012) 89 177– 186.
5. Guowen Zhang, Yadi Ma, Lin Wang, Yepeng Zhang, Jia Zhou Food Chemistry (2012) 133 264–270.
6. Jinghua Yu, Lei Ge, Jiadong Huang, Shenguang Ge 3rd International Conference On Bioinformatics And Biomedical Engineering (2009) 1(11) 2588-2590.
7. D. Suznjevic, M. Erceg, D. Vuceli Microchemical Journal (2001) 69 59-71.
8. Sang Hak Lee, Jung Kee Suh, Ming Li Bull. Korean Chem. Soc. (2003) 24(1) 45-48.
9. Siddhartha Shrivastava, Debabrata Dash Nano-Micro Lett. (2010) 2 164-168.
10. Can Serkan Keskin, Semra Yilmazer Keskin, Abdil Özdemir Rev. Chim. (2012) 63(7) 598-602.
11. Can Serkan Keskin, Semra Yilmazer Keskin, Abdil Özdemir Journal of Nano Research (2012) 18-19 63-76.
12. Haibing Li, Zhimin Cui, Cuiping Han Sensors and Actuators B (2009) 143 87–92.

Quercetin Isolation from Hydrolyzed Black Tea Extract Using Quercetin Imprinted Polymer

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Molecular imprinted polymers (MIPs) are solid polymeric materials containing templates which have recognizing abilities chemically of specific molecules (or their derivatives). MIPs offer distinct advantages such as ease of preparation, low cost, tolerance to extreme thermal and chemical conditions, long shelf life, and enhanced versatility in experimental design compared to natural proteinaceous receptors [1,2].

Quercetin (3,3',4',5,7-pentahydroxyflavone, QC) widely occurring in leaves, fruits, and flowers of many plants is a flavone that has become the topic of increasing interest based on its antioxidant, antiviral and antitumor properties [3]. So preconcentration and/or separation of quercetin in complex multicomponent plant materials is an important research area. Tea that is recognized significant health protecting activity due to its high polyphenol content with many experimental studies is also the most consumed beverage worldwide [4].

In this work, imprinted polymer for the isolation of QC was synthesized. This polymer was prepared thermally through bulk polymerization by using quercetin as the template molecule, 4-vinylpyridine (4VP) as the functional monomer, ethylene glycol dimethacrylate (EDMA) as the cross-linker and 2,2'-azobisisobutyronitrile (AIBN) as the initiator in the porogen of acetone. Non-imprinted polymers (NIPs) were also synthesized without template. QC imprinted polymer with 1:4:20 molar ratio (template:monomer:cross-linker) was established as the most suitable polymer for recognition of QC due to having high selectivity for quercetin according to the other structurally related compounds [5]. Molecularly imprinted solid phase extraction (MISPE) using prepared quercetin imprinted polymer was applied to hydrolyzed black tea extract. The recovery yields from black tea of quercetin and kaempferol as a quercetin derivative were 66 % and 43 % respectively.

Keywords: Molecularly Imprinted Polymer, Quercetin Imprinted Polymer, Quercetin, Black Tea.

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References:

1. Yan, H., Row, K. H. International Journal of Molecular Sciences (2006) 7 155-178.
2. Haupt, K. Analytical Chemistry (2003) 75 376-383.
3. Song, X., Li, J., Wang, J., Chen L. Talanta (2009) 80 694–702.
4. Turkmen N., Sari F., Velioglu Y. S. Food Chemistry (2006) 99 835-841
5. Karaman Ersoy S., Tütem E., Sözgen Başkan K., Apak R., Nergiz C. Journal of Chromatography B (2016) 1017 89–100

Rosmarinic Acid Isolation from Rosemary Extract using Caffeic Acid Imprinted Polymer

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Molecular imprinted polymers (MIPs) having distinct advantages such as ease of preparation, low cost, tolerance to extreme thermal and chemical conditions, and long shelf life are solid polymeric materials containing templates which have chemical recognition abilities for specific molecules (or their derivatives) [1,2].

Caffeic acid (CA) is a hydroxycinnamic acid derivative which is present in many plants and beverages. It accounts for up to 70% of the total hydroxycinnamic acid content in fruits. Caffeic acid can slow down the process of inflammation, thereby providing protection from the hazardous effects of free radicals and against endothelial damage, *etc.* [3]. Rosmarinic acid (RA) is an ester of caffeic acid and 3,4-dihydroxyphenyllactic acid and has a number of interesting biological activities such as antiviral, antibacterial, antiinflammatory and antioxidant [4]. A large number of polyphenolic compounds, of which rosmarinic acid is the most abundant with antioxidant activity, have been identified in rosemary (*Rosmarinus officinalis*) extracts. In addition, rosemary extracts are used in medicine as antiinflammatory and antimicrobial agents [5].

In this work, caffeic acid imprinted polymer was synthesized thermally through bulk polymerization by using caffeic acid as the template molecule, 4-vinylpyridine (4VP) as the functional monomer, ethylene glycol dimethacrylate (EDMA) as the cross-linker and 2,2'-azobisisobutyronitrile (AIBN) as the initiator in the porogen of tetrahydrofuran (THF). Non-imprinted polymers (NIPs) were also synthesized without template. CA imprinted polymer with 1:4:16 molar ratio (template:monomer:cross-linker) was established as the most suitable polymer for recognition of CA due to its high selectivity for CA compared to other structurally related compounds. Also in this study preconcentration and purification of RA was performed by using CA-MIPs. Sorption parameters of the MIPs and NIPs were calculated by using Freundlich and Langmuir isotherms using RA solutions in ACN. Molecularly imprinted solid phase extraction (MISPE) using the prepared CA imprinted polymer was applied to rosemary extract. The recovery yield from rosemary of RA was 84 %.

Keywords: Molecularly imprinted polymer, Caffeic acid imprinted polymer, Rosmarinic acid, Rosemary.

References:

1. Yan, H., Row, K. H. International Journal of Molecular Sciences (2006) 7 155-178.
2. Haupt, K. Analytical Chemistry (2003) 75 376-383.
3. Maurya, D. K., Devasagayam, T. P. A. Food and Chemical Toxicology (2010) 48 3369-3373.
4. Petersen M., Simmonds, M. S.J. Phytochemistry (2003) 62 121-125.
5. Del Baño, M.J., Lorente, J., Castillo J., Bnevente-García, O., Del Río, J. A., Ortuño, A., Quirin, K.-W., Gerard, D. Journal of Agricultural and Food Chemistry (2003) 51 4247-4253

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Changes in Phenolic Profile and Antioxidant Activity of Black Table Olives During Fermentation Process

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Olive is an ancient fruit and it is extremely rich in bioactive compounds, which contributes to its antimicrobial, anticarcinogen and antioxidant properties. Changes in total phenolics, phenolic profile and antioxidant activity (CUPRAC) of olive fruits of Edremit cultivar during black table olive production were investigated. Olive samples (n=4) were collected at days 120 and 240 of fermentation process and were compared to samples from beginning of the fermentation. Significant changes were observed in total phenolic compounds (from 4331.5 mg GA/kg to 2024.5 mg GA/kg) and antioxidant activities (from 10.84 mg TR/g to 6.89 mg TR/g) during fermentation period ($P<0.05$). Both the total phenolic content and CUPRAC values of olive fruits significantly decreased 54% and 37% respectively after 240th days of fermentation. Oleuropein, hydroxytyrosol, tyrosol, vanilin, rutin and apigenin 7 glucoside were identified and quantified by HPLC analysis as phenolic compounds of Edremit cultivar variety black olives. Decrease in oleuropein content was significant and it was around 50% during fermentation period resulting in increases in hydroxytyrosol, which was expected. Hydroxytyrosol is one of the principal degradation products of oleuropein. Final concentrations of oleuropein, hydroxytyrosol, tyrosol, vanilin, rutin, and apigenin 7 glucoside were 127.3, 3021.2, 361.8, 50.1, 26.4 and 174.9 mg/kg respectively, in olive fruits to ready for consumption.

Keywords: Black Table Olive, Fermentation, Phenolic Compounds, Antioxidant Activity

Production of Volatile Organic Compounds by Five Species of Microalgae: the Use of Solid Phase Microextraction (Spme) Coupled to Gc-Ms as A Method of Analysis

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There is an increasing demand for integration of microalgae as a whole biomass or their metabolites in a variety of foodstuffs. When the microalgal biomass/metabolites is integrated in food products, the investigation of their chemical and sensory properties are of importance. Additionally, in recent years, obtaining volatile organic compounds from vegetable and animal sources or using biotechnological methods in their production becomes prominent due to consumer preferences. Microalgae can also be a source from this aspect for production of these natural volatile compounds (Nor Qhairul Izzreen and Vijaya, 2011; Güneşer et al., 2015).

In this study the volatile organic compounds (VoCs) of five species of microalgae were studied by using solid phase microextraction (SPME) coupled to GC-MS as a method of analysis. Three species of marine microalgae (*Cryptocodinium cohnii*, *Schizochytrium limacinum* and *Tetraselmis chuii*) and two fresh water microalgae (*Chlorella vulgaris* and *Chlorella protothecoides*) were investigated. Microalgae species were cultivated in heterotrophic/mixotrophic conditions and biomass were harvested at the end of logarithmic phase and fresh microalge pastes were used for VoCs analysis. Data analysis revealed that the freshwater microalgae *C. vulgaris* and *C. protothecoides* had relatively simple VoCs mainly composed of several ketones and alcohols compared to other species. *C. cohnii* which is relatively rich in polyunsaturated fatty acids had at high concentrations of sulphuric and ester compounds. Additionally, aldehydes were proved to be the most prevalent in *Cryptocodinium cohnii* and *Schizochytrium limacinum* species.

Keywords: Microalgae, Heterotrophic/Mixotrophic Growth, Volatile Organic Compounds, SPME-GC-MS

References:

1. Nor Qhairul Izzreen, M.N. and Vijaya Ratnam, R. Volatile compound extraction using Solid Phase Micro Extraction coupled with Gas Chromatography Mass Spectrometry (SPME-GCMS) in local seaweeds of *Kappaphycus alvarezii*, *Caulerpa lentillifera* and *Sargassum polycystem*. *International Food Research Journal* (2011) 18(4): 1449-1456
2. Guneser, O., Demirkol, A., Karagül Yüceer, Y., Ozmer Togay, S., İşleten Hoşoğlu, M., Elibol, M. Bioflavour production from tomato and pepper pomaces by *Kluyveromyces marxianus* and *Debaryomyces hansenii* Bioprocess Biosyst Eng (2015) 38 1143–1155.

Effects of Different Pretreatment Methods on Production of Some Volatile Organic Compounds from Tomato and Pepper Pomaces

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In recent years, obtaining volatile organic compounds from vegetable and animal sources or using biotechnological methods in their production becomes prominent due to consumer preferences. Production of these natural volatile compounds by utilizing lignocellulosic or organic agricultural or industrial wastes, which are abundant and sustainable sources, becomes more and more important in terms of both decreasing production costs and developing processes in which the present wastes can be utilized.

In our country, especially in the Marmara and Aegean regions, a significant amount of tomato and pepper pulp comes out as a natural biologic waste in paste production industry. In our previous study, it was demonstrated that those pomaces have a potential to use for the production of natural volatile compounds via fermentation (Güneşer ve ark., 2015). In this study, firstly, a series of pretreatments (ultrasound, dilute acid and enzymatic hydrolysis and their combinations) were undertaken for an effective conversion of tomato and pepper pomaces into fermentable sugar. Secondly, the yeast *K. marxianus* which find industrial application due to its GRAS status was cultivated on pretreated mediums. Effects of different pretreatments on production of volatile organic compounds by *K. marxianus* were evaluated by HS-SPME-GC-MS analysis. Results were also compared with the control group and the yeast growing on Yeast Extract Peptone Dextrose (YPD) medium. The yeast grown in the medium obtained by ultrasound-assisted acid hydrolysis (2% H₂SO₄ solution) produced higher amount of ethyl acetate (21.6 mg/kg), isoamyl acetate (9.2 mg/kg) and phenylethyl acetate (17 mg/kg) compared to control and YPD grown group. Also, ultrasound-assisted enzyme application on pepper pomaces led to an increase especially in the amount of fusel alcohols (isoamyl alcohol and phenyl ethyl alcohol) produced by *K. marxianus*. Experiments demonstrated that the amount of volatile organic compounds differed according to the type of hydrolysis applied to pomaces. Additionally, ultrasound-assisted pretreatment seemed to increase the yield for chemical and enzymatic hydrolysis, showing a promising technology to be used for hydrolysis for tomato and pepper pomaces. Therefore, Response Surface Methodology (RSM) has been applied for the optimization of pretreatment methods on tomato and pepper pomaces.

Keywords: Tomato And Pepper Pomace, Ultrasound, Dilute-Acid Pretreatment, Enzymatic Hydrolysis, Response Surface Methodology

References:

1. Güneşer, O., Demirkol, A., Karagül Yüceer, Y., Özmer Togay, S., İşleten Hoşoğlu, M., Elibol, M. Bioflavour production from tomato and pepper pomaces by *Kluyveromyces marxianus* and *Debaryomyces hansenii* Bioprocess Biosyst Eng (2015) 38 1143–1155.

Effect of Acidification Process on the Physicochemical Properties of Licorice Root Sherbet

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Licorice plant is being used for production of traditional beverage known as Licorice root sherbet in Eastern and Southeastern part of Turkey due to health promoting effects since ancient times. During the traditional production process of licorice root sherbet, conservation methods such as thermal treatment are not applied, so the sherbet becomes undrinkable in a short period. Glycyrrhizin, a substance from the licorice plant, 50 times sweeter than sucrose, makes it inconsumable for lots of people. Objective of this study was to develop new sherbet product to increase consumption rate and shelf life. Therefore, licorice root sherbet (pH 6.09) was produced in acidified form by decreasing the pH value to 4.2. In this work, chemical composition of acidified sherbet (AS) was compared with normal sherbet (NS). The effect of acidification process was determined by analyzing the physicochemical properties (pH, brix, color, total phenol, total flavonoid, glycyrrhizic acid and antioxidant capacity) of sherbet. The difference between normal and acidified sherbet was statistically significant ($P < 0.05$) for all physicochemical properties. After the acidification process, phenolic compounds and glycyrrhizic acid were separated from acidified sherbet as a precipitate. Glycyrrhizic acid content of sherbet had a significant loss of about 85%. Total phenol content and total flavonoid content were 379.72 and 25.18 for NS respectively whereas the same parameters were 308.28 and 6.56 for AS respectively. Similarly, antioxidant activity in NS ($6.45 \mu\text{mol Trolox} / \text{mL}$) was higher than AS ($3.49 \mu\text{mol Trolox} / \text{mL}$). In terms of the lightness (L^*) values, AS samples had higher values than NS samples.

Keywords: Licorice Root Sherbet, Acidification

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Kinetics of Anthocyanin Degradation and Polymeric Color Formation in Black Mulberry (*Morus nigra*) Juice During Heating

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The degradation of total monomeric anthocyanins and changes in the proportion of polymeric color (%PC) and total phenolic content of mulberry (*Morus nigra*) juice were studied during heating at 70, 80 and 90°C. Analysis of kinetic data suggested a first-order reaction for the thermal degradation of black mulberry anthocyanins. As expected, degradation rates of anthocyanins in black mulberry juice increased with increasing temperature. At 70, 80 and 90°C, the rate constants were determined as 0.75×10^{-3} , 1.7×10^{-3} and $4.05 \times 10^{-3} \text{ min}^{-1}$, respectively. The formation of %PC followed zero order reaction kinetics and the rate constants were found to be 0.096, 0.045 and 0.025 %PC/min, respectively. The temperature dependence of degradation of anthocyanins and formation of %PC were adequately modeled by Arrhenius equation. The activation energy values for the degradation of anthocyanins and formation of %PC were found as 87.35 and 69.42 kJ/mol, respectively. Total phenol content of black mulberry juice changed slightly during heating. However, no fitting kinetic model was found for the change in total phenol content.

Keywords: Black Mulberry, Monomeric Anthocyanins, Polymeric Color, Kinetics, Thermal Treatment, Total Phenol

Effect of Vinegar Processing on Bioactive Compounds and Antioxidant Properties of Black Mulberry Juice

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Black mulberry (*Morus nigra*) fruits present valuable income in the food industry due to their high content of phenolic compounds. In this study, black mulberry vinegar as a condiment was produced from black mulberry juice by following a two steps process including alcoholic and acetic fermentation. The changes in terms of bioactive compounds (phenolics and anthocyanins) together with antioxidant properties (TEAC, CUPRAC, DPPH, FRAP) were investigated during vinegar making process. Total phenolics of the black mulberry juice (BMJ) were measured both after alcohol fermentation (AF) and after acidification (AC). The differences were small enough to be non significant ($P>0.05$). However, significant increases were observed in catechin, caffeic acid and chlorogenic acid content of BMJ ($P<0.05$). Major anthocyanins of BMJ were cyanidin-3*O*-glucoside (115.54 mg/L) and cyanidin-3*O*-rutinoside (100.04mg/L) followed by smaller amounts of pelargonidin-3*O*-glucoside (10.96 mg/L). Anthocyanins are responsible for the distinctive color of BMJ and they are also an important quality parameter for the sensorial desirability of the final product. Anthocyanins found in BMJ had a significant loss of about 88% after the vinegar making process. Conversely, antioxidant properties of BMJ samples in terms of TEAC, DPPH, CUPRAC and FRAP values showed an increasing tendency as a result of the fermentation processes. The increases in antioxidant potential in terms of TEAC, DPPH and CUPRAC values of AC samples were large enough to be significant compared to both BMJ and AF samples ($P<0.05$).

Keywords: Black mulberry, vinegar, bioactive compounds, antioxidant activity

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Oleuropein Content and Antioxidant Activity of Herbal Tea Made From Olive Leaves of Fourteen Different Cultivars

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Olive leaves have lately received significant attention due to their medicinal properties and positive health effects, which mainly due to their high content of bioactive compounds. In this study, olive leaf tea made from fourteen different olive cultivars were investigated in terms of total phenolic, total flavanoid and oleuropein contents and antioxidant activities (DPPH and CUPRAC). Olive tree leaves (*Olea europaea* L.) from varieties of Arbequine, Ascolana, Ayvalık, Domat, Edincik Su, Gemlik, Gordales, Karamürsel Su, Manzanilla, Memecik, Negral, Samanlı, Uslu, Verdial were harvested from Edremit/Turkey and were dried at 80°C for 4 hours. The teas were prepared from fine powder of the dried olive leaves by infusion at 80°C for 10 min. Tea from Manzanilla variety had the highest content of total phenolics (302,46±19,66 mg GA/L) and total flavanoids (7,57±0,42 mg QE/L) compared to the other cultivars (P<0.05). HPLC analyses indicated that oleuropein content of tea from Manzanilla (178,53±4,54 mg/L) was the highest followed by tea from Ascolana (93.72±4.54 mg/L) and tea from Domat (87.28±4.54 mg/L). Tea from Gemlik (27.34±4.54 mg/L) had the lowest oleuropein content among the fourteen olive cultivars. In terms of the antioxidant activities of tea products, tea from Manzanilla had the lowest EC₅₀ value (15.61±7.22 µL) and had the highest CUPRAC value (490.50±39.14 mg Trolox/L). CUPRAC values of the tea products were ordered as Manzanilla >Samanlı >Memecik >Arbequine >Domat >Ayvalık >Karamürsel Su >Negral >Gordales >Ascolana >Uslu >EdincikSu >Verdial >Gemlik. There were high correlations between total phenolics and the antioxidant activity revealed by the DPPH and CUPRAC methods. The pearson correlation coefficients were always higher than 86% (P<0.0001).

Keywords: Olive leaf tea, Oleuropein, Antioxidant activity

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Development of a Capillary Electrophoretic Method for Determination of Phenolic Compounds in Carob Molasses

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The main purpose of this study was to develop and validate a capillary electrophoretic method for the determination of phenolic compounds in carob molasses. For this purpose, parameters including pH, voltage and loading time which influence capillary electrophoretic separation were investigated to determine the optimum conditions. The results of the study showed that phenolic compounds could be well separated within 18 min. in a 55 cm length capillary at a separation voltage of 30 kV with 40 mM borate buffer at pH 8.9 at room temperature. The linearity was determined at the range of 2.5 -100 ppm for 18 phenolic compounds with high correlation coefficient (<0.98) and also satisfactory recoveries (<90 %). Optimized capillary electrophoretic method was applied to five carob molasses samples provided from local producer in Uşak for the determination of phenolic compounds. As a results, gallic acid was determined as major phenolic compound in carob molasses. The concentrations of gallic acid in the molasses samples ranged from 15.02-87.98 ppm.

Keywords: Phenolic Compounds, Capillary Electrophoresis, Carob Molasses,

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Mineral Content of Carob Pekmez (Molasses) from Different Regions in Turkey

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The aim of this study was to determine the contents of some macro and micro elements in carob pekmez provided from different regions in Turkey. For this purpose, 35 samples of carob pekmez from Marmara, Aegean, Mediterranean, Central, Eastern and Southeastern Anatolia Regions were collected and analyzed in 2015-2016. Levels of Na, K, Mg, Ca, Fe, Cu, Zn, Mn, Al, Cr and Mo in carob pekmez samples were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

As results, significant differences were observed between carob pekmez samples in terms of the contents of Ca, Cr and Mo. Carob pekmez from Aegean region had the highest Ca content while the highest Mo content was observed in carob pekmez from Aegean region. Moreover, carob pekmez from Mediterranean region had the lowest Cr content. The concentration ranges in the carob pekmez samples were found to be 0.2-55.80, 1.68-6.47, 1.34-10.69, 1.19-28.46 mg/kg for Na, K, Mg, Ca, respectively. Among the micro elements, the concentrations of Fe, Cu, Zn, Mn and Al in the pekmez samples ranged from 0.2-3.07, 0.02-0.07, 0.07-0.50, 0.06-0.15 and 0.02-0.48 mg/kg, respectively.

Keywords: Carob Pekmez, Macro Elements, Micro Elements, ICP-MS,

Acknowledgements

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Investigation of The Light Effect on Ascorbic Acid Level in Some Local Fruit Juices

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Ascorbic acid (AsA; or vitamin C) is the most abundant antioxidant in the plant cells and plays important roles in a wide range of processes such as photosynthesis, growth regulation and senescence. Additionally, AsA is a cofactor for enzymes and affects the expression of genes involved in defense and hormone signaling pathways [1].

The content of vitamin C in fruits and vegetables is not only directly affected by endogenous factors and developmental signals, but may also be regulated by several external factors such as handling procedures, climatic conditions and cultural practices [1,2]. Temperature and light have a capital influence on the levels of vitamin C and fruits. There are different studies investigating the light effect on the AsA level in harvested plant or fruit juices as much as cultured plants or juices [1,4].

In this study, the affect of exposure light wavelength on the AsA concentration in some local mandarin juices will be investigated by using UV light, yellow light, red light, fluorescent light and darkness. At the beginning of the study, this effect will be evaluated on standard solution of AsA exposed to different wavelengths as blank. Determination of AsA amount will be made by titration method. Fruit juices contain a lot of different materials. Due to complex matrix, determination of the AsA will be planned by using an HPLC method in mandarin juices.

Keywords: Ascorbic Acid, Vitamin C, Light Exposure, Mandarin Juice, HPLC

References:

1. Joanna Lado, Enriqueta Alós, María Jesús Rodrigo, Lorenzo Zacarías, Plant Science (2015) 231 138-147.
2. Lancui Zhanga, Gang Maa, Kazuki Yamawakia, Yoshinori Ikomab, Hikaru Matsumotob, Terutaka Yoshiokab, Satoshi Ohtab, Masaya Katoa, Plant Science (2015) 233 134-142.
3. Lakshmi Nimmagadda, GuruprasadKadurNarayanaswamy, Journal of Plant Physiology (2009) 166 329-332.
4. Lijuan Zhan, Jinqiang Hub, Zhilu Ai, Lingyun Pang, Yu Li, Meiyun Zhu, Food Chemistry (2013) 136 273–278.

Antioxidant and Anticholinesterase Potential of Some Medicinal Plants

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Aphanes arvensis L., *Rosmarinus officinalis* L., *Silybum marianum* L. Gaertner, *Malva sylvestris* L. and *Urtica dioica* L. have been commonly used in traditional medicine all around the world. The hexane, acetone and ethanol extracts of these plants were prepared to determine their total phenolic/flavonoid contents, antioxidant and anticholinesterase activities in the present study.

Total phenolic and flavonoid contents of the crude extracts were carried out as pyrocatechol and quercetin equivalents, respectively (1, 2). The antioxidant activity was performed by DPPH free radical, ABTS cation radical and superoxide anion radical scavenging activities (3-5). The anticholinesterase activity was determined by Ellman method (6).

Total phenolic and flavonoid contents of *A. arvensis* ethanol extract were found to be higher than those of other plant extracts. *A. arvensis* ethanol, *M. sylvestris* hexane and acetone extracts exhibited almost the same free radical scavenging activity with standards (BHA and α -tocopherol) in DPPH assay at 50 and 100 $\mu\text{g/mL}$ concentrations. The acetone and ethanol extracts of *A. arvensis* and *R. officinalis* showed the same ABTS cation radical scavenging activity with BHA and (+)-catechin at 100 $\mu\text{g/mL}$ concentration. None of the extracts indicated superoxide anion radical scavenging effect. *U. dioica* ethanol extract showed higher inhibition against butyrylcholinesterase than galanthamine.

Keywords: Medicinal Plant, Antioxidant, Anticholinesterase, Phenolic Content, Flavonoid Content

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References:

1. Slinkard K, Singleton VL. Am J Enol Vitic (1977) 28 49–55.
2. Moreno MI, Isla MI, Sampietro AR, Vattuone MA. J Ethnopharmacol (2000) 71 109–114.
3. Blois M. S., Nature (1958) 181 1199–1200.
4. Re R, Pellegrini N, Proteggente A, Pannala A, Yang M, Rice-Evans C. Free Radic Biol Med. (1999) 26 1231–1237.
5. Liu, F.; Ooi, V. E. C.; Chang, S. T. Life Sci. (1997) 60 763-771.
6. Ellman G. L., Courtney K. D., Andres V., Featherston R. M., Biochem Pharmacol (1961) 7 88–95.

Inhibitory Effect of Rosmarinic Acid on Human Cervix Carcinoma in Vitro

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Abstract

Origanum bilgeri P.H. Davis including rosmarinic acid was collected from Antalya, Turkey. Aerial parts were extracted with hexane and ethyl acetate. Rosmarinic acid was isolated from ethyl acetate extract by chromatographic techniques (column chromatography, semi preparative HPLC) and the structure was elucidated by spectroscopic method basically 1D-, 2D-NMR and LC-TOF/MS. Antiproliferatif activity of of rosmarinic acid was executed on HeLa (human cervix carcinoma) cell lines and was revealed to possess high inhibitory effect.

Keywords: *Origanum Bilgeri*, Rosmarinic Acid, Hela.

Introduction

The utilization of plants for production of natural recombinant compounds of commercial interest has gained attention over past decades. Natural products have been the source of most of the active ingredients of medicine. 80% of drug substances were natural products or inspired by a natural compound.¹ Bioactive compounds isolated from plants have been used extensively in pharmaceutical, agrochemical, food and pesticide industries.² *Origanum* genus, important aromatic and medicinal plant, mainly distributed in the Eastern Mediterranean region, belonging to the Lamiaceae family is represented by 23 species and six hybrids in the flora of Turkey, 14 of which are endemic³. Due to the wide range of application in food, cosmetic and medicinal industries, *Origanum* is cultivated in several European, Asian and African countries.⁴ Phenolic acids, secondary metabolites of plants, are naturally occurring polyphenolic compounds found extensively in vegetables, fruits and beverages. They are often added into the human diet due to the great health benefits to mankind. Rosmarinic acid is used as a fragrant additive in cosmetics and a food additive to prevent food spoilage.⁵ In this work, rosmarinic acid was isolated from *O. bilgeri* ethyl acetate extract and antiproliferative activity was investigated on HeLa (human cervix carcinoma) cell lines. The result indicated that the rosmarinic acid has strong inhibitory effect on HeLa cell lines.

Materials&Methods

Plant material

O. bilgeri is an endemic species, distributed in Antalya. Its flowering time is July. Its habitat is forestry area, calcareous side of hill, rocky places, and dry stream beds. The aerial parts of *O. bilgeri* were collected from Mahmutlar, Bucak, Cokelek area of Antalya, altitude of 1353 m, coordinate of N: 36° 36' 45" E: 32° 20' 02".

2.3. Extraction and isolation

The areal parts of the plant material were dried and then extracted (0.5 kg) with hexane and ethyl acetate sequentially. Rosmarinic acid was isolated from ethyl acetate extract (2.0 g) by column chromatography (2.5 × 50 cm) using the sephedex LH-20 (50 g) as a stationary phase and methanol as mobile phase.⁶ The structure was identified by spectroscopic methods including 1D-NMR, 2D-NMR and LC-TOF/MS.

Cell proliferation assay

The antiproliferative activity of rosmarinic acid against HeLa cell lines was tested by cell proliferation assay using BrdU Cell Proliferation ELISA kit (Roche). A cell suspension containing nearly 5×10^3 cells in 100 μ L was pipetted into the well cell culture plates (96-well cell). The treatments of cells with compounds in DMSO and 5-Fluorouracil (5 FU) in DMSO separately at concentration 25, 50, 75, 100, 125 150, 175, 200 μ g/mL were carried. The final volume of the wells was adapted to 200 μ L by DMEM and reaction mixture was incubated at 37 °C with 5% CO₂ for overnight⁷.

Results & Discussion

Rosmarinic acid is commonly found in plants belonging to the Lamiaceae family. It was reported to reveal antioxidant, antiinflammatory, anticancer and antiviral activities.⁸ In this work, rosmarinic acid was isolated and antiproliferative effect was investigated on HeLa cell lines and was demonstrated to have excellent antiproliferative activity (Fig. 1).

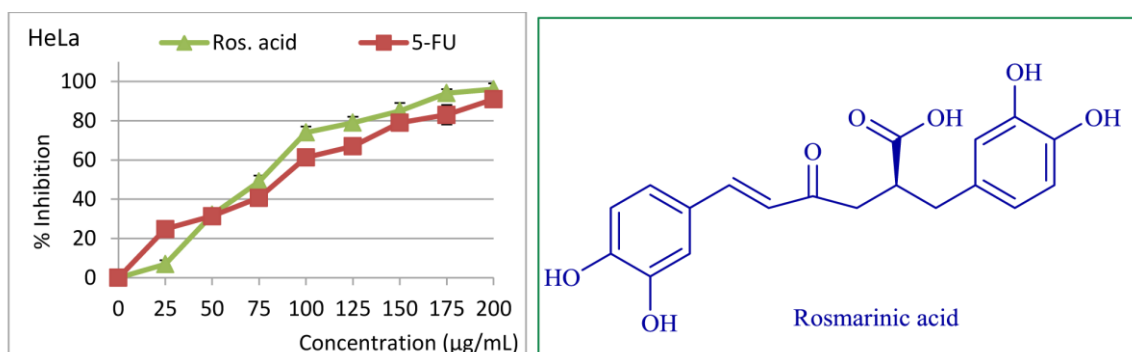


Figure 1. Antiproliferative activity and structure of rosmarinic acid

Rosmarinic acid activity is better than standard, 5-fluorouracil at the concentration of 50 μ g/mL and upper concentrations. This indicates that it has a potency to be a drug against cervix cancer.

Conclusion

Rosmarinic acid is very important compound for pharmaceutical and food industries. Hence, it has a potency to be a drug candidate. Due to the main constituent of the *Origanum* species is rosmarinic acid, cultivation of *Origanum* should be supported to produce the rosmarinic acid. The in vivo and clinical work should be carried out to present the drug potency of rosmarinic acid.

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References

1. Harvey, A. L. (2008), *Drug Discov Today*, 13, 894-901.
2. Newman, D. J. and Cragg, G. M. (2007), *J Nat Prod*, 70, 461-477.
3. Davis, P. H. (1982), *Flora of Turkey and the East Aegean Islands*, Edinburgh University Press, Edinburgh.
4. Erenler, R., Sen, O., Aksit, H., Demirtas, I., Yaglioglu, A. S., Elmastas, M. and Telci, I. (2016), *J Sci Food Agric*, 96, 822-836.
5. Peng, X., Wang, X. C., Qi, W., Su, R. X. and He, Z. M. (2016), *Food Chem*, 192, 178-187.
6. Aksit, H., Celik, S. M., Sen, O., Erenler, R., Demirtas, I., Telci, I. and Elmastas, M. (2014), *Records of Natural Products*, 8, 277-280.
7. Okten, S., Cakmak, O., Erenler, R., Yuce, O. and Tekin, S. (2013), *Turk J Chem*, 37, 896-908.
8. Petersen, M. and Simmonds, M. S. J. (2003), *Phytochemistry*, 62, 121-125.

Efficient Extraction Method of *Origanum rotundifolium* Boiss for High Phenolic Contents and Strong Antioxidant Activity

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Abstract

The dried aerial part of *Origanum rotundifolium* was extracted with hexane, ethyl acetate, methanol and water. The aqueous part of water extract was partitioned with ethyl acetate. After the filtration and removing of the solvents, hexane extract (Extract 1), ethyl acetate extract (Extract 2), methanol extract (Extract 3), water extract (Extract 4) and water to ethyl acetate extract (Extract 5) were obtained. The antioxidant activities of all these extracts were carried out using different antioxidant assays, including 1,1-diphenyl-2-picryl-hydrazyl free radical (DPPH) scavenging, 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) radical scavenging, reducing power. Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and trolox were used as standards. Total phenolic contents of extracts were also determined. In comparison of the extracts, Water to EtOAc extract displayed the most antioxidant activities on all assays and it included the most total phenolic compounds. While the partition of water extract with ethyl acetate, the antioxidant compounds passed to ethyl acetate phase which were responsible for antioxidant activity. Therefore it was presented the best extraction technique for strong antioxidant activity.

Key Words: Antioxidant, Extraction Method, *Origanum Rotundifolium*

Introduction

Due to the consequence of traditional medicine acknowledged by many researchers as an important source of health care, the extraction and purification of bioactive compounds from natural sources have gained the great significance for usage of natural products in the preparation of food ingredients, pharmaceutical and cosmetic products. Therefore extraction techniques play a crucial role in phytochemistry.¹ Due to the difficulty of synthesis, polyphenols, bioactive natural products, play an important role in humans needing to satisfy their phenolic requirements through a daily consumption of fruits and vegetables. Phenolic compounds are effective in treatment of chronic and acute diseases such as cancer, cardiovascular disorders and inflammations². *Origanum* genus belongs to the Lamiaceae family and has 23 species and six hybrids in Turkey flora, 14 of which are endemic.³ *Origanum* widely used in food industry and traditional medicine in many countries is important medicinal and aromatic plant.⁴ Due to the biological and chemical diversities, the demand of *Origanum* in world market has increased steadily. Free oxygen radicals, called reactive oxygen species (ROS), comprising hydroxyl radical, superoxide and singlet oxygen can yield the cellular harm leading to diseases such as DNA damage, cancer, cardiovascular diseases, Parkinson and Alzheimer's disease.⁵ Even though ROS are formed by metabolic functions, they could be scavenged by compounds existence in fruits, vegetables and herbs. Hence, the extracts of fruits, vegetables and herbs containing most antioxidant compounds are important for pharmacology

and food industry⁶. Antioxidants, revealing significant effects for health by reduction of the oxidative stress are used to prevent food from oxidative deterioration.⁷

Materials&Methods

Plant material

The plant materials were collected from Artvin, east part of Turkey during the flowering period and identified by Prof.Dr. Ozgur Eminagaoglu, specialists of Plant Taxonomy at department of Forestry Engineering, Faculty of Forestry, Artvin Coruh University where a voucher specimen was deposited (No: ARTH 5247).

Extraction

Origanum rotundifolium aerial part was dried and powdered (10 g) then extracted with hexane (3 × 100 mL) for a week at room temperature, filtered and solvent was removed to obtain hexane extract (Extract 1). Solid material of hexane extract was re-extracted with ethyl acetate (3 × 100 mL) for a week at room temperature, filtered and after removal of the solvent, ethyl acetate extract was achieved (Extract 2). Methanol extract (Extract 3) was acquired by extracting (3 × 100 mL) the solid part of ethyl acetate extract of *O. rotundifolium* for a week at rt. The solid part of methanol extract was heated with distilled water (200 mL) at 80 °C for 2 hours, filtered then 100 mL of which was lyophilised to get the water extract (Extract 4). The other portion of the water extract (100 mL) was partitioned with ethyl acetate, ethyl acetate phase was separated by separator funnel, dried with (MgSO₄), filtered then solvent was removed to obtain the water to ethyl acetate extract (Extract 5). All extracts were dried and kept in freeze to be analysis.

Antioxidant assays

Determination of total phenolic compounds

Total phenolic contents,⁸ DPPH[•] scavenging assay,⁹ ABTS^{•+} scavenging assay,¹⁰ Ferric ions (Fe³⁺) reducing antioxidant power assay (FRAP)¹¹ were determined according to the literatures.

Results & Discussion

Total phenolic contents

In this work, effective extraction method was developed by a series of extraction techniques to yield the strong antioxidant activities. Interestingly, the total phenolic content of water to ethyl acetate extract (Extract 5) consists of four times as much as phenolic compounds than the methanol extract (Extract 3) which is the second one. This also led to the best antioxidant activities. The order of total phenolic content is as follow: gallic acid/kg extract, Extract 5 (620.5) > Extract 3 (164.7) > Extract 4 (134.6) > Extract 2 (44.9) > Extract 1 (21.9) (Fig.1).

DPPH free radical scavenging activity

The mechanism of DPPH[•] scavenging activity is based on the hydrogen or electron releasing capability of antioxidant molecules to DPPH[•] molecules to form the non radical DPPH-H and the measurement of the reducing ability of antioxidants. In this work, extract 5

exhibited the best DPPH[•] scavenging activity. The scavenging effects of *O. rotundifolium* extracts and standards on the DPPH[•] decreased in the order of Extract 5 > BHA > Extract 3 > BHT > Extract 4 > Extract 2 > Extract 1 that showed the coherence between the activity and total phenolic content.

ABTS radical cation decolorization assay

In this assay, ABTS is oxidised to its radical cation form, ABTS^{•+} which is blue-green coloured. The antioxidant ability of extracts is measured by detecting the decreasing colour due to the reaction of extracts with ABTS^{•+}. The results indicated that except hexane extract, *O. rotundifolium* extracts have high ABTS radical cation scavenging activity, which exhibited the following order (IC₅₀, µg/ml): Extract 5 > BHT > Extract 3 > BHA > Extract 2 > Extract 4 > Extract 1 (Fig.1).

Reducing power

Reduction of Fe⁺³ to Fe⁺² is determined by measuring the absorbance of Perl's Prussian blue complex¹². The reduction capacity of extract exhibits that it has a significant antioxidant potential. Antioxidant compounds in extracts are able to donate electrons to radicals which are reduced to more stable and unreactive species. The reducing power of extracts was investigated by Fe⁺³ to Fe⁺² transformation assay. The reducing power of extracts and standards decreases in the following order (40 µg/ml): BHA (2.74) > Trolox (2.16) > Extract 5 (2.10) > Extract 3 (1.88) > BHT (1.27) > Extract 2 (0.48) > Extract 1 (0.20). This results indicate that water to ethyl acetate extract exhibits as good activity as trolox, better than BHT.

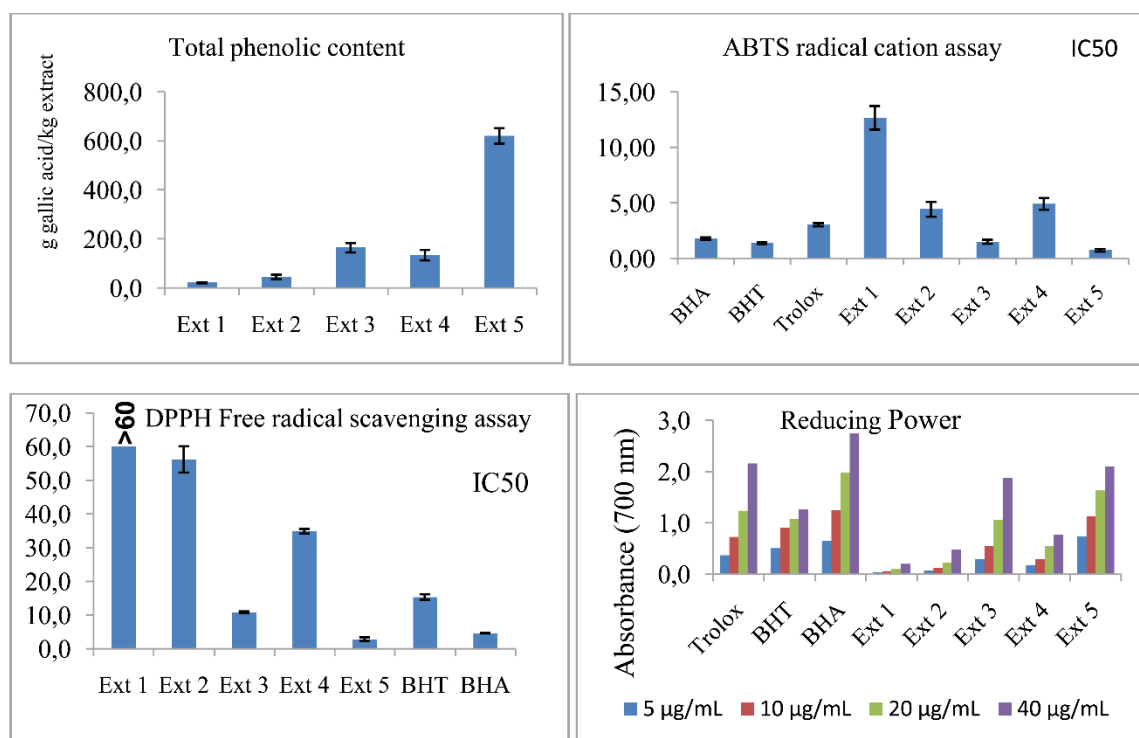


Figure 1. Antioxidant activity and total phenolic content of *Origanum rotundifolium*

Conclusion

The efficient extraction method was developed to yield the high phenolic contents and excellent antioxidant activity. *origanum rotundifolium* has the potency to be used in food industries for natural antioxidant.

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Reference:

1. Zhu, C. P., Zhai, X. C., Li, L. Q., Wu, X. X. and Li, B. Food Chem, (2015) 177, 139-146.
2. Baiano, A., Bevilacqua, L., Terracone, C., Conto, F. and Del Nobile, M. A. J Food Eng, (2014) 120 135-145.
3. Baser, K. H. C. Pure Appl Chem, (2002) 74 527-545.
4. Wakim, L. H., El Beyrouthy, M., Mnif, W., Dhifi, W., Salman, M. and Bassal, A. Nat Prod Res, (2013) 27 1378-1387.
5. Rottkamp, C. A., Nunomura, A., Raina, A. K., Sayre, L. M., Perry, G. and Smith, M. A. Alzheimer Disease & Associated Disorders, (2000) 14 S62-S66.
6. Bae, H. J., Jayaprakasha, G. K., Jifon, J. and Patil, B. S. Food Chem, (2012) 134 1912-1918.
7. Narita, Y. and Inouye, K. Food Chem, (2012) 135 943-949.
8. Slinkard, K. and Singleton, V. L. American Journal of Enology and Viticulture, (1977) 49-55.
9. Blois, M. S. Nature, (1958) 26 1199-1200.
10. Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M. and Rice-Evans, C. Free Radical Bio Med, (1999) 26 1231-1237.
11. Oyaizu, M. Japanese Journal of Nutrition, (1986) 44 307-315.
12. Gulcin, I. Chemico-Biological Interactions, (2009) 179 71-80.

Green Synthesis of Magnetic NPs from Red Cabbage Extract and Their Effect on the Antioxidant Activity

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Nanoparticles have been commonly synthesized by wet traditional chemical techniques, green approaches are emerging novel and alternative techniques for biosynthesis of metal nanoparticles. Those approaches are usually inexpensive, natural, safe, and promising for nanoparticles synthesis and their use in biomedical applications. In here, we report a green and rapid technique using red cabbage (*Brassica oleracea* var. *capitata*) plant extract solution as both reducing and capping agents for the biosynthesis of iron oxide nanoparticles without any chemical additives. We characterized Fe₃O₄-NPs with scanning electron microscopy (SEM), dynamic light scattering (DLS), and Zeta potentials and measured their antioxidant activity to 2,2-Diphenyl-1-picryl-hydrazyl (DPPH) antioxidant assay. The magnetic property of Fe₃O₄-NPs also allowed us to use them repeatedly in antioxidant activity measurement.

Keywords: Biosynthesis, Ironoxide Nanoparticles, Red Cabbage, Antioxidant Activity

Biosynthesized Ag NPs from Berry Fruits (Strawberry, Blackberry, and Raspberry) and Their Effect on Antioxidant Activity

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Many studies have focused on nanoparticles synthesis using plants in the last decade due to their effectiveness in reducing and stabilizing agents. Using plant extract for nanoparticles synthesis is relatively cheap, safe, and simple compared to the use of chemical materials. Herein, we report the biosynthesis of silver nanoparticles (Ag NPs) using extracts of strawberry, blackberry, and raspberry, which are source of antioxidant molecules. The Ag NPs were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy, UV–vis spectroscopy, dynamic light scattering, and zeta potential. Although some plant directed NP showed higher antioxidant activity than free plant extract, we systematically demonstrated that both silver ions (Ag⁺) and Ag NPs cause the severe reduction in antioxidant activity of berries when measured towards 2,2-Diphenyl-1-picryl-hydrazyl (DPPH) antioxidant assay.

Keywords: Green Synthesis, Silver Nanoparticles, Berries, Antioxidant

Chemical Composition and Antioxidant Activities of Extracts Obtain from Mosses of Ida Mountain (Kazdagi) (Canakkale, Turkey)

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Recent pharmacological investigations of bryophytes have proven that the active principles present in these plants are quite unique and having potential chemical application and antioxidant capacity. The mosses of *Plagiomnium undulatum* (Hedw.) T.Kop, *Plagiothecium undulatum* (Hedw.) B.S.G, *Neckera complanata* (Hedw.) Hub., *Platyhypnidium alopecuroides* (Brid.) A.J.E.Sm.were collected from different locations the Ida Mountain (Kazdagi) Canakkale, Turkey, and dried accordingly. Volatiles were isolated from the samples by solid phase microextraction. Gas Chromatography-Mass Spectrometry (GC-MS) was used to identify volatile compounds. Antioxidant activities of moss were tested by Ceric Ion Reducing Antioxidant Capacity (CERAC) and Cupric Reducing Antioxidant Capacity (CUPRAC) methods[1,2]. Trolox equivalent value (TEAC) from water extract of mosses was calculated at concentration range between 0.0109(±0.0008)-0.0212(±0.0009) -trolox/g mosses and from methanol extract 0.0259(±0.0013)-0.0058(±0.0012) by CERAC method and from water extract 0.0027(±0.0006)-0.0083(±0.0012) trolox/g mosses and from methanol extract 0.0035-0.0095(±0.0005) by CUPRAC method. Samples of infusion have higher antioxidant capacity than methanol/water extraction samples. Total flavonoid content was determined as mmol gallic acid/g mosses by AlCl₃/NaNO₂ colorimetric method. The contents of total phenolics were determined by a Folin–Ciocalteu colorimetric method. On the basis of the results it is suggested that the extract of mosses species determined here could be of use as an easily accessible source of natural antioxidant for the treatment. Volatile compounds determined in aldehydes, ketones, alcohols and terpenes. 1-octen-3-one, 1-octen-3-ol, 3-octanone and 3-octanol were common eight-carbon volatiles in all samples.

Keywords: Mosses, Antioxidant Activity, Volatiles, Spectrophotometry, Colorimetry

References:

1. R. Apak, K Güçlü, M Özyürek, SE Karademir, J Agric Food Chem (2004) 52 7970–7981.
2. D. Ozyurt, B. Demirata, R. Apak, Talanta (2007) 71 1155–1165.

Free Radical Scavenging Activity of Extracts Obtain from Some Moss species in Turkey

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Recent pharmacological investigations of bryophytes have proven that the active principles present in these plants are quite unique and having potential chemical application and radical scavenging capacity. The mosses of *Oxystegus tenuirostris* (Hooker & Taylor) A. Smith, *Eurhynchium striatum* (Schreb. ex Hedw.) Schimp, *Rhynchostegium murale* (Hedw.) Schimp were collected from different locations of the Turkey, and dried accordingly. Antioxidant activities of these mosses were tested by Free radical scavenging activity (DPPH• assay) of chloroform, ethanol, methanol and water extracts according to the procedures described by Srinivasan et al. [1]. Moss extract of 0.1 ml were mixed with 1.5 ml of DPPH• reagent and allowed to stand at room temperature for 30 minutes in the dark. The absorbance was taken at 518 nm. RSD is calculated by measuring the average and the third the preparation of each sample. Results are calculated as % reduction. Trolox standard of comparison shows 89 % reduction. Trolox equivalent value from chloroform extract of *Oxystegus tenuirostris* was calculated as reduction 29.03 (±1.36) % , from ethanol extract as 18.92 (±0.99) %, from methanol extract as 46.07 (±4.42) % and from water extract as 24.98 (±1.16) % trolox/g mosses by DPPH method. Trolox equivalent value from chloroform extract of *Eurhynchium striatum* was calculated as reduction 33.94 (±1.77) %, from ethanol extract as 23.92 (±1.16) %, from methanol extract as 24.23 (±0.13) % and from water extract as 26.04 (±0.42) by DPPH method. Trolox equivalent value from chloroform extract of *Rhynchostegium murale* was calculated as reduction 67.12 (±1.48) %, from ethanol extract as 22.74 (±0.51) %, from methanol extract as 20.91 (±1.80) % and from water extract as 12.56 (±1.70) % by DPPH method.

Keywords: Different Solvent Extract Of Mosses, DPPH• Radical Scavenging Activity, Spectrophotometry

References:

1. R. Srinivasan, MJN. Chandrasekar, MJ. Nanjan, B. Suresh, J Ethnopharmacol (2007)113 284–91.
2. Karadağ A. Ozcelik, B. Saner S. Food Anal Methods (2009) 2 41-66
3. Molyneux, P. Songklanakarin J. Sci. Technol. (2004) 26 2 211-219.

Stability Studies on Extracts of Anthocyanins obtained from Berries

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Anthocyanins are important phenolic substances and they have been used as pigmented materials in food industry. Also they exist inside of a large number of fruits and flowers as natural colouring agent and make them colourful from blue to red and purple^[1,2].

There are some studies on stability of anthocyanins at different pH and temperatures by interaction between anthocyanins and the complex organic molecules^[3] and type of interaction^[4,5]. The aim of this study* is to present stabilities of anthocyanin extracts obtained from fruits of blueberry and cranberry after applications of different extraction techniques by using spectrophotometric method.

Keywords: Anthocyanin, Extraction, Extract, Stability, Blueberry, Cranberry.

References:

- [1] Celemente, E., Gali, D. International Journal of Science (2013) 2 12-18.
- [2] L. Vargas y Vargas, M., Tamayo Cortez, J.A., S. Duch, E., P. Lizama, A., H. Herrera Mendez, C. Food and Nutrition Science (2013) 4 1221-1228.
- [3] Mazzaracchio, P., Pifferi, P., Kindt, M., Munyaneza, A., Barbiroli, G. International Journal of Food Science and Technology (2004) 39 53-59.
- [4] Dangles, O., Saito, N., Brouillard, R. mPhytochemistry (1993) 34 119-124.
- [5] Baranac, J.M., Petranovic, N.A., Dimitric-M., J.M., Agricultural and Food Chemistry (1996) 44 1333-1336.

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Determination of Some Phenolic Acids in Walnut (*Juglans regia* L.) Species

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Plants are used as therapeutic since the start of mankind history. Non-consumed part of plants (seed, husk, leaf etc.) are used in pharmacology and alternative medicine. Antioxidants which the plants contain highly are the substances that enable plants to be used for treatment.

Antioxidants are matter that neutralize free radicals, prevent rancidity in foods and deterioration of foods. The structures that provide antioxidant effects are know that phenolic acids, flavanoids, tocopherols. Different parts of plants (roots, leafs, husks, fruits, seeds etc.) are usually rich with regard to phenolic compounds.

It is important to search natural products for human health which contain antioxidant. Because we need to get rid of harmful effects from accumulating toxic matters in our body. So, we need antioxidant matters.

In this study, determination of some phenolic acids (rosmarinic acid, caffeic acid, vanillic acid and ferulic acid) in two types of walnuts (Yalova and Kaman) leaves, green husks and kernels were intended. HPLC-DAD was used in conjunction with C18 column for determination of phenolic acids.

Keywords: Walnut, Antioxidant, HPLC, Phenolic Acids.

References:

1. Akyüz E. (2007) Polygonum bistorta ssp. Carneum bitki ekstraktlarının kromatografik yöntemlerle kimyasal bileşiminin belirlenmesi ve antioksidan ve antimikribyal aktiviteleri, *Yüksek lisans tezi*, Trabzon.
2. Wollgast J. ve Anklam E. (2000) *Food Res. Int.* 33 423-347.
3. Nizamlıoğlu, N.M., Nas, S. (2010) Meyve ve sebzelerde bulunan fenolik bileşikler; yapıları ve önemleri, *Electronic Journal of Food Technologies*, 5 20-35.
4. Tepe B. (2006) Rozmarinik asitin *Satureja hortensis* L. kallus kültürlerinde üretimi ve optimizasyonu, *Yüksek Lisans Tezi*, Cumhuriyet Üniversitesi Fen Bilimleri Enstitüsü.

Comparison of Seven Different C₁₈ Analytical Columns for the Analysis of Pantoprazole Sodium Impurities

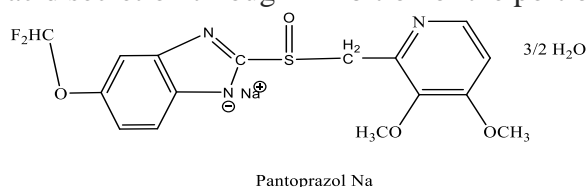
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Pantoprazole sodium a substituted benzimidazole derivative is an irreversible proton pump inhibitor and was developed for the treatment of acid-related gastrointestinal disorders. As with other drugs of its class (e.g., omeprazol or lansoprazole), pantoprazole reduces gastric acid secretion through inhibition of the portion on the gastric parietal cell (1).



In this study, a rapid analytical method was developed and validated against standard method for the pharmaceutical ingredient of Pantoprazole Sodium and these methods was intended to give the results in less time than Ph. Eur. (European Pharmacopoeia) method.

The performance of seven different C₁₈ analytical columns varied with different lengths, particle sizes and porosities were compared for the analytical merits of the developed method). Chromatographic parameters including retention time, limit of detection, limit of quantification, number of theoretical plates and reduced plate height were obtained and compared (2).

During the method development studies, good separation (resolution) could not be achieved or some impurities could not be detected in the chromatogram obtained with silica C₁₈ column. The analysis times of developed methods for determination of impurities are better than Ph. Eur. (European Pharmacopoeia) method. HPLC method was less 15 min. than Ph. Eur. (European Pharmacopoeia) method and UPLC method was less 30 min. than Ph. Eur. (European Pharmacopoeia) method. Analytical method validation was performed for these developed method by meeting the acceptance criterias (3).

Seven different columns were compared: Waters X-Terra RP C₁₈ 4,6x150mm 5µm; Agilent Rapid Resolution C₁₈ 4,6x150mm 1,8µm; Hypersil Gold Termo Separation 4,6x150mm 3µm; Agilent Rapid Resolution C₁₈ 4,6x250mm 5µm; Thermo Separation Hypersil C₁₈ 4,6x250mm 5 µm; Agilent Zorbax SB Phenyl C₁₈ 4,6x250mm 5µm; Restek Ultra Biphenly C₁₈ 2,1x100mm 3µm.

Keywords: Analysis Time, Comparison C₁₈ Column, EP (European Pharmacopoeia), Pantoprazole Sodium And Impurities

References:

1. Badwan A., Lina N. Nabulsi, M.M. Al Omari, Nidal H. Daraghme, Mahmoud K. Ashour, Ahmad M. Abdoh and A. M. Y. Jaber, Analytical Profile of Drug Substances and Excipients (2002) 29 215-257.
2. Y. Sultan, N. Magana, A. Medina, Journal of Chromatography B (2014) 971 89-93.
3. European Pharmacopoeia 7.0 (2011).

A Novel Liquid-Liquid Extraction for the Determination of Naphthalene in Tap Water at Trace Levels by GC-MS with Deuterated Anthracene as Internal Standard

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Polycyclic aromatic hydrocarbons have carcinogenic and mutagenic impacts on human health and also disrupt endocrine system. Naphthalene as the simplest in structure of polycyclic aromatic hydrocarbons has been used in industrial processes for a long time and present in air, soil, and water. Hence, it requires a regulation of its concentration in environmental samples (1, 2). In this study, a simple and fast analytical method was developed to determine the naphthalene in water samples at trace levels by gas chromatography-mass spectrometry after liquid-liquid extraction. All parameters in extraction procedure were optimized to improve extraction recovery, thus reducing the limit of detection. Under the optimum conditions, the limit of detection (LOD) and quantification (LOQ) for naphthalene were found to be 4.4 ng mL⁻¹ and 14.6 ng mL⁻¹, respectively. Deuterated anthracene as internal standard was used to increase the precision of proposed method; thereby relative standard deviation was calculated as 4.3%. The percent recovery of naphthalene from tap water was found in the range 93.8-102.2%.

Keywords: Liquid-Liquid Extraction, Naphthalene, Anthracene D-10, Gas Chromatography Mass Spectrometry

References:

1. Cavalieri E., Rogan E., (1998) "Mechanisms of tumor initiation by polycyclic aromatic hydrocarbons in mammals, in: A.H. Neilson (Ed.), The Handbook of Environmental Chemistry, Part J. PAHs and Related Compounds", Volume 3, Springer-Verlag, Berlin, 81.
2. Coons S., Byrne M., Goyer, M. (1982) "An exposure and risk assessment for benzo(a)pyrene and other polycyclic aromatic hydrocarbons Volume II. Naphthalene. Final draft report", US Environmental Protection Agency, Office of Water Regulations and Standards, Washington, DC.

Analysis of Inorganic Anions in Wines Using Suppressed Ion Chromatography

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The purpose of this study is to determine inorganic anions in wines using suppressed ion chromatography with conductivity detection. Mixed solution of sodium carbonate and sodium hydroxide was used as the mobile phase (Mobile phase: 8.0 mM Na₂CO₃, 1.5 mM NaOH, flow rate: 0.9ml/min.-). Precision of method was found to be high and proposed method was applied for the determination of the inorganic anions in all wines produced in different parts of Turkey.

The results except for fluoride, sulphate anions and all the other anions were determined below the limit value. Limit values of fluoride, chloride, nitrite+nitrate, sulphite, sulphate, phosphate -anions are, respectively, 1 mg.L⁻¹...5 mg.L⁻¹, 60 mg.L⁻¹, 0.3%, 0.2 g.L⁻¹ (ammonium sulphite), 0.3 g.L⁻¹ (ammonium sulphate), 0.3 g.L⁻¹ (diammonium phosphate) according to TKG (Turkish Food Codex), Wine Analysis and Production Book and OIV, the results were evaluated statistically. The sulphite, phosphate was found higher than limit sulphite, phosphate in some wine. White wine sulphite results is found higher than red wine sulphite results. Nitrate and sulphate anions has been found to be high in wine produced in Şarköy. Phosphate anions has been found to be high in wine produced in Denizli.

Keywords: Wine, Anion, Ion Chromatography

References:

1. G. Giovenelli, Susanna Buratti. Food Chemistry (2009) 112 903–908.
2. Dugo, G., Pellicano, T. M., La Pera, L. Food Chemistry (2007) 102, 599–605

Capillary Electrophoretic Determinations of Some Anions in Different Foodstuffs

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Nitrate and nitrite ions occur naturally in the environment and found in most of food products¹. The presence of nitrate in foodstuffs may be considered hazardous because during storage of food prior to ingestion or during digestion in human body they can be reduced to nitrite which may react with naturally present amines to form carcinogenic nitrosamines².

The objective of this research was to determine the concentrations of nitrate and nitrite in variety of foodstuff: i.e. some vegetables, fruits, fruit juices, dairy products, baby foods and herbal tea products, by using capillary electrophoretic method. Experimental conditions used were: pH 3,5, phosphate running buffer (50 mM); temperature 30 °C; applied voltage (-20 kV).

Analyzed vegetables were kale, spinach, chard, carrot and sultane pea. The average amount of nitrate in fresh kale leaves (2016 ± 519 mg/kg) was greater than in spinach and lower than in chard³. Fruits studied were strawberry, apple, pear, quince and plum in both fresh and dry matter. Nitrate and nitrite ions were maximum in strawberries with values (140 ± 2 mg / kg) and (38 ± 24 mg / kg) respectively in fresh fruit. Commercial carrot-apple puree and apple juice were selected as baby foods for this study. Nitrite was not detected in both products. Nitrate content of carrot-apple puree was higher (107 ± 2 mg / kg) than apple juice (29 ± 3 mg / kg). Dairy products (yogurt, fresh kasar cheese, halloumi cheese, cottage cheese and Turkish white cheese) were also examined. Nitrate content was found between 1.30 - 115.64 mg/kg in different cheese samples. Nitrate level in fresh kasar cheese and Halloumi cheese samples were found higher than the maximum acceptable level that is given by Turkish Food Codex (2002)⁴. Nitrate content was found between 1.92 – 8.56 mg/L in different herbal tea samples. The nitrite content of herbal tea products were less than the limit of detection, so nitrite concentrations of herbal tea samples were not determined. All of food products were purchased from local market places in Samsun, Turkey.

Keywords: Nitrate, Nitrite, Foodstuff, Electroosmotic Flow Reversal

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References:

1. S. D. Gangolli, P. A. van den Brandt, et all. European Journal of Pharmacology (1994) 292, 1–38.
2. B. Schuster, K. Lee, J. Food Sci. (1987) 52 1632.
3. B.Yavuz Erdoğan, A. N. Onar. Journal of Animal and Veterinary Advanced (2011) 10 2051-2057
4. Türk Gıda Kodeksi Yönetmeliği (2002) 63 Ek 16- Ek 3.

Environment-Friendly Organic Fertilizers

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Soil samples were taken from Istanbul. This samples excavated from 0-20 cm depth. Then soil samples passed through 2 mm sieve in the laboratory. After some physical, chemical and biomedical analysis were done to soil and made some experiments; for example total nitrogen kjeldal (1), organic matter and ash (2), receivable phosphate (2).

Used waste compost, mushroom compost, chicken manure, sheep manure, goat manure, quail manure, bat manure, obtained from various farm in İstanbul. That fertilizers micro and macro element analysis, pH and C/N ratio was investigated on the soil. And also search leonardit and liquid chicken manure effected on the soil. We want find which organic fertilizers are the most suitable.

In our experiments with sheep manure C/N ratio has risen to 20. Pigeon and sheep manure are rich in organic matter. We find soil pH at 6,79. We examined in fertilizers % N, maximum ratio was found in bat manure. Garbage compost, mushroom compost, cow manure, poultry manure application on the soil after C/N ratio increase in 8, 16, 32, and 45 days in research that is applied to the soil. Organic waste as the dose increases, from the beginning to the end of the study C/N ratio has increased. The effect of liquid chicken manure and leonardit search different doses together on the same soil. Leonardit and liquid chicken manure effects are examined on the pH, when that dose are increased, pH dose also increased. Then find liquid chicken manure provides more efficient results as compared to leonardit.

Organic Fertilizers	time				
	0. day	8. day	16. day	32. day	45. day
Garbage compost	36.88	58.64	41.13	32.18	61.14
mushroom compost	46.41	51.90	37.61	27.52	38.25
cow manure	27.25	35.57	25.45	21.18	32.55
chicken manure	29.78	62.48	34.18	19.99	32.90

C/N rate effects of organic fertilizers on soil

Fertilizers Applications	Leonardit		liquid chicken manure	
	Total N (%)	pH (1/2.5)	Total N (%)	pH (1/2.5)
control	0.099	6.79	0.099	6.79
1. dose	0.212	7.36	0.125	7.11
2. dose	0.216	7.38	0.138	7.13
3. dose	0.219	7.48	0.147	7.16

Total N and pH effect of leonardit and liquid chicken manure on soil

Keywords: Natural Fertilizers, Artificial Fertilizers, Farming

References:

1. Bremner, J.M., (1965) Methods Of Soil Analysis, Part 2, Chemical And Microbiological Properties. In Ed. C.A. Black, American Society Of Agronomy, Inc Pub, Argon Series, No.9., Madison, Wisconsin, U.S.A.
2. Kacar, B. (1972) Bitki ve Toprağın Kimyasal Analizleri II. Bitki analizleri. Ankara Üniversitesi Basımevi, Ankara 646 ss

Tooth-Friendly Chocolate Production

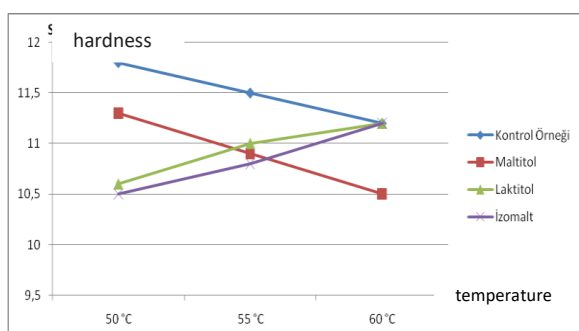
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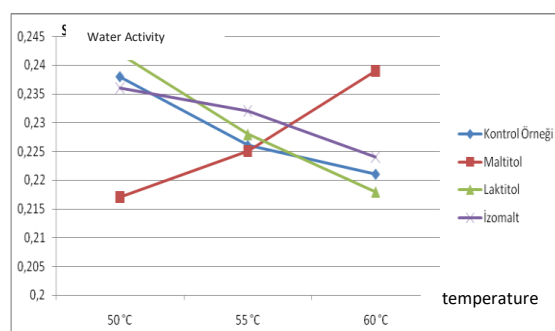
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In this study, as the sugar alcohol maltitol, lactitol, isomalt are used. As the ratio of sugar alcohol in samples of milk chocolate 40% is based on the level of sucrose. Conching temperature: 50, 55 and 60 °C on chocolates textural and sensory structure will be evaluated. 20 micron particle size is performed using products. Conching time 6 hours; 40% provide substitutes for sucrose, maltitol, lactitol, and isomalt containing acesulfame K and aspartame were added in examples the degree of sweetness for balance. Purposes has been prepared. 6 hours of conching operation; 50 °C, 55 °C and 60 °C It was performed on temperature. In the sensory evaluation of the chocolate samples Farzanmehr and Abbasi (2009) changes in the method used by has been used by those who are punished (1). Sokmen and Güneş (2006) study about hardness analysis conducted by applied inflicted by certain changes in the method of used (2). We study hardness analysis change to Sokmen and Güneş methods. Color parameters of chocolate samples were determined by colorimetric method and laser diffraction particle size analyzer used. After the refining process that is applied during the sample preparation stage, the targeted value was determined as 20 µm. Undesired odours from the raw material in chocolate, the removal of aldehydes and ketones according to the working principle of our system and the existing conching time 6 hours, it was observed that the process is ideal. In addition, a control sample and samples containing maltitol shows the increase in hardness of chocolate with the decrease of conching temperature. Lactitol, isomalt decrease in hardness with decrease conching temperature. We have observed that it is more efficient according to maltitol other sugar alcohol. Maltitol gives us better flavour and texture result than the other sugar alcohols. The supply of raw materials can be supplied easily and in a short time maltitol other sugar alcohol is suitable dosage according to use and the cost. Maltitol recommended for tooth friendly chocolate production.



Maltitol and control sample conching temperature — hardness (N) —
İzomalt and lactitol sample conching temperature — hardness (N) —



Maltitol conching temperature — Water Activity —
Control sample, İzomalt and lactitol conching temperature — Water Activity —

Keywords: Tooth-Friendly Chocolate, Maltitol, Acesulfame K

References:

1. Farzanmehr, H., Abbasi, S. (2009) Journal of Texture Studies, 40, 536-553.
2. Sökmen, A., Güneş, G. (2006) Swiss Society of Food Science and Technology. LWT 39 1053-1058.

Simultaneous Determination of Two Preservatives in Various Foods by Capillary Electrophoresis

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Abstract

A simple and rapid capillary electrophoretic method is reported for simultaneous determination of benzoic acid (BA) and sorbic acid (SA) in food products using direct UV detection. Background electrolyte was 20 mM borate buffer, at pH 9.3; internal standard was cinnamic acid. Under the optimized conditions acids were separated in 3.5 min. The concentration ranges of the calibration curves were 0.005 – 0.4 mM. The correlation coefficients for each standard curve exceeded 0.999. Good reproducibility and recovery results were obtained using internal standard. Detection limits of BA and SA (Signal-to-noise ratio=3) are 0.405 µg/mL for BA and 0.415 µg/mL for SA.

Keywords: Capillary Electrophoresis, Benzoic Acid, Sorbic Acid, Foods

Introduction

Sorbic acid (SA) and benzoic acid (BA) are common food additives, which are used to prevent the growth of yeasts, molds, and bacteria in food and beverages. They are considered as generally safe food additives. However, these preservatives in high doses may be harmful to consumers due to their tendency to induce allergic reactions. The use of these preservatives have been limited. Consequently, in order to protect consumer health, the development of analytical methods for detecting additives and their levels in food products has practical demand for ensuring compliance to existing government regulations. Various analytical methods for the determination of preservatives in food products have been reported, including GC [1] HPLC [2-4], CE [5-7]. HPLC is the most common analytical procedure for the detection and quantification of these preservatives in foods. The drawback of HPLC is the need of pre-separation step before injecting the sample to the packed columns and the high amount of consumed organic solvents. Capillary electrophoresis (CE) is a powerful separation technique that can provide high resolution efficiency and is becoming a standard tool for the analysis of many compounds. Good resolution and low sample consumption are common advantages attributed to this technique. In CE, even if the sample contains a matrix, it can be injected with minimal sample preparation without decreasing the separation performance. The capillary between injections is rapidly flushed with fresh buffer. It is therefore a suitable method for the analysis of food products.

Both BA and SA are the most active in foods of low pH due to their pK_a values (4.19 and 4.76 respectively). These two acidic preservatives are used as a substitute for each other. However, the combinations of these preservatives are often used in some consumed food products in Turkey.

In the present study, a CE method was applied to various food samples in the Turkish markets for the simultaneous determination of BA and SA. The samples were dissolved or suspended in water/methanol solution and injected directly to a simple buffer solution without any other pretreatment step. In order to improve the quantitative determination of the preservatives, cinnamic acid (CA) was used as internal standard, of which migration time was well match with BA and SA peaks.

Materials&Methods

All experiments were carried out with an Agilent CE system from Agilent Technologies (Waldbronn, Germany). A diode array detector was employed for the detection. The wavelength was set at 220 nm. Instrument control and data analysis were performed by use of Agilent CE ChemStation on a PC. In separations, a 38cmx50µm I.D. fused silica capillary (Polymicro Technologies, Phoenix, AZ, USA) was used. The total length of capillary was 46 cm. The temperature of the capillary tubing was maintained at 25⁰ C during electrophoresis. The electrophoretic separation was performed with an electric potential of 28 kV. Samples were pressure 50 mbar for 4s. The capillary was flushed with 1M NaOH, water and running buffer each for 10min at the beginning of each day. A washing step of 1 min with buffer between runs was applied. All chemicals were analytical reagent grade. All of the food samples were bought at a local market. Stock solutions of BA, SA, and CA were prepared in water as 1 mM of each, and stored in a refrigerator.

1-2 g of homogenized samples were weighed in a beaker. 20 mL of methanol-water solution (40/60, v/v) was added and mixed for 30 min. The samples were centrifuged a 7000 rpm for 5 min and filtered through a 0.45µm membrane filter. Fatty foods were weighed (about 0.1 g) and then dissolved in 1 mL of hexane. 5 mL of 5 mM borate buffer was added and extracted. Internal standard solution was added to filtrates and extracts, they was diluted to suitable volume. The resulting solution was injected directly. Liquid samples were diluted ten times with water. For recovery experiments, the known amount of BA and SA solutions were added to the food sample solutions.

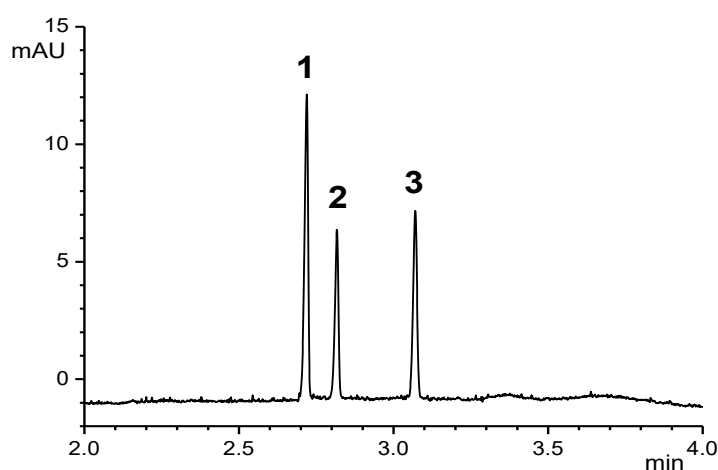


Fig.1. Electropherogram of standards. Peaks: (1) CA, (2) SA, (3) BA. Experimental conditions: 20 mmol/L Borate, pH 9,3; injection, 4 s at 50 mbar; temperature 25⁰C; run voltage 28 kV.

Results&Discussion

The borate buffer was used for analyzing of BA, SA, and CA. Optimum conditions were achieved by using 20 mM borate buffer at pH 9.3. Fig.1 shows the electropherogram of a standard sample mixture at optimum conditions. BA and SA samples are injected directly to the simple borate buffer and peaks come less than 3.5 min.

Method validation

Calibration curves between the concentrations of anions and peak area ratios (A_a/A_{IS}) were used for quantitative determinations. Regression equations for BA and SA were $y = 8.140 \cdot 10^{-1} x - 9.558 \cdot 10^{-4}$ and $y = 6.474 \cdot 10^{-1} x - 3.459 \cdot 10^{-3}$ respectively. The calibration curves show linear dynamic ranges from 0.005-0.4 mmol/L with an average correlation coefficient of 0.9998 and 0.9999 respectively for BA and SA. The detection limits of the CE method were sufficiently low for the determination of anions in food samples. Limit of detection (LOD) for BA corresponding to a signal/noise ratio of 3 is 0.405 µg/mL and for SA is 0.415 µg/mL.

Repeatability (interday and intraday) was studied to obtain the method precision. Intraday analysis was established by the injection of the standard mixture of cations five times at the same day. Interday repeatability was determined by analysing the standard mixture on 3 different days. The relative standard deviations (R.S.D., %) of the intraday and the interday studies are $\leq 0.55\%$ and $\leq 2.54\%$ for migration time and $\leq 2\%$ and $\leq 3.44\%$ for peak area, respectively. The accuracy of method was checked with both peak purity analysis with diode array detector and the determination of analytes in food samples spiked with standards. The recovery values for the analytes in ketchup and margarine samples ranged from 97%-103%.

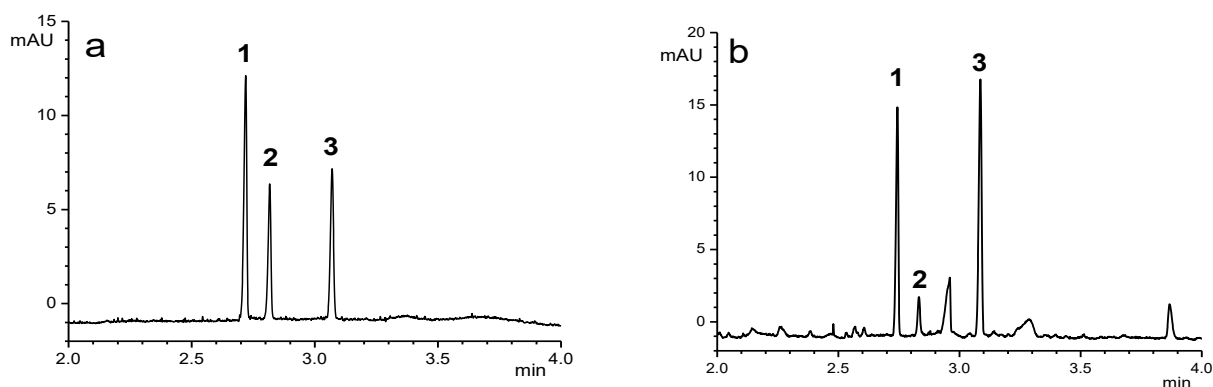


Fig.2. Electropherogram of analytes in the soft drink (a) and candied chestnut (b). Other conditions as in Fig. 1.

Application to food samples

Thirteen food products were analyzed using the optimized CE method. The electropherogram of soft drink sample are presented in Figs. 2. Sample solutions were prepared as described above and a known amount of CA solution was added as internal standard to all injection samples.

As seen from Fig. 2b, in the electropherograms of some samples, there were unknown peaks in working region, but peaks of analytes were seen clearly. Table 1 gives the results of analysis food products.

Table 1. Results for the determination of BA and SA in various food products.

Food Sample	BA (mg/kg or mg/L)	SA (mg/kg or mg/L)
Lemon sauce	4.36 ± 0.121	235.5 ± 0.9
Pickle	126.98 ± 1.1	127.3 ± 0.9
Soft drink	234.9 ± 0.9	178.5 ± 0.7
Ketchup A	463.2 ± 1.0	75.29 ± 1.8
Ketchup B	452.7 ± 1.4	n.d.
Candied chestnut	200.5 ± 1.9	251.5 ± 1.9
Green Olive	13.09 ± 1.7	600.7 ± 1.5
Pepper paste	495.5 ± 1.8	10.51 ± 0.44
Pepper sauce	182.8 ± 1.6	188.5 ± 1.2
Cake	n.d.	600.7 ± 2.0
Pomegranate syrup	341,6 ± 1.8	297,6 ± 1.8
Margarine	n.d.	905,3 ± 2.7
Mayonnaise	n.d.	1019 ± 3.6

Conclusion

A simple, fast and reliable CE method with direct UV detection for the simultaneous determination of BA and SA in foods was described. The advantages of the method for food samples are short sample preparation and analysis time, low electrolyte and sample consumption. It provides good reproducibility, recovery and selectivity. The CE method is a good alternative to HPLC for the analysis of preservatives in food products. Fused silica capillaries are less expensive than chromatographic columns, easily washed between runs and free of irreversible contamination of the matrix, unlike the packed columns. The results indicate that the proposed method is useful for routine simultaneous analysis of BA and SA in many kinds of food samples.

References:

1. Sun Y, Wang X, Huang Y, Pan Z, Wang L, *J. Sep. Sci.* (2013) 36 2268-2276.
2. Can NO, Arli G, Lafci Y, *J. Sep. Sci.* (2011) 34 2214-2222.
3. Kamankesh M, Mohammadi A, Tehrani ZM, Ferdowsi R, Hosseini H, *Talanta* (2013) 109 46-51.
4. Molognoni L, de SáPlôêncio LA, Valse AC, Lindner JDD, Daguier H, *Talanta* 147 (2016) 370-382.
5. Xue Y, Chen N, Luo C, Wang X, Sun C *Anal Methods* (2013) 5 2391-2397
6. Ding XJ, Xie N, Zhao S, Wu YC, Li J, Wang Z, *Food Chem.* (2015) 181 207-214.
7. Hsu, SH, Hu, CC, Chiu, TC, *Anal. Bioanal. Chem.* (2014) 406 635-641.

A Screening Study: Analysis of Umbelliferone in Different Plants from Apiaceae Family by Capillary Electrophoresis

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Plants have been the main source of medicines since ancient times because they contain components of therapeutic value. Furthermore, the increasing use of plant extracts as therapy against diseases requires a vast investment of research. In order to find active compounds, a systematic analysis of medicinal plants is required. Umbelliferone, also known as 7-hydroxycoumarin, is a widespread natural product of the coumarin family with confirmed with antioxidant and anti-inflammatory activities [1]. The main focus of this study is to screen the amount of umbelliferone in different medicinal plants. Since the bioactivities of plants can be related to coumarins, umbelliferone has been suggested for use as a marker compound for the quality of plants.

In this study, separation of this compound was successfully achieved by capillary electrophoresis (CE). The background electrolyte (BGE) was selected as borate. β -cyclodextrin (β -CD) served as the modifier that was added in BGE to improve the sensitivity. Considering these factors, an optimal buffer condition, which was 20 mM borate with 5 mM β -CD at pH 9.6 was constructed for the determination of umbelliferone. The method was applied for several plants namely *Angelica Sylvestris*, *Ammi visnaga*, *Ammi majus*, *Anethum graveolens*, *Conium Maculatum*, *Heracleum Graveolens*, , and *Chaerophyllum aureum*. Seeds and aerial parts of the plants were dried and finely powdered. 0.5 gram of the dried materials were placed into 10 mL of methanol and submitted to ultrasonicator for 1 hour.

The LOD and LOQ value for the developed method were 1.05 and 3.50 μ g/mL for umbelliferone, respectively. The developed method is simple, reliable and yields short analysis time (about 3.0 min).

Keywords: Apiaceae, Umbelliferone, Capillary Electrophoresis, β -CD.

References:

1. Jiang, Q., Yi, M., Guo, Q., Wang, C., Wang, H., et al. Int. Immunopharmacol. (2015) 29 370–376.

Comparison of Gas Phase Volatile Organic Compounds' (VOC) Concentrations in Samples taken by Active and Passive Sampling Techniques

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Volatile Organic Compounds (VOCs) consists of plenty compounds with different boiling points and molecular weights. To estimate the VOC levels in air samples, active and passive sampling techniques are the most preferred methods. However, there is lack information regarding the associations between both techniques. Levels of indoor VOCs were measured in 6 homes located in three different towns of Canakkale, Turkey. In this study, indoor VOC samples were collected by both active and passive sampling techniques and air samples were collected throughout a year. VOC samples were collected on to Tenax TA-Carbograph1TD dual-bed sorbent tubes and analyzed by Thermal Desorber-GC-Flame Ionization Detector with a capillary column. Concentrations of benzene, toluene, xylenes, and total volatile organic compounds (TVOC) were assessed. TVOC concentrations were quantified as toluene-equivalent. Indoor VOC samples were collected by a low-flow air sampling pump once a month by active sampling (US EPA, 1999), while a sampling tube was located into the sampling sites for about 1 month-period by passive sampling technique. Concentrations of benzene toluene, and xylenes in the passive samples were estimated according to the uptake rates given for the sorbents used in this study by ISO standard (ISO, 2003). Calculated concentrations from passive and active samples were compared for each target compound. Estimated concentrations of the target compounds in passive and active samples showed variations. A total of 53 sample-pairs were categorized according to concentration ratio between pairwise Active and Passive samples (A/P). Toluene, xylenes, and TVOC levels were found to be higher in more than half of the passive samples, while benzene levels were found to be higher in 64,7% of the active samples (see Table 1). Furthermore, total score (0-4) for each sample calculated by summing up each $A/P \geq 1$ pair for all 4 target compounds, showing that all 4 compounds were observed in 66% of the sample pairs and concentrations found to be underestimated in 28% of the samples by active sampling.

Table 1. Frequencies (%) of A/P ratios for target compounds

Target compound	N	Frequency (%) of $A/P \geq 1$	Frequency (%) of $A/P < 1$
TVOC	53	48	52
Benzene	34	64,7	35,3
Toluene	43	21	79
Xylenes	41	43,9	56,1

Keywords: Volatile Organic Compounds, Air Sampling, Passive sampling, Active Sampling.

Acknowledgement: This study was financially supported by The Scientific and Technological Research Council of Turkey (TUBITAK). Project no: 112Y059.

References:

1. ISO (2003). ISO 16017-2: Indoor, ambient and workplace air-Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography - Part 2, ISO.
2. US EPA (1999). Compendium Method for the Determination of Organic Compounds in Ambient Air TO-17, EPA/625/R-96010b.

Amperometric Determination of Putrescine Over Polyfuran Film

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Small organic molecules with multiple amine groups are ubiquitous in living organisms, in food products and in the environment. One of these organic compounds called biogenic amine, putrescine is an aliphatic diamine base that has an important role at synthesis of nucleic acid and protein in cell. Putrescine is formed in the process of decarboxylation of the amino acids, arginine and ornithine. Despite its vital function in human organism, it also has toxic effect due to its excessive endogenous production or intake from the exogenous sources [1]. Moreover, it has been reported that certain types of cancer produce an increase of putrescine concentration in some human tissues [2]. Thus, putrescine is listed as a tumor marker and its determination in clinical samples can be important for diagnosis of malignancy and even for monitoring the efficiency of treatments, such radio or chemotherapy diseases [3, 4]. Putrescine content in food can also be considered as a freshness marker and be used as an indicator of microbial spoilage [5]. The electrochemical synthesis and properties of conducting polymers have been studied primarily because of their technological interest. In particular polyaniline, polypyrrole, polythiophene, and their derivatives have been the subject of several studies. Polyfuran (PF), however, has not received similar attention due to the low conductivity, need high polymerizing potential and low stability. But PFu can be more conductive polymer when polymerized with different electrolytes containing perchlorate [6]. Furthermore, PF is not overoxidized in aqueous media at high potentials that other conducting polymers are. So, PF is more suitable for amperometrically determining biogenic amines required high oxidation voltage in aqueous media [7].

In this work, polyfuran modified platinum electrode (Pt/PF) prepared for determination of putrescine in human serum. Black adherent polyfuran film was deposited on Pt electrode by potentiostatically (2.30V) in the acetonitrile solution containing tetrabutylammonium perchlorate and the experiments were carried out in a buffer solution (pH 2.0) consisting NaHSO₄/Na₂SO₄. The experimental results indicate that the current response is more sensitive than Pt electrode. The limit of detection (LOD), limit of quantification (LOQ), linear dynamic range and the regression coefficient (R^2) of Pt/PF modified electrode determined as 6.60×10^{-4} , 2.21×10^{-3} , 2.21×10^{-3} to 125 mM and 0.997 at 1.20 V, respectively. The reproducibility was investigated by using three different PF films and good analytical results were obtained. The modified electrode was successfully employed to determine putrescine in human serum with good recoveries.

Keywords: Polyfuran, Biogenic Amine, Putrescine, Amperometry

References:

1. N. Minois, D. Carmona-Gutierrez, F. Madeo, Aging (Albany NY) (2011) 3 716–732.
2. L. Nagy, G. Nagy, R. Neuman, E. Lindner, J. Biochem. Biophys. Methods (2002) 53 165–175.
3. S. Nowotarski, P. Woster, R. Casero Jr., Expert reviews in molecular medicine (2013) Feb 22;15:e3.
4. M. Park, K. Igarashi, Biomolecules & Therapeutics (Seoul) (2013) 21 1–9.
5. Silla Santos MH. International Journal of Food Microbiology (1996) 29 213–31.
6. M. González-Tejera, E. Sánchez de la Blanca, I. Carrillo, Synthetic Metals (2008) 158 165–189.
7. M. Koppang, M. Witek, J. Blau, G. Swain, Analytical Chemistry (1999) 71 1188–1195.

Preparation of Graphene Based Hydrogen Peroxide Sensitive Biosensor for Determination of Glucose

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Graphene, a thinnest two-dimensional carbon material, can provide an ideal platform for metal nanomaterials deposition or enzyme adsorption on electrodes due to its unusual electronic conductivity, electron flexibility and mobility, large specific surface area, excellent mechanical stability [1]. We design a sensitive electrochemical sensor for glucose based on a glassy carbon electrode that was modified with a nanocomposite containing graphene, gold nanoparticles (Au-NPs) and nafion.

High-quality graphene (GR) was produced by an effective chemical method using Hummers' method. [2-3] GR/NFN(Nafion) preparation, the NFN solution was added to obtain 0.25 (m/v) nafion concentration in the GR solution. The quantification of glucose can be achieved via electrochemical detection of the enzymatically unchained H_2O_2 . The immobilization of glucose oxidase (GOD) over Nafion-solubilized metal nanoparticles dispersed graphene and electrode has been achieved by cross-linking with glutaraldehyde. The performances of the biosensor have been investigated by electrochemical method at an optimum potential of +0.6V in pH 7.0 phosphate buffer. In our study glucose biosensor based on immobilization of GOD in Au nanoparticles/graphene/NFN nanocomposite film is responsive to a low concentration of H_2O_2 ($\sim 5\mu\text{M}$) and two different linear determination ranges of 10^{-4} - 10^{-3} M (shown in figure-1) and 10^{-3} - 10^{-1} M are detected. According to literature values [4-6] our sensor has low detection limit and long linear range among to other studies. This properties shows us our sensor is good candidates for biochemical applications.

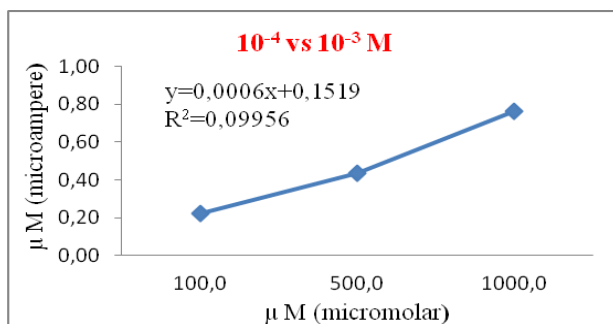


Figure 1 Concentration vs. Current between 10^{-4} - 10^{-3} M H_2O_2 +0.6V in pH 7.0 phosphate buffer

Keywords: Graphene, Biosensors,

References

1. Y.Fang, D.Zhang, Y.Guo, Q.Chen Sensors and Actuators B (2015) 221 p.265-272.
2. W.S.Hummers, R.E.Offeman, J.am.Chem.Soc. (1958) 80 1339.
3. R. Ning, W.B. Lua, Y.W. Zhang, X.Y. Qin, Y.L. Luo, J.M. Hu, A.M. Asiri, A.O. Al-Youbi, X.P. Sun Electrochimica Acta, (2012) 60.
4. E. Jin, X.F. Lu, L.L. Cui, D.M. Chao, C. Wang Electrochimica Acta (2010) 55 p. 7230.
5. X.X. Liu, H. Zhu, X.R. Yang Talanta (2011) 87 p. 243.

Graphene-based Modified Electrode for the Simultaneous and Sensitive Determination of Chlorogenic Acid, Vanillin and Caffeine in Food Samples

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Chlorogenic acid (CGA), a biologically important phenolic compound, is a member of hydroxycinnamic acid group found in apples, pears, peaches, plums, cherries, and among other fruits, and also in beverages such as coffee and tea. Vanillin (VAN) is a unique and highly prized food additive as flavor enhancer. This compound is widely used to contribute to the fragrance of commercial foods such as pudding, ice-cream, custard, cookies, chocolate, and beverages. Caffeine (CAF) is a naturally occurring alkaloid widely distributed in natural products, commonly used as a flavoring agent in a variety of beverages. CAF may be also considered as the most widely used drug in the world. With respect to the above mentioned facts, the individual and/or simultaneous determination of CGA, VAN and CAF is important for the quality (taste and health benefit of the product) in foods. Despite the fact that these molecules are electrooxidizable at several electrodes, however, bare electrode materials have rarely been used for their analysis. The main reason is the problem of electrode surface fouling and regeneration for CGA and VAN, or high oxidation potentials of VAN and CAF where oxygen evolution current interferes. Our research group has recently reported some papers dealing with the voltammetric determination of CGA [1], VAN [2], and CGA+CAF [3] using boron-doped diamond electrode.

In this work, a graphene-modified glassy carbon electrode was fabricated and used for the simultaneous determination of CGA, VAN and CAF. The electrochemical behaviors of these three compounds were investigated by cyclic voltammetry, and square-wave adsorptive anodic stripping voltammetry. By using stripping mode in phosphate buffer solution at pH 2.5 for simultaneous determination of CGA, VAN and CAF, their electrochemical oxidation peaks appeared at +0.54, 0.83 and 1.40 V, and good linear current responses were obtained with the detection limits of 0.0013, 0.046 and 0.055 µg mL⁻¹, respectively.

The proposed electrochemical sensor was successfully applied for quantifying CGA, VAN and CAF in commercial food samples using a simple pretreatment.

Keywords: Chlorogenic Acid, Vanillin, Caffeine, Graphene-Based Modified Glassy Carbon Electrode, Simultaneous Determination, Food Samples

Acknowledgements

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References:

1. Y. Yardım, J. Food Sci. (2012) 77 C408-C413.
2. Y. Yardım, M. Gülcan, Z. Şentürk, Food Chem. (2013) 141 1821-1827.
3. Y. Yardım, E. Keskin, Z. Şentürk, Talanta (2013) 116 1010-1017.

A Novel Glucose and H₂O₂ Biosensor Based on Nafion and Amine Functionalized Reduced Graphene Oxide

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Herein, we have fabricated a novel enzymatic glucose biosensor using glucose oxidase (GOx) immobilized onto amine functionalized reduced graphene oxide (rGO-NH₂) modified glassy carbon electrode (GCE) and a non-enzymatic H₂O₂ sensor. The electrochemical properties of the modified electrode was investigated using electrochemical impedance spectroscopy, cyclic voltammetry, and amperometry. The resulting nafion/rGO-NH₂/GOx/GCE and nafion/rGO-NH₂/GCE composites showed good electrocatalytical activity toward glucose and H₂O₂ respectively. The nafion/rGO-NH₂/GCE exhibited a linear range concentration for H₂O₂ from 0.03 to 6.1018 mM with a correlation coefficient of 0.994 and a detection limit of 0.018 mM. The nafion/rGO-NH₂/GOx/GCE showed a linear range concentration for glucose from 0.05 to 3.960 mM with a correlation coefficient of 0.999 and a detection limit of 0.025 mM. Besides, the fabricated biosensors showed a sensitivity of 10.83 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and an acceptable selectivity for glucose and a sensitivity of 7.16 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ for H₂O₂.

Keywords: Amine Functionalized Reduced Graphene Oxide, Gox, Nafion, H₂O₂.

References:

1. Binesh Unnikrishnan, Selvakumar Palanisamy, Shen-Ming Chen. Biosensors and Bioelectronics (2013) 39 70-75.
2. Zhimin Luo , Lihui Yuwen, Yujie Han, Jing Tian, Xingrong Zhu, Lixing Weng, Lianhui Wang. Biosensors and Bioelectronics (2012) 36 179–185.
3. Muhammet Guler, Vedat Turkoglu, Arif Kivraf. Int. J. Biol. Macromol (2015) 79 262–268.

An Enzymatic Glucose Biosensor and Sensitive Enzyme-Free H₂O₂ Sensor Based on Reduced Graphene, Co₃O₄, Aad Ionic Liquid Nanocomposites Modified Glassy Carbon Electrode

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A nanocomposite material consisting of amine functionalized graphene oxide (GO-NH₂), Co₃O₄, room temperature ionic liquid (IL: 1-Butyl-3-methylimidazolium hexafluorophosphate), and glucose oxidase (GOx) was prepared and used to construct a glucose biosensor for the detection of glucose in biological fluids. The incorporation of IL into Co₃O₄@GO-NH₂ has increased the sensitivity of both Co₃O₄@GO/IL/GOx/GCE and Co₃O₄@GO-NH₂/IL/GCE. The Co₃O₄@GO/IL/GOx/GCE biosensor showed good electrochemical performance for glucose. The linear response of the biosensor to glucose was from 0.04 to 3.747 mM with a correlation coefficient of 0.999, sensitivity of 73.02 $\mu\text{A mM}^{-1}\text{ cm}^{-2}$, and limit of detection of 25 μM . Also, the Co₃O₄@GO-NH₂/IL/GCE exhibited good response to H₂O₂. The linear response of the sensor to glucose was from 0.029 to 5,235 mM with a correlation coefficient of 0.996, sensitivity of 170.98 $\mu\text{A mM}^{-1}\text{ cm}^{-2}$, and limit of detection of 12 μM . According to these results, the fabricated biosensor and sensor can be used for glucose and H₂O₂ in real samples.

Keywords: Amine Functionalized Reduced Graphene Oxide, Gox, Co₃O₄, H₂O₂, Ionic Liquid.

References:

- 1 J.R, Anusha, Hee-Je Kim, Albin T. Fleming, S. Jerome Das, Kook-Hyun Yu, Byung Chul Kim, C. Justin Raj. Sensors and Actuators B (2014) 202 827-833.
- 2 Shibu Saha, Sunil K. Arya, S.P. Singh, K. Sreenivas, B.D. Malhotra, Vinay Gupta. Biosensors and Bioelectronics (2009) 24 2040-2045.
3. Jinping Liu , Yuanyuan Li, Xintang Huang, Zhihong Zhu. Nanoscale Research Letters (2010) 5 1177 1181.

Electrochemical Glucose Biosensing via New Generation Conducting Polymers/Gold Nanoparticles/Glucose Oxidase Modified Electrodes

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The biosensors can be described as chemical sensors in which the recognition system utilizes a biochemical mechanism [1]. In this study, a novel approach for constructing different glucose biosensors using conducting polymers of 4-(4H-dithiynol[3,2-b:2',3'-d]pyrrol-4-yl)aniline (DTP-Ph-NH₂) and 4-(4H-dithiynol[3,2-b:2',3'-d]pyrrol-4-yl)-[1,1'-biphenyl]-4-amine (DTP-Ph-NH₂) is proposed. The synthesis of derivatives of dithione pyrrole (DTP) is a hot subject that has been studied extensively. After the synthesis and characterizations of the dithione pyrrole type monomers, they were used in glucose biosensing applications. The surface of gold electrode was modified with mercaptoethane sulfonic acid and paminothiophenol functionalized gold nanoparticles (AuNPs) and aniline modified Glucose oxidase (GOx). Electrochemical measurements were carried out by following the consumed oxygen due to the enzymatic reaction of glucose oxidase. DTP-Ph-NH₂/AuNP/GOx and DTP-Ph-Ph-NH₂/AuNP/GOx biosensors showed very good linearity between 0.1 and 2.5 mM, and 0.05 and 1 mM for glucose, respectively. LOD value was obtained for pDTP-Ph-NH₂/AuNP/GOx as 5.00×10^{-2} mM and for pDTP-Ph-Ph-NH₂/AuNP/GOx as 9.86×10^{-5} mM using S/N ratio. Optimization of molar ratio amount of AuNP/GOx, cycles amount to immobilize AuNP/GOx, conducting polymer thickness were examined. Finally, under optimized conditions, the amount of glucose in spiked human serum samples and recovery experiments were conducted [2].

Keywords: Glucose Biosensors, Conducting Polymers, Gold Nanoparticles, Aniline Modified Glucose Oxidase

References:

1. D.R. Thevenot, K. Toth, R.A. Durst, G.S. Wilson, Electrochemical biosensors: recommended definitions and classifications, *Biosens. Bioelectron* (2001) 16 121–131.
2. Azak, H., Kurbanoglu, S., Yildiz, H. B., Ozkan, S. A. Electrochemical glucose biosensing via new generation DTP type conducting polymers/gold nanoparticles/glucose oxidase modified electrodes. *Journal of Electroanalytical Chemistry* (2016) 770 90-97.

Gold Electrodeposited and Graphene Immobilized Glassy Carbon Electrode as Non-enzymatic Electrochemical Cholesterol Sensor

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Cholesterol is an important compound which needed for biosynthesis of hormones, vitamin D or forth substances [1]. The overabundant of this essential lipid may cause several diseases such as brain thrombosis, anemia, hypolipoproteinemia, malnutrition hypertension, septicemia and arteriosclerosis etc. [2]. To avoid of these diseases accurately and reliable determination of cholesterol in human serum is very important. For this aim, colorimetric, fluorometric and chromatographic techniques and hybrid systems have been used [3].

This study includes the preparation of new surfaces through the immobilization of graphene onto the glassy carbon electrode and electrodeposition of gold at the graphene decorated surface. Bare glassy carbon and modified carbon electrode surfaces were characterized with atomic force microscope and scanning electron microscope.

The microscopic characterization results showed us that the graphene film on the glassy carbon electrode surface provided an ideal matrix for electrodeposition of gold as compared to the bare electrode surface. The modified surfaces were evaluated for the design of non-enzymatic cholesterol sensor. The electrochemical results approved the high sensitivity of proposed system for cholesterol determination.

Keywords: Cholesterol Sensor, Electrochemistry, Electrodeposition, Graphene, Gold Nanostructures

References:

1. A.N. Kozitsina, A.V. Okhokhonin, A.I. Materna, Journal of Electroanalytical Chemistry (2016) 772 89-95.
2. A. Hayat, W. Haider, Y. Raza, J. L. Marty, Talanta (2015) 143 157-161.
3. X. Lin, Y. Ni, S. Kokot, Sensors and Actuators B: Chemical (2016) 233 100-106.

Conducting Polymer of 10-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)decan-1-amine] As an Immobilization Matrix for Microbial Biosensing Based on Gluconobacter Oxydans

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Microbial based biosensors are suitable for the control of biochemical processes. Microbial based biosensors involving bacteria, yeast or fungi find applications such as in waste water treatments, brewing industries and detection of pesticides [1-3]. The advantages of microbial based biosensors are found in many places, can be adapted to different conditions, they are more resistant than the enzyme electrode. Cells are particularly useful for multi catalyzes. Recent research efforts have been directed towards entrapping biomolecules within electrochemically synthesized conjugated polymers. These polymers were frequently used in amperometric microbial electrodes to enhance the electron transportation reaction between electrode and microbial reactions via branched conducting network.

In this work, novel amperometric microbial biosensor was developed using amine functionalized conducting polymer with G. Oxydans. Biological materials were immobilized with the help of glutaraldehyde. pH optimization, polymer thickness optimization studies were performed for biosensor and the analytical characterizations of the biosensor well achieved. Designed conducting polymer have the biocompatible character due to its amine functional group resulted in a microbial biosensor.

Keywords: Microbial Based Biosensor, Conducting Polymers, G. Oxydans

Reference:

1. A. Gupta, V.K. Singh, G.N. Qazi, A. Kumar, J. Mol. Microbiol. Biotechnol (2001) 3 445–456.
2. Y. Lei, W. Chen, A. Mulchandani, Anal. Chim. Acta (2006) 568 200–210.
3. I. Vostiar, E.E. Ferapontova, L. Gorton, Electrochem. Commun (2004) 7 621–626.

Preparation of Screen-printed Carbon Electrode Modified Rosmarinic Acid: Application as Redox Mediator for Biosensor

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Rosmarinic acid (RA) is a hydroxycinnamic acid derivative and a naturally occurring phenylpropanoid that is commonly found in species of the Boraginaceae family, the subfamily Nepetoideae of the Lamiaceae family. The antioxidants are redox agents, and both electrochemical and chemical oxidations of these compounds have been studied [1]. Dehydrogenase based biosensor need nicotinamide adenine dinucleotide (NAD⁺) as a coenzyme. Reduced form NADH generated in the enzymatic reaction is oxidizing on the electrode surface at suitable potential and electrooxidation of NADH is detected. Electrooxidation of NADH at high overvoltage causes irreversible formation of enzymatically inactive forms of NAD⁺ and contamination (fouling) of electrode surface due to adsorption of these products which results in background currents leading to interferences in the analysis of real samples. Various mediators, polymers and nanomaterials (NMs) have been widely used in modification of electrodes to lower this high overpotential and thus minimize the side reactions [2]. The main aim of the present research is used by RA as new redox material to the electrooxidation of NADH at lower potential. As the biosensor application of RA modified SPCE is utilized determination of ethanol.

RA was deposited on SPCE by potential cycling between -0.1 to +0.8 V for 5 cycles in at a scan rate of 20 mV s⁻¹ a solution containing 1 mM RA, 50 mM pH 7.0 PBS. 1 mg ADH was dissolved in 10 µL 50 mM PBS of pH 7.0. Then 5 µL of this solution was spread over the working electrode surface of RA modified SPCE (SPCE/RA). It was then allowed to dry 1 hour at 4 °C. In order to stabilize the activity of biosensing enzyme layer, ADH was cross-linked with GA.

Figure 1 represents the cyclic voltammograms of 0.5 mM ethanol, 2 mM NAD⁺ and buffer obtained with SPCE/RA/ADH. The cyclic voltammograms were obtained in a series of concentrations of ethanol and are given in Figure 2. The anodic current was an enhancement with the addition of ethanol. Ethanol was detected amperometrically by applying a potential of +0.20 V (vs. Ag pseudo reference electrode). Measured current plotted vs ethanol concentration gave a sensitivity and a correlation coefficient of 1.14 µA.mM⁻¹ and 0.993, respectively.

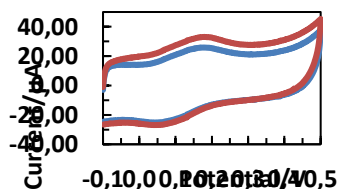


Figure 1. CVs obtained with SPCE/RA/ADH at a scan rate of 50 mV s⁻¹ in 50 mM pH 7.0 PBS (in 0.1 M KCl) containing no ethanol (inner CV) and containing 0.5 mM ethanol (outer CV)

Keywords: Rosmarinic Acid, Alcohol Biosensor, Screen-Printed Electrode, Antioxidant

References:

1. Park, S.U., Uddin, M.R., Xu, H., Kim, Y.K., Lee, S.Y., Afr. J. Biotechnol (2008) 7 4959-4965.
2. Sahin, M., Ayranci, E., Electrochimica Acta (2015) 166 261–270.

Pulsed Deposited MnOx-VOx/Gold Nanoparticles and Carbon Nanotubes Modified Glassy Carbon Electrode and Its Biosensing Applications

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Transition metal oxides are used in a wide range of applications in various fields due to their abundant sources and low cost. Molybdenum and manganese oxides have received a special attention owing to their remarkable electronic, catalytic, and electrochromic properties depending on the synthesis procedure. The nature of the deposit can also be controlled by changing the deposition parameters and a mixed-valent metal oxide (MeOx) film can be produced by this means on a glassy carbon electrode [1]. Electrochemical Pulsed Deposition (PD) technique is becoming popular as the pattern of applied potential determines the composition and morphology of MeOx [2]. A recent study has shown that PD deposited Mn-Mo oxide film on glassy carbon electrode (GCE) and further decorated with Pt nanoparticles can be used as a catalytic platform for monitoring oxygen reduction reaction (ORR) [3].

Dissolved oxygen is usually consumed during the enzymatic reactions thus; its detection is very interesting for the development of biosensors. This study reveals the catalytic activity of gold nanoparticle modified manganese and vanadium oxide film (AuNPs/MnOx-VOx) co-deposited on carbon nanotube modified glassy carbon electrode (GCE) towards ORR and their use in biosensing technology, i.e. glucose sensing.

The biosensor was prepared by mixing the glucose oxidase enzyme (GOx), chitosan and ionic liquid with 25 μ L of pH 7.0 sodium phosphate buffer solution. Afterwards, 25 μ L of this mixture were dropped onto the AuNPs/MnOx-VOx/CNT/GCE surface and kept in a refrigerator for 1 h in +4 °C. The electrode was then dipped into the sodium phosphate buffer solution and kept in 5 min. These novel electrodes were tested upon glucose biosensors (Fig.1).

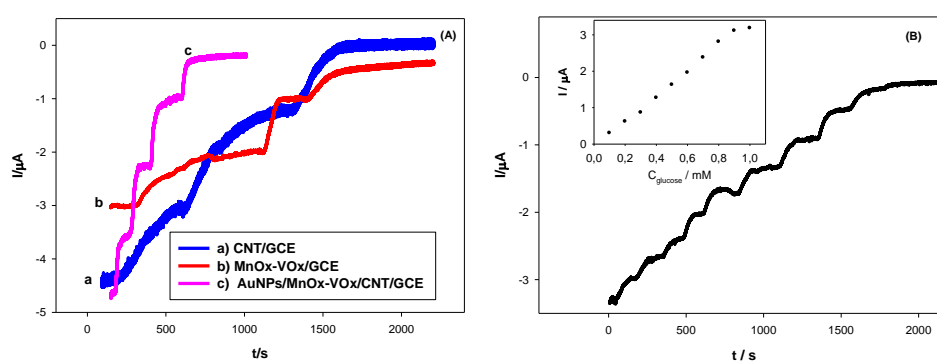


Fig.1. Chronoamperometric response for glucose concentration at the different modified biosensor platforms (A) and calibrations graphs (B).

Keywords: Pulsed Deposition, Metal Oxide, Oxygen Reduction Reaction, Sensors

References:

1. E. Yavuz, K.V. Özdokur, I. Çakar, S. Koçak, F.N. Ertaş, *Electrochim. Acta* (2015) 151 72–80.
2. S.H. Lee, H. Lee, M.S. Cho, J.D. Nam, Y. Lee, J. Mater. Chem. A (2013) 1 14606–14611.
3. K.V. Özdokur, B. Demir, E. Atman, A.Y. Tatlı, B. Yılmaz, D.O. Demirkol, S. Kocak, S. Timur, F. N.Ertas, *Sensors and Actuators B: Chemical* (2016) 237 291-297.

Simultaneous Determination of B-Group Vitamins at Metal Nanoparticle Poly(Taurine) and Carbon Nanotube Modified Electrode by Voltammetry

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Vitamins constitute a group of compounds, which are essential for the normal growth and functioning of the human body. Vitamin deficiency can lead to many diseases, thus there is an increasing interest in the development of suitable and reliable methods for quantifying vitamin on complex samples in many fields [1,2]. Some chromatographic, spectrophotometric/fluorimetric and electrophoretic methods were recently proposed for determining vitamin B. Moreover, microbiological assays, biosensor and potentiometric methods were also proposed. Voltammetric methods were also reported, since they are particularly suitable due to their high sensitivity and low cost [3].

In the present work, we have observed the electrochemical behaviour of vitamin B6 and B9 was investigated at Pt and Au nanoparticles modified poly(taurine)/GC electrodes. Modified electrodes were characterized with electrochemical impedance spectroscopy (EIS), Atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques. The best catalytic activity was obtained at Au nanoparticles modified electrodes for simultaneous determination of vitamins (Figure 1). Finally, modified electrodes are used for the determination of B vitamins in pharmaceutical preparations.

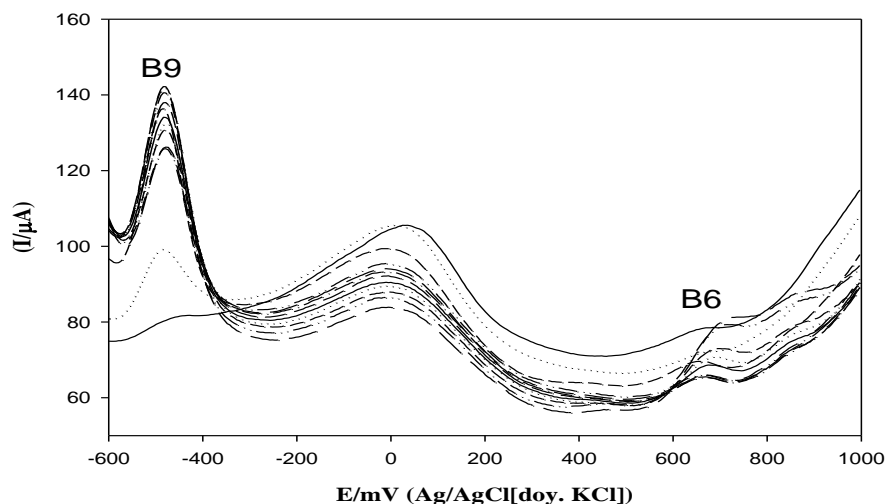


Figure 1. Square wave voltammograms for vitamins B9 and B6 at AuNPs/Poly(Taurine)/CNT/GCE

Keywords: Metal Nanoparticles, Poly(taurine), Vitamin B.

References:

- 1 R.C. Barthus, L.H. Mazo, R.J. Poppi, J. Pharmaceut. Biomed. Analysis (2005) 38 94–99
- 2 B. Brunetti, E. Desimoni, J. Food Comp. Analysis. (2014) 33 155–160
- 3 Z. Zhoub, C. Tanb, Y. Zheng, Q. Wang, Sens. Actuator. B (2013) 188 1176–1182

Determination of Sesamol in Tahini Halva Samples at Boron Doped Diamond Electrode by Square Wave Voltammetry

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Sesamol (3,4-methylenedioxyphenol), a phenolic component of lignans and a major natural component of sesame seed oil, has been shown to have cardioprotective, antiatherogenic, chemopreventive, and anti-aging properties, and even anti-cancer effects [1,2]. Most of all, sesamol is best known for its antioxidant, as well as anti-inflammatory, effects [3]. Tahini halva is consist of sesamol.

Boron doped diamond (BDD) is a one of the novel carbon-based material, which has been studied more in detail in last 20 years [4]. The most relevant feature of this material is high overpotential for the oxygen and hydrogen evolution causing the fact that BDD electrodes have absolutely the widest working potential range of currently using working electrodes [4].

In this work, we developed an electrochemical method for detection of sesamol. Square wave voltammetry (SWV) had a good sensitivity for detection of sesamol on the BDD electrode. The electrochemical behavior of sesamol oxidation was investigated at BDD electrodes in 0.1 M H₂SO₄ solution. The linear concentration ranges were found between 0.5 to 1000 µM ($R^2 = 0.9981$) (Fig.1). The limit of detection (LOD) and limit of quantitation (LOQ) values were calculated to 0.15 µM and 0.5 µM, respectively. Finally, BDD electrode is used determination of sesamol in different tahini halva samples. This electrode has good stability, sensitivity, reproducibility and selectivity. The proposed method has also been practically and successfully applied for the determination of sesamol.

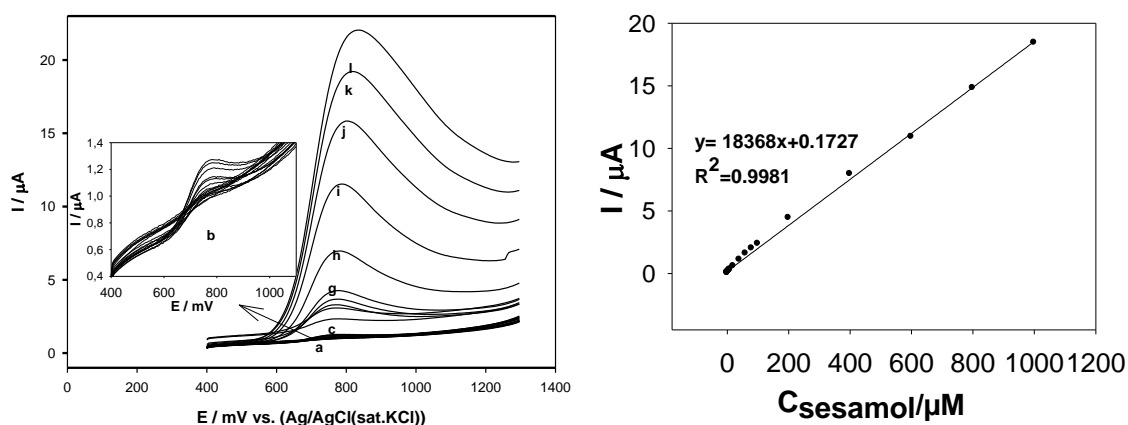


Figure 1. Square wave voltammograms of different sesamol concentrations at (a) 0.1 M H₂SO₄, (b) 0.5- 10 µM, (c) 20, (d) 40, (e) 60, (f) 80, (g) 100, (h) 200, (i) 400, (j) 600, (k) 800, (l) 1000 µM.

Keywords: Sesamol, BDD Electrode, Tahini Halva, Square Wave Voltammetry.

References:

1. A. Kuhad, K. Chopra, Exp. Brain Res. (2008) 185 411-420.
2. D.Z. Hsu, Y.W. Chen, P.Y. Chu, S. Periasamy, M.Y. Liu, Biomed. Res. Int. 2013 (2013) 481827.

3. O.Tokusoglu, S. Koçak, S.Aycan, Grasas Y Aceites, (2009) 60 2 119-124.
4. K. Pecková, J. Musilová, J. Barek, Cr. Rev. Anal. Chem. (2009) 39 148-172.

P2-72

Determination of C-Reactive Protein by ITO Based Disposable Biosensor System: A New Immunosensor Design from an Old Molecule

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C-reactive protein (CRP) is a member of the pentraxin family of proteins that participates in the systemic response to inflammation. In humans, CRP is the most sensitive acute phase reactants, with serum levels rising as much as 1000- fold following injury or infection and measures of plasma CRP levels are used clinically as a biomarker of inflammation. The identification and validation of biomarkers for diagnosing Alzheimer's disease (AD) and other forms of dementia are increasingly important. Considerable studies proof that inflammation process is associated with Alzheimer's disease (AD) pathology, CRP level is increased in the brain and serum of patients with Alzheimer's disease(AD). Based on the importance of CRP in patients with AD, novel, cost effective and disposable biosensor system has been designed to determine C-reactive protein for diagnosis and monitoring treatment. The biosensor was based on the indium tin oxide (ITO) electrodes modified by 11 cyanoundecyltrimethoxysilane which is very new organo-functional silanes. Anti C-reactive protein (anti-CRP) was covalently immobilized on to poly amidoamine dendrimer (PAMAM). To monitor immobilization and optimization steps of biosensor, cyclic voltammetry (CV), square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS) techniques were applied. To achieve reproducible and repeatable biosensor system, all parameters such as self assembled mono layers (SAMs) concentration, antibody concentration, and PAMAM concentration were optimized. The present biosensor has wide determination range and showed repeatable and reproducible characteristics which are hopeful for using in medical fields as a diagnostic tools.

We are thankful for financial support from the Scientific and Technological Research Council of Turkey (TÜBİTAK, Project number: 113 Z 678).

Keywords: ITO (indium tin oxide), Alzheimer Disease, CRP, Immunosensor

References:

1. C. Reitz, Alzheimer disease: Epidemiology, diagnostic criteria, risk factors and biomarkers Biochemical Pharmacology (2014) 88 640-651
2. Koji Yasojima, Claudia Schwab, Human neurons generate C-reactive protein and amyloid P: upregulation in Alzheimer's disease, Brain Research, (2000) 887 80-89

Study of Disposable ITO Electrode Modified with Organosilanes to Determine SOX2 : A Novel Sensitive and Regenerative Biosensor

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SOX2 plays critical roles in the embryonic development of several tissues and in organogenesis[1,2]. In recent years, SOX2 has been investigated intensively and found to be associated with induced pluripotent stem cells [3]. It also contributes to tumorigenesis and the recurrence of certain types of human cancer. Overexpression of SOX2 has been demonstrated in small-cell lung cancer, pancreatic intra-epithelial neoplasia, cancers of the stomach, prostate and colon, and squamous cell carcinomas of different organ sites [4].

In this study, an ITO (indium tin oxide) based biosensor was designed to determine SOX2. Firstly ITO electrodes were modified with $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ to obtain the OH groups on the surface. Later, the surface of ITO electrodes were modified with 11-cyanoundecyltrimethoxysilane. After SAM formation, anti-SOX2 was covalently immobilized onto the electrodes. All parameters such as 11-cyanoundecyltrimethoxysilane (11-CUTMS) concentration, anti-SOX2 concentration and incubation time, SOX2 incubation time were optimized to prepare a sensitive, reproducible, repeatable and stable biosensor. For determining the immobilization steps and optimization of the biosensor, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were used. To determine analytical characterization of proposed biosensor; linear range, repeatability, reproducibility, regeneration studies were done. In optimum conditions, the linear range biosensor of the biosensor was determined as 0,02 pg/mL – 2 pg/mL. Square wave voltammetry technique was applied to the biosensor. These steps were realised in $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ redox probe. Shelf life of designed biosensor was investigated. SEM (Scanning Electron Microscope) technique was used to determine the morphology of the surface in every step. To determine whether the impedance spectra of the designed biosensor are affected from the deviation obtained because of external factors, Kramer's Kronig transform was used. Finally, the designed biosensor was applied to real human serum and hopeful results were obtained.

We are thankful for financial support from the Scientific and Technological Research Council of Turkey (TÜBİTAK, Project number: 113 Z 678).

Keywords: SOX2, electrochemical impedance spectroscopy, ITO electrodes

References

1. Kamachi Y, Uchikawa M, Kondoh H. Pairing, Trends Genet. (2000) 16 182–187.
2. Graham V, Khudyakov J, Ellis P, Pevny L, Neuron (2003) 39 749–765.
3. Takahashi K, Tanabe K, Ohnuki M, Cell (2007) 131 861–872.
4. Maier S, Wilbertz T, Braun M, Hum. Pathol. (2011) 42 1078–1088.
5. Neumann J, Bahr F, Horst D, BMC Cancer (2011) 11 518.

Electrochemical Determination of H₂O₂ in Flow Injection Analysis System with Using Platinum Nanoparticles Modified Pencil Graphite Electrode

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Hydrogen Peroxide (H₂O₂) is a significant molecule in many fields like food science, chemistry, environmental sciences, pharmaceutical and clinical applications. Also H₂O₂ forms from many enzymatic reactions containing peroxidase enzymes [1]. Moreover its toxic effects are well known in living organisms [2]. Due to these reasons, fast, sensitive and selective detection of H₂O₂ is important in construction of sensors/biosensors. Many methods have been proposed for its determination including spectrometry, titrimetry, and electrochemistry. Among them, electrochemical methods have found great attention because of its high sensitivity, ease of operation, and low cost [3]. Accordingly, researchers are focusing on the new electrocatalysts to decrease the overpotential and increase the kinetics of electron transfer [4]. Among them, metal nanoparticles (Au, Pd, Pt, Ag) have been widely used in increasing electron transfer between electrode surface and substrate because of their high conductive properties, large surface areas and they also show high catalytic activity to many molecules [5, 6].

In this work, Pt nanoparticles modified Pencil Graphite Electrode (PGE) was used for the electrocatalytic oxidation of H₂O₂. For this, Platinum nanoparticles (PtNPs) electrochemically deposited on PGE surface by recording cyclic voltammograms of 1.0 mM of H₂PtCl₆ solution in 0.1 M KCl at scan rate of 50 mV/s with 30 cycles. Surface morphologies of PGE and modified electrodes (PtNPs- PGE) were examined by recording their Scanning Electron Microscope (SEM) images which indicate PtNPs were successfully decorated on PGE. Finally, electrochemical oxidation of H₂O₂ was investigated by recording cyclic voltammograms of PGE and also PtNPs-PGE in 0.1M NaOH solution at scan rate of 50 mV/s. Cyclic voltammograms show that the peak potential of H₂O₂ oxidation shifts from +700-800 mV at bare PGE to +50 mV vs. Ag/AgCl /KCl (sat) at PtNPs-PGE. This result showed that PtNPs-PGE exhibit a good electrocatalytic activity towards oxidation of H₂O₂. Then, electrocatalytic determination of H₂O₂ was performed in Flow Injection Analysis (FIA) system under optimized conditions using a new homemade electrochemical flow cell which was constructed for PGE for the first time. As a result, it can be concluded that this study shows the first study on the amperometric FIA determination of H₂O₂ using PtNPs modified PGE.

Keywords: Hydrogen Peroxide, Pencil Graphite Electrode, Flow Injection Analysis, Platinum Nanoparticles.

References:

1. Md. Abdul Aziz, Abdel-Nasser Kawde Microchimica Acta (2013) 180 837-843.
2. Barbara E. Watt, Alex T. Proudfoot, J. Allister Vale Toxicological Review (2004) 23 51-57.
3. M. A. Aziz, A. N. Kawde, N. Baig, Y. Temerk J. Electroanalytical Chemistry (2015) 740 68-74.
4. L. Challier, F. Gal, G. Carrot, H. Perez, V. Noel Electrochemistry Communications (2013) 28 118-121.
5. X. L. Luo, A. Morrin, A. J. Killard, M. R. Smyth Electroanalysis (2006) 18 319-326.
6. W. W. Zhao, M. Xiong, X. R. Li, J. J. Xu, H. Y. Chen Electrochemistry Comm. (2014) 38 40-43.

Electrocatalytic Determination of NADH in Flow Injection Analysis System at Pyrocatechol Violet (PCV) Modified Pencil Graphite Electrode

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NADH (induced form of β - Nicotinamide adenine dinucleotide) is an important coenzyme for production of energy in human cells [1]. NADH plays roles in many biosynthetic reactions. It is also known that it catalysis more than 250 enzymes [2] and has been used for the construction of electrochemical biosensors. The electrochemical oxidation of NADH has received considerable attention due to these important functions. Chemically modified electrodes (CMEs) have been widely used for electrocatalytic oxidation of NADH [1-3] due to its highly irreversible oxidation with a great overpotential at a bare electrode. For this aim many redox mediators have been used for electrocatalytic oxidation of NADH. Among them, Pyrocatechol violet (PCV), which is a sort of sulfone phthalein dye obtains from pyrocatechol and *o*-sulphobenzoic acid anhydride, has also been used as a an effective redox mediator [4]. However, our literature search showed that PVC modified Pencil graphite electrode (PGE) has not been used for the electrocatalytic determination of NADH in Flow Injection Analysis (FIA) system.

In this work, electrocatalytic determination of NADH has been described in FIA using PCV modified PGE for the first time. Modified PGE was prepared through immersion of PGE into 10^{-2} M PVC solution in water for 10 min. Cyclic voltammograms of bare PGE and modified PGE were recorded in the absence and presence of NADH in Phosphate Buffer solution (PBS at pH 7.0) at scan rate of 20 mV/s. Cyclic voltammetric studies show that the peak potential of NADH oxidation shifts from +450 mV at bare PGE to +200 mV vs. Ag/AgCl /KCl (sat) at PVC/PGE. This result showed that PVC modified PGE exhibit a good electrocatalytic activity towards oxidation of NADH. Then, electrocatalytic determination of NADH was performed in FIA system under optimized conditions using a new homemade electrochemical flow cell which was constructed for PGE for the first time. The electrocatalytic currents obtained from amperometric measurements in FIA at +200 mV vs. Ag/AgCl /KCl (1.0 M) and at pH 7.0 PBS containing 1.0 M KCl were linearly related to the concentration of NADH. As a result, it can be concluded that this study shows the first study on the amperometric FIA determination of NADH using PVC modified PGE.

Keywords: NADH, Pyrocatechol Violet, Pencil Graphite Electrode, Flow Injection Analysis

The authors are grateful to TUBİTAK (Project Number: 115Z235) for financial support.

References:

1. L. Gorton, E. Dominguez Encyclopedia of Electrochemistry, Bioelectrochemistry (Ed:G.S.Wilson) Wiley-VCH, Weinheim (2002) 9 67-143.
2. E. Simon, P. N. Barlett Biomolecular Films, Design, Function and Applications (Ed:J. F. Rushling), Marcel Dekker, New York, (2003) 499-544.
3. Kumar, Jun Zhu, Xiao-Yan Wu, Dan Shan , Pei-Xin Yuan, Xue-Ji Zhang, Talanta (2014) 155 78–84.

The Electrochemical Determination of Cu(II) from Different Copper Salts by the Application of The Graphene Oxide-modified Glassy Carbon Electrode

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Heavy metal composition of environmental samples is of interest because of their essential or toxic nature. For this reason the evaluation of heavy metal concentration is of special interest and it has been attracted considerable attention [1]. To accurate and precise determination of these ions several analytical techniques such as flow injection, amperometric, gravimetric, optic and stripping analysis etc. are available for the determination of metals with sufficient selectivity [2]. One of the ways to perform these applications has been possible by electrochemical and/or chemical modification of electrode surfaces [3,4]. Due to its relative low cost and good analytical performance, electrochemical instruments are the main device for the determination of metals in many laboratories. From the point of this view, in this study graphene oxide (GO) and reduced graphene oxide (rGO) nanoparticles were synthesized by Hummers method. Then application of graphene oxide-modified glassy carbon electrode (GO/GC) for the electrochemical determination of Cu(II) from different copper salts such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and CuCl_2 was performed by differential pulse voltammetry, square wave voltammetry and open circuit potential. The GO/GC electrode was found to be suitable for selective determination of Cu(II) in the solutions containing the mixture of heavy metal ions and showed high stability and reproducibility.

Keywords: Electrochemical Determination, Copper Salts, GO, rGO, Heavy Metal.

References:

1. Tokaloğlu S., Gurbuz F., *Food Chem.* (2010) 183-187.
2. Pena-Pereira F., Lavilla I., Bendicho C., *Spectrochim. Acta B*, (2009) 1-15.
3. Oztekin Y., Ramanaviciene A., Ramanavicius A., *Electroanalysis*, (2011) 701-709.
4. Oztekin Y., Ramanaviciene A., Yazicigil Z., Solak A.O., Ramanavicius A., *Biosensors and Bioelectronics*, (2011) 2541-2546.

The Investigation of Electrochemical Behavior of Amine Compounds on Glassy Carbon Electrode

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The modified electrodes are given targeted properties with the modification of a conductive substrate and these electrodes have different properties from unmodified substrate. Also knows that; electrochemical behaviors of electrodes is able to change with various materials which are absorbed to electrode surface.

In this study; the electrochemical behaviors of diphenylamine, triphenylamine and triphenylphosphine on the Glassy Carbon (GC) electrode surface in both aqueous and non-aqueous media were investigated by using of cyclic voltammetry (CV). Pt wire, Ag/AgCl and glassy carbon electrode were used as counter, reference and working electrode, respectively. In order to provide aqueous media for the modification experiments, Britton Robinson (BR) buffer solution was chosen at pH=7. Electrochemical characterization was realized with CV technique in the presence of redox probes as potassium hexacyanoferrate III (HCF(III)) and Ferrocene in the suitable conditions of their own potential range, scan rate and solvent. After that the result was obtained and compared with the bare GC. It has been realized that the all electrodes modified with amine compounds used.

After that the differences for capacity of metal holding were examined. From these results, Cu compound was selected and the optimum conditions was determined. For this, copper solutions (1.10^{-2} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) with Br buffer solutions at pH 2, 5, 8 and 11 were prepared. DPV (Differential pulse voltammetry) method was used for experiment of holding metal capacity. The optimum pH was found to be as 5 for copper solutions. Then a stock solution of copper was prepared for finding the optimum concentration. Different concentration of copper solution (1.10^{-2} , 1.10^{-4} , 1.10^{-6} , 1.10^{-8}) was prepared. Optimum concentration was found to be as 1.10^{-2} . GC electrodes with used compounds was modified and the these electrodes in copper solutions which prepared in optimum conditions. After all these experiments, it was obtained that the used compounds have different capacity for holding metal.

Keywords: Diphenylamine, Triphenylamine, Triphenylphosphine, GC, DPV, Metal Holding Capacity

References:

1. Burcu Kömürcü, "Amine compounds' electrochemical modifications, characterization and applications of modified surfaces" MSC thesis (in progress) Selcuk University, Graduate School of Sciences, Master thesis (in progress)

Amperometric Determination of Hydroquinone in The Presence Of Phenol and Catechol in River Water over Polycarbazol - Polyaniline Copolymer Film

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Phenol compounds are plentiful in nature. They are extremely harmful to animals, plants, and aquatic environments even at very low concentrations. It is a widely used as stabilizer in the paint industry, a lightening agent in dermatology, an antioxidant for fats and in cosmetics, medicines, varnishes, photography, motor fuels, oils, dyes, photostabilizer, plasticizers, pesticides and some pharmaceuticals^[1-3]. It is a highly reactive molecule and can produce active oxygen species through redoxcycle. Therefore, it can be metabolized to benzoquinones which are potentially haematotoxic, genotoxic and carcinogenic compounds^[4]. Every year, it was estimated that living beings and environment were exposed to this substance from many sources. Due to the exposure of alives, it can cause sensitization and irritation in the nose, throat and eyes, tiredness, headache, tachycardia and kidney damage^[5].

For determination of HQ, Polycarbazole homopolymer and polycarbazole - polyaniline copolymer films were synthesized on the Pt electrode in dichloromethane (CH₂Cl₂) medium containing 33 mM HClO₄, 100 mM TBAP by potentiodynamic method for the first time and optimum conditions were determined. The characterization of the synthesized films was carried out by using some methods, such as cyclic voltammetry, FT-IR, Raman, UV-vis, SEM and EDS. In the second part of the study, electrochemical behavior of the films was examined using cyclic voltammetry in aqueous solution containing NaHSO₄ / Na₂SO₄ (pH 2.0- 6.5) and the optimum condition was determined as to be the pH 4.0^[6]. Electroanalysis of hydroquinone with amperometric I - t method (between from 0.40 V to 0.60 V) was successfully performed using these modified electrodes. The best analytical data (limit of detection (LOD) , limit of quantification (LOQ), linear range and regression coefficient (R²) were calculated as to be 2.43x10⁻⁴ mM, 8.08x10⁻⁴ mM, 8.08x10⁻⁴ – 85.0 mM and 0.9982, respectively) in optimum conditions (pH 4.0 and 0.55 V) was obtained by the use of PC- PANI film. The results were compared with uncoated Pt electrode. The reusability of films was tested in the optimum conditions in which the best analytical results were obtained. Determination of hydroquinone in the presence of phenolic compounds containing hydroxyl group using artificially contaminated river water samples with hydroquinone, phenol- hydroquinone, catechol- hydroquinone and fenol-catechol- hydroquinone was carried out and high satisfactory recovery values were obtained.

Keywords: Polycarbazole, Polyaniline, Copolymers, Hydroquinone, Amperometry

References:

1. M.U. Anu Prathap, B. Satpati, R. Srivastava, Sensors and Actuators B (2013) 186 67–77.
2. JJ Nordlund, PE Grimes, JP Ortonneş, Journal of the European Academy of Dermatology and Venereology (2006) 20 781–787.
3. D. Davidson, R.Courage, C. Rushton, L. Levy, Occupational Env. Med. (2001) 58 2–13.
4. W. Tang, M. Zhang, W. Li, X. Zeng, Talanta (2014) 127 262–268.
5. Yanli Zhanga, Shixiu Xiao, Jinling Xie, Zhongming Yanga, Pengfei PangaYuntao Gao, Sensors and Actuators B (2014) 204 102-108.
6. Muammer Kavanoz, Gözde Kılıç, Journal of Turkish Chemical Society, Section A: Chemistry, JOTCSA (2015) 2(3) 42-46.

Synthesis and Characterization of Polyaniline - 1,10 Phenanthroline Modified Electrode and Sensitivity to Fe(II) Ion

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Phenanthroline is a heterocyclic organic compound. It is a white solid that is soluble in organic solvents. It is used as a ligand in coordination chemistry, it forms complexes with different metal ions^[1]. The 1,10-phenanthroline family has been extended to the use of dihydroxy, dimethyl, nitro and diphenyl derivatives. The spectrophotometric determination method of a red-orange complex that forms between iron(II) and 1,10-phenanthroline is practical and sensitive. 1,10-Phenanthroline is a well-known benchmark ligand and has often been used in the coordination chemistry for the complexation of transition metal ions, such as Fe²⁺, Ni²⁺ and Co²⁺ [2].

In this study, Polyaniline – 1,10-phenanthroline (PANI –Fnt) film deposited using the polymerization solution containing aniline, 1,10-phenanthroline, HClO₄ and tetrabutylammoniumperchlorat (TBAP) in dichloromethane (CH₂Cl₂) medium on the Pt electrode surfaces between -0.40 V and 1.80 V vs. Ag / AgCl and electrochemical synthesis of the PANI - FNT film obtained by depositing of Fnt on the PANI film as separate layer between -0.10 V and -1.20 V using solution containing Fnt, HClO₄ and TBAP were performed for the first time. The characterization of the synthesized films was carried out by using methods, such as cyclic voltammetry, FT-IR, UV-vis, SEM and EDS. In the second part of the study, electrochemical behavior of the films was examined using cyclic voltammetry in aqueous solution containing NaHSO₄ / Na₂SO₄ (pH 2,0- 6,5) and the optimum condition was determined as the pH 4,0. In the optimum working pH medium, interacting with Fe²⁺ of films was determined by cyclic voltammetry method.

Keywords: Polyaniline, 1,10 Phenanthroline, Sensitivity to Fe(II) Ion, Cyclic Voltammetry

References:

1. C.R. Luman, F.N. Castellano (2003) "Phenanthroline Ligands" in Comprehensive Coordination Chemistry II, Elsevier. ISBN 978-0-08-043748-4.
2. N. Demirhan, F. Tuncel Elmalı, Turk J Chem (2003) 27 315 – 321.

A Voltammetric Determination of Bisphenol A in Polycarbonate Tableware Materials Using a Modified Carbon Paste Electrode

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In recent years, a great many interest about bisphenol A (BPA), [2, 2-bis (4-hydroxyphenyl) propane], that is one of the most common chemicals to which we are exposed in everyday life in order the production of the single use utensils has been enlarged. BPA is a monomer that is used for production of polycarbonate (PC), a hard, clear plastic, and it is also used in the manufacture of epoxy resins found in many common consumer products such as water bottles, including some baby bottles, disposable tableware, coatings on the inside of many food and beverage cans, and food storage boxes. A PC material may include BPA in its structure due to incomplete polymerization reaction during their production. Migration of this compound into food from PC tableware and the other material has also caused concern due to estrogenic activity of BPA [1, 2]. BPA has been identified as an important endocrine disrupting compound. It has been also found that BPA could possibly cause cancer, diabetes, hyperactivity, and obesity. Therefore, it is very important to remove BPA from the environment and to determine its presence [3, 4].

A method for determining the amount of BPA in the polycarbonate eating utensils due to an incomplete polymerization reaction during their production was investigated in this study. For this purpose, polyvinyl benzyl chloride - ethylene glycol dimethacrylate (PVBC-EGDMA) resin modified CPE was prepared in order to develop a stable and sensitive voltammetric method to determine BPA quantitatively in polycarbonate materials, in a simple, fast, and inexpensive manner.

The optimum voltammetric response was achieved in a pH 9 BR buffer. Additions of BPA using a quantitative voltammetric determination exhibited a linear detection range between 0.02 and 270 μM BPA. The limit of detection and the limit of quantitation were found to be 0.011 μM and 0.037 μM , respectively. The method developed was successfully applied to the determination of BPA content of real samples.

Keywords: Bisphenol A, Modified Electrode, Cyclic Voltammetry, Differential Pulse Voltammetry

References:

1. A.Beronius, C. Rudén, H. Håkansson, A. Hanberg Reprod. Toxicol. (2010) 29 132–146.
2. C.Liao, K. Kannan, Environ. Sci. Technol. (2011) 4 9372-9379
3. M.Yang, J.H. Ryu, R. Jeon, D. Kang, K.Y. Yoo, Arch. Toxicol. (2009) 83 281–285.
4. J.Li, D. Kuang, Y. Feng, F. Zhang, M. Liu, Microchim. Acta (2011) 172 379–386.

Potentiometric Acid Dissociation Constants Determination of Some Novel Polysubstitued Thiohydantoin Derivatives

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Acid dissociation constants are important physicochemical parameters, which give critical information about drug properties such as solubility, lipophilicity, acidity [1-3], transport behavior, bonding to receptors [2–4], and permeability [5]. Hence, the relationship between the acid dissociation constants and structure in drug design studies is crucial [2, 3, 6]. Acid dissociation constants are also key parameters for the selection of the optimum conditions in the development of analytical methods [5] and provide information about the stereochemical and conformational structures of active centers of enzymes [7].

Thiohydantoin, and their some derivatives are known to show a range of biological activity such as, antiviral, anticonvulsant [8a], antimicrobial [8b], anti-inflammatory [8c], antitumour [8d], antiandrogenic [8e] properties and agricultural applications [8f]. Due to these valuable biological and pharmaceutical properties of thiohydantoin and their derivatives are attractive to study to investigate more potent derivatives.

As part of our ongoing research work [9] acid ionization constants for 2×10^{-4} M of the synthesized thiohydantoin derivatives were determined in acetonitrile-water (20:80, (v/v)) hydroorganic solvent system at 25 ± 0.1 °C by using potentiometric titration method in the presence of sodium chloride and hydrochloric acid, and sodium hydroxide were used as titrant. Acid ionization constants were determined potentiometric titration method from obtained data by Molspin Titration System using HYPERQUAD computer program.

Keywords: Acid Dissociation Constants, Potentiometric Titration, Thiohydantoin

References:

1. M. Meloun, S. Bordovska, A. Vrana, *Analytica Chimica Acta* (2007) 584 2 419-432.
2. G. Roda, C. Dallanocce, G. Grazioso, V. Liberti, M. de Amici *Analytical Sciences* (2010) 26 51-54.
3. M. Sanchooli, *Journal of Chemistry* (2013) Article ID 989362.
4. A. E. Pütün, G. Bereket, E. Keskin *Journal of Chemical & Engineering Data* (1995) 40 1 221-224.
5. I. Narin, S. Sarıoğlu, B. Anılanmert, H. Sarı *Journal of Solution Chemistry* (2010) 39 10 1582 1588.
6. S. Şanlı, Y. Altun, N. Şanlı, G. Alsancak, J. L. Beltran, *Journal of Chemical & Engineering Data* (2009) 54(11) 3014-3021.
7. C. Öğretir, S. Yarlğan, Ş. Demirayak, T. Arslan *Journal of Molecular Structure: THEOCHEM* (2003) 666-667 609-615.
8. a. Smit B, Pavlovic RZ, Mihailovic AR, Dosen A, Curcic MG, Seklic DS, Zivanovic MZ. *J. Serb. Chem. Soc.* (2013) 78(2) 217-227 b. Arani NM, Safari J. *Ultrasonic Sonochemistry*, (2011) 18 640-643 c. Blanc M, Cussac M. Boucherle A, Leclerc G. *Eur. J. Med. Chem.* (1992) 27 267-275. d. Jung ME, Ouk S, Yoo D, Sawyers CL, Chen C, Tran C, Wongvipat J. *J. Med. Chem.*, (2010) 53 2779-2796. e. Tachibana K, Imaoka I, Shiraishi T, Yoshino H, Nakamura M, Ohta M, Kawata H, Taniguchi K, Ishikura N, Tsunenari T, Saito H, Nagamuta M, Nakagawa T, Takanashi K, Onuma E, Sato H. *Chem Pharm Bull* (2008) 56(11) 1555-61. f. Cao S, Zhu L, Zhao C, Tang X, Sun H, Feng X, Qian X *Monatsh. Chem.* (2008) 139 923-926
9. Y. Nural, HA. Döndaş, H. Sarı, H. Atabey, S. Belveren, M. Gemili *International Journal of Analytical Chemistry* (2014) Article ID 634194,

Determination for Sildenafil Citrate at Trace Levels by Using Magnetic Hybrid Nano Composite

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Sildenafil (SD) is a typical phosphor diesterase-5 inhibitor which is abused as drugs and health products to treat male erectile dysfunction [1-2]. It has also adverse effects such as head ache, vertigo, the reduction of blood pressure and aggravation of cardiovascular disease. Magnetic solid-phase extraction (MSPE) is known a new type of solid-phase extraction (SPE) based on the use of magnetic particle as [3] as the adsorbent. MSPE is a useful and simple extraction method for trace analytes with high extraction efficiency. In addition, MNP possesses large specific surface area owing to nano structure, and the equilibrium time between the sorbents and sample solution is greatly shortened, resulting in relatively higher extraction capacity and detection sensitivity [4].

In this study, magnetic nanoparticles (MNPs) was developed including graphene oxide and nano diamond hybrid material as solid-phase extraction adsorbent. A thermal synthesis equipment was used to obtain new adsorbent. The prepared material was characterized by Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD) spectrometry and scanning electron microscopy (SEM). The functionalized MNPs showed excellent dispersibility in aqueous solution and they were applied to magnetic solid phase extraction (MSPE) of sildenafil from model solutions followed by high performance liquid chromatographic analysis. Experimental variables were investigated in detail such as the amount of MNPs, pH and salt concentration of sample solution, extraction and desorption time, and the volume of desorption solvent. Under the optimum MSPE conditions, the developed method showed satisfactory reproducibility with intra-day and inter-day relative standard deviations less than 2.8 % and low limits of detection of 1.51 ng mL⁻¹. The proposed material possessed good water compatibility and demonstrated excellent applicability for real samples.

Keywords: Sildenafil, Magnetic Solid Phase Extraction, HPLC

References:

1. Cirino, G., Fusco, F., Imbimbo, C., Mirone, V., Pharmacol.Ther.111 (2006) 400–423.
2. Aguilar-Arteaga, K., Rodriguez, J.A., Barrado, E., Anal.Chim.Acta 674 (2010) 157–165.
3. Chen, L., Wang, T., Tong, J., Trac-Trends Anal.Chem. 30 (2011) 1095–1108.
4. Tang, M., Wang, Q., Jiang, M., Xu, L., Shi, Z., Zhang, T., Liu, Y., Talanta 130 (2014) 427–432.

Electrochemical Polymerization of Purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole)

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Electrodes chemically modified using monomers are uncommon are arousing great interest in the area of electrochemistry, due to easy preparation and by possibility of those materials (1). Many ways of anchoring compounds electrochemically active in the surface have been investigated in order to shorten the distance between the sites of oxidation-reduction involved in electronic transfer reactions (2).

4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, also known as purpald, is a chromogenic agent that is widely used in the determination of aldehyde (3). Purpald possesses S–C–N linkages and displays potential ligands for metal complexes that may also be biologically active just like some other amine- and thione-substituted triazoles. In this study, electrochemical behaviour of purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole) was investigated by cyclic voltammetry (CV). Then, purpald modified pencil graphite electrode (PGE) was prepared by using cyclic voltammetry methods. As a results of cyclic voltammogram, purpald modified pencil graphite electrodes were optimized (scan rate, number of cycle, pH) and this process 0.0 V - 0.6 V potential range carried out in the 0.1 M pH 8 BR (Britton-Robinson) buffer. Purpald modified pencil graphite electrode was washed with BR buffer solution dried at room temperature before use.

The polymeric film was then characterized by electrochemical impedance spectroscopy (EIS) methods. The polymeric film compared to bare pencil graphite electrode, purplad and p-phenylenediamine modified pencil graphite electrodes, respectively. As a results of electrochemical impedance spectroscopy (EIS), electrochemical polymerization was determined electrode on surface.

Keywords: Purpald, Pencil Graphite Electrode, Electrochemistry, Electropolymerization

References:

1. Sharma P.S., Pietrzyk-Le A., D'Souza F., Kutner W. Analytical Bioanalytical Chemistry (2012) 402 3177-3204.
2. Afzal A., Iqbal N., Mujahid A., Schirhagl R. Analytica Chimica Acta (2013) 787 36-49
3. Zarrok H., Zarrouk A., Hammouti B., Salghi R., Jama C., Bentiss F. Corrosion Science (2012) 64 243-252

Electrocatalytic Activity of Cyanex 921 on Cu(II) Determination

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Water has become a valuable source for the world due to the rapid growth of population, urbanization and industrialization. Increasing water stress not only in the arid or semi-arid regions but also in the regions without any water shortage leads to the application of efficient techniques for water recovery and reuse. Heavy metals can be listed as one of the most critical pollutants for various water bodies. Heavy metal pollution of water sources triggers various research studies due to their potential ecological effects and possible health concerns on humans. Thus, efficient techniques for the rapid and accurate detection of heavy metals became important. Development of the heavy metal selective electrodes is a simple, robust and fast way of determining heavy metal ions in aqueous phase.

In this study, graphite is selected for the electrode material. Pencil graphite electrode, polypyrrole electrode and Cyanex 921-polypyrrole electrode are employed as the working electrode. Cyanex 921 compound is used as a modifier for the first time in the literature for the voltammetric determination of Cu(II). Modified electrodes are developed by the cyclic voltammetry method and their performances in the determination of Cu(II) ions are analyzed by the differential pulse voltammetry. Effect of the pH on Cu(II) determination is investigated with the Britton-Robinson buffer solution which is suitable for the applications in a wide pH range (1.0-7.0). Effects of Cyanex 921 concentration, cycles (1-12), and scan rate (20-120 mV/s) on the performance of electrodes are also studied. Interferences of various ions during the determination of Cu(II) ions are also evaluated. Developed electrodes, which are prepared under optimum conditions, have linear responses in a defined concentration range. Moreover, developed electrodes are applied for the real industrial wastewater samples in order to prove the efficient Cu(II) determination under harsh conditions of industrial effluents.

Keywords: Cu(II) Ion, Cyanex 921, Graphite Electrode, Polypyrrole Electrode, Voltammetry.

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Development of Chitosan/PVA/Silver Membrane with Antimicrobial Activity

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Chitosan is known as an abundant and cheap bio-material. Chitosan has a strong antimicrobial property against fungi, yeasts and bacteria. Also, chitosan has negligible toxicity against mammalian cells. Therefore, it is widely applied in the food industry. Moreover, chitosan is also used in the areas of photography, cosmetics, biotechnology and water purification [1, 2]. Silver is one of the most toxic elements against pathogen microorganisms. Thus, various silver based compounds are developed and applied due to its strong antimicrobial activity. In this study, chitosan/polyvinyl alcohol membranes doped with various amounts of silver (CS/PVA/Ag) are developed, characterized and tested for the antimicrobial activity.

In this study, CS/PVA/Ag membranes are synthesized by solution casting method. The morphology of the prepared membranes is investigated by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The presence of silver ions in the membrane matrix is also detected by energy dispersive analysis of SEM-EDAX and X-ray diffraction (XRD) analyses. The antimicrobial activity against the selected twelve bacteria types (*Escherichia coli* ATCC 25922, *Salmonella typhimurium* ATCC 14028, *Micrococcus luteus* ATCC 9341, *Staphylococcus aureus* ATCC 25923, *Staphylococcus epidermidis* ATCC 12228, *Klebsiella pneumonia* ATCC 13882, *Pseudomonas aeruginosa* ATCC 35032, *Proteus vulgaris* ATCC 33420, *Serratia marcescens* ATCC 13880, *Enterobacter aerogenes* ATCC 13048, *Bacillus cereus* ATCC 11778, *Bacillus subtilis* ATCC 6633) and two yeasts (*Candida albicans* ATCC 10231, *Saccharomyces cerevisiae* ATCC 9763) are studied by disc diffusion method. The results are demonstrated that CS/PVA/Ag membranes have excellent antimicrobial effect. Antimicrobial activity of developed CS/PVA/Ag membranes is increased with the higher silver concentrations as expected. The excellent antimicrobial properties are suggested that the obtained CS/PVA/Ag membranes could be applied in various areas.

Keywords: Antimicrobial Activity, Chitosan, Membrane, Poly (Vinyl Alcohol), Silver.

References:

1. Ahmed. M. Youssef, Hussein Abou-Yousef, Samah M. El-Sayed, Samir Kamel International Journal of Biological Macromolecules (2015) 76 25-32.
2. Anna Regiel, Silvia Irusta, Agnieszka Kyzioł, Manuel Arruebo, Jesus Santamaria Nanotechnology (2013) 24 1-13.

POSTER SESSION 3

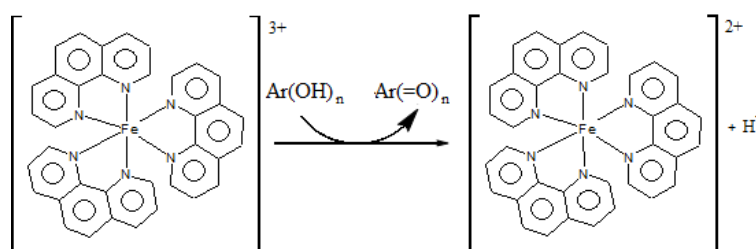
Development of Ferric Ion-Based Optical Sensors for Measurement of Antioxidant Capacity in Food Extracts

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The accumulation of reactive oxygen species (ROS) in the organism, unless counterbalanced by antioxidants intaken through diet, may cause oxidative damage to DNA and cellular membranes under ‘oxidative stress’ conditions eventually giving rise to certain human diseases, especially cardiovascular disease and some types of cancer.¹ Optical sensors are recently attracting remarkable attention because of their advantages in biomedical sensing, environmental monitoring, and industrial process control applications by *in situ*/on site measurements.² Rapid and low-cost chemical sensing of antioxidants with the use of sensors has recently gained importance. The main purpose of this study is develop a low-cost and widely used novel polymer film-based optical sensor using the *o*-phenanthroline colorimetric method originally developed for the determination of antioxidant capacity by Berker *et al.*³ The reagent, Fe(III)-*o*-phenanthroline (Fe(III)-phen) complex, was immobilized onto a cation-exchanger film, and the absorbance changes associated with the formation of the highly-coloured Fe(II)-phen chelate as a result of reaction with antioxidants was measured at 510 nm.



Yellow-orange Fe(III)-phen reagent

Red-orange Fe(II)-phen product, $\lambda_{\max} = 510 \text{ nm}$

Figure 1. The 1,10-phenanthroline method reaction and chromophore: Fe(II)-phen chelate cation.

This assay was validated through linearity, additivity, precision and recovery, demonstrating that the assay is reliable and robust. The developed optical sensor was used to screen total antioxidant capacity (TAC) of some commercial fruit juices without preliminary treatment, and showed a promising potential for the preparation of antioxidant inventories of a wide range of food plants.

Keywords: 1,10-phenanthroline method, Optical Sensors, Antioxidants, Antioxidant Capacity

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References:

1. Gutteridge, J. M. C., Halliwell, B. (1994) *Antioxidants in nutrition, health, and disease*, Oxford University Press, New York.
2. Ojeda, C. B., Rojas, F. S. *Sensors* (2006) 6, 1245-1307.
3. Berker, K. I., Güçlü, K., Tor, İ., Apak, R. *Talanta* (2007) 72(3), 1157-1165.

Determination of Some Antioxidants in Different Types of Pine Barks in Turkey

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Pine barks have been used since ancient times as medicine, syrup, edema reliever and etc. and due to these reasons they are drunk after boiling or applied for wounds. Old people knew this based on their experiences and this information was known and verified by the development of science in our era. Finally, scientists have named this mixture extracted from pine barks as pycnogenol. Pycnogenol is a mixture composed of many constituents like proanthocyanidins, flavonoids and etc. It has been known to have antioxidant properties of 50 times more potent than Vitamin C and 30 times more potent than Vitamin E when compared. Pycnogenol is obtained from *Pinus nigra* in France near the seaside and is commercially available.

In this study, pycnogenol components of different types of pine barks collected from Manisa, Bilecik and Adana regions were analyzed qualitatively and quantitatively after the optimization of gradient HPLC method. At first, the extraction procedure was performed according to the studies in literature. However, oxidation of pycnogenol components were observed during the removal of ethyl acetate phase. For this reason, removal of ethyl acetate step was realized under vacuum using argon gas. The collected pine bark samples were thoroughly grounded, 20 g of pine bark was weighed and then it was extracted in 150 mL of hot water. The sample was filtrated to remove the barks after cooling to room temperature. After, salt was added until saturation and it was re-filtrated. Then, the filtrate was extracted with ethyl acetate and this phase was collected. Sodium sulfate was added to this ethyl acetate phase in order to remove the remaining water. Later, sodium sulphate was also filtered and the ethyl acetate was removed by argon with vacuum. The solid residue which was off-white was dissolved in 25 mL of 25% methanol-water (v/v) mixture. Afterwards, the solution was injected to the instrument.

The samples were analyzed only after the optimization of mobile phase composition. As the mobile phase composition, water, methanol and acetonitrile were used each containing 0.1% ortho-phosphoric acid. The flow rate was adjusted to 1 mL/min. and gradient elution was used. The qualitative and quantitative analyses of pine barks (karaçam, kızılçam, sarıçam, fıstıkçamı, halepçamı) that contain catechin, epicatechin, epicatechingallate, ferulic acid and taxifolin have been performed. According to the types of pine barks analyzed, the pycnogenol components were found to be as: 0.209 mg/g taxifolin, 0.086 mg/g catechin, 0.076 mg/g epicatechin, 0.022 mg/g ferulic acid in karaçam; 23.16 mg/g taxifolin, 1.454 mg/g catechin, 0.027 mg/g epicatechin in kızılçam; 1.923 mg/g catechin, 1.801 mg/g taxifolin in fıstıkçamı; 0.066 mg/g epicatechin, 0.065 mg/g catechin, 0.025 mg/g epicatechingallate, 0.015 mg/g taxifolin, 0.010 ferulic acid in sarıçam; 0.219 mg/g taxifolin, 0.093 mg/g catechin, 0.046 mg/g epicatechin in halepçam.

Keywords: HPLC, Pycnogenol, Proanthocyanidin, Pine bark, Catechins.

References:

1. Rohdewald, P. Bioavailability and metabolism of Pycnogenol®. Eur Bull Drug Res (1999) 7(2) 5-7.
2. Masquelier J, Michaud J, Laparra J, et al. Flavonoides and pycnogenols (1979) 49 307–311.

Total Antioxidant Capacity and Radical Scavenging Activity of Beta-Carotene Encapsulated with Methyl- β -Cyclodextrin in Aqueous Medium

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Abstract

The hydrophobic property of β -carotene (BC) limited their effective usage as antioxidant character in many applications. We have investigated the ability of BC in the form of inclusion complex with methyl- β -cyclodextrin (M- β -CD), that increases water solubility and chemical stability for the evaluation of the antioxidant capacity and radical scavenging activity of BC in aqueous medium. Formation of inclusion complex was monitored by FTIR technique. The antioxidant capacity/activity of β -carotene-M- β -CD (BC-M- β -CD) inclusion complex were tested by cupric ion reducing antioxidant capacity (CUPRAC) assay, ABTS-persulphate assay, peroxy radical scavenging assay (ORAC) and hydroxyl radical scavenging assay in this study.

Keywords: β -Carotene, methyl- β -cyclodextrin, inclusion complexes, antioxidant capacity, radical scavenging activity.

Introduction

The encapsulation with oligosaccharides such as cyclodextrins (CDs) can be applied as a convenient technique to enhance the solubility, bioavailability and stability of hydrophobic guest molecules such as β -Carotene (BC). Cyclodextrins have hydrophobic inner cavity and hydrophilic external surface that provide CDs solubilizing several non-polar guest molecules.¹ Due to the polarity of hydrophilic exterior walls, CDs are able to generate inclusion complexes with hydrophobic guest molecules incorporated into the inner cavity by displacing water in aqueous medium.²

The encapsulation of carotenoids with various cyclodextrins has been studied in the literature.³⁻⁵ Many studies emphasized the characterisation of carotenoid-inclusion complexes such as water solubility, bioavailability, and stability. However, very scarce information on antioxidant capacity and radical scavenging activity of carotenoid-cyclodextrin complexes were performed.^{6,7} The objective of this study is to determine total antioxidant capacity and radical scavenging activity of BC encapsulated within M- β -CD in aqueous medium. Due to its hydrophobicity, there is no specific study on the antioxidant characteristics of BC at aqueous medium. This is the first time that the total antioxidant capacity and the quenching ability of these complexes containing β -carotene molecules against ROS such as hydroxyl and peroxy radical were reported.

Materials & Methods

Inclusion complexes of BC were prepared by using M- β -CD.⁸ β -carotene stock solution was added to ethanolic solution of CD. The mixture was incubated for 24 h in a shaking water bath kept at 37 °C. At the end of this period, the solvent mixture was evaporated to dryness under vacuum at 30 °C using rotary evaporator. The dried residue was redissolved in water and filtered through a 0.45 μ m membrane filter before analysis to remove free BC. Carrots and apricots samples were extracted and at the end, solvent mixture was removed with the aid of rotary evaporator and the dried residue was redissolved in DCM.⁹ The inclusion complexes of real sample extracts were prepared according to the procedure mentioned above.

Antioxidant capacity of the BC-M- β -CD was determined using the CUPRAC method as described by Apak et al.¹⁰ and ABTS-Persulphate method as described by Re et al.¹¹ Trolox equivalent antioxidant capacity (TEAC) coefficients were calculated by dividing the molar absorptivity of each inclusion complex to the molar absorptivity of trolox under the specified conditions ($\epsilon_{\text{CUPRAC}}=1,67 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$; $\epsilon_{\text{ABTS}}= 2.59 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$). Hydroxyl radical scavenging activity of BC-MBCD was determined by using terephthalate (TP) probe which produces a fluorescent product, hydroxyterephthalate (hTP), upon hydroxylation.¹² Hydroxyl radical was generated by Fenton reaction system. At the end of this period the fluorescence intensity ($\lambda_{\text{ex}}=315 \text{ nm}$, $\lambda_{\text{em}}=450 \text{ nm}$) of the reaction mixture was recorded.

The inhibition ratio of scavengers (%) was calculated using the following formula:

$$\text{Inhibition ratio (\%)} = (A_0 - A)/A_0 \quad (\text{Eq. 2})$$

where A_0 and A are the absorbances of the system in the absence and presence of a CD inclusion complex, respectively. IC_{50} value (the half maximal inhibitory concentration) were determined by means of a linear plot of inhibition percentage as a function of scavenger concentration.

Peroxyl radical scavenging activity of the BC-M- β -CD was determined using the ORAC method as described by Ou et al.¹³ The fluorescence intensity ($\lambda_{\text{ex}}=493 \text{ nm}$, $\lambda_{\text{em}}=515 \text{ nm}$) of the reaction mixture was recorded. $\text{ROO}\cdot$ scavenging activity was calculated using the following equation:

$$\text{Inhibition \%} = (I_2 - I_1)/(I_0 - I_1) \quad (\text{Eq. 3})$$

I_0 is the initial fluorescence intensity of the fluorescein probe, and I_1 and I_2 are the fluorescence intensities of fluorescein probe subjected to peroxyl radical action in the absence and presence of a scavenger compound respectively.

Results & Discussion

The concentration of BC encapsulated in M- β CDs were calculated 0.283 mg mL^{-1} using the calibration equation of free BC ($A_{450}=25.44c_{\text{BC}}+000.7$; $r= 0.9996$) constructed as absorbance (A) versus concentration where c_{BC} was in mg mL^{-1} according the study of Kaur et al.⁷ The FT-IR spectra of BC-M- β -CD complex was compared to the pure M- β -CD and free BC by utilizing the difference of shape and position of absorption bands. Some significant differences can be seen in the FT-IR spectrum of the inclusion complexes as compared to the corresponding spectra of BC, as displayed in Figure 1.

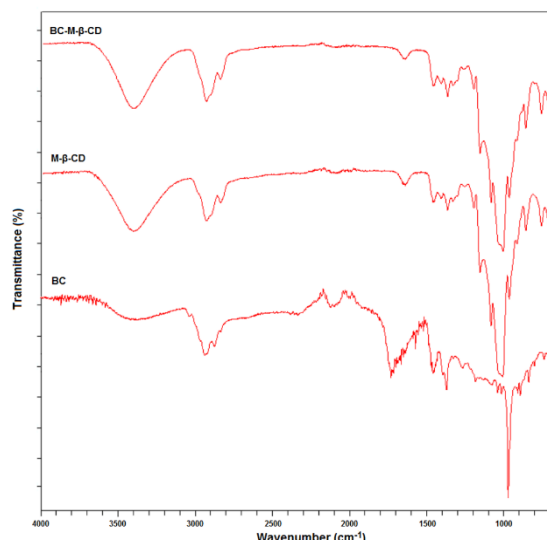


Figure 1. FT-IR spectra of solid β -carotene (BC) alone, M- β -CD alone and inclusion complex of BC with M- β -CD.

Antioxidant capacities of BC in the absence and presence of CDs were measured using electron transfer-based TAC assays, CUPRAC assay and ABTS-persulphate assay. Both CUPRAC and ABTS assays were successively applicable to hydrophilic and lipophilic antioxidants in polar and nonpolar solvent medium for measuring antioxidant capacity because they involve univalent-charged chromophore species (i.e., $\text{ABTS}^{\bullet+}$ and $\text{Cu}(\text{Nc})_2^+$) capable of being solvated by both water and alcohols as well as by less polar solvent mixtures. TEAC coefficients, peroxy and hydroxyl radical scavenging activities (IC_{50} ($\mu\text{g/mL}$)) of inclusion complex of BC with M- β -CD were assayed (Table 1). We found that the complexed BC with M- β -CD was less effective antioxidant than free BC compared to the TEAC value of BC in acetonated medium given as 1.75.¹⁴ Inclusion complexation phenomenon is competitive to redox behaviour, and is expected to decrease antioxidant capacity due to the difficult release of BC in the complex. The total antioxidant capacities, peroxy and hydroxyl radical scavenging activities of the encapsulated carrot extract (CE) and apricot extract (AE) with M- β -CD were evaluated using capacity and activity methods (Table 1).

Table 1. Total antioxidant capacities, peroxy and hydroxyl radical scavenging activities of inclusion complexes

Inclusion Complex	TEAC		$\text{IC}_{50}(\mu\text{g mL}^{-1})$	
	CUPRAC	ABTS	ROO^{\bullet}	$\bullet\text{OH}$
BC-M- β -CD	1.02	0.26	9.89	0.20
	TAC (mg TR g^{-1} sample)		Inhibition %*	
	CUPRAC	ABTS	ROO^{\bullet}	$\bullet\text{OH}$
CE-M- β -CD	0.22 ± 0.01	0.21 ± 0.02	71.3 ± 1.4	90.1 ± 0.5
AE-M- β -CD	0.21 ± 0.01	0.16 ± 0.02	68.3 ± 0.9	75.7 ± 1.2

Data presented as mean \pm SD (N = 3)

* The inhibition percentage of hydroxyl and peroxy radicals was calculated for 1:50 and 1:10 diluted extract, respectively.

Standard calibration curves of BC-M- β -CD inclusion complexes in the absence and presence of apricot extract were given in Figure 2. The antioxidant capacities of the tested inclusion complexes were additive. The parallelism of the linear calibration curves effectively

demonstrated that there was no chemical interactions of intereferent nature among the BC-M- β -CD complex and the real matrix solution.

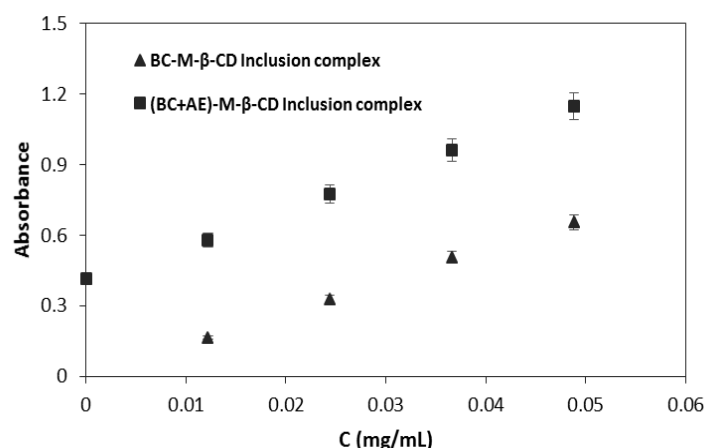


Figure 2. Standard calibration curves of BC-M- β -CD inclusion complex alone and in the presence of apricot extract (AE)

Conclusion

In this study, antioxidant capacity and scavenging activity of water-soluble inclusion complex of β -carotene in M- β -CD were evaluated. The complexed form of BC showed 1:1 stoichiometry. The results indicated that the complex of a β -carotene/M- β -CD inclusion is more soluble in water than β -carotene alone. β -carotene could be protected from degradation by encapsulation to the M- β -CD cavity.

Acknowledgement

The authors wish to express their gratitude to Istanbul University – Application and Research Center for the Measurement of Food Antioxidants (Istanbul Universitesi Gida Antioksidanlari Olcumu Uygulama ve Arastirma Merkezi) for the donation of antioxidant samples.

References:

1. Y. Cai, S. H. Gaffney, T. H. Lilley, D. Magnolato, R. Martin, C. M. Spencer and E. Haslam, J. Chem. Soc. Perkin Trans. (1990) 2, 2197-2209.
2. T. Loftsson and D. Duchêne, Int. J. Pharm (2007) 329, 1-11.
3. V.E. Oliveira, E.W.C. Almeida, H.V. Castro, H.G.M. Edwards, H.F.D. Santos and L.F.C. Oliveira, J. Phys. Chem. A (2011) 115, 8511–8519.
4. N.E. Polyakov, T.V. Leshina, T.A. Konovalova, E.O. Hand and L.D. Kisperty, Free Radic. Biol. Med. (2004) 36, 872-880.
5. E. Rodrigues, L.R.B. Mariutti, A.F. Faria and A.Z.M. Rodrigues, Food Chem. (2012) 134, 704-711.
6. C. Yuan, L. Dua, Z. Jinb and X. Xu, Carbohydr. Polym. (2013) 91, 385-389.
7. M. Kaur, M. Bawa and M. Singh, J. Glob. Sci. (2016) 5, 3665-3675.
8. I. Pfitzner, P.I. Francz and H.K. Biesalski, Biochim. Biophys. Acta (2000) 1474, 163-168.
9. K. Sözen Başkan, E. Tütem, N. Özer and R. Apak, J. Agric. Food Chem. (2013) 61, 11371-11381.
10. R. Apak, K. Güçlü, M. Özyürek and S. E. Karademir, J. Agric. Food Chem. (2004) 52, 7970-7981.
11. R. Re, N. Pellegrini, A. Proteggente, A. Pannala, M. Yang and C. Rice-Evans, Free Radic. Biol Med. (1999) 26, 1231-1237.
12. X. Qu, L.J. Kirschenbaum and E.T. Borish, Photochem. Photobiol. (2000) 71, 307-313.
13. B. Ou, M. Hampsch-Woodill and R.L. Prior, J. Agric. Food Chem. (2001) 49, 4619-4626.
14. M. Özyürek, B. Bektaşoğlu, K. Güçlü, N. Güngör and R. Apak, Anal. Chim. Acta (2008) 630, 28-39.

Microencapsulation of Antioxidants Using Biopolymer Mixtures

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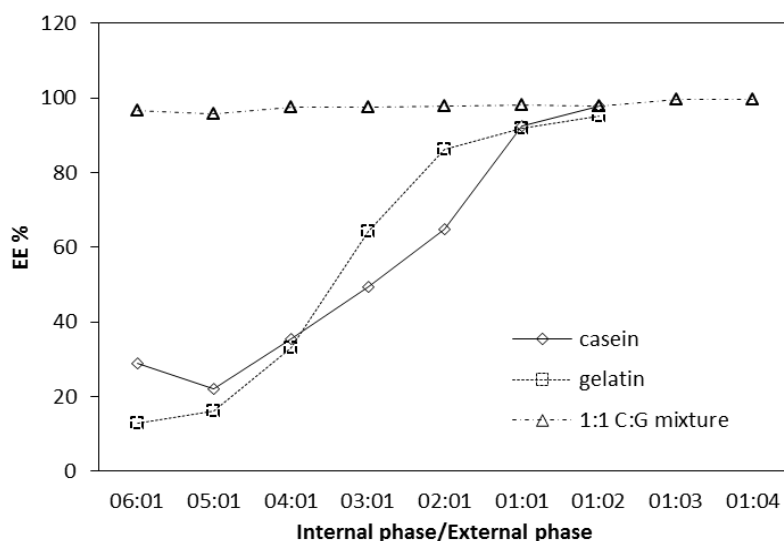
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Microencapsulation retards degradation of food additives and drug active materials so it causes expanded shelf life and controlled releasing of core materials through gastrointestinal system. Coating of surface takes place via secondary interaction between core and shell material. The encapsulation process is used to inhibit the interaction of core material with air and other molecules, and to decrease rate of mass transfer to the environment (1). Using proteins as wall material in encapsulation of antioxidants leads to enhancing in antioxidant efficiency of core material (2).

In this study, gallic acid, ascorbic acid and quercetine were used as core phase; casein, gelatin, stearic acid and their mixture were used as shell phase. Formed microcapsules are powdered using freeze dryer. Encapsulation efficiency for each encapsulated combination was calculated. Unreacted core materials were quantitatively determined by using CUPRAC method. As a result, when used single type of external phase, maximal encapsulation efficiency was calculated over 90% for 1:4 internal phase:external phase ratio. On the other hand, usage of binary external phase solution (having 1:1 ratio) led to higher encapsulation efficiency for 6:1 core/shell ratio. Using of binary shell mixtures enhance the encapsulation efficiency, and result in less external phase requirement for more internal phase.



The variation of Encapsulation Efficiency depending the type of external phase and core:shell ratio

Key words: Microencapsulation, Casein, Gelatin, Stearic Acid, Antioxidant

References:

1. Gharsalaoui A., Gaelle R., Chambin O., Voilley A., Saurel R., Food Research International (2007) 40 1107-1121.
2. Almajano M.P., Delgado M.E., Gordon M.H., Food Chemistry (2007) 102 1375-1382.

Antioxidant Activity Determination Using N,N-dimethyl-*p*-phenylenediamine Probe with Fe₃O₄ Magnetic Nanoparticles

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During normal cellular oxidative metabolism, ROS and RNS are formed in small quantities and can be removed effectively by natural defense mechanisms. However, uncontrolled and excessive generation of ROS/RNS have been implicated in the pathogenesis of various diseases including cancer, cardiovascular and neurodegenerative diseases as well as aging [1,2]. The main features of most antioxidant assays are based on an efficient generation system of free radicals, a suitable oxidation reaction induced by free radicals and an appropriate measurement of the suppressive signal [3]. In this regard, one of the antioxidant detection methods with a nanotechnological approach is to use NPs to generate free radicals that were further trapped by various antioxidants and detected using different strategies or techniques [4]. In this study, it is targeted to measure the hydroxyl radical (•OH) scavenging activity of antioxidants with the use of a N,N-dimethyl-*p*-phenylenediamine (DMPD) probe. In accordance with this aim, magnetite (Fe₃O₄)-NPs can be used to generate reactive oxygen species (ROS, mainly •OH) from a hydrogen peroxide (H₂O₂) source, which in turn converts the DMPD probe to colored products composed of DMPD-Q⁺ quinonic radical cations. In the presence of antioxidant compounds, these colored quinones are produced less, and the difference in absorbance enables an indirect determination of hydroxyl radical scavenging activity. The proposed assay was optimized with respect to a number of parameters such as the mode of preparation and concentration of magnetite NPs, probe and buffer concentrations, pH, temperature, etc. When optimized parameters were applied to quercetin solutions at final concentration ranging between 2x10⁻⁵-1x10⁻⁴ M, linear calibration curve was obtained as: A₅₅₃=9.96x10³c_{QR}-2.96x10⁻² (r=0.9981), where c_{QR} is the molar concn. of quercetin. This study can be applicable to polyphenol class antioxidants.

Keywords: Antioxidant Activity Measurement, Reactive Oxygen Species (ROS), Colorimetric Sensor, Magnetite Nanoparticles (Fe₃O₄-NP).

Acknowledgement

The authors wish to express their gratitude to Istanbul University – Application and Research Center for the Measurement of Food Antioxidants (Istanbul Universitesi Gıda Antioksidanları Olcumu Uygulama ve Araştırma Merkezi) for the donation of antioxidant samples.

References:

1. Bourdon, E., Blache, D. The importance of proteins in defense against oxidation. *Antioxid. Redox Signaling* (2001) 3 (2) 293–311.
2. Niki, E. Assessment of Antioxidant Capacity in vitro and in vivo. *Free Radical Biol. Med.* (2010) 49 503–515.
3. Wang, Y., Calas-Blanchard, C., Cortina-Puig, M., Baohong, L., Marty, J.-L. An electrochemical method for sensitive determination of antioxidant capacity. *Electroanalysis* (2009) 21 1395–1400.
4. Vasilescu, A., Sharpe, E., Andreescu, S. Nanoparticle-based technologies for the detection of food

Determination of Oxidative Protein Damage Using Modified CUPRAC Method

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An imbalance between oxidative species and antioxidants in favor of oxidants is defined as oxidative stress. Oxidative stress conditions can cause harmful effects on certain biologically important macromolecules such as proteins, lipids and DNA. Hydroxyl radical ($\bullet\text{OH}$) is one of the most dangerous oxidative species since it can rapidly react with a large number of different molecules non-specifically. The degree of oxidative damage is related to certain conditions including abundance and location of the target molecule and kinetic factors as well. In this point of view proteins in the human body are suitable for $\bullet\text{OH}$ damage. In the presented study, $\bullet\text{OH}$ was produced in the reaction medium using the Fenton reaction between Fe(II) and H_2O_2 , and bovine serum albumin (BSA) was chosen as standard protein sample. Fenton reaction was slightly modified from Bektaşoğlu et al.'s work¹. The decomposition products of BSA after $\bullet\text{OH}$ attack were subjected to CUPRAC reaction. Although BSA reacts with CUPRAC reagent (Cu(II)-neocuproine complex) weakly, oxidation products can react easily. Fenton reaction was performed in pH=7 phosphate buffered medium and stopped with HCl. To generate $\bullet\text{OH}$ and decompose BSA; phosphate buffer, BSA solution, Na_2EDTA and Fe(II) were mixed in this order and diluted with distilled water. To start Fenton reaction H_2O_2 solution was added to the reaction mixture and it was incubated in a water bath at 37°C for 10 min. The Fenton reaction was stopped with 1M HCl. Na_2CO_3 solution was added to neutralize the acidic sample. Modified CUPRAC method was applied as stated: Cu(II), Neocuproine (Nc), urea buffer, Na_2CO_3 , incubated sample (acidified with HCl) were mixed and the resulting yellow color was read at 450 nm. When the procedure was optimized, it was applied to different protein samples such as casein, egg white and meat. Water soluble proteins were directly dissolved with water, while meat protein was extracted using protein extraction buffer. Extracted protein was precipitated with TCA and redissolved with a protein dissolution buffer, as stated earlier in Sözgen et al.'s study².

Keywords: Oxidative Damage, Fenton Reaction, Reactive Oxygen Species, Protein

References:

1. B. Bektaşoğlu, M. Özyürek, K. Güçlü, R. Apak, Talanta (2008) 77(1) 90-97.
2. K. Sözgen, S. Demirci Çekiç, E. Tütem, R. Apak, Talanta (2006) 68(5) 1601-1609.

An Approach to Improve the Relation Between Silver Nanoparticle Formation Rate and Antioxidant Capacity of Aqueous Plant Leaf Extracts

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Correlation between the antioxidant capacity and silver nanoparticle formation rates of pomegranate (*Punica granatum*), quince (*Cydonia oblonga*), chestnut (*Castanea sativa*), fig (*Ficus carica*), walnut (*Juglans cinerea*), black mulberry (*Morus nigra*) and white mulberry (*Morus alba*) leave extracts is investigated at constant illumination. Silver nanoparticles formed in all plant leaf extracts possess round shapes with average particle size of 15-to-25 nm, whereas corresponding surface plasmon resonance peak wavelengths vary between 422 nm and 451 nm. Cupric reducing antioxidant capacity technique is used as a reference method to determine total antioxidant capacity of the plant leaf extracts. Integrated absorbance over the plasmon resonance peaks exhibit better linear relation with antioxidant capacities of various plant leaf extracts compared to peak absorbance values, with correlation coefficient values of 0.9333 and 0.7221, respectively.

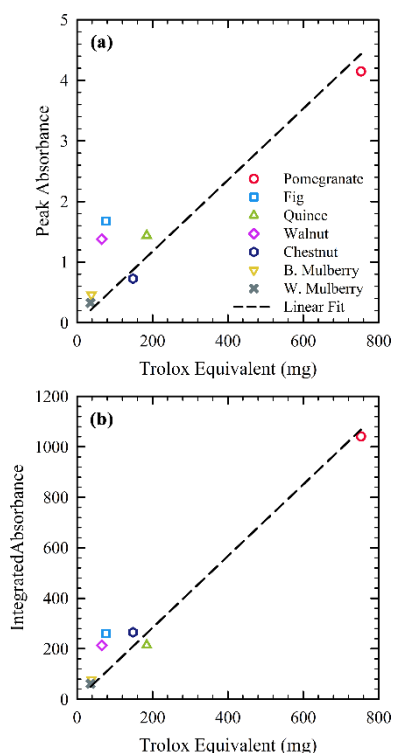


Figure. SPR peak absorbance (a) and integrated absorbance between 300 and 800 nm (b) for the mixtures of plant leaf extracts and AgNO₃ against the trolox equivalence of corresponding extracts. Dashed lines indicate the best fits to data.

Keywords: Antioxidant Capacity, Silver Nanoparticle, Plant Leaf Extract, Integrated Absorbance, Trolox Equivalence.

Variation of Quantitative Composition of Phenolic Compounds in the Apricot (*Prunus armeniaca* L.) Leaves During the Growth Season

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Plants, which are potential source of antioxidants, prevent the oxidative stress caused by oxygen and photons at the same time. Interest of antioxidant compound has been increased for last years. Therefore, it is believed that an increased intake of food, which is rich in natural antioxidant, is associated with a lower risk of degenerative diseases(1-2).

In this study, the changes in phenolic compounds in leaves of 5 different apricot cultivars taken from April (23.04.15), July (18.07.15) and November (14.11.15) during one year was examined. Phenolic compounds were determined in the leaves of apricot fruits of "Hacıhaliloglu" "Hasanbey" "Kabaası" "İsmailaga" and "Cekirge" cultivars in natural habitats of Apricot during their growth season by using the HPLC method. which were harvested from the Directorate of Malatya Apricot Research institute during 2015/04 and 2015/11 harvest year were investigated.

For the analysis of phenolics the most suitable extraction method was determined to extract these components from apricot leaves. In this sense, prior to the extraction of polyphenols from different apricot leaves sample, operational parameters of the ASE technique were established. Extraction procedure was performed under the conditions of 1,500 psi pressure, 60°C temperature, ethanol–water (80:20, v/v) extraction solution and 60 min static extraction time. All criteria examined in this study were changed depending on the cultivars and sampling months. It was determined that phenolics including chlorogenic acid, rutin, catechin and naringin are available in apricot leaves. The most abundant phenolic acid was chlorogenic acid while rutin, catechin and naringin found the highest levels as flavonoids in leaves.

At the end of the growth season, chlorogenic acid and naringin contents in ethanol–water extracts of apricot leaves samples exponentially decreased. However, rutin and catechin increased. During the growth season catechin and naringin was not detected in some leave samples. Dried apricot leaves showed higher total chlorogenic acid (167.75-91.94 mg/100g dw leaves) Rutin (24.78 -146.48 mg/100g dw leaves) and catechin (12.62- 6.79 mg/100g dw leaves) and naringin (48.68-13.71 mg/100g dw leaves).

Keywords: Apricot Leave, Polyphenol, HPLC.

References:

1. Ratnam V.D, Ankola D.D, Bhardwaj D.K, Sahana M.N.V., Ravi K., (2006) 113 189-207.
2. Thomas R.H., Bernards M.A., Drake E.E., Guglielmo G.C., (2010) 23 244-252.

Assessment of Some Water Soluble Vitamin Composition in Wild Edible Plant: Hawthorn

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Hawthorn is a plant that grows in many regions in Turkey, used in a variety of heart and circulatory diseases. Main ingredients such as fructose, flavonoids, proanthocyanidins, triterpenes, organic acids, vitamins and minerals found in hawthorn berries are changed according to hawthorn type, geographic location and harvest time. When used hawthorn extract, the pressure heart rate shows a decrease. Results show that there is a significant benefit from hawthorn extract as an adjunctive treatment for several diseases especially chronic heart failure [1-3]. However, active compounds which are responsible for this beneficial effect is still unknown.

In this study present, red and yellow colored hawthorn fruits which grow naturally and consumed much, were collected and analyzed in terms of fat-soluble and water-soluble vitamin composition. Red and yellow hawthorn samples were collected in season at the town Beydagi in Malatya-Turkey and analyzed. Vitamin analyses were performed by HPLC-DAD applying gradient elution. According to the obtained data, both colors hawthorn were rich in terms of water-soluble vitamins and especially they identified as an important potential of vitamin C. But in both colors hawthorn, fat-soluble vitamins were below the detection limits.

Keywords: Hawthorn, vitamins, HPLC-DAD

This study was a part of the project supported by Tunceli University Scientific Investigations Project Unit (TÜNİBAP MFTUB013-23).

References

1. Pittler M.H, Schmidh K., Ernest E., The American Journal of Medicine (2003) 114 665-674.
2. Chang Q., Zuo Z., Harrison F., Choww M.S.S., J. Clin. Pharmacol. (2002) 42 605-612.
3. Yildirim N.C., Turkoglu S., Kaplan Ince O., Ince M., Cell. Mol. Biol. (2013) 59 1882-1888.

Element Composition and Antioxidant Activity of *Teucrium polium* L. Consumed as Condiment

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Reactive oxygen species (ROS) could be vital provocative agents of numerous health problems especially in human. In order to protect against harmful free radicals, antioxidant components have a major role in human diet. Recently, it is believed that the regular consumption of food that have antioxidants may reduce the risk of serious health problems such as cancer, Alzheimer's disease, cardiovascular disease, age-related functional decline, and diabetes besides other health benefits [1-3]. Besides fruits and vegetables, some dried condiment especially *Teucrium polium* L. contain many compounds with antioxidant activities, such as vitamins, [4-6], in which recent studies have shown to be good contributors to the total antioxidant capacity of the foods that contain them [7]. Phenolic compounds are important constituents of the human diet and widely distributed in plant foods.

The aim of this work was to investigate elemental composition and antioxidant activity of *Teucrium polium* L. plant. It was determined 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity, ABTS and total phenolic content. DPPH, ABTS and total phenolic content in methanol extracts were found 15.77 ± 0.89 mg TEAC g⁻¹, 25.27 ± 0.62 mg TEAC g⁻¹ and 8.27 ± 0.10 mg GAE g⁻¹, respectively. On the other hand, results show that these condiments have rich in terms of macro and micro elements source especially sodium (Na), potassium (K) calcium (Ca) and magnesium. Elemental composition of *Teucrium polium* L. was determined by using flame atomic absorption spectrophotometer (FAAS).

Keywords: *Teucrium polium* L., antioxidant activity, element composition, FAAS

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References

1. Knekt, P., Kumpulainen, J., Jarvinen, R., Rissanen, H., Heliovaara, M., Reunanen, A., American Journal of Clinical Nutrition (2002) 76, 560–568.
2. Martí'nez-Gonza'lez, M. A., Ferna'ndez-Jarne, E., Martí'nez-Losa, E., Prado-Santamar'ía, M., Brugarolas-Brufay, C., & Serrano-Martí'nez, M., European Journal of Clinical and Nutrition, (2002) 56, 715–722.
3. Hassimoto, N. M. A., Genovese, M. I., & Lajolo, F. M. Journal of Agricultural and Food Chemistry, (2005) 53, 2928–2935.
4. Sa'ñchez, C., Plaza, L., Ancos, B., & Cano, P. Food Chemistry (2006) 98, 749–756.
5. Yildirim N.C., Turkoglu S., Ince O.K., Ince M., Cell. Mol. Biol. (2013) 59 1882-1888.
6. Vinson, J. A., Su, X., Zubik, L., & Bose, P. Journal of Agricultural and Food Chemistry, (2001) 49, 5315–5321.
7. Zulueta A., Esteve M. J., Frassetto I, Fri'gola A., Food Chemistry (2007) 103, 1365–1374.

A Study of the Comparative of Hawthorn Fruit Extract in Different Solution in terms of Some Chemical Properties

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Hawthorn is a plant that grows in many regions in Turkey especially East Anatolia. Hawthorn fruit has been shown several health benefits such as hypotensive, cardiovascular protective and hypocholesterolemic. On the other hand, it has long been used as a folk medicine because of long-term medicinal benefits and little side effect. Recently, there are several studies associated with effect of pharmacological and toxicological impact about hawthorn fruits. Several studies reported that there is a significant benefit from hawthorn extract as an adjunctive treatment several disease especially chronic hearth failures besides its extract was clinically effective in reducing total plasma cholesterol and blood pressure [1-3]. However, active compounds which are responsible for this beneficial effect is still unknown.

In this study present, antioxidant activity of red and yellow colored hawthorn fruits was determined by ABTS (2,2-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid)), DPPH (1,1-diphenyl-2-picrylhydrazyl) radical scavenging activity besides total phenolic content in different solution. Total phenolic content of hawthorn fruits was determined according to the Folin-Ciocalteu method [4,5]. The absorbance was recorded at 517 nm by UV-VIS spectrophotometer. Gallic acid was used for calibration curve. The results were expressed as mg gallic acid equivalents (GAE) per 100 g of sample in dry weight (mg GAE 100 g DW⁻¹). All samples were analyzed in triplicate. The dry hawthorn fruit was extracted successively with methanol, acetonitrile and water. The methanol fraction was the highest than the other fraction. ABTS, DPPH radical scavenging activity and total phenolic content were found 6.29±0.38 mg TEAC g⁻¹, 2.49±0.13 mg TEAC g⁻¹, 1.20±0.07 mg GAE g⁻¹, respectively for yellow hawthorn and higher than red hawthorn.

Keywords: Hawthorn, DPPH, ABTS, Antioxidant Activity

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References

1. Pittler M.H, Schmidh K., Ernest E., The American Journal of Medicine (2003) 114 665-674.
2. Chang Q., Zuo Z., Harrison F., Choww MSS., J. Clin. Pharmacol. (2002) 42 605-612.
3. Zhang Z, Chang Q, Zhu M, Huang Y, Ho W.K.K., Chen Z.Y., The Journal of Nutritional Biochemistry (2001) 12, 144-152.
4. Maria I., Francisco A., Barbwra N., Betty H.P., Adel A.K., Journal of Agriculture and Food Chemistry (2002) 50 4976-4982.
5. Yildirim N.C., Turkoglu S., Ince O.K., Ince M., Cell. Mol. Biol. (2013) 59 1882-1888.

Phenolic Content of *Teucrium polium* L.: A Case of Tunceli

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Plant materials such as herbs, fruits and vegetables extracts rich in terms of phenolics are increasingly interest in the food industry as they retard lipids oxidative degradation and in this way improve the nutritional value and food quality. These compounds are found in plants in the form of glycosides. Recently, because of medicinal values in diets, wild species have a great importance. Wild plant species provide vitamins, essential fatty acids, minerals and fibre especially phenolic compounds. Phenolic compounds that belong to natural antioxidants, are reported as they inhibit oxygen-derived free radicals [1,2]. According to several studies, phenolic compounds have been shown to neutralize free radicals [3,4]. Polyphenols, including vitamins, pigments and flavonoids, possess antimutagenic properties as well as blood glucose decreasing activity. The antioxidant effect of polyphenols has been demonstrated in many systems from in vitro studies (human low density lipoprotein, liposomes) [5,6] to investigations in normal human subjects, although their effects remain controversial.

In this study, thirteen different phenolic compounds such as gallic acid, (+)-catechin, (-)-epicatechin, chlorogenic acid, caffeic acid, *p*-coumaric acid, naringin, hesperidine, phlarizidinedihydrate, rutin, ellagic acid, myricetin and quercetin in *Teucrium polium* L. were investigated using high performance liquid chromatography-diode array detector (HPLC-DAD). Flow rate, injection volume and column temperature were applied 1.0 mL min⁻¹, 10 µL and 30 °C, respectively.

Keywords: *Teucrium polium* L., Phenolic Compounds, HPLC-DAD

This study was a part of the project supported by Tunceli University Scientific Investigations Project Unit (TÜNİBAP MFTUB016-03).

References

1. Wanasundara U.N., Shahidi F., Food Chemistry (1998) 63, 335-342.
2. Yuting C., Rongliang Z., Zhongjian J., Young J., Free Radic Biol Med. (1990) 9, 145–150.
3. Ruchrj., Cheng S., & Klaunig J.E., Carcinogenesis (1989) 1003-1008.
4. Shon M., Kim T., Sung N, Food Chemistry (2003) 82, 593–597.
5. Teissedre P.L., Frankel E.N., Waterhouse AL, Peleg H., & German J.B., J Sci Food Agric (1996)70, 55-61.
6. Wiseman SA., Balentine D.A., & Frei B., Critical Reviews in Food Science and Nutrition, (1997) 37, 705-718.

Antioxidant and Some Vital Elements Sources: *Allium Tuncelianum*

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Oxidation is essential to living organisms in order to product of energy during biological processes. At the same time, free radicals that oxygen-centered and other reactive oxygen species (ROS), which are continuously, produced in vivo, result in tissue damage and cell death. Oxygen radicals have been caused many diseases, including diabetes, cardiovascular diseases, and cancer, etc. Antioxidants are critical substances which possess the ability to protect the body from damage caused by free radical induced oxidative stress. Recently, there is an increasing interest in natural antioxidants especially polyphenols due to prevent oxidative damage [1]. Polyphenols have ideal chemical structural because of free radical scavenging activity, and they have been shown to be more effective antioxidants in vitro [2,3].

In human diet, vegetables and other foods are a good source in terms of valuable nutrients and minerals. *Allium tuncelianum* possesses a big popularity among these products, because of its acceptability for consumers as well as its nutritional properties and several useful influences on human health especially in respect to elemental composition. Because especially infants grow rapidly during early months and need more nutrients including trace elements. The objective of this study was to evaluate some elements and antioxidant activity of *Allium tuncelianum*. Some vital element contents such as zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu) in *Allium tuncelianum* were compared using ICP-OES and FAAS. In addition, antioxidant activity of *Allium tuncelianum* was investigated. Samples were extracted with acidified solvents such as water, acetonitrile, methanol and ethanol. Antioxidant activity tests such as ABTS, reduction power and total phenolic content were applied to these extracts. ABTS and reduction power tests of acidified methanol extract was found higher than other extracts. Total phenolic contents were found the highest in acidified water extracts.

Keywords: *Allium tuncelianum*, antioxidant activity, elements, ICP-OES, FAAS

References

1. Silva B.A., Ferreres F., Malva J.O., Dias A.C.P. Food Chemistry, 90 (2005) 157-167.
2. Ozsoy N., Can A., Yanardag R., Akev N., Food Chemistry 110 (2008) 571-583.
3. Yildirim N.C., Turkoglu S., Ince O.K., Ince M., Cell. Mol. Biol. (2013) 59 1882-1888.

Why is Legumes Important in Human Diet? Is Elemental Content Possible?

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Elements are present in different forms in the nature, and these elements are very essential for body to perform different functions. Trace elements are very important for cell functions at biological, chemical and molecular levels. These elements mediate vital biochemical reactions by acting as cofactors for many enzymes, as well as act as centers for stabilizing structures of enzymes and proteins. Some of the trace elements control important biological processes by binding to molecules on the receptor site of cell membrane or by alternating the structure of membrane to prevent entry of specific molecules into the cell. The functions of trace elements have a dual role. In normal levels, they are important for stabilization of the cellular structures, but in deficiency states may stimulate alternate pathways and cause diseases. These trace elements have clinical significance and these can be estimated using different analytical methods. Our body needed nutrients supply by daily food including leucine, isoleucine, methionine, lysine, phenylalanine, threonine, valine and amino acids. Legumes are rich nutrients in terms of protein and amino acids. Legumes contain 2-3 times more protein than wheat, are considered as major source of the high-carbohydrate [1].

In this study, Zn, Fe, Mn and Cu contents in legumes such as chickpeas and haricot bean grown in Tunceli were determined using flame atomic absorption spectrophotometry (FAAS). Samples were digested using dry ash and microwave digest system. Each result is the mean value of the three separate portion of the same sample. Zn, Fe, Mn and Cu average concentrations of legumes samples using dry ash were found 35.25 ± 0.87 mg kg⁻¹, 43.62 ± 2.56 mg kg⁻¹, 26.74 ± 0.80 mg kg⁻¹ and 7.59 ± 0.32 mg kg⁻¹ for chickpeas and 29.60 ± 1.52 mg kg⁻¹, 55.24 ± 3.32 mg kg⁻¹, 14.13 ± 0.38 mg kg⁻¹ and 6.71 ± 0.21 mg kg⁻¹ for haricot bean, respectively. Zn, Fe, Mn and Cu average concentrations of legumes samples using microwave digest system were found 37.53 ± 1.78 mg kg⁻¹, 36.39 ± 2.92 mg kg⁻¹, 27.01 ± 0.32 mg kg⁻¹ and 9.20 ± 0.23 mg kg⁻¹ for chickpeas and 34.26 ± 0.47 mg kg⁻¹, 53.43 ± 3.83 mg kg⁻¹, 13.99 ± 0.16 and 9.24 ± 0.27 mg kg⁻¹ for haricot bean, respectively.

Keywords: Microwave digest system, metals, legumes, FAAS

References

1. Prashanth L., Kattapagari K.K., Chitturi RT., Baddam V.R.R., Prasad L.K., A review on role of essential trace elements in health and disease, Journal of Dr. NTR University of Health Sciences (2015) 4, 75-85.

Assessment Phenolic Content of Strawberry

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Many kinds of diseases have been treated with herbal remedies since ancient times. Herbal remedies are still being used extensively in many countries. Therefore, research on biologically active extracts and compounds from natural sources have been of great interest to scientists in an attempt to discover new sources for drugs that may be useful in combating infectious diseases. Phenolic compounds are widely reported to be beneficial to health, having been shown to possess anti-carcinogenic, anti-tumor and anti-oxidative properties [1]. In developed countries, one out of every four people will eventually suffer cancer, claiming over 6 million lives each year worldwide.

Many authors reported that it was necessary to establish a rational relationship between chemical, biological and therapeutic activities in traditional medicine [2,3]. In recent years, there has been a resurgence of interest in evaluating plants possessing antibacterial activities for various diseases.

The objective of this work was to investigate the assessment phenolic content of strawberry and as consequence to exploit its potential as a natural preservative food source. For this aim, thirteen different phenolic compounds such as gallic acid, (+)-catechin, (-)-epicatechin, chlorogenic acid, caffeic acid, *p*-coumaric acid, naringin, hesperidine, phlarizidinedihydrate, rutin, ellagic acid, myricetin and quercetin in strawberry were investigated using high performance liquid chromatography-diode array detector (HPLC-DAD). Flow rate, injection volume and column temperature were applied 1.0 mL min⁻¹, 10 µL and 30 °C, respectively. It was determined chlorogenic acid, caffeic acid, *p*-coumaric acid, naringin, ellagic acid and quercetin in strawberry. This study clearly showed that this plant constitutes an excellent source of phenolic compound and makes it a potential source of dietary regime. Because of this potential it can play a protective role against serious diseases.

Keywords: Strawberry, phenolic compounds, HPLC-DAD

References

1. Christopoulou G.E., Stavropoulou A., Anastassopoulos G., Panteliou S.D., Papadaki E., Karamanos NK., Panagiotopoulos E., Journal of Pharmaceutical and Biomedical Analysis (2006) 41 891-897.
2. Khlebnikov A.I., Schepetkin I.A., Domina N.G., Kirpotina L.N., Quinn M.T., Bioorg. Med. Chem. (2007) 15 1749-1770.
3. Fura A., Drug. Disc. Today (2006) 11 133-142.
4. Yildirim N.C., Turkoglu S., Ince O.K., Ince M., Cell. Mol. Biol. (2013) 59 1882-1888.

Determination of Phenolic Compounds in Cranberry Using HPLC-DAD

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Phenolic compounds find in many foods and beverages such as fruits, vegetables, flowers, wine and tea. They are a group of organic compounds having one or more hydroxyl groups on the aromatic ring and/or rings. These compounds known as polyphenols have a wide range from simple phenols to complex compounds. One of the most important members of phenolic compounds are highly diverse in terms of both their chemical structure and proposed biological functions [1-3].

The purpose of the study is to investigate phenolic compounds in cranberry that exhibit antioxidant, anticancer, anti-atherosclerotic, anti-inflammatory and anti-neurodegenerative properties. For this aim, thirteen different phenolic compounds which consisted of (+)-catechin, gallic acid, chlorogenic acid (-), epicatechin, caffeic acid, *p*-coumaric acid, naringin, hesperidine, phlarizidinedihydrate, rutin, ellagic acid, myricetin and quercetin in cranberry were investigated using high performance liquid chromatography-diode array detector (HPLC-DAD). Chlorogenic acid, caffeic acid, *p*-coumaric acid, naringin and ellagic acid were determined in cranberry.

Keywords: Phenolic Compounds, cranberry, HPLC-DAD

References

1. Robards K., and Antolovich M., Analyst (1997) 122 11R-34R.
2. Karaaslan N.M., Yaman M., European Food Research and Technology (2016) 242 127-135.
3. Mišan AČ., Mimica-Dukić N.M., Mandić A.I., Sakač M.B., Milovanović I.L., Sedej IJ., Cent. Eur. J.Chem. (2011) 9 133-142.

The Antioxidant Activities of Some *Salvia* Species

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The *Salvia* genus belongs to the subfamily *Nepetoideae* in *Lamiaceae* family. The genus consists of about 900 species (1). Many *Salvia* species are used as herbal tea and for food flavoring, as well as in cosmetics, perfumery and the pharmaceutical industries throughout World (2). *Salvia* species are generally known for their multiple pharmacological effects including their antibacterial, antiviral, antioxidative, antimalarial, anti-inflammatory, antidiabetic, cardiovascular, antitumor and anticancer (3). Also, some studies showed that a part of these activities depended on essential oil composition (4,5). The essential oil of this *Salvia* was tested for antioxidant (β -Carotene-linoleic acid test system, DPPH free radical scavenging activity, ABTS cation radical decolorisation and cupric reducing antioxidant capacity) activities in our study. Essential oil samples were obtained by a Clevenger apparatus from the whole parts of plants which were crumbled into small pieces and soaked in distilled water for 3 h. Then, these samples were dried over anhydrous Na₂SO₄ and stored at +4°C for a sufficient period of time.

The antioxidant activities of essential oils of four *Salvia* species were determined medium and low values, generally. The essential oil of *S. palaestina*'s was show as a good activity with β -Carotene-linoleic acid testing system method, especially. The essential oils of *S. macrochlamys*, *S. sclarea* and *S. hypargeia* were determined as a good activity with ABTS cation radical decolorisation method. Also studied four essential oils were show low activity with cupric method, but its were show no activity with DPPH free radical scavenging method.

Keywords: *Salvia Sclarea*, *Salvia Macrochlamys*, *Salvia Hypargeia*, *Salvia Palaestina*, Essential Oil, Antioksidant

References:

1. Çadirci E, Süleyman H, Kuruüzüm UA, Güvenalp Z, Demirezer LÖ Turkish Journal of Biology (2012) 36 59-64.
2. Baytop T (1999) Türkiye’de Bitkiler Ile Tedavi (2nd ed.), Nobel Tip Kitapevleri Ltd Sti. Istanbul.
3. Deans SG and Simpson EJM (2000) Antioxidants from *Salvia officinalis*, In: Kintzios SE Sage Harwood Academic Publishers.
4. Tepe B, Daferera D, Sokmen A, Sokmen M, and Polissou M *Food Chemistry* (2005) 90 333–340.
5. Alizadeh A, Shaabani M *Advances in Environmental Biology* (2012) 6 (1) 221-226.

The Anticholinesterase Activity and Total Phenolic Content of Some *Salvia* Species from Anatolia

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The *Salvia* genus belongs to the subfamily *Nepetoideae* in *Lamiaceae* family. The genus consists of about 900 species (1). Many *Salvia* species are used as herbal tea and for food flavoring, as well as in cosmetics, perfumery and the pharmaceutical industries throughout World (2). *Salvia* species are generally known for their multiple pharmacological effects including their antibacterial, antiviral, antioxidative, antimalarial, anti-inflammatory, antidiabetic, cardiovascular, antitumor and anticancer (3). Also, some studies showed that a part of these activities depended on essential oil composition (4,5). The essential oil of this *Salvia* was tested for anticholinesterase (Acetyl- and butyrylcholinesterase enzymes) activities and total phenolic in our study. Essential oil samples were obtained by a Clevenger apparatus from the whole parts of plants which were crumbled into small pieces and soaked in distilled water for 3 h. Then, these samples were dried over anhydrous Na₂SO₄ and stored at +4°C for a sufficient period of time

The essential oils of studied four *Salvia* species were determined the similar results as total phenolic content. Their butyrylcholinesterase enzyme activity were determined as high.

Keywords: *Salvia Multicaulis*, *Salvia Pinnata*, *Salvia Spinosa*, *Salvia Montbretii*, Essential Oil, Antioxidant

References

1. Çadirci E, Süleyman H, Kuruüzüm UA, Güvenalp Z, Demirezer LÖ Turkish Journal of Biology (2012) 36 59-64.
2. Baytop T (1999) Türkiye’de Bitkiler ile Tedavi (2nd ed.), Nobel Tıp Kitapevleri Ltd Sti. Istanbul.
3. Deans SG and Simpson EJM (2000) Antioxidants from *Salvia officinalis*, In: Kintzios SE Sage Harwood Academic Publishers.
4. Tepe B, Daferera D, Sokmen A, Sokmen M, and Polissou M *Food Chemistry* (2005) 90 333–340.
5. Alizadeh A, Shaabani M *Advances in Environmental Biology* (2012) 6 (1) 221-226.

Total Phenolic-Flavonoid Contents, Antioxidant and Anticholinesterase Activities of *Salvia Pseudeuphratica*

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Salvia is a large and widespread genus with a diversity of ethnobotanical uses. Many plants from *Salvia* genus have been used for centuries (1). Many of *Salvia* species are named “Adaçayı” in Anatolia, Turkey, and used as herbal tea due to their antiseptic, stimulant, diuretic and wound healing properties (2). *Salvia* species are generally known for their several pharmacological effects including antibacterial, antituberculous, antiviral, cytotoxic and cardiovascular activities (3). In this study, we aimed determination of total phenolic-flavonoid contents, antioxidant and antialzheimer activities of different parts (stems, leaves, flowers, roots and mixed parts) of *Salvia pseudeuphratica*. Chloroform extract of mixed parts of *S. pseudeuphratica* is rich in phenolic (pyrocatechol equivalent) and flavonoid (quercetin equivalent) contents with 92.94 ± 1.99 µg PEs/mg extract and 30.84 ± 0.90 µg QEs/mg extract, respectively. Ethanol extracts of *S. pseudoeuphratica* root have been found better antioxidant activities in studied antioxidant tests, namely β-caroten-linoleic acid test system, DPPH free and ABTS cation radical scavenging activities with $IC_{50}: 22.15 \pm 0.72$ µg/mL, 31.95 ± 0.59 µg/mL and 34.15 ± 0.59 µg/mL values, respectively. Ethanol extracts of *S. pseudoeuphratica* root have better activity in CUPRAC-cupric reducing antioxidant capacity assay. Ethanol extract of *S. pseudeuphratica* leaves has good antibutyrylcholinesterase activity with 74.69 ± 1.19 % inhibition at 200 µg/mL.

Keywords: *Salvia Pseudeuphratica*, Total Phenolic-Flavonoid Content, Antioxidant, Anticholinesterase

Acknowledgements: The research was funded by grant: KBAG 114Z801 from TUBITAK, The Scientific and Technological Research Council of Turkey.

References:

1. Wu, Y-B., Ni, Z-Y., Shi, Q-W., Dong, M., Kiyota, H., Gu, Y-C., Cong, B. Chemical Reviews (2012) 112 5967-6026.
2. Baytop T. (1984). Therapy with medicinal plants in Turkey. University of İstanbul Press. İstanbul.
3. Topcu, G., Öztürk, M., Kuşman, T., Barla-Demirkoz, A., Kolak, U., Ulubelen, A. Turkish Journal of Chemistry, (2013) 37 619-632.

LC-MS/MS Analysis of Different Parts of *Salvia Pseudeuphratica*

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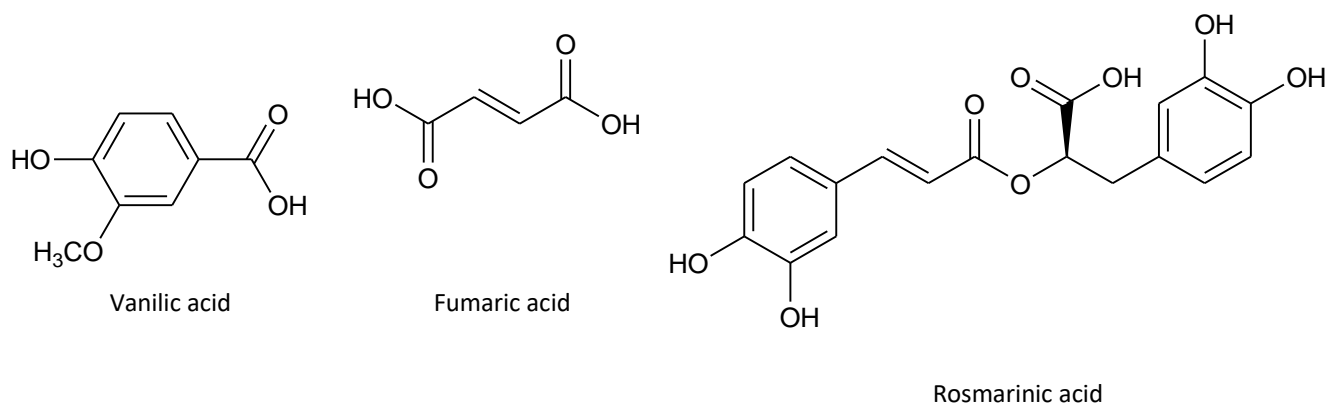
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The genus *Salvia* (Lamiaceae) is represented by 95 species in Turkish flora. Endemism ratio of this genus is approximately 50% in Turkey (1). The genus *Salvia* is an important source of terpenoids, flavonoids and other phenolics with antioxidant, anti-tuberculous, anti-inflammatory, neuroprotective and anticholinesterase properties. (2). In this study, secondary metabolite profile (37 phytochemicals including 15 Phenolic acids, 17 flavonoids, 3 nonphenolic organic acids, 1 phenolic aldehyde and 1 penzopyrane) of ethanol extracts of different parts (stems, leaves, flowers, roots and mixed parts) of *Salvia pseudeuphratica* was determined with LC-MS/MS. LC-MS/MS method validation was developed for the qualitative and quantitative analysis of 37 phytochemicals. Rosmarinic acid was the main compound of leaves, flowers, roots and mixed (EtOH) parts (11256.23 ± 8.03 , 14088.73 ± 10.05 , 3604.27 ± 2.57 , 5510.05 ± 3.93 $\mu\text{g g}^{-1}$ extract, respectively); fumaric acid for mixed (chloroform) part (248.86 ± 0.03 $\mu\text{g g}^{-1}$ extract); and vanillic acid for stem part (1058.98 ± 0.54 $\mu\text{g g}^{-1}$ extract) of the *Salvia pseudeuphratica*.



Keywords: *Salvia Pseudeuphratica*, Phenolic Content, LC-MS/MS

Acknowledgements: The research was funded by grant: KBAG 114Z801 from TUBITAK, The Scientific and Technological Research Council of Turkey.

References

1. Kocak, M.S., Sarıkürkçü, C., Cengiz, M., Kocak, S., Uren, M.C., Tepe, B. Industrial Crops & Products (2016) 85 204-212.
2. Topcu, G. and Kuşman, T. Bezmialem Science, (2014) 1 1-25.

Biological Activities of *Salvia Cerino-Pruinosa* var. *Elazigensis*

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Different *Salvia* species are reported to show many biological activities and medicinal properties, such as antimicrobial, antioxidant, antibacterial, anti-inflammatory, antitumoral, anxiolytic, antidiabetic, anti-inflammatory, antifungal, antiparasmodial, hypoglycaemic and anticarcinogenic effects (1, 2). *Salvia* species are used as herbal tea due to their antiseptic, stimulant, diuretic and wound healing properties in Turkey (3). The aim of our study is determination of total phenolic-flavonoid contents, antioxidant and antialzheimer activities of different parts (stems, leaves, flowers, roots and mixed parts) of *Salvia cerino-pruinosa* var. *elazigensis*. Ethanol extract of leave parts of *Salvia cerino-pruinosa* var. *elazigensis* is rich in phenolic (pyrocatechol equivalent) and flavonoid (quercetin equivalent) contents with 229.94 ± 2.00 µg PEs/mg extract and 65.95 ± 0.90 µg QEs/mg extract, respectively. Ethanol extract of *Salvia cerino-pruinosa* var. *elazigensis* root has been found better antioxidant activity than the other extracts in β -caroten-linoleic acid test system (IC_{50} : 28.95 ± 0.11 µg/mL). Ethanol extract of *Salvia cerino-pruinosa* var. *elazigensis* leaves has the highest antioxidant activity among all extracts and standards in DPPH free and ABTS cation radical scavenging assays with IC_{50} : 5.72 ± 0.71 µg/mL and 2.43 ± 0.21 µg/mL values, respectively. Besides that, ethanol extract of the plant flowers has strong antioxidant activities in same methods. Ethanol extracts of root, leave and flower parts of *Salvia cerino-pruinosa* var. *elazigensis* have better activity than the other extracts and standards which are BHA and α -tocopherol in CUPRAC-cupric reducing antioxidant capacity assay. Ethanol extract of *Salvia cerino-pruinosa* var. *elazigensis* roots has moderate antibutyrylcholinesterase activity with 57.28 ± 1.36 % inhibition at 200 µg/mL.

Keywords: *Salvia Cerino-Pruinosa* var. *Elazigensis*, Total Phenolic-Flavonoid Content, Antioxidant, Anticholinesterase

Acknowledgements: The research was funded by grant : KBAG 114Z801 from TUBITAK, The Scientific and Technological Research Council of Turkey.

References:

1. Jeshvaghani, Z.A., Rahimmalek, M., Talebi, M., Sayed Amir Hossein Goli, S.A.M. Industrial Crops & Products (2015) 77 409-415.
2. Topcu, G., Öztürk, M., Kuşman, T., Barla-Demirkoz, A., Kolak, U., Ulubelen, A. Turkish Journal of Chemistry (2013) 37 619-632.
3. Baytop T. (1984). Therapy with medicinal plants in Turkey. University of İstanbul Press. İstanbul.

Phytochemical Analysis of Different Parts of *Salvia Cerino-Pruinosa* var. *Elazigensis* by Using LC-MS/MS

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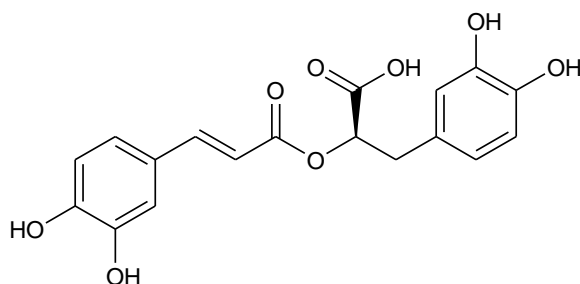
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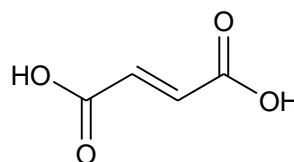
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Salvia is one of the largest genera of Lamiaceae and encompasses about 900 species distributed throughout the world (1). The genus *Salvia* (Lamiaceae) is represented by 95 species in Turkish flora. Endemism ratio of this genus is approximately 50% in Turkey (2). The phytochemical analyses of *Salvia* species exhibited the presence of various types of compounds including terpenoids and phenolic compounds, which consist of phenolic acids, phenolic glycosides and flavonoids (3). In this study, secondary metabolite profile (37 phytochemicals including 15 Phenolic acids, 17 flavonoids, 3 nonphenolic organic acids, 1 phenolic aldehyde and 1 penzopyrane) of ethanol extracts of different parts (stems, leaves, flowers, roots and mixed parts) of *Salvia cerino-pruinosa* var. *elazigensis* was determined with LC-MS/MS. Rosmarinic acid was the main compound of leaves, flowers, roots, stems and mixed (EtOH) parts (34638.42 ± 24.70 , 14898.05 ± 10.62 , 7107.27 ± 5.07 , 1701.59 ± 1.21 , $15666.13 \pm 11.17 \mu\text{g g}^{-1}$ extract, respectively) and fumaric acid for mixed (chloroform) part ($269.82 \pm 0.03 \mu\text{g g}^{-1}$ extract) of the *Salvia cerino-pruinosa* var. *elazigensis*.



Rosmarinic acid



Fumaric acid

Keywords: *Salvia Cerino-Pruinosa* var. *Elazigensis*, Phenolic Content, LC-MS/MS

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References:

1. Jeshvaghani, Z.A., Rahimmalek, M., Talebi, M., Sayed Amir Hossein Goli, S.A.M. Industrial Crops & Products (2015) 77 409-415.
2. Kocak, M.S., Sarıkürkçü, C., Cengiz, M., Kocak, S., Uren, M.C., Tepe, B. Industrial Crops & Products (2016) 85 204-212.
3. Topcu, G, Kuşman, T. Bezmialem Science (2014) 1 1-25.

Fatty Acid Composition of Some Endemic Salvia Species by Using GC/MS

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The aim of this study was to determine the fatty acid composition of petroleum ether extracts of *Salvia cerino-pruinosa* var. *cerino-pruinosa*, *Salvia siirtica*, *Salvia rosifolia* and *Salvia kurdica*. (*S. siirtica*, *S. kurdica*, *S. cerino-pruinosa* var. *cerino-pruinosa* and *S. rosifolia* species were collected from the east of Turkey (Hakkari, Şırnak, Elazığ and Kars, respectively) and identified by Mehmet Fırat) (Yüzüncü Yıl University, Faculty of Education, Department of Biology, TR-65080 Van,). Voucher specimens were deposited in the Herbarium of Van Yuzuncu Yıl University, Faculty of Science (*S. siirtica* VNF 30755, *S. kurdica* VNF32564, *S. cerino-pruinosa* var. *cerino-pruinosa* VNF 32538, *S. rosifolia* VNF32536). Powdered form of the whole plant material was weighed (100 g) and macerated three times with petroleum ether (250 mL each) at 25 °C for 24 hours. Esterification of the petroleum ether extract and GC/MS procedures were applied as described by Ertas et al (1). Thermo Scientific Polaris Q GC-MS/MS instrument was used. The major fatty acid components were identified as oleic acid (27.88%) for *S. cerino-pruinosa* var. *cerino-pruinosa*, erucic acid (29.03%) for *S. siirtica*, erucic acid (44.61%) for *S. rosifolia* and nervonic acid (19.46%) for *S. kurdica*.

Keywords: *Salvia*, Fatty acid, GC-MS

Acknowledgements: The research was funded by grant : KBAG 114Z801 from TUBITAK, The Scientific and Technological Research Council of Turkey.

References:

1. Ertas A., Boğa M., Haşimi N., Yeşil Y., Gören A.C., Topcu G., Kolak U. Turkish Journal of Chemistry (2014) 38 592-599.

Chemical Profile of *Salvia Cerino-Pruinosa* var. *Cerino-Pruinosa* and *Salvia Rosifolia* by Using LC-MS/MS

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Since ancient times, *Salvia* species have been used in folk medicine for the treatment of diabetes and skin diseases such as psoriasis and eczema. These species have been the subject of extensive pharmacognosic researches that were intended to identify biologically active compounds (1, 2). Particular attention has been shown to the members of the genus *Salvia* due to their wide range of important biological activities such as antifungal activity, antitumor activity, antibacterial activity, antiviral activity, cytotoxic activity, antioxidant activity, treatment of heart disease, and antimycobacterial activity (3). In this study, secondary metabolic profile of ethanol extracts of *Salvia cerino-pruinosa* var. *cerino-pruinosa* and *Salvia rosifolia* were investigated using LC-MS/MS. A comprehensive LC-MS/MS method validation was developed for the qualitative and quantitative analysis of 37 phytochemicals including 15 Phenolic acids, 17 flavonoids, 3 nonphenolic organic acids, 1 phenolic aldehyde and 1 penzopyrane. The phenolic profile of the ethanolic extracts of different parts (stems, leaves, flowers, roots and mixed parts) of two *Salvia* species were determined quantitatively by LC-MS/MS. It was observed that both species (notably their root extracts) possess high amounts of rosmarinic acid. Besides, leaf and stem extracts of both species were rich in terms of fumaric acid and hesperidin.

Keywords: *Salvia Cerino-Pruinosa* var. *Cerino-Pruinosa* and *Salvia Rosifolia*, Phenolic Content, LC-MS/MS

Acknowledgements: The research was funded by grant : KBAG 114Z801 from TUBITAK, The Scientific and Technological Research Council of Turkey.

References:

1. Baytop T. Therapy with medicinal plants in Turkey. University of İstanbul Press. İstanbul (1984).
2. Lu Y, Foo LY. Phytochemistry (2002) 59 114-140.
3. Tepe B, Daferera D, Sokmen A Food Chemistry (2005) 90 333-340.

Total Phenolic-Flavonoid Content and Anticholinesterase Activities of Two Endemic *Salvia* Species from East Anatolia

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Salvia species, commonly known as sage, have been used since ancient times for more than sixty different ailments of aches, epilepsy, colds, bronchitis, tuberculosis, hemorrhage, and menstrual disorders (1). The aim of this study was to determine the total phenolic (2) and flavonoid (3) content and anticholinesterase activities of different parts and extract (4) of *Salvia cerino-pruinosa* var. *cerino-pruinosa* and *Salvia rosifolia*. The anticholinesterase potential of the extracts was indicated by Ellman method. The amounts of total phenolic and flavonoid components in crude extracts were determined by expressing as pyrocatechol and quercetin equivalents, respectively. Ethanol extract of *Salvia cerino-pruinosa* var. *cerino-pruinosa* was determined to be rich in total phenolic content and chloroform extract was rich in total flavonoid content. It was determined that ethanol extract of especially leaves of these species is richer both in total phenolic and total flavonoid content. As for *Salvia rosifolia*, petroleum ether extract was determined to be richer than the ethanol and the chloroform extracts in terms of both in phenolic and flavonoid content. Therefore, it can be said that phenolic and flavonoid compounds of these species are mostly non-polar structure. All type extract of both species were determined to have no acetylcholinesterase activity. While all type extract of *S. rosifolia* have no butyrylcholinesterase enzyme activity, all type extract of *S. cerino-pruinosa* var. *cerino-pruinosa* have shown good activity in this method.

Keywords: *Salvia Cerino-Pruinosa* var. *Cerino-Pruinosa*, *Salvia Rosifolia*, Total Phenolic, Total Flavonoid, Anticholinesterase.

Acknowledgements: The research was funded by grant : KBAG 114Z801 from TUBITAK, The Scientific and Technological Research Council of Turkey.

References:

1. Topcu G., Journal of Natural Products (2006) 69 482–487
2. Slinkard, K.; Singleton, V.L. American Journal of Enology and Viticulture (1977) 28 49-55.
3. Moreno, M.I.N.; Isla, M.I.; Sampietro, A.R.; Vattuone, M.A. Journal of Ethnopharmacology (2000) 71 109-114.
4. Ellman, G.L.; Courtney, K.D.; Andres, V.; Featherstone, R.M. Biochemical Pharmacology (1961) 7 88-95.

Biological Activities of *Thymus Cariensis* and *Thymus Convolutus* Endemic to Turkey

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The genus *Thymus* L. is a member of Lamiaceae family and represented by 318 species in the world, 40 species in Turkey and 18 of them are endemic for Turkey (45%) (1). In Turkish folk medicine it is used for its antihelmintic, palliative, stomachic, lowering blood circulation effects, and for protection of mouth and teeth health (2). In this study, determination of total phenolic-flavonoid contents, antioxidant and antialzheimer activities of two endemic *Thymus* species were aimed. Ethanol extracts of whole plant of *Thymus cariensis* rich in phenolic (pyrocatechol equivalent) content; and ethanol extract of aerial part of *Thymus convolutus* rich in flavonoid (quercetin equivalent) contents with 58.07 ± 0.60 µg PEs/mg extract and 25.51 ± 0.85 µg QEs/mg extract, respectively. All extracts did not show antioxidant activity in β-caroten-linoleic acid test system. Ethanol extract of *Thymus cariensis* showed better antioxidant activity than the other extracts in DPPH free radical scavenging activity with $IC_{50}: 34.97 \pm 1.00$ µg/mL value. Ethanol extract of *Thymus convolutus* root showed very strong ABTS cation radical scavenging activity ($IC_{50}: 9.43 \pm 0.33$ µg/mL). None of extracts showed antiacetylcholinesterase activity; only the ethanol extract of *Thymus cariensis* showed antibutyrylcholinesterase activity with 32.26 ± 0.27 % inhibition at 200 µg/mL.

Keywords: *Thymus Cariensis*, *Thymus Convolutus*, Antioxidant, Antialzheimer

Acknowledgements: The research was funded by grant : 14-EZF-69, Dicle University Scientific Research Projects Coordinator

References:

1. Ertaş, A., Boğa, M., Yilmaz, M.A., Yesil, Y., Tel, G., Temel, H., Haşimi, N., Gazioğlu, I., Öztürk, M., Uğurlu, P. Industrial Crops and Products, (2015) 67 336-345
2. Baytop T. Therapy with medicinal plants in Turkey. University of İstanbul Press. İstanbul; 1984.

Essential Oil Analysis of Two Endemic Thymus Species: *Thymus Cariensis* and *Thymus Convolutus*

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The genus *Thymus* L. is a member of Lamiaceae family and represented by 318 species in the world, 40 species in Turkey and 18 of them are endemic for Turkey (45%) (1). In Turkish folk medicine it is used for its antihelmintic, palliative, stomachic, lowering blood circulation effects, and for protection of mouth and teeth health (2). Among the aromatic plants which belong to the family Lamiaceae, essential oils and extracts of the genus *Thymus* are remarkable for its high antimicrobial and antioxidant effects compared to other plants (1). Essential oils are natural, volatile, complex compounds known for their antibacterial, antifungal, antiviral, antioxidant and medicinal properties (3). In this study, we aimed essential oil analysis of two endemic *Thymus* species namely *Thymus cariensis* and *T. convolutus*. Essential oils of the two plants were obtained by using a Clevenger apparatus from the aerial parts. The major components of the essential oils were identified as carvacrol (43.0%), germacrene D (19.0%) for *Thymus cariensis*, camphor (12.7%), α -pinene (10.2%), 1,8-cineole (10.1%) and cubenol (8.1%) for *Thymus convolutus*.

Keywords: *Thymus Cariensis*, *Thymus Convolutus*, Essential Oil, GC-MS

Acknowledgements: The research was funded by grant: 14-EZF-69, Dicle University Scientific Research Projects Coordinator

References:

1. Ertas, A., Boğa, M., Yilmaz, M.A., Yesil, Y., Tel, G., Temel, H., Haşimi, N., Gazioğlu, I., Öztürk, M., Uğurlu, P. Industrial Crops and Products (2015) 67 336-345
2. Baytop T. Therapy with medicinal plants in Turkey. University of İstanbul Press. İstanbul; 1984.
3. Boubakera, H., Karima, H., El Hamdaoui, A., Msanda, F., Leach, D., Bombarda, I., Vanloot, P., Abbad, A., Boudyach, E.H., Ait Ben Aoumar A. Industrial Crops and Products (2016) 86 95-101

Chemical Profile of *Salvia Sclarea* by LC-MS/MS Using the Ethanol Extract

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Salvia species are generally known for their multiple pharmacological effects including their antibacterial, antiviral, antioxidative, antimalarial, anti-inflammatory, antidiabetic, cardiovascular, antitumor and anticancer (1). In this study, secondary metabolic profile of ethanol extracts of *Salvia sclarea* were determined using LC-MS/MS. A comprehensive LC-MS/MS method validation was developed for the qualitative and quantitative analysis of 37 phytochemicals including 15 Phenolic acids, 17 flavonoids, 3 nonphenolic organic acids, 1 phenolic aldehyde and 1 benzopyrane (2). *S. sclarea* was collected from east Turkey (Van Bahçesaray) in June 2015 and characterized by Mehmet Firat (Yüzüncü Yıl University, Faculty of Education, Department of Biology, TR-65080 Van,). Voucher specimens were deposited in the Herbarium of Van Yuzuncu Yıl University, Faculty of Science (VANF30657). The powdered plants (stems, leaves, flowers, roots and mixed parts) were extracted three times with ethanol (50 mL each) at room temperature for 24 h. Afterwards, the extracts obtained were combined, filtered and evaporated under low pressure. Dry filtrates were reconstituted in ethanol at a concentration of 250 mg L⁻¹ and filtered through the 0.2 µm PTFE filter prior to LC-MS/MS analysis. Especially, the all extracts of *S. sclarea* were determined to possess very high amounts of rosmarinic acid. Besides, root and stem extracts of both species were rich in terms of fumaric acid.

Keywords: *Salvia Sclarea*, LC-MS/MS, Phenolic Content

References:

1. S.G. Deans, E.J.M. Simpson (2000) Antioxidants from *Salvia officinalis*. In: Kintzios SE Sage. Harwood Academic Publishers, pp.185-192.
2. A. Ertas, M.A. Yilmaz, M. Firat, Nat. Prod. Res. (2015) 29(6) 529–534.

The Biological Activities of *Salvia Suffruticosa* from Anatolia

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Salvia species are generally known for their multiple pharmacological effects including their antibacterial, antiviral, antioxidative, antimalarial, anti-inflammatory, antidiabetic, cardiovascular, antitumor and anticancer (1). In this research, total phenolic and flavonoid content, antioxidant and anticholinesterase activities of extracts obtained from various parts of (roots, leaves, stems, flowers and mixed) *Salvia suffruticosa* were compared. *S. suffruticosa*, which was collected from east Turkey (Van Gürpınar) in May 2015 and characterized by Mehmet Firat (Yüzüncü Yıl University, Faculty of Education, Department of Biology, TR-65080 Van,). Voucher specimens were deposited in the Herbarium of Van Yuzuncu Yıl University, Faculty of Science (VANF30657). β -Carotene method, ABTS cation radical decolorisation method, cupric reducing antioxidant capacity assays and DPPH free radical scavenging activity were carried out to indicate the antioxidant activity (2-5). The anticholinesterase potential of the extracts were indicated by Ellman method (6). The amounts of total phenolic and flavonoid components in crude extracts were determined by expressing as pyrocatechol and quercetin equivalents, respectively. Among the studied extracts which prepared from parts of the flower was found to be richer in terms of both total phenolic and total flavonoid. It was determined that working in all extracts not show acetylcholinesterase activity but show a moderate butyrylcholinesterase activity. Furthermore, all of the extracts prepared from the various parts of this species as the four working methods of antioxidant activity was determined to have high antioxidant potential.

Keywords: *Salvia Suffruticosa*, Antioksidant, Anticholinesterase, Total Phenolic-Flavonoid

References:

1. S.G. Deans and E.J.M. Simpson (2000) Antioxidants from *Salvia officinalis*. In: Kintzios SE Sage. Harwood Academic Publishers, pp.185-192.
2. H.E. Miller J. Am. Oil Chem. Soc. (1971) 48 91.
3. M.S. Blois Nature (1958) 181 1199-1200.
4. R. Re, N. Pellegrini, A. Proteggente, A. Pannala, M. Yang, C. Rice-Evans Free Radical Bio. Med. (1999) 26 1231-1237.
5. R. Apak, K. Guçlu, M. Özyurek, S.E. Karademir J. Agric. Food Chem (2004) 52 7970-7981.
6. G.L. Ellman, K.D. Courtney, V. Andres, R.M. Featherstone Biochem. Pharmacol. (1961) 7 88-95.

The Determination of Trace Metal Content of Different Parts of *Euphorbia Denticulata* and *E. Fistulosa*

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Euphorbia is one of the largest genus which belongs to the Euphorbiaceae family, and represented by 105 species in Turkey [1]. *Euphorbia* species are named as ‘Sütleğen’ and ‘Xaşıl’ [2]. *Euphorbia* species are commonly used in Turkish folk medicine for the treatment of rheumatism, swelling as well as a wart remover. However, inflammation and diarrhoea are the two potential side effects that might occur during the treatment [2]. It’s known that plant’s root parts are accumulate trace metal elements more than plant’s other parts. Additionally some *Euphorbia* species show accumulating few metals effect was known in literature [3]. In this study, different parts of *Euphorbia denticulata* and *Euphorbia fistulosa* species (root, stem, leaves, flower, seed and also mixed parts separately) were dried and then homogenized. Homogenized plant samples were digested by microwave oven. Heavy metal contents of prepared samples were observed by ICP-MS instrument. Depending on our results, different parts of the studied species were observed to contain different amounts of trace metals. Moreover, Cu and Zn elements were found to be the richest metals in the studied *E. denticulata* and *E. fistulosa* species. *E. fistulosa* that was collected from Diyarbakır was determined to have higher Pb concentration compared to *E. denticulata* that was collected from Kayseri. As a result, it was observed that *E. denticulata* and *E. fistulosa* species accumulate Cu, Pb, Cr, Ni, Co and Se elements.

Keywords: *Euphorbia Denticulata*, *Euphorbia Fistulosa*, Heavy Metal, ICP-MS

References:

1. Oztekin M.; Euphorbia L.; Güner A.; Aslan S.; Ekim T, Vural M.; Babac M.T.; Editors. (2012) A checklist of the flora of Turkey (vascular plants). Istanbul: Nezahat Gökyiğit Botanic Garden (NGBB), ANG Foundation and Flora Research Society; p. 414–424.
2. Baytop T. (1994) Türkçe Bitki Adları Sözlüğü [Dictionary of Vernacular Names of Wild Plants of Turkey]. Ankara: Türk Tarih Kurumu Basımevi, 385 pp.
3. Malayeri, B.E.; Chhregani, A.; [Mohsenzadeh, F.](#); [Kazemeini, F.](#); [Asgari, M.](#) (2013) Toxicological And Environmental Chemistry, 95, 434-444.

Chemical Profile by LC-MS/MS the Methanol Extract of *Euphorbia Denticulata*

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The family Euphorbiaceae is widely distributed in temperate regions of the world. Within the family Euphorbiaceae, the sixth largest flowering genus *Euphorbia* L., with well over 1000 species, is subdivided into many subgenera and sections, a number of which have been treated as distinct genera[1]. Plants belonging to *Euphorbia* spp. have been the subject of many investigations for their biologically active components [2, 3]. Their biological activities, including skin irritant, tumor promotion, and pro-inflammatory properties are attributed to the presence of specific classes of macro- and polycyclic diterpenes. Some species of *Euphorbia* have been used for the treatment of skin diseases, gonorrhea, migraine, intestinal parasites, and warts, and as anti-inflammatory agents in folk medicine [4]. A literature survey of the genus showed that many of its constituents are highly bioactive in phytochemical analysis. Many different parts of the *Euphorbia* species like roots, seeds, latex, stem, stembarks, leaves and whole plants have been studied. Moreover, it is found that the plants in the Euphorbiaceae family are well known for the chemical diversity of the isoprenoid constituents. The major constituents of the genus are diterpenoids. Many biological activities of the constituents of the *Euphorbia* species have been reported for a decade [5]. Root and aerial parts (stem, leave, flower and seed) of *E. denticulata* was collected from Kayseri in flowering period. Powdered form of the parts plant material was weighed (1 g) and macerated three times with methanol (10 mL each) at 25 °C for 24 hours. After filtration, the solvent was evaporated to get the crude extracts. Phenolic components in the methanol extract was quantified by LC-MS/MS. LC-MS/MS analysis of the phenolic compounds was performed by using a Nexera model Shimadzu UHPLC coupled to a tandem MS instrument. In the current study, twenty-four phenolic compounds (flavonoids, flavonoid glycosides, phenolic acids, phenolic aldehyde, coumarin) and three non-phenolic organic acids which are widespread in plant materials were qualified and quantified in *E. denticulata*. Among 27 compounds, malic acid, hesperidin, Quinic acid, Tannic acid, Hyperoside and rutin were found to be the more abundant compound in *E. denticulata*.

Keywords: *Euphorbia Denticulata*, LC-MS/MS, Phenolic Content

References:

1. Kupchan, S. M., Uchida, I., Branfman, A. R., Dailey, R. G. and Fei, B.Y, *Science*, (1976) **191** 571.
2. Di Stefano, V., Pitonzo, R. and Schillaci D., *Chem. Nat. Compd.*, (2011) **47** 660.
3. Kang, W., Wang, J. and Cao N., *Chem. Nat. Compd.*, (2012) **48** 886.
4. Demirkiran, O., Topcu, G., Azarpira, A. Choudhary, M.I., *Chem. Nat. Compd.*, (2014) **50** 810-813.
5. Ertaş, A., Yılmaz, M. A., Firat M., *Nat. Prod. Res.*, (2015) **29**(6) 529–534.

The Total Phenolic-Flavonoid Content, Cytotoxic, Antioxidant and Anticholinesterase Activities of Ethanol Extract of *Allium Scabriscapum*

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In Turkey, traditionally consumed *Allium* genus like kormen, rock garlic, savage onion, savage garlic, dog onion and shepherd garlic are also used as food or used in treating aims (1)

In this research, total phenolic and flavonoid content, antioxidant and anticholinesterase activities of the extracts obtained from various parts of *Allium scabriscapum* were compared. *Allium scabriscapum* was collected from east of Turkey (Van, Gürpınar) in April 2015. Voucher specimens were deposited in the Herbarium of Van Yuzuncu Yıl University, Faculty of Science (VANF31171). The powdered plant was extracted three times with ethanol (50 mL each) at room temperature for 24 h. Afterwards, the extract obtained was combined, filtered and evaporated under low pressure. β -Carotene-linoleic acid, ABTS cation radical decolorisation, cupric reducing antioxidant capacity and DPPH free radical scavenging assays were carried out for the antioxidant activity (2-5). The anticholinesterase potential of the extracts was studied spectrophotometrically (6). The total phenolic and flavonoid contents in crude extracts were determined as pyrocatechol and quercetin equivalents, respectively. The ethanol extracts exhibited good activity in ABTS assay. However, when compared with the standards the extracts indicated mild activity in other antioxidant activity assays. In addition, these both ethanol extracts were in active against acetylcholinesterase and butyrylcholinesterase enzymes. The last but not the least is these both extract exhibited moderate activity against DLD-1 (colon cancer) cancer cell lines.

Keywords: *Allium Scabriscapum*, Cytotoxic, Antioxidant, Anticholinesterase, Total Phenolic-Flavonoid

References:

1. Güner, A., Aslan, S., Ekim, T., Vural, M., Babaç, M.T. (eds.) (2012) *Türkiye Bitkileri Listesi (Damarlı Bitkiler)*. Nezahat Gökyiğit Botanik Bahçesi ve Flora Araştırmaları Derneği Yayını, İstanbul.
2. Miller, H.E. J. Am. Oil Chem. Soc. (1971) 48 91-91.
3. Blois, M.S. Nature (1958) 181 1199-1200.
4. Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M., Rice-Evans, C. Free Radical Bio. Med. (1999) 26 1231-1237.
5. Apak, R., Guçlu, K., Özyurek, M., Karademir, S.E. J. Agric. Food Chem (2004) 52 7970-7981.
6. Ellman, G.L., Courtney, K.D., Andres, V., Featherstone, R.M. Biochem. Pharmacol. (1961) 7 88-95.

NMR Studies on the Secondary Metabolites of *Tricholoma Anatolicum*

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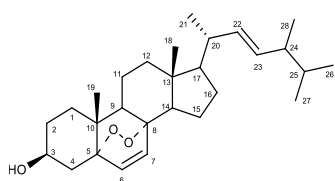
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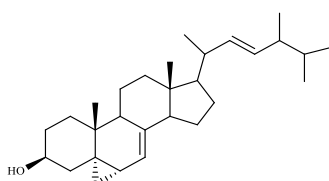
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Wild mushrooms have been used since ancient times as food and medicinal purposes. Recently, the mushrooms have been interested by the researchers due to their biologically active compounds. Anticancer, antiviral, antioxidant and immunomodulatory agents were isolated from the mushrooms [1]. The studies indicated that the mushrooms can also be used for medicinal purposes. *Tricholoma anatolicum* H.H. Doğan & Intini, growing naturally in Fethiye-Muğla and Kozan-Adana during September time, is exported 50 tons every year to Japan. Due to the economic importance and delicious taste the secondary metabolites of the mushroom were studied. The isolated and elucidated compounds using the spectroscopic techniques were also screened for their bioactivities.

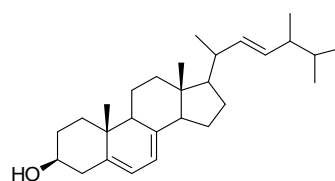
In this study *Tricholoma anatolicum* were collected from Fethiye-Muğla. It was extracted with petroleum ether, acetone and methanol at room temperature, successively. The acetone and methanol extracts were subjected to column chromatography. After purification the ergostane type steroids, which some of the structures of them were given following, were elucidated using ¹H-NMR, ¹³C-NMR, DEPT, HSQC, HMBC and MS spectroscopic techniques.



1



2



3

Keywords: *Tricholoma Anatolicum*, Isolation, Chromatography, NMR Spectroscopy, MS Spectrometry, Structure Elucidation

Acknowledgements: This study is supported by the TUBITAK with the project number SBAG-113R012.

References:

1. El Enshasy, H.A., Hatti-Kaul, R. Trends in Biotechnology (2013) 31 668–77.

The Phenolic Content Analysis of *Allium Scabriscapum* by LC-MS/MS

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Allium genus represented 800 species in the world and 179 species in Turkey [1]. Species that featured in *Allium* genus are splits some parts between each other. The most known species of *Allium* genus are onion, garlic and leek. Some species are also in the group whose head smells like onion, and generally appeared on Northern hemisphere (specially, on the area located between east of Europe and west of Asia) [1]. Kormen, rock garlic, savage onion, savage garlic, dog onion and shepherd garlic which are traditionally consumed *Allium* species are also used medicinally in Turkey [2]. In this study, secondary metabolic profile of ethanol extract of *Allium scabriscapum* was determined using LC-MS/MS. A comprehensive LC-MS/MS method validation was developed for the qualitative and quantitative analysis of 27 phytochemicals [3]. The powdered plant was extracted three times with ethanol (50 mL each) at room temperature for 24 h. Afterwards, the extracts obtained were combined, filtered and evaporated under low pressure. Dry filtrates was reconstituted in ethanol at a concentration of 250 mg.L⁻¹ and filtered through the 0.22 µm PTFE filter prior to LC-MS/MS analysis. In general, the LC-MS/MS study indicated that the species is poor in phenolic compounds; however, in the ethanol extract of aerial parts of species rutin and hesperidin were quantified in high amounts.

Keywords: *Allium Scabriscapum*, Phenolic Content, LC-MS/MS

References:

1. Güner, A., Aslan, S., Ekim, T., Vural, M., Babaç, M.T. (eds.) (2012) *Türkiye Bitkileri Listesi (Damarlı Bitkiler)*. Nezahat Gökyiğit Botanik Bahçesi ve Flora Araştırmaları Derneği Yayını, İstanbul.
2. Fritsch, R.M., Blattner, F.R., Gurushidze, M. *Phyton* (2010) 49 145-220.
3. Ertas, A., Yilmaz M.A., Fırat, M., *Nat. Prod. Res* (2015) 29 529–534.

Characterization of Phenolic Compounds of *Abies Numidica* by LC-ESI-MS/MS with Antioxidant and Anticholinesterase Activities

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The genus *Abies* (Pinaceae) consists of 51 species mainly distributed in temperate and boreal regions of the Northern hemisphere, essentially in mountainous regions [1, 2].



The cones of *Abies numidica* de Lannoy ex Carrière were used in folk medicine against cold, indigestion, stomach ache, pulmonary, vascular and venereal diseases [3]. Therefore, it is aimed to investigate the compounds of fractions (Fr.2, Fr.3, Fr.4) of cones of *Abies numidica* using LC-ESI-MS/MS along with antioxidant (DPPH, ABTS, β -carotene-linoleic acid and CUPRAC assays) and anticholinesterase (Ellman method against acetylcholinesterase and butyrylcholinesterase enzymes) activities.

Organic acids and phenols were identified for the first time in the genus *Abies* by LC-MS/MS. Quinic acid (214.9-829.7 $\mu\text{g/g}$ of dry extract), malic acid (766.3- 770.5 $\mu\text{g/g}$), hyperoside (204.6-35.3 $\mu\text{g/g}$), vanillin (148.9-152 $\mu\text{g/g}$), tannic acid (128.2- 141.7 $\mu\text{g/g}$), rosmarinic acid (106.3-114.9 $\mu\text{g/g}$), coumarin (68.3- 77.3 $\mu\text{g/g}$) and quercetin (88.1 $\mu\text{g/g}$ of dry extract) were some of the compounds identified in cones.

The Fr.3 showed the strongest antioxidant activity especially in the ABTS assay ($\text{IC}_{50} = 1.5 \pm 0.4 \mu\text{g/mL}$). Fr.2 showed better acetylcholinesterase inhibitory activity ($\text{IC}_{50} = 693.4 \pm 2.4 \mu\text{g/mL}$) while Fr.4 ($\text{IC}_{50} = 83.9 \pm 0.8 \mu\text{g/mL}$) exhibited the highest butyrylcholinesterase inhibitory activity.

Keywords: *Abies Numidica*, LC-MS/MS, Antioxidant Activity, Anticholinesterase Activity.

References:

1. Farjon, A., Rushforth, K.D. A classification of *Abies* Miller (Pinaceae). Notes Roy. Bot. Garden. Edinburg (1989) 46 59–79.
2. Uçar, G., Uçar, M.B. Rec. Nat. Prod. (2014) 8 56-60.
3. Fujita, T., Sezik, E., Tabata, M., Yeşilada, E., Honda, G., Takeda, Y., Tanaka, T., Takaishi Y. Econ Bot. (1995) 49 406–422.

Cytotoxic Activity of *Tricholoma Focale*

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Medicinal mushrooms are gaining interest because of their promising activities beside their nutritional properties. Unique odor and taste of wild edible mushrooms makes them preferred. Recently, many researchers have been investigated medicinal mushrooms to understand the origin of various bioactivities. Various biologically active compounds; such as, terpenes, steroids, lectins and glucans indicating anticancer, immunomodulatory, antioxidant, anticholinesterase activities have been isolated from mushrooms [1-2].

Tricholoma focale (Fr.) Ricken. grows naturally in conifer forests, and collected from Muğla region. The dried mushroom material was extracted with petroleum ether, acetone and methanol, and then with hot water, successively. The cytotoxic activity of extracts of *Tricholoma focale* against MCF-7 (breast cancer) and H1299 (lung cancer) cell lines were studied by WST method.

Tricholoma focale extracts showed toxic effects on MCF-7 and H1299 cell lines. Toxicity increased with increasing concentrations. Against MCF-7 acetone extract was the most active (15% cell viability at concentration of 75 µg/ml) while the water extract had notably activity. Against H1299 methanol extract was the most active (24% at concentration of 75 µg/ml). The acetone extract, however, exhibited also good cytotoxic effect.

Keywords: *Tricholoma Focale*, Cytotoxic Activity, MCF-7 (breast cancer cell line) and H1299 (lung cancer cell line)

Acknowledgements: This study is supported by the TUBITAK with the project number SBAG-113R012.

References:

1. Hassan, M.A.A., Rouf, R., Tiralongo, E., May, T.W., Tiralongo, J. International Journal of Molecular Sciences (2015) 16 7802–7838.
2. Kikuchi, T., Masumoto, Y., In, Y., Tomoo, K., Yamada, T., Tanaka, R. European Journal of Organic Chemistry (2015) 4645–4649.

Development and Validation of An RP-HPLC Method for Quantification of Galantamine in the Plant Extracts and Pharmaceutical Formulation

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Galantamine is a tertiary alkaloid and found generally in *Galantus Species* such as snowdrops, daffodils and *Leucojum aestivum*. These plants comprise galantamine in up to %0.3 concentration. It is cholinesterase inhibitor and is used in treatment of alzheimer, polio, narrow-angle glaucoma and as an antidote after poisonings and is still being investigated for use in treatment of alcohol and nicotine dependence, schizophrenia and cognitive memory disorders.

In this study, in the first step, a simple, accurate and sensitive HPLC method was developed for determination of galantamine. The chromatographic separation was carried out on RP C₁₈ ACE column (250 × 4.6 mm, 5µm) using mobile phase 0.5 M **potassium dihydrogen phosphate**: methanol in the ratio of 80:20 v/v at flow rate 1 ml/min with UV detection at 290 nm. Retention time was 5.8 minutes. The calibration curve was linear (r = 0.9997) in the concentration range 50-250 µg/ml. The method was statistically validated for precision, accuracy, LOD, LOQ, robustness and recovery.

In the second step, ultrasound-assisted extraction (UAE) was applied to the extraction of galantamine from *Galanthus woronowi* leaves. The galantamine were quantified and analyzed by high performance liquid chromatography coupled with UV detection (HPLC-UV). The extraction pH, extraction temperature and extraction time parameters, the three main factors for UAE, were optimized with response surface methodology (RSM) to obtain the highest extraction efficiency. The optimal conditions were extraction pH of 7, extraction time of 30 min and extraction temperature of 45 °C. Under this optimized conditions, the experimental yield of galantamine is % 2.85, which is well matched with the predicted yield of % 2.87. The analysis of variance indicated a high goodness of model fit and the success of RSM method for optimizing galantamine extraction from *Galanthus woronowi* leaves.

Keywords: Galantamine, Extraction, Optimization.

Optimisation of Extraction Conditions for Phenolic Compounds from Mountain Tea (*Sideritis Akmanii*) Leaves

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Sideritis, also known as mountain tea, is a genus of flowering plants well known for their use as herbal medicine, commonly as an herbal tea. They are abundant in Mediterranean regions, the Balkans, but can also be found in Central Europe and temperate Asia. *Sideritis akmanii* is an endemic plant of Afyonkarahisar located in Turkey. It has been traditionally used to aid digestion, strengthen the immune system and suppress common cold, the flu and other viruses, allergies and shortness of breath, sinus congestion, even pain and mild anxiety. Studies indicate a positive effect on many common ailments. It is known scientifically to be anti-microbial, anti-inflammatory, and anti-oxidant. Active elements include diterpenoid and flavonoids

In this study, the extraction conditions for phenolic compounds from mountain tea (*Sideritis akmanii*) leaves was optimised by using response surface methodology (RSM). Box-Behnken design (BBD) was applied to determine the effects of ethanol concentration (%), extraction temperature (°C), and extraction time (min) on total phenolic content (TPC) from mountain tea (*Sideritis akmanii*) leaves. The independent variables were coded at three levels and their actual values were selected based on the results of single factor experiments. Results showed that ethanol concentration was the most significant factor affecting the TPC. The optimum extraction conditions were found to be ethanol concentration of 53 %, extraction temperature of 48 °C, and extraction time of 45 min. Under the optimised conditions, the experimental value for TPC was 52.8 mg GAE/g DW, which reasonably close to the predicted value (53.0 mg GAE/100g DW).

Keywords: Mountain Tea (*Sideritis Akmanii*) Leaves, Phenolic Compounds, Antioxidants, Total Phenolic Content (TPC); Response Surface Methodology (RSM)

The Investigation of Biological Activities and HPLC-DAD-MS Analysis of Phenolic Compounds of Achillea vermicularis

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In this study, it is aimed to investigate antioxidant and antiurease effects of *Achillea vermicularis* extracts. The extraction techniques included soxhlet extraction and maceration with three different solvent systems including hexane, chloroform and ethanol. Three methods were applied for the evaluation of extracts' antioxidant properties: DPPH (1,1-diphenyl-2-picrylhydrazyl), TEAC/ABTS (*trolox equivalent antioxidant capacity*), CUPRAC (cupric reducing antioxidant capacity) assays and also, the amount of total phenolic (TPC) and total flavonoid contents (TFC) were analysed by using Folin-Ciocalteu and aluminium chloride colorimetric assays, respectively. In addition, urease inhibitory activities of the extracts from *A. vermicularis* were determined according to a reported method (1).

In vitro screening tests indicated that ethanol extract of *A. vermicularis* had the highest amount of TPC and TFC and showed the highest biological activities among the different solvent extractions and methods.

Subsequently, we tried to identify and quantify of the major phenolic compounds in ethanol extract using ESI-Q-TOF LC/MS (electrospray ionization-quadrupole-time of flight liquid chromatography mass spectrometry) and HPLC-DAD (high-performance liquid chromatography equipped with a photodiode array detector) methods. Major phenolic compounds identified and quantified in the extract were rutin, chlorogenic acid and dicaffeoylquinic acid.

These results showed that ethanol extract of *A. vermicularis* have good antioxidant and antiurease activity. These can be attributed to the high concentration of phenolic compounds in this extract.

Keywords: Phenolic Compounds, Biological Activity, HPLC-DAD-MS, *A. Vermicularis*

References:

1. Ghous T, Akhtar K, Nasim FUH, Choudhry MA, Biology and Medicine (2010) 2(4) 64-69.

Phytochemical Analysis and Evaluation of In Vitro Anti-Urease and Antimicrobial Activities of Methanol Extract from Geranium purpureum

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There are 35 *Geranium* (Geraniaceae) species recorded in the flora of Turkey. *Geranium* species are used as antiasthmatic, antiallergic, antioxidant, antidiarrhoeic, antihepatotoxic, diuretic, tonic, haemostatic, stomachic and antidiabetic in folk medicine. Leaves of some *Geranium* species are consumed as food in Anatolia. The aerial parts of *G. purpureum* in Kocaeli are used as vegetable. Plants from the genus *Geranium* are known to contain flavonoids, tannins, lignans and essential oils (1,2).

The aim of this work is to analyse qualitative and quantitative phytochemical and evaluate *in vitro* anti-urease and antimicrobial activities of methanol extract from *G. purpureum* aerial parts.

Preliminary phytochemical analysis for alkaloids, cardiac glycosides, flavonoids, glycosides, phenols, saponins, tannins and triterpenoids and quantitative phytochemical analysis for total phenolics, total flavonoids, tannins, saponins and proanthocyanidin were made by following standard procedures (3,4,5). The urease inhibitory activity of the extract were determined according to a reported method (6). In addition, antimicrobial activity of extract were investigated using the disc diffusion and microdilution methods (7,8). The methanol extract of *G. purpureum* showed good anti-urease activity while this extract had weak antimicrobial activity. Subsequently, we tried to identify the phenolic compounds in the methanol extract by HPLC-DAD/ESI-Q-TOF LC/MS.

Keywords: *G. Purpureum*, Phenolic Compounds, Biological Activity, ESI-Q-TOF LC/MS

References:

1. Şöhretoğlu D, [Ekizoğlu M](#), [Özalp M](#), Sakar MK, Hacettepe University Journal of the Faculty of Pharmacy (2008) 28(2) 115-124.
2. Neagu E, Paun G, Moroeanu V, Radu GL, Rev. Roum. Chim., (2010) 55(6) 321-325.
3. Harborne JB, (second ed.) Chapman and Hall, London (1998) 54-84.
4. Kokte CK, Vallabh Prakashan (2000) 218.
5. Sharma V, Agarwal A, Indian Journal of Pharmaceutical sciences (2015) 77(6) 729-734.
6. Ghous T, Akhtar K, Nasim FUH, Choudhry MA, Biology and Medicine (2010) 2(4) 64-69.
7. National Committee for Clinical Laboratory Standards. Reference, Wayne, PA. (2002) 22(15).
8. NCCLS, 940 West Valley Road, Suite 1400, Wayne Pennsylvania, USA (1999) 19087-1898

Comparative Evaluation of Different Extraction Methods and Solvents for Biological activities of Endemic Achillea lycaonica

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The genus *Achillea* L. belongs to Asteraceae, which is the largest family of vascular plants and represented by more than 140 perennial herbaceous species worldwide (1). Turkey is one of the main centers of diversity for the genus *Achillea*. A total of 54 *Achillea* taxa are indigenous to Turkey, of which 31 are endemic (2,3). *Achillea* species are important in Turkish folk medicine for matters such as stomachache, hemorrhoids and inflammation (4).

The aim of this study was to investigate phenolic composition and compare evaluation of different extraction methods and solvents for biological activities of *A. lycaonica* growing in Turkey.

In the present study, three different extraction methods were employed to recover extracts from *A.lycaonica* aerial parts. The total phenolic, total flavonoids contents and antioxidant, anti-urease, antimicrobial activities of *A.lycaonica* extracts obtained by ultrasonic bath, soxhlet extraction and maceration techniques were compared. The efficiency and selectivity of processes were determined in terms of extraction yield and biological activities. The extracts were quantitatively analyzed for total phenolic and flavonoid contents using spectrophotometric methods. Antioxidant activity of the extracts was measured using the DPPH[•], ABTS^{•+} scavenging activities and FRAP assay. The urease inhibitory activities of the extracts were determined according to a reported method (5). In addition, antimicrobial activities of extracts were investigated using the disc diffusion and microdilution methods (6,7).

The ethanol extract of *A.lycaonica* had the highest amounts of total phenolics and total flavonoids and showed the highest biological activity. Subsequently, we tried to identify the phenolic compounds in the ethanol extract by HPLC-DAD/ESI-Q-TOF LC/MS.

Keywords: *A.lycaonica*, Phenolic Compounds, Biological Activity, ESI-Q-TOF LC/MS

References:

1. Turkmenoglu FP, Ağar OT, Akaydin G, Demirci B, *Molecules* (2015) 20(6) 11432-11458.
2. Yaeesh S, Jamal Q, Khan AU, Gilani AH, *Phytother Res* (2006) 20 546–551.
3. Karamenderes C, Apaydin S, J. *Ethnopharmacol.* (2003) 84 175–179.
4. Demirci F, Demirci B, Gürbüz İ, Yeşilada E & Başer KHC, *Turkish J Biol.* (2009) 3 3129-136.
5. Ghous T, Akhtar K, Nasim FUH, Choudhry MA, *Biology and Medicine* (2010) 2(4) 64-69.
6. National Committee for Clinical Laboratory Standards. Reference, Wayne, PA. (2002) 22(15).
7. NCCLS, 940 West Valley Road, Suite 1400, Wayne Pennsylvania, USA (1999)19087-1898.

Evaluation of Energy Dispersive X-ray Fluorescence Spectroscopy for the Determination of Light Rare Earth Elements in Geological Material

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The aim of the present work was to evaluate the performance of Energy Dispersive X-ray Fluorescence (EDS XRF) Spectroscopy for geological material analysis. The method was compared with laboratory analysis of certified reference materials (CRMs) using Inductively Coupled Plasma Atomic emission spectroscopy (ICP-AES) and Instrumental Neutron Activation Analysis (INAA) as established methods for the light Rare Earth Elements (REE) determination in geological material. The elements Ce and La were chosen as representative of their group in geological material and six reference materials were employed for the investigation. The reference materials were 1633b a fly ash provided by NIST as well as an andesite AGV 1 and a basalt BHVO 1 both by USGC. In addition to these CRMs three laboratory reference materials, prepared at our lab with accepted values determined against existing CRMs, were analyzed. The figures of merit principally accuracy and precision, as well as the values of goodness of fit (r^2) were calculated and compared. The strengths and limitation of EDS XRF were assessed and suggestion are made for the optimization of the methodology.

Keywords: Light Rare Earth Elements, Energy Dispersive X - Ray Fluorescence Spectroscopy, Geological Material

Silver Nanoparticles – Efficient Sorbent for Trace Elements Determination by Total Reflection X-ray Fluorescence

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Silver nanoparticles were synthesized by completely green method using raffinose as reducing and stabilizing agent and characterized by UV-VIS spectroscopy, SEM and TEM analysis. Their high active surface area and chemical reactivity implied their high extraction efficiency toward chemical elements. The aim of present study was to optimize chemical conditions for quantitative sorption of Cd(II), Cu(II), Co(II), Hg(II), Fe(III), Ni(II) and Pb(II) on the surface of Ag nanoparticles (AgNPs) as a first step and to optimize instrumental parameters for Total reflection X-ray Fluorescence (TRXRF) measurement of retained analytes as a second step. Quantitative sorption for all studied analytes was achieved at pH 8.5 reached with 5 M ammonia solution for less than 5 min. AgNPs were centrifuged at 14000 rpm and suspended in Milli-Q water. The whole analytical procedure was performed in small centrifuge tube – sample solution 2 ml was used for sorption of trace elements. The volume of final suspension was 50 µL, which were transferred on the glass support and analyzed by TRXRF. The developed analytical procedure was applied for different types of surface wastewaters. Recoveries achieved for fresh waters varied in the range 92-97%, however for Black sea water aggregation of AgNPs was observed and recoveries were below 80%. Additional experiments for stabilization of AgNPs in salted waters are needed to solve this problem. Analytical procedure proposed for fresh waters was validated by analyses of certified reference materials.

Keywords: Surface Waters, Silver Nanoparticles, TRXRF, Trace Elements

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Self-Organizing Maps as a Tool for Classification of Different Kinds of Bulgarian Monofloral Honey

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Trace elements Al, Ba, Co, Cu, Fe, Mn, Ni, Sr and Zn, major elements K, P, S, Na, Ca and Mg as well as toxic elements Cd and Pb were all determined in 17 Bulgarian monofloral honey samples, with defined botanical origin: sunflower, lime, acacia, thistle and honey dew, by using electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES). Monofloral honey samples were produced in different years however in the same geographical region for each year. Self-organizing maps (SOM), as one type of the neural networks, are commonly used for visualizing and also for clustering of multidimensional data. In this study SOM were tested as efficient statistical approach for data mining and successful identification of botanical origin of honeys. Various calculations performed showed that the proper choice of element markers is the most important factor for correct separation of honeys with different botanical origin. The proper classification of honey samples was achieved after optimization of the set of the most important elements – markers: Al, K, Cu and Sr and it was proven that chemical elements in combination with powerful statistical methods might be proposed as reliable tool for monofloral honey classification. According to U-matrix all studied honey samples formed 3 major groups. Two of them were populated with honey dew samples and lime honey samples. The last one consists of the rest monofloral honeys – sunflower, acacia and thistle, but there was also good separation inside this group.

It was shown that the year of honey production was not a factor of honey behavior in the used multivariate statistical approach for classification. Even more monofloral honeys produced in different years were correctly separated applying proposed approach.

Keywords: Monofloral Bulgarian Honeys; Self-Organizing Maps; ETAAS; ICP-OES

Investigation of binding characteristics of two hydrazone derivatives with nucleic acids by spectral methods

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The interaction studies between fluorescent dyes and DNA are significant to design new probes and the quantitative detection of nucleic acids. Many fluorescence assays have been reported for DNA measurement by using of fluorescent dyes, metal ions and metal complexes that exhibit fluorescence quenching or enhancement in the presence of DNA. The possible interaction models between these small molecules and DNA generally include the electrostatic or surface, the groove and the intercalation binding. Hydrazones are attractive targets for researchers worldwide due to their widespread applications in biology and medicinal chemistry, exhibiting potential therapeutic properties. Because of the ease of preparation and tendency toward crystallinity, they are also important compounds for drug design.

In the present work, hydrazone derivatives, AN1 and AN3, were synthesized and the interactions with ct-DNA were investigated by fluorescence quenching method. The fluorescence quenching mechanisms of derivatives by ct-DNA were studied by means of Stern-Volmer modeling. The experimental results showed that the interaction of both derivatives with ct-DNA resulted with complex formation. In addition, the binding properties of ct-DNA-derivative complexes were investigated based UV-vis absorption spectra, ionic strength, iodide ion quenching and thermodynamic parameters. The Stern-Volmer quenching constant, binding constant, binding sites and the corresponding thermodynamic parameters ΔH , ΔS and ΔG were calculated at different temperatures.

Keywords: *Stern-Volmer* equation, hydrazone dyes, fluorescence quenching, groove binding

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References:

1. Lakowicz JR (2006) Principles of Fluorescence Spectroscopy, 3rd Edition, Springer, New York.
2. Ding C, Zhong H, and Zhang S, Biosensors and Bioelectronics (2008) 23 1314-1318.

Use of SERS for characterization of interaction between phthalocyanine complex and amyloid fibrils

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The insoluble beta-pleated aggregates of proteins, called as amyloid fibrils, are associated with the pathogenesis of a large number of human diseases such as neurodegenerative disorders (Alzheimer's, Parkinson's), diabetes type II and various amyloidosis. The accumulation of amyloid aggregates causes to the disfunction of the cell and cell death and this leads the emergency request for the development and investigation of the agents able to suppress the protein fibril formation, or promote the fibril degradation processes.

Recently the strong effect of cyclic tetrapyrroles- phthalocyanines on protein aggregation process is reported and the anti-fibrillogenic properties of the phthalocyanine complexes of Zr and Hf containing axially coordinated substituents were discovered [1]. The ability of these macrocyclic metal complexes to interact with the mature amyloid fibrils was also shown [2].

In the present study the SERS on Ag nanoparticles was used to characterize the interaction between the axially coordinated Hf phthalocyanine (Figure 1) with mature fibrils of amyloidogenic protein insulin.

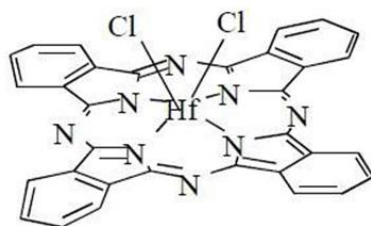


Figure 1. Structure of Hf phthalocyanine.

The spectra of free phthalocyanine contain the bands in the range 485- 1530 cm⁻¹ and the metal surface enhancement of about 10⁴ times was registered. Addition of fibrillar insulin leads to the decrease of the SERS intensity of phthalocyanine bands that is attributed to the increase of the phthalocyanine to metal surface distance due to the binding of phthalocyanines with fibrils. This effect does not demonstrate noticeable dependence on the procedure of sample preparation (first incubation of phthalocyanine with nanoparticle and the addition of amyloid fibrils on it or vice versa procedure). This could point on the pronounced binding of phthalocyanine molecules with the mature fibrils. Besides, since the addition of amyloid fibrils did not lead to the formation of the new bands in Raman spectra of phthalocyanines, which suggest that phthalocyanine molecules do not undergo chemical bounding upon the interaction with fibrils.

Keywords: SERS, amyloid fibrils, phthalocyanine

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References:

1. V. Kovalska, V. Cherepanov, M. Losytskyy, S. Chernii, A. Senenko, V. Chernii, I. Tretyakova, S. Yarmoluk, S. Volkov *Bioorganic and Medicinal Chemistry* (2014) 22 6918-6923.
2. V.B. Kovalska, M.Y. Losytskyy, S.V. Chernii, V.Y. Chernii, I.M. Tretyakova, S.M.Yarmoluk, S.V.Volkov *Biopolymers and Cell* (2013) 29 473-479.

CTAB-Free Generation of SERS Active Gold Nanoparticle and Lateral Flow Immunoassay Application

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Surface Enhanced Raman Spectroscopy (SERS) has great potential in biological applications due to high sensitivity in complex biological matrix or even single molecule detection. Fabrication of novel gold nanostructures is also important in SERS since SERS amplification strongly depends on plasmons on the surface of gold nanoparticles. Novel gold particles as SERS substrates can be used to maximize signals for intended analytes and makes the ultra-sensitive analysis possible with a Raman spectrometer. However colloidal stability and reproducibility should be taken into account in a quantitative analysis. For these reasons, a lot of effort has been made in generation of rapid, simple and cheap methods for gold nanoparticles. Among these effective methods, seed mediated synthesis procedures are widely used using toxic CTAB surfactant [1]. In the present study, we report a robust synthesis of gold nanoparticles with different shape by using benzalkonium chloride. Significantly, benzalkonium chloride coated gold nanoparticle was able to demonstrate the long lasting stability (over one year) and exhibited the SERS activity.

The sandwich format of LFIA was optimized for the determination of *Escherichia coli* by visual inspection and SERS detection. For this purpose, we optimized experimental parameters using benzalkonium coated gold nanoparticles which is used for labeling. To test the efficiency of present method, varied cell concentrations of *E. coli* (1.5×10^1 - 1.5×10^8 cfu mL⁻¹) were analyzed in optimized conditions and related to the colorimetric and SERS measurements. The proposed method shows a clear advantage over traditional methods and the combination of excellent SERS activity and chemical stability enable a lateral flow immunoassay *E.coli* detection.

Keywords: SERS, *E.coli*, Benzalkonium Coated Gold Nanoparticles, Lateral Flow Immunoassay

Acknowledgements: The authors would like to thank TUBITAK for financial support (Project No: 114Z783).

References:

1. Wild, D. G., John, R., Sheehan, C., Binder, S., He, J. (2013) The Immunoassay Handbook: Theory and Applications of Ligand Binding, ELISA and Related Techniques, Elsevier Ltd., Oxford.

Preparation and Characterization of Silver-PESeE Film Deposited on ITO Glass Surface as a Surface Enhanced Raman Scattering Substrate

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Surface enhanced Raman scattering (SERS) is known as a very attractive technique for the characterization and detection of a variety of chemical and biological molecules due to their impressive characteristics such as giving spectral fingerprint of vibrations, high sensitivity and insensitivity to water. One of the most important points of the SERS technique is the requirement for producing a substrate having an ideal surface morphology to facilitate the achievement of the most favorable enhancement.[1,2]

Here a novel, simple, reliable, and reproducible one-step electrochemical method for the preparation of surface enhanced Raman-active polymer-mediated silver nanoparticles (Ag NPs) on planar indium tin oxide (ITO) coated glass substrates was reported. Poly (4,7-di-2,3-dihydrothieno [3,4-b] [1,4] dioxin-5-yl-2,1,3 benzoselena diazole) (PESeE) film was used as a support material for dispersing silver nanostructures on the surface homogeneously. The morphologies of the prepared substrates have been investigated by field emission scanning electron microscopy (FE-SEM). The effect of the thickness of PESeE polymer film and the amount of silver particles on the polymer film on the SERS response were studied as well as repeatability and stability of prepared substrates. Brilliant cresyl blue (BCB) has been used as Raman probes to evaluate the properties of the new SERS substrates.

Keywords: Raman Spectroscopy, SERS, Polymer Film, Silver Nanoparticles, Electrochemically Prepared SERS Substrate

References:

1. Stiles, P. L., Dieringer, J., Shah, N. C., Duyne, R. P. Annu. Rev. Anal. Chem. (2008) 1 601–26.
2. Sharma, B., Frontiera, R. R., Henry, A.-I., Ringe, E. , Van Duyne, R. P. Mater. Today (2012) 15 16–25.

Preparation of Noble Metal and Polymer Added Titanium Based Magnetic Photocatalytic Nanocomposite Material and Usage in Environmental Remediation

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Due to the increasingly polluted environment the development of high efficiency renewable technologies and eco-friendly methods for environmental remediation is highly important. Wastewaters discharged from the textile industry contain huge amounts of toxic and non-degradable dye molecules known as carcinogenic. Therefore finding effective treatment methods and extending the treatment units which use them is necessary. Semiconductor based photocatalytic materials for the photodegradation of organic pollutants in wastewater has gained importance due to its potential application in environmental remediation. Formations of organic/inorganic nanocomposite materials with the addition of polymers becoming important research are to increase the efficiency of semiconductors.[1] Another important issue besides the increase in catalytic activity is the recovery and reuse performance of the catalytic materials. Generally, removal of heterogeneous catalysts from the solution requires centrifugation or filtration steps. But, with the addition of magnetic nanoparticles to the structure, catalyst can be separated by using external magnetic field and can be used in next cycle.[2]

In this study, multifunctional organic-inorganic nanocomposite photocatalysts was developed to provide environmental remediation with the removal of organic dyes founded in waste waters from industry with photocatalytic degradation. For this purpose, magnetically recyclable, Poly (3, 4-ethylenedioxythiophene (PEDOT) and silver added TiO₂ based (CoFe₂O₄-PEDOT-TiO₂-Ag) nanocomposite material with high photocatalytic activity and well-separation property was produced. The comparative photocatalytic activity of the prepared nanocomposites was investigated in the degradation of organic dye, methylene blue (MB), known as a typical pollutant in the textile industry.

Keywords: Photocatalyst, TiO₂, PEDOT, Noble Metals Magnetic Separation, Waste Water Treatment

References:

1. Zhang, J.; Wu, Y.; Xing, M.; Khan Leghari, S. A.; Sajjad, S., Energy Environ. Sci. (2010) 3 715–726.
2. Polshettiwar, V., Varma, R. S. Chem. Soc. Rev. (2008) 37 1546-1570.

Multiplexed and Sensitive Detection of Glucose via Fluorescence and Surface Enhanced Raman Spectroscopy

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The sensitive and specific detection of biochemical molecules such as carbohydrates with low concentration in solution has gained great importance in the fields such as biomedical research and diagnosis. An ideal technique to make the identification and determination of the important biochemical molecules should be fast, reliable, accurate and inexpensive. Of these techniques, particularly, fluorescence and SERS based ones have gained much attention due to advantages of sensitivity, selectivity. Boronic acids derivatives are utilized to achieve attachment of diol containing molecules through the agency of formation of reversible boronate ester. Therefore, this tight binding provides opportunity to phenylboronic acids (PBA) to be used for recognition and separation of diol-containing compounds. Recently, a fluorescent competitive assay that includes a chromophore such as Alizarin Red S (ARS) has been developed. When diol molecule is added to ARS-PBA complex solution, fluorescence intensity decreases providing the quantitative determination of glucose. Unfortunately, the technique suffers from low sensitivity. Alternatively, this disadvantage can be eliminated via development of a new technique based on surface enhanced Raman spectroscopy (SERS). For this, Raman dye based tags (such as Rhodamine-based) was developed to achieve conjugation with glucose via reductive amination reaction. Dye-conjugated carbohydrates provide low detection limit nearly as 1 nM in concentration with 632.8 nm HeNe laser. Besides the enhancement in SERS detection, tagged carbohydrates enables the fluorescence detection that shows the superiority of designed tag-system for multimodal spectroscopic characterization.

Keywords: Multiplex Detection, Glucose, Fluorescence, Raman-Dye Tag, Surface-Enhanced Raman Scattering (SERS)

References:

1. M. Li, W. Zhu, F. Marken, T. D. James. Electrochemical Sensing Using Boronic Acids, *Chem. Commun.*, 2015 51 14562-14573.
2. A. C-Fdez, T. L-Luke, A. T-Castro. Glucose Determination Using SERS with Multi-Branched Gold Nanostructures in Aqueous Medium, *RSC Adv.*, 2014 4 59233-59241.
3. T. Nguyen, M. B. Francis. Practical Synthetic Route to Functionalized Rhodamine Dyes, *Org. Lett.*, 2003 5 3245-3248.

Application of Photonics in Diagnosis of Papillary Thyroid Carcinoma Tissues by FT-IR and Raman Spectroscopy

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Photonics is the science of light ([photon](#)) generation, detection, and manipulation through [emission](#), [transmission](#), [modulation](#), [signal processing](#), switching, [amplification](#), and [detection/sensing](#). Though covering all [light](#)'s technical applications over the whole [spectrum](#), most photonic applications are in the range of visible and near-[infrared](#) light. The term photonics developed as an outgrowth of the first practical semiconductor light emitters invented in the early 1960s and optical fibers developed in the 1970s.

In this study, it is aimed to diagnose and detect cancer cells in tissue samples of human thyroid. In order to carry out the study, different healthy and cancered tissues were collected from Ataturk University, Department of Pathology. Diagnosis of tissues was already achieved by histopathological tests.

Samples were deparafinized and 20 micron of each sample were located on a coverslip. Both healthy and cancered tissues exposure to Mid-Infrared light between wavenumber of 100-4000 cm⁻¹. Obtained spectrum was evaluated on MATLAB software, PLS Toolbox package program. O-PLS and PARAFAC analysis were applied in order to separate cancer cells and healthy cells. Mapping of tissues was performed by Raman Spectroscopy including two-laser beam by filtering Ray-Leigh scattering.

In conclusion, it is claimed that this method make it enable to diagnose papillary thyroid carcinoma in human thyroid tissue without any sample preparation, extraction or any other pre-treatment procedure. This easy and cheap method do not need any chemical for diagnosis of papillary thyroid carcinoma tissues. Photonics studies exhibit a new perspective on qualitative determination of specific diseases.

Keywords: Photonics, FT-IR, Raman Spectroscopy, Papillary Thyroid Carcinoma

References:

1. Chai Yeh. (2012) Applied Photonics, Academic Press inc. California, USA.

Application of Differential Scanning Calorimetry and Fourier Transform Infrared Spectroscopy to the Study of Some Drug-Excipient Compatibility

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Studies of drug active compound-excipient suitability represent an important phase in the preformulation stage of the development of all dosage forms. The possible physical and chemical interactions between drugs and excipients can affect the chemical nature, the stability and bioavailability of drugs and, consequently, their therapeutic efficacy and safety [1]. Drug – excipients compatibility studies lays a foundation in careful selection of most appropriate excipients and helps in designing a chemically stable and effective dosage form [2,3]. The purpose of the present investigation was to evaluate the compatibility of metoprolol, lisinopril, and estriol with various pharmaceutical excipients to be used in the nanoparticle formulations utilizing the different analytical techniques such as Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR). The thermograms of the drug and excipient were obtained using DSC (PE DSC 400). All the samples were placed in a pre-weighed stainless steel pan and sealed carefully with a sealer supplied by the manufacturer. The sealed pan was weighed to obtain the sample mass. Another sealed empty stainless steel pan was used as the reference. The sample was equilibrated heated from - 20 °C to 400 °C at a rate of 10 °C/min. ZnSe-ATR equipment was used as well as KBr pellet technique. The FTIR measurements were formed on a PE Frontier spectrometer. Thermal methods especially DSC can be used for a wide range of drug applications ranging from the qualification and characterisation of pure substances to the evaluation of drug–excipient interactions through the appearance, shift, or disappearance of endo- or exothermal effects and/or variations in the appropriate enthalpy values. FTIR of any compound given information about the functional group present in particular compound [4-9].

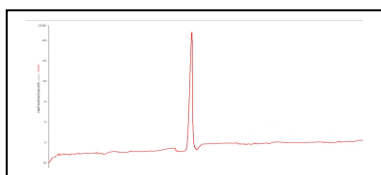


Figure 1: DSC thermograms of mannitol

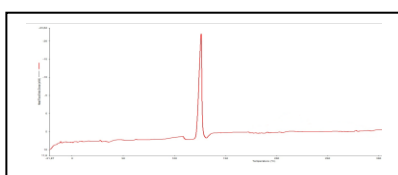


Figure 2: DSC thermograms of metoprolol

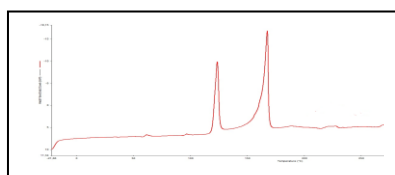


Figure 3: DSC thermograms of metoprolol+ mannitol

Keywords: Drug, excipient, DSC, FTIR

References:

1. S. Sonali, B.S. Bharate, A.N. Bharate, J. Bajaj. Excipients and Food Chem (2010) 1 3-26.
2. P. Pandian, K. Kannan, M. Manikandan, R. Manavalan. Int J Pharm Pharm Sci (2012) 4 342-347.
3. ME. Aulton. (2002). Pharmaceutics The scientific principles of dosage form design. Churchill Livingstone.
4. D. Giron, J. Pharm. Biomed. Anal (1986) 4 755–770.
5. S.A. Botha, A.P. Lotter. Drug Dev Ind. Pharm (1990) 16 673–683.
6. S.Y. Lin, R.Y. Han. Pharmazie (1992) 47 266–268.
7. F. Giordano, G.P. Bettinetti. J Pharm Biomed Anal (1988) 6 951–955.
8. K.R. Verma, S. Garg. J Pharm Biomed Anal (2004) 35 449–458.
9. M. Tomassetti, A. Catalani, V. Rossi, S. Vecchio. J Pharm Biomed Anal (2005) 37 949–955.

The Solute Descriptor That Account for the Ionization of Some Propionic Acid and Acetic Acid Class of Non-steroidal Anti-Inflammatory Drugs for Determination of Dissociation Constants

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Non-steroidal anti-inflammatory drugs (NSAIDs), and principally naproxen, ibuprofen, diclofenac, flurbiprofen and ketoprofen, are drugs with analgesic, antipyretic and anti-inflammatory effects [1,2]. Most NSAIDs act as non-selective inhibitors of the enzyme cyclooxygenase, inhibiting both the cyclooxygenase-1 (COX-1) and cyclooxygenase-2 (COX-2) isoenzymes. Most NSAIDs are weak acids, with pK_a of 3-5. The retention of an ionizable compound in RP-LC is different from the retention of a neutral one. Retention behaviour of acidic solutes is greatly influenced by the pH of the mobile phase in conventional reverse phase HPLC. Small changes in pH can significantly alter chromatographic retention, particularly when it is close to the dissociation constant (pK_a) of the solute. A weak acid presents equilibrium between its unionised (HA) and anionic (A) forms related by the dissociation constant. The observed retention time (t_r) is an average of the retention factors of the unionised ($t_{r,HA}$) and ionized forms ($t_{r,A}$) [1]. The pH dependence of chromatographic retention for weak acidic solutes in reversed phase liquid chromatographic separation was proposed by Horváth [3]. The equation modified and proposed as linear equation by Poole et al [2-4].

Nowadays, some researchers have focused attention the effect of ionisation degree on retention behavior of ionisable analyte since this is the easiest way to predict retention in LC. The linear relationship between $\log t_r$ and f parameter have been widely used to predict retention in reversed phase liquid chromatography. In this study, retention behavior of five compounds (naproxen, ibuprofen, diclofenac, flurbiprofen and ketoprofen) in 40%, 45%, and 55% MeCN:H₂O binary mixtures by chromatographic method. A Gemini C6 phenyl analytical column provided by Phenomenex (150×3.0 mm×5μm, USA) was used for all of the determinations at 25°C. General models for the influence of ionization on retention of these acids were applied. The $\log [1-D(1-f)]$ parameter taken as a solute descriptor that accounts for the ionization of the compound. The results show that this descriptor is an appropriate solute descriptor for the ionization.

Keywords: NSAIDs, f Parameter, Solute Descriptor.

References:

1. Bunaciu AA, Grasu A, Aboul-Enein HY. *Analitica Chimica Acta* (1995) 311 193–197.
2. Somasundaram S, Rafi S, Hayllar J, Sigthorsson G, Jacob M, Price AB, Macpherson A, Mahmood T, Scott D, Wrigglesworth JM, Bjarnason I. *Gut* (1997) 41 344–353.
3. Horváth C. *Analytical Chemistry* (1977) 49 142–154.
4. Roses M, Bolliet D, Poole CF. *Journal of Chromatography A* (1998) 829 29–40.

Development of A New Index for Phenolic Compounds Using Unique Colour Transitions of Rhodium Nanoparticles

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Abstract

In this work, we describe for the first time an unknown phenomenon triggered by the interaction of Rh-nanoparticles with antioxidant compounds. Trihydroxy and dihydroxy benzoates were found to induce several size transitions in citrate capped RhNPs yielding at the same time unprecedented colorimetric and spectral changes in the UV/VIS region. These interactions stem from the binding of antioxidants on the RhNPs surface from the hydroxyl groups further augmented by the presence of carboxylate moieties which act both as size regulators and stabilizers. On the basis of these phenomena, our findings could provide a springboard for the development of a facile approach for one-pot aqueous-based synthesis of bio-compatible RhNPs with variable sizes and absorption properties in the UV /Vis region for new applications in catalytic, field emission, magnetic and sensory applications. On this line of thinking, we demonstrate a few proof-of-concept applications for the determination of tea quality.

Keywords: Rhodium Nanoparticles, Phenolic Compounds, Molecular Spectrometry, Optical Sensors.

Introduction

Noble metal nanoparticles have found numerous applications mainly due to their unique optical, catalytic and mechanical properties [1]. One of their most characteristic properties is their interaction with light, causing coherent oscillation of the free electrons of the metals locally around each nanoparticle with a frequency known as the localized surface plasmon resonance (LSPR) [2].

Among the different types of noble metal nanoparticles, those of gold and silver (AgNPs) are most commonly used in chemical and biochemical analyses. Rhodium nanoparticles (RhNPs) have also been employed for analytical purposes, but only as electrochemical mediators for the determination of hydrogen peroxide [3]. To the best of our knowledge, analyte-mediated changes in the LSPR properties of RhNPs have not been used for the spectrophotometric determination of any analyte.

This article reports for the first time that the interactions of citrate-capped RhNPs with phenolic compounds (i.e., catechins, gallates, cinnamates, and dihydroxybenzoic acids) can cause changes in the size of RhNPs, and give rise to analyte-specific spectral and color transitions in the suspensions of the RhNPs. As proof-of-concept applications, we developed an RhNPs-based photometric method for the determination of the total phenolic content of tea samples.

Materials & Methods

UV-Vis spectra were recorded in a Jenway 6405 UV/Vis spectrophotometer with matched quartz cells of 1 cm path length. Atomic force microscopy (AFM) images were obtained in tapping mode with a Multimode Nanoscope 3D. Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano ZS instrument. A Zeiss Libra 120 energy filter transmission electron microscope (TEM) operating at 120 kV in bright field mode was employed for the morphological characterization of the RhNPs.

2.3 Synthesis of citrate-capped rhodium nanoparticles (RhNPs)

We synthesized citrate-capped RhNPs by mixing equimolar amounts of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and tri-sodium citrate (0.5 mL, 10.0 mM) under stirring into 19.5 mL of doubly distilled water. Then 2.5 mM NaBH_4 (0.5 mL, 0.10 M) were added. Stirring was continued for another 15 min at room temperature.

We determined the total phenolic content (TPC) of tea samples by adding 100 μL of a dilute aqueous tea extract into 1900 μL of a suspension of citrate-capped RhNPs. The mixture was incubated for 25 min at room temperature and the increase of the absorbance peak at 450 nm was measured and correlated with the total phenolic content of the tea samples. The results were expressed as gallic acid equivalent (GAE) concentration.

Results & Discussion

Analysis of the citrate-capped RhNPs using AFM showed that the nanoparticles were relatively uniform devoid of aggregates. Based on the topographical height profile (section analysis) the size of the particles lied between 3.5 and 8.0 nm with an average size of 7.2 nm (depth profile analysis), while DLS experiments calculated the average hydrodynamic diameter of the particles to be equal to 8.7 nm.

Trihydroxybenzoate derivatives such as gallic acid and pyrogallol induced a unique visual color change (Figure 1) to the suspensions of citrate-capped RhNPs from dark green-brown (citrate-capped RhNPs without phenolic compounds) to blue, due to the appearance of absorption bands at 350, 450 and 575-580 nm. On the other hand, dihydroxybenzoate derivatives, such as catechin and caffeic acid, that bear an aromatic vicinal diol group, caused the appearance of absorbance bands at 350 and 425-450 nm (Figure 1) accompanied by the appearance of an orange coloration. This coloration is evident by the unattended eye even in low catechin concentrations ($<0.1\text{mM}$). Other phenolic compounds such as coumaric acid, vanillic acid, cinnamic acid, epicatechin gallate and catechol, caused a small but measurable monotonic enhancement in the absorbance of the suspension of citrate-capped RhNPs throughout the UV-Vis region without causing any color changes or inducing new absorption bands.

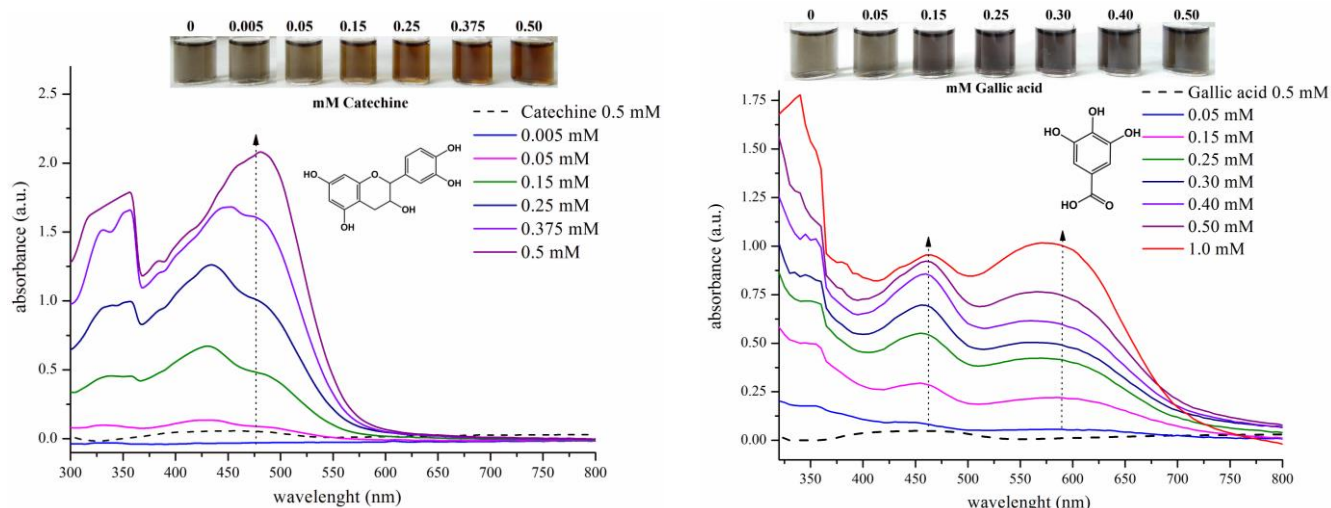


Figure 1. Normalized UV-Vis spectra and color transitions of citrate-capped RhNPs in the presence of various concentrations of (a) catechin and (b) gallic acid. Spectral lines are normalized to blank (citrate-capped RhNPs without phenolic compounds). Dot lines show the absorbance spectra of the phenolic compounds at a concentration of 0.5 mM.

Using AFM, DLS and TEM (Figure 2) we measured the size of citrate-capped RhNPs after reaction with various concentrations of phenolic compounds. We found that the size of the nanoparticles increased from 8.7 nm to 18.2 nm with increasing gallic acid concentration and to 24 nm with increasing catechin concentration.

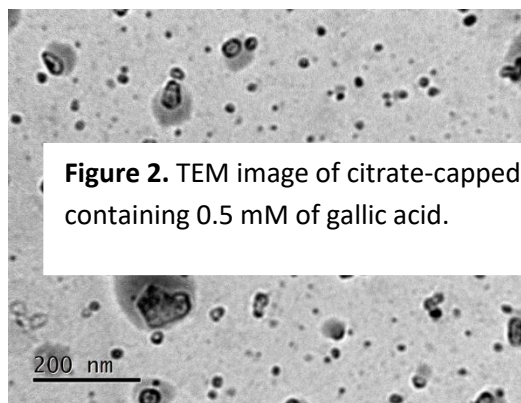
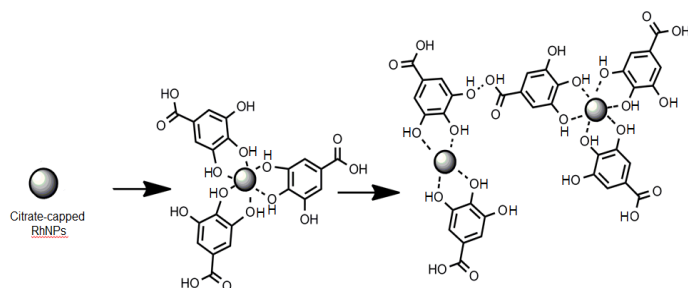


Figure 2. TEM image of citrate-capped RhNPs containing 0.5 mM of gallic acid.

Based on the above observations a tentative mechanism is illustrated in Figure 3.



Under the optimum experimental conditions, we prepared response curves of the absorbance values vs. the concentration of the tested compound (Table 1). We concluded that there is a linear dependence of the absorbance of the citrate-capped RhNPs with the logarithm of the concentration of phenolic compounds enabling detection to be carried out even at the

mid- μ M concentration levels (Table 1).

Table 1. Analytical response curves of absorbance (at 450 and/or 580 nm) vs the concentration of phenolic compounds.

Phenolic compound	λ_{max}	Linear range (μ M)	Calibration function	Correlation coefficient (r)	Limit of Detection (μ M)*	GAE
Catechin	450	0.0-500	$y = 4.2 \times 10^{-3} (\pm 2 \times 10^{-4}) \times C + 0.89 (\pm 5 \times 10^{-3})$	0.9937	39	2.1
Catechol	450	0.0-500	$y = 5 \times 10^{-4} (\pm 2 \times 10^{-5}) \times C + 0.79 (\pm 8 \times 10^{-3})$	0.9921	49	0.24
	580	0.0-500	$y = 4 \times 10^{-4} (\pm 2 \times 10^{-5}) \times C + 0.58 (\pm 1 \times 10^{-3})$	0.9820	77	
Gallic acid	450	0.0-500	$y = 2 \times 10^{-3} (\pm 1 \times 10^{-4}) \times C + 0.84 (\pm 3 \times 10^{-3})$	0.9916	49	1.0
	580	0.0-500	$y = 1.6 \times 10^{-3} (\pm 4 \times 10^{-5}) \times C + 0.61 (\pm 1 \times 10^{-3})$	0.9970	29	
Caffeic acid	450	0.0-500	$y = 7 \times 10^{-4} (\pm 3 \times 10^{-5}) \times C + 0.75 (\pm 1 \times 10^{-3})$	0.9931	46	0.38
Coumaric acid	450	0.0-500	$y = 1.7 \times 10^{-4} (\pm 7 \times 10^{-6}) \times C + 0.78 (\pm 3 \times 10^{-3})$	0.9913	57	0.08
Vanillic acid	450	150-500	$y = 1 \times 10^{-4} (\pm 3 \times 10^{-6}) \times C + 0.79 (\pm 3.4 \times 10^{-3})$	0.9845	103	0.053
Cinammic acid	450	150-500	$y = 1 \times 10^{-4} (\pm 8 \times 10^{-6}) \times C + 0.78 (\pm 3 \times 10^{-3})$	0.9863	91	0.052
Epillocatechin gallate	450	50-400	$y = 6 \times 10^{-4} (\pm 4 \times 10^{-5}) \times C + 0.87 (\pm 1 \times 10^{-3})$	0.9615	68	0.30
Pyrogallol	450	0.0-500	$y = 2 \times 10^{-3} (\pm 5 \times 10^{-5}) \times C + 0.86 (\pm 1.4 \times 10^{-3})$	0.9987	30	1.11
	580	0.0-500	$y = 1.1 \times 10^{-3} (\pm 5 \times 10^{-5}) \times C + 0.64 (\pm 2 \times 10^{-3})$	0.9899	55	

* Three times the signal-to-noise ratio. GAE = ratio of slope of the response curve of the examined compound to the slope of the response curve of gallic acid at 450 nm. The intensity of the absorbance was measured after 25 min at 450 nm and after 15 min at 580 nm.

On the grounds of the above observations, the determination of TPC of aqueous tea extracts was based on the additive effect of antioxidants to the absorbance of the citrate-capped RhNPs suspension at 450 nm. The results from the analysis of 6 different tea varieties exhibit statistically significant linear correlation with the total phenolic content ($r=0.9273$, $p=0.05$) determined by the Folin-Ciocalteu assay [4].

Conclusion

In this work, we report a new method for the determination of phenolic compounds based on citrate-capped RhNPs. Phenolic compounds were found, for the first time, to interact with citrate-capped RhNPs and induce size transitions which can be observed as changes in the absorbance spectra of suspensions of citrate-capped RhNPs. We tested a variety of phenolic compounds at different concentration levels and correlated their reactivity with their chemical structure and concentration. On the basis of these findings, we developed an RhNPs-based assay that enable to obtain a “fingerprint” of the total phenolic content of tea samples. The results of the RhNPs-based assays correlated satisfactorily with the Folin-Ciocalteu assay that is commonly used to assess the phenolic content of natural products.

References:

1. M. Rycenga, C.M. Cobley, J. Zeng, W. Li, C.H. Moran, Q. Zhang, D. Qin, Y. Xia, Chem. Rev. (2011) 111 3669-3712.
2. S.K. Ghosh, T. Pal, Chem. Rev. (2007) 107 4797-4862.
3. V.A. Gatselou, D.L. Giokas, A.G. Vlessidis, M.I. Prodromidis, Talanta (2015) 134 482-487.
4. V.A. Gatselou, D.C. Christodouleas, A. Kouloumpis, D. Gournis, D.L. Giokas, Anal. Chim. Acta (2016) 932 80-87.

Relationship between Soil Properties and Different Fractions of Cd, Cu, Ni, Pb and Zn in Roadside Agricultural Soils from Athens, Greece

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In general, soils are mostly exposed to trace metal contaminants because they are the largest receiving body among the other components of the ecosystem (1). The natural trace metal concentration of agricultural lands usually is dependent on the composition of parent rocks. On the other hand, trace metal contamination of agricultural soils originates from anthropogenic sources, such as amendments of sewage sludge, high fertilization, emissions from industrial activities and traffic, particularly when agricultural land extends at the margins of highways. The relationships between the trace metals in environmental samples and different geochemical fractions of the soils components basically depend on the physicochemical conditions encountered in the environment (2). The present study was initiated to examine the relationships between soil properties and different fractions of Cd, Cu, Ni, Pb and Zn in roadside agricultural soils along two major highways of the Metropolitan city of Athens in Greece. Samples were collected from roadside agricultural soils located in ten sites in the vicinity of two major highways in Greece. Five sites were selected from the National Road Athens-Lamia. Another five sites were selected from the Attiki Odos highway, leading to the Athens International Airport. The modified BCR (former European Community Bureau of Reference, now Standard Measurement and Testing) sequential extraction procedure was employed to determine the fractions of Cd, Cu, Ni, Pb and Zn in the soil samples (3). Trace metal contents were separated into four fractions, the acid soluble, reducible, oxidizable and the residual fraction. Pearson correlation was applied to current data to identify the relationships between soil physicochemical properties (pH, soil organic matter content, calcium carbonate content and clay content) and the amount of metals in each fraction. Current findings reveal that soil organic matter and calcium carbonate contents were significantly correlated with the fractions of trace metals in soils. Generally, positive relationships between soil organic matter and especially oxidizable fraction of metals (except for Ni) indicated that organic structures may have formed complexation with metals depending on the soil organic matter contents. Thus, increased contents of soil organic matter constitute a critical host and accumulation medium for metals.

Keywords: Sequential Extraction, Roadside Agricultural Soils, Soil Properties, Trace Metals

References:

1. Sparks, D. L. Elements (2005) 1(4) 193–197
2. Sungur, A., Soylak, M., Ozcan, H. Chemical Speciation and Bioavailability (2014) 26(4) 219-230.
3. Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P. (1999) Journal of Environmental Monitoring 1(1) 57-61.

Analysis of Some Honey Samples Using Microtiter Plate Reader (MPR)

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Honey itself exhibits antioxidant property which is attributed to its polyphenolic content, and holds very important place in our diet for this reason. In this work, in order to analysis the honey samples consuming locally, the Microtiter Plate Reader (MPR) apparatus [1,2] were used. Each microtiter plate has 96 wells, and thus in comparison with a routine spectrophotometric analysis; it is obvious that we can measure absorbances 96 times more rapidly. We can also consider this as time and sample savings since only 300 μ L aliquots of sample solutions are placed in the wells, as shown in Figure 1.

In this study, feasibility of the analysis of polyphenolic substances in a variety of honey samples consumed in Bolu, have been examined by "Microtiter Plate Reader". As the very rapid measurements can be performed by means of Microtiter Plate Reader and can be studied within very small volumes of samples a suitable highly reliable and practical analytical procedure for routine analysis of the polyphenolic substance contents are introduced.

We determined the antioxidant activities and amounts of the total polyphenolic substances of seven different honey examples consumed in Bolu by using 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) [3,4,5] and Folin-Ciocaltaeu [6] reagents, respectively. However, the most important and biggest difference here is that the measurements are made not in the normal spectrophotometer but on a Microtiter Plate Reader (MPR) device. We clearly demonstrated the potential analytical applications of microtiter plate reader for the honey analyses. Microtiter plates and readers are essential equipment in all life sciences and analytical laboratories, and since the microtiter plate reader can provide high sample throughput (96 samples in less than 5 min), this method should be attractive to many researchers and quality control chemists who need to analyze the honey samples.

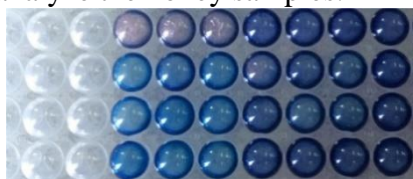


Figure 1. An example for Microtiter Plate

Keywords: Microtiter Plate Reader, Honey, Polyphenolics.

References

1. N. Dürüst, M.E. Meyerhoff, N. Ünal, S. Naç. *Anal Chim Acta* (2011) 699 107- 112.
2. N. Dürüst, S. Nac, N. Ünal. *Sensors and Actuators B: Chemical* (2014) 203 181–186.
3. W. Brand-Williams, M.E. Cuvalier, C. Berset. *Food Sci. Tech.* (1995) 28(1) 25–30.
4. Y. Ruiz-Navajas, M. Viuda-Martos, J. Fernandez-Lopez, J.M. Zaldivar-Cruz, V.Kuri, J.A.Perez-Alvarez. *Int. J. Food Prop.* (2011) 14 459-470.
5. G. Miliauskas, P.R. Venskutonis, T.A. van Beek. *Food Chem.* (2004) 85 231-237.
6. C.H. Wu, H.N. Murthy, E.J. Hahn, K.Y. Paek. *Arch. Pharm. Res.* (2007) 30 945–949.

Determination of Some Heavy Metal Ions Using Optical Sensors with Microtiter Plate Reader (MPR)

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Approximately a million different pollutants including heavy metals are being released to the global environment by means of industrial processes [1]. This kind of metal ions can be either essential or toxic to human beings and their determination is therefore of tremendous interest. Heavy metals are defined as metals of a density higher than 5 g/cm³ [2]. They occur as pure elements, as ions and complexes. Heavy metals are being brought into the environment by human activities.

In this study, usabilities of polymeric films in microtiter plate formate (MPR) for the determination of several heavy metal ions have been examined. We have used Microtiter Plate Reader (MPR) method [3,4], due to its advantages over other spectrophotometric sensing systems. Since very quick determinations can be made in MPR apparatus, it is possible to run a great number of measurements in a very short time for each determination. Each microtiter plate has 96 wells, and thus in comparison with a routine spectrophotometric analysis it is obvious that absorbances can be read out 96 times more rapidly. In addition, this method is sample saving since only 300 µL aliquots of sample solutions are placed in the wells. On the other hand, coating the uniform films on the glass slide is too difficult for normal spectrophotometric studies. In the MPR method, the films can be prepared so uniformly by casting 10 µL into each well (Figure 1). Other methods require high cost analytical instruments.

The potential analytical applications of ion sensitive microtiter plate-format optodes (MPOs) for the measurement of some heavy metal ions were clearly demonstrated. Microtiter plates and readers are essential equipment in all life sciences and analytical laboratories, and since microtiter plate-format optodes can provide high sample throughput, this new method should be attractive to many researchers and quality control chemists who need to measure low levels of analytes. As a result, it may also be considered as too much appropriate for the routine analysis.



Figure 1. An example for Microtiter Plate.

Keywords: Microtiter Plate Reader (MPR), Optical Sensors, Polymeric Films.

References:

1. U. Förstner, G. T. Wittmann (1981) Metal Pollution in the Aquatic Environment, Springer, Berlin.
2. E. Merian, (1991) Metals and Their Compounds in the Environment, VCH, Weinheim.
3. N. Dürüst, M.E. Meyerhoff, N. Ünal, S. Naç. Anal Chim Acta (2011) 699 107-112.
4. N. Dürüst, S. Naç, N. Ünal. Sensors and Actuators B: Chemical (2014) 203 181-86.

Major Ion Chemistry, Quality and Assessment Nitrate Levels and in Groundwaters

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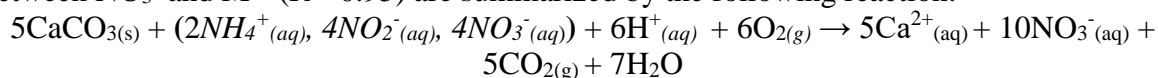
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Groundwater is a major source of water for domestic, industrial and agricultural uses in many parts of word as well as Turkey where arid environments are common. The distribution of freshwater resources is often highly skewed. Groundwater is the major source of municipal, industrial and agricultural water in both urban and rural Gaziantep as well as other parts of Turkey, due to the scarcity of surface water. Because of the high demand for groundwater in multiple applications, there is a substantial risk of overexploitation and resource degradation. Water chemistry is an important factor in determining how the water will be used for domestic, irrigation or industrial purposes, and/or how the water must be treated before use.

Limestone (CaCO_3) was the most common mineral in the study area, with a magnesium limestone variant, dolomite ($\text{CaMg}(\text{CO}_3)_2$), being found at substantial levels in some locations. Given the predominance of limestone and dolomite, it is not surprising that groundwater cation chemistry is dominated by Ca^{2+} , with Mg^{2+} being a dominant feature in some groundwater samples. Bicarbonate (HCO_3^-) was the dominant anion throughout the collected samples, yielding the major dissolved ion forms of $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. In some locations HCO_3^- was overshadowed by SO_4^{2-} or NO_3^- , resulting in the dissolved forms of MSO_4 and $\text{M}(\text{NO}_3)_2$ where the total alkaline earth metal ion ($\text{Ca}^{2+}+\text{Mg}^{2+}$: M^{2+}) is at an excess concentration of $\text{Ca}^{2+}+\text{Mg}^{2+}$ over HCO_3^- .

There was a strong linear correlation between NO_3^- ion concentration and total alkaline earth metal ion (M^{2+}) concentration in excess of $\text{Ca}^{2+}+\text{Mg}^{2+}$ over HCO_3^- ($[\text{Ca}^{2+}+\text{Mg}^{2+}]-[\text{HCO}_3^-]$). The limestone-bearing mineral unit serves as an N source to groundwater. Moreover, calcite absorbs N species, and provides a permeable structure. Nitrate occurring in the soil as a result of natural and anthropogenic activities is expected to react with CaCO_3 , which aids in the transport of NO_3^- to groundwater via natural processes. The strong linear relationships between NO_3^- and M^{2+} ($R^2=0.95$) are summarized by the following reaction:



These data and associated analyses indicate that elevated NO_3^- concentrations can be a result of both natural and anthropogenic activities, while migration to groundwater sources is associated with natural processes that can be explained through examination of geochemistry and local hydrology.

Keywords: Groundwater; Hydrochemistry; Major Ion Chemistry; Nitrate Levels; Water Quality

The Research on Heavy Metal Content Of Soils Which are Received From the Different Agricultural Areas in Karaman

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The definition of heavy metal occurs mostly when environmental problems are seen and relatively it is defined as toxic or noxious metal which has got high concentration and even in low concentration. Metals which are more than 60 metals such as lead, cadmium, chrome, iron, cobalt, copper, nickel, mercury and zinc are involved in this group. That some of heavy metals in soils such as Cd, Cr, Cu, Ni and Zn have got too much concentration causes that natural water and territorial ecosystems are destroyed [1]. Some of heavy metals are important micro-elements for poor plants; but high dosages prevent that most of plant species grow and can cause metabolic irregularity [2,3].

The main goal of this study is to determine on the amount of heavy metals such as As, Bi, Cd, Co, Cu, Cr, Mn, Ni, Pb and Zn in soils collected from agricultural areas of Karaman. Our province, Karaman has got quite important place in agricultural area. It is thought that some of heavy metal will accumulate in soils with the effect of environmental factors. It is very important to research this subject in terms of living creatures and human life. Soil samples have been taken from Karaman city center and various towns. The desiccated soil samples are made solution as the processes of solubilisation are applied. Samples have been assessed on whether there is pollution or not as they are measured by AAS method in terms of heavy metal contents. Results have been compared with standard values and it has been found in centers where the measurement has been done that the mean concentration of Cu and Ni elements is high; Zn is low and Cd, Co, Cr, Mn and Pb are normal.

Keywords: Heavy Metals, AAS, Soil Pollution.

References:

1. Meagher, R.B., Phytorematadion of Toxic elemental and organic pollutants. C.Op. in Plant Biol., 2000 3 153-162.
2. Fernandes, J.C. ve Henriques, F.S., Biocehmical,physiological and structural effects of excess copper in plants.The Botanical Rewiev, 1991 57 246-273.
3. Claire, L.C., Adriano, D.C., Sajwan, K.S., Abel, S.L., Thoma, D.P. ve Driver, J.T., Effects of selected trace metals on germinating seeds of six plant species. Water, Air, and Soil Pollution. 1991 59 231-240.

Modification of Tris(hydroxymethyl)aminomethane Functions onto Crosslinked Poly (Vinyl Benzyl Chloride (PVBC)–co-Ethylene Glycole dimethacrylate) for Removal of Boron From Water

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Abstract

A cross-linked polystyrene based resin with tris(hydroxymethyl)aminomethane functional groups was synthesized and characterized. The sorption behavior of the resin was investigated using a batch system.

The resulting polymeric sorbent has been demonstrated to be an efficient and regenerable specific sorbent for removal of boron in parts per million (ppm) levels. Kinetics of boron sorption and regeneration of the polymer was investigated.

Keywords: Boron Removal, Polymeric Sorbent, Adsorption

Introduction

Many industries use boron compounds as their raw materials. Their uses are in the production of fiberglass insulation, borosilicate glass, and detergents. Also, they are used in fertilizers, nuclear shielding and metallurgy [1].

Boron compounds are present in small amounts in seawater (5 ppm) and some in mineral waters. Although small quantities of boron are vital for the growth of plants and vegetation, elevated levels of boron may be injurious and even lethal to living organisms [2]. Boron contamination is a serious threat to crops as they are very sensitive to high levels of boron in the irrigation waters [3].

For boron removal, main processes that have been studied are: (1) precipitation–coagulation, (2) reverse osmosis, (3) electro dialysis, (4) solvent extraction, (5) membrane filtration, and (6) adsorption (including ion exchange adsorption) [4,5]. Among these methods, adsorption is a very useful and economical technique at low boron concentration [4-6].

Molecules with three or more hydroxyl functions tend to bind boric acid tightly by forming either neutral boron ester or borate complex anion with a proton as counter ion. A typical example of boron selective resins that is early reported is Amberlite IRA 743, prepared by the condensation of N-methylglucamine with cross-linked chloromethylated polystyrene [7].

In this study, tris(hydroxymethyl)aminomethane was interacted with PVBC resin to obtain boron selective sorbent.

The obtained sorbent has been demonstrated to be an efficient sorbent for removal of boron. In this study, the kinetics of boron sorption and regeneration conditions of the sorbent has been investigated.

Materials&Methods

Materials

Polyvinyl benzyl chloride (Aldrich), ethyleneglycole dimethacrylate (EGDMA), Sorbitol (Fluka), Boric acid (Fluka) and all the other chemicals, solvents utilized were analytical grade commercial products.

Preparation of polyvinyl benzyl chloride (PVBC) resin

Crosslinked PVBC microspheres were prepared by suspension polymerization according to the literature. The details are as follows: VBC (5.0 mL, 31.9 mmol), EGDMA (1.5 mL, 7.8 mmol), and AIBN (0.12 g, 0.71 mmol) were dissolved in toluene (7.2 mL). The resulting solution was dispersed in an aqueous medium, prepared by dissolution of PVA (0.25 g) in water (80 mL). The polymerization was carried out in a magnetically stirred glass flask (100 mL) at 78 °C for 8 h. After polymerization, the PVBC microspheres were washed exhaustively with ethanol, and then with water, to remove the diluent and unreacted monomer. They were subsequently dried in vacuum at 50 °C. The microspheres were sieved and a proper size fraction (200-500 µm diameter) was isolated.

Modification of PVBC with tris(hydroxymethyl)aminomethane

PVBC resin (5 g.) was added portion wise to a stirred of , tris(hydroxymethyl)aminomethane 4 g in 2-methyl pyrrolidone (NMP) 30 mL at 0 °C. The mixture was shaken with a continuous shaker for at room temperature. The reaction content was poured into water (500 mL), filtered and washed with excess water and methanol respectively. The EP-PS resin dried under vacuum at room temperature for 24 h. The yield was 7 g.

Determination of the Boron Loading Capacity of Sorbent.

The capacity of the sorbent was determined by batch method as follows: 0.1 g of the sorbent sample was mixed with 10 mL of H₃BO₃ solution (0.49 M) and was stirred for 24 h at room temperature. For the determination of residual boric acid content of the filtrate, 2 mL of the filtrate was mixed with 10 mL of 0.50 M D-sorbitol solution and titrated with 0.1 M NaOH solution in the presence of phenolphthalein as a color indicator. Boron sorption capacities of the resin were also studied by using different boron concentration.

Boron Sorption Kinetics of Sorbent

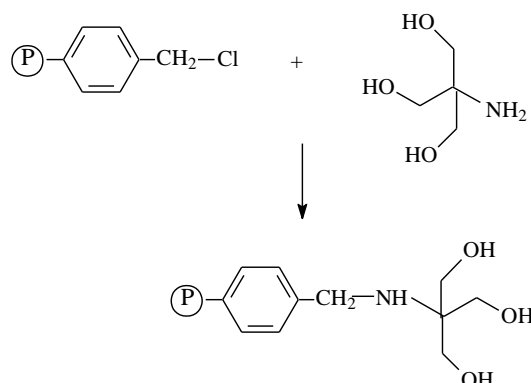
0.1 g of the sorbent was soaked into 5 mL of water and left for 2 h. Then, 90 mL of H₃BO₃ solution (1.0×10⁻³ M) was added to the wetted sorbents at room temperature. The mixture was stirred with a magnetic stirring bar. 3 mL of aliquots were taken and transferred to sample-bottles at appropriate time intervals using a filter paper. The carminic acid method was used to determine boron content of the solution (λ=585 nm) [8].

Desorption of the Boron from Loaded Sorbent.

Acid leaching method was used for desorption of the boron as follows: Loaded sorbent sample (0.1 g) was left in contact with 3 mL of water for 4 h. 10 mL of 2.0 M HCl solution was added and stirred at room temperature for 24 h. After filtrating, 2 mL of the filtrate was titrated with 0.1 M NaOH solution in the presence of phenolphthalein indicator. At the end of the neutralization of the excess HCl, 10 mL of 0.5 M D-sorbitol solution was added to the mixture.

Results&Discussion

In this study, crosslinked PVBC resin was prepared by using suspension polymerization method in the presence of toluen as porogen and AIBN as initiator at 70°C for 8 h . The PVBC resin was reacted with tris(hydroxymethyl)aminomethane to obtain tris hydroxy amine functions (Scheme1).



Scheme1.Preparation of the resin

Boron Sorptions

Boron sorption experiments were performed depending on different boron concentrations (Table 1). Hydroxyl functions incorporated into the polymer structure act as chelating agent for boric acid, by forming cyclic boron esters. Boron loading capacity of the sorbent is 2.62 mmol g⁻¹ in non-buffered conditions. According to Table 1, boron sorption capacity depends on boron concentration and loading capacity of the resin increases with increasing boron concentration.

Table 1. Maximum boron sorption capacities of the resin.

Concentration (M)	Boron Sorption Capacity (mmol/g)
0.12137	0.44
0.24275	1.15
0.36413	1.50
0.4855	2.62

Also, boron sorption capacities of the resin was investigated in the presence of foreign ions such as Mg²⁺ and Ca²⁺ and capacities do not change drastically (Table 2).

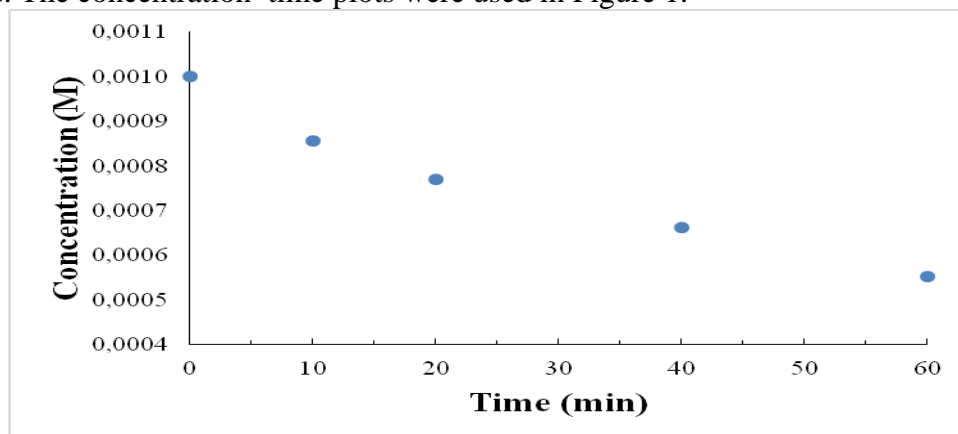
Table 2. Maximum boron and ion sorption capacities of the resin

H ₃ BO ₃ (M)	Ion (0.14M)	Boron capacity (mmol/g)	Ion Capacity (mmol/g)
0.485	Mg ²⁺	2.17	0.24
0.485	Ca ²⁺	1.67	0.24
-	Mg ²⁺	-	0.98
-	Ca ²⁺	-	0.69

Boron Sorption Kinetics of the Resin

Batch kinetic experiments were performed by using highly diluted boric acid

solutions. The concentration–time plots were used in Figure 1.



The kinetics of sorption is an important aspect of the process control of removal of pollutants. As shown in Fig. 1, there was a rapid uptake kinetics and adsorption equilibrium, which would be attained within about 60 min.

Conclusion

In this work, tris hydroxyl modified PVBC polymeric sorbent was synthesized to prepare an alternative adsorbent for removal of boron from wastewater. The desorption capacity of the sorbent was found as 2.0 mmol g⁻¹. Desorption experiment was conducted with regenerated resin again and the sorbent was desorbed completely.

References:

1. Power, P.P. and W.G. Woods. *Plant and Soil* (1997) 193(1-2) 1-13.
2. D. Hou, J.Wang, X. Sun, Z. Luan, C. Zhao, X. Ren. *J. Hazard. Mater.* (2010) 177 613–619.
3. A. Farhat, F. Ahmad, H. Arafat. *Desalination* (2013) 310 9–17.
4. N. Öztürk, D. Kavak. *J. Hazard. Mater.* (2005) 127 81–88.
5. Z. Yazicigil, Y. Oztekin. (2006) 190 71–78.
6. I. Yilmaz, N. Kabay, M. Brjyak, M. Yuksel, J. Wolska, A. Koltuniewicz. *Desalination* (2006) 198 310–315.
7. W.R. Lyman, A.F. Preuss, US Patent 2 (1957) 813-838
8. Hatcher, J. T.; Wilcox, L. V. *Analytical Chemistry* (1950) 22 567-569.

Assessment of Essential Element Bioaccessibilities in Baby & Toddler Foods Using Response Surface Methodology Approach

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Minerals are required for many biological functions in the body. Therefore, providing an appropriate diet especially in growing period of children is important and low intake or bioavailability of nutrients may cause body function impairment.^{1,2} Although breast milk is recommended for the first 6 months of life of infant, it may not sufficient alone to meet the increasing nutritional requirements.^{3,4} So, various commercial infant complementary foods mostly contain fruits, vegetables or cereals and in powder, liquid-concentrate and ready-to-feed forms are intended for consumption from the beginning of some periods of life depending on the pediatric guidelines.³⁻⁵

Infants consume more food than adults relative to their body weight. On the other hand, essential micronutrients can be toxic when taken in excess.⁶ Therefore, elemental content of baby foods together with the amount of the available fractions for absorption in the body are crucial factors. In our study, total concentrations and bioaccessibility of some essential and trace elements in commercial baby complementary foods were determined by inductively coupled plasma mass spectrometer after using response surface methodologies. Enzymatic in vitro digestions were performed by consecutive pepsin and pancreatin enzymes at pH 1.9 and 6.9, in respectively to simulate the stomach and the intestine conditions. A five-level, three-factor central composite design, consisting of 20 runs with six replicates of the central points, was applied to optimize and evaluate the sample, pepsin and/or pancreatin amounts and sample dilutions on the bioaccessibility of selected elements using the Design Expert software. Rice flour and baby food composite certified reference materials analysis were applied to optimize the digestion parameters and evaluate the accuracy of the optimized method. Interferences were screened by analyzing the certified reference materials and monitoring different isotopes of elements. Finally, bioaccessible data with improved quality were used for the risk assessment of baby foods.

Keywords: Baby Food, Essential Elements, Bioaccessibility, ICP-MS.

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References:

1. Melo, R., Gellein, K., Evje, L., Syversen, T. Food And Chemical Toxicology (2008) 46 3339–3342.
2. Zand, N., Chowdhry, B.Z., Zotor, F.B., Wray, D.S., Amuna, P., Pullen, F.S. Food Chemistry (2011) 128 123–128.
3. Ljung, K., Palm, B., Grander, M., Vahter, M. Food Chemistry (2011) 127 943–951.
4. Frontela, C., Haro, J.F., Ros, G., Martinez, C. Journal of Agricultural and Food Chemistry (2008) 56 3805–3811.
5. Erkekoglu, P., Baydar, T. Nutrition Research Reviews (2010) 23 323–333.
6. Pandelova, M., Lopez, W.L., Michalke, B., Schramm, K.W. Journal of Food Composition and Analysis (2012) 27 120–127.

An Experimental Design Approach to Evaluate Leaching Characteristics of Nickel Laterites with Different Analytical Techniques Used for Analysis

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Approximately 60% of the world production of nickel ores is obtained from sulphide ores and the rest from nickel laterites. Due to rapid growth of nickel consumption and the lack of sulphide ores, laterite ore has become a major source of nickel¹. Complex mineralogy of laterite ores and low nickel content leads to difficulties for recovery of nickel directly². Nowadays, as the typical metallurgical methods, the ammonia leaching followed pre-treatment roasting-reduction and the high pressure acid leaching are used to process nickel laterite ores³.

This work is aimed to describe the atmospheric sulphuric acid leaching characteristics of Uzunpinar (Kayseri, Turkey) laterite ore⁴. The leaching of nickel from laterite ore was investigated by using response surface methodology (RSM). Central composite design (CCD) combined with RSM was used to examine and optimize the effects of leaching parameters. The quadratic model was defined by three independent variables (initial acid concentration, temperature and ore/acid ratio). The significance of the effects was checked by ANOVA and the optimum values of the selected variables were found. According to the statistical analysis, the temperature played the most significant roles in the leaching of nickel. The nickel recovery determined as 99.96% by the model was experimentally found as 97.99%±1.83 (N=3) in the acceptable level.

Analysis of nickel in the leached solutions was carried out with calibration curves and standard addition techniques by flame atomic absorption spectrometry. Two analytical techniques were compared statistically. In addition, to determine the precision of the calibration curve and the accuracy of the standard addition technique were investigated. These techniques were first applied to real samples using the RSM approach and received good results and were validated.

Keywords: Calibration Curve Technique, Leaching, Nickel, Response Surface Methodology (RSM), Standard Addition Technique.

References:

1. Wang B., Guo Q., Wei G., Zhang P., Qu J., Qi T., Hydrometallurgy (2012) 129 7-13.
2. Whittington B.I., Muir D., Miner. Process. Extr. Metall. Rev. (2000) 21 527-599.
3. McDonald R.G., Whittington B.I., Hydrometallurgy (2008) 91 35-55.
4. Çetintas S., Bingöl D., Anal. Methods (2016) 8 3075-3087.

Elemental Distribution and Fatty Acid Profile of Raw Goat Milk: Effect of Dietary Olive Pellets on Milk Nutritional Value

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Milk is the most valuable drink for adults and babies. Milk serves as the source of macronutrients such as protein, lipids and carbohydrates and micronutrients such as minerals, vitamins and enzymes¹⁻². In this study, the effect of dietary olive pellets on nutritional value of raw goat milk were investigated by elemental fractionation and fatty acid analysis. Experimentally, previously suggested sequential fractionation procedure was applied on milk samples and lipid, protein and serum fractions were separated. The elements Fe, Cu, Zn, Mn, Mg, Ca, Cr, Ni, Mo, Al, Ba, Pb, Sn, V, Co and Cd were determined by inductively coupled plasma optic emission spectrometry (ICP-OES) in separated fractions. The elements Ca, Mg, Mn, Ba, Mo and Zn were mainly found in serum fraction. On the other hand, Fe and Cu was predominantly bounded to protein fraction. Fatty acid profile of the milk samples were determined using gas chromatograph. The results demonstrated that feeding the goats with olive pellets increase the MUFA and PUFA contents in milk. Correspondingly, principal component analysis was showed that, milk samples of basal diet fed and olive pellet fed goats were separated into two groups. Accordingly, milk of basal diet fed goats was rich in SFA and medium chain FA and milk of olive pellet fed goats were rich in PUFA, MUFA and long chain FA.

References:

1. S. Bağdat Yaşar, E. Köse Baran, F. Tokay, Spectroscopy Letters (2013) 46 100-108.
2. S. Bağdat Yaşar, E. Köse Baran, F. Tokay, International Journal of Food Science and Technology (2014) 49, 392-398.

Retinoic Acid: A Spectroscopic Approach on Binding Studies of DNA with The Copper(II) Complex

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Retinoic acid (RA) is a metabolite of vitamin A (retinol) that mediates the functions of vitamin A required for growth and development. During early embryonic development, retinoic acid generated in a specific region of the embryo helps determine position along the embryonic anterior/posterior axis by serving as an intercellular signaling molecule that guides development of the posterior portion of the embryo [1].

In this study, Cu(II) complex of RA was synthesized and characterized via spectroscopic and analytical techniques. The thermal behavior of the complex was also analyzed. The electrochemical properties of complex have been analyzed by cyclic voltammetry using glassy carbon electrode. The biological activities of the compounds were evaluated through examining their capacity to bind to fish sperm double strand DNA (FSdsDNA) with absorption spectroscopy. Absorption studies of the interaction of the RA and its Cu(II) complex with FSdsDNA have indicated that these compounds could bind to FSdsDNA, and the binding constants were calculated.

Keywords: Characterization, electrochemical properties, DNA binding

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References:

1. G. Duester, *Cell*, 2008 134(6): 921–31.

Spectrophotometric Methods for The Calculation of DNA Binding of Metal Based Drugs: Recent Trends and Developments

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Spectrophotometry is a mighty analytical technique that is increasing in benefit in the DNA binding studies. Spectroscopic techniques employ light to interact with matter and thus probe certain features of a sample to learn about its consistency or structure. Light is electromagnetic radiation, a phenomenon exhibiting different energies, and dependent on that energy, different molecular features can be probed. Spectrophotometric techniques are used as an alternative or complementary technique to electrochemical and separation techniques due to its high sensitivity, speed of analysis and sample consumption, and low operating cost compared to other analytical methods. These techniques are the principal method for evaluating quantity and quality of nucleic acids. In aqueous solution, DNA has maximal absorbance near 260 nm with an extinction coefficient of 50; protein absorbs light strongly near 280 nm. This study gives recent DNA binding studies used for each techniques of spectrophotometry. This study will also describe recent developments for DNA binding studies of metal based drugs, DNA types, and kind of. Selected studies on these subjects are given as examples [1,2].

Keywords: DNA, binding constant, spectrophotometry

References:

1. J. Wang, Anal. Chim. Acta. 469, 63 (2002).
2. G. Psomas, J. Inorg. Biochem. 102, 1798 (2008).

Spectrofluorometric Determination of Zinc in Pharmaceutical Preparations by Using the Manganese Displacement from Manganese-Zinpyr-1 Complex

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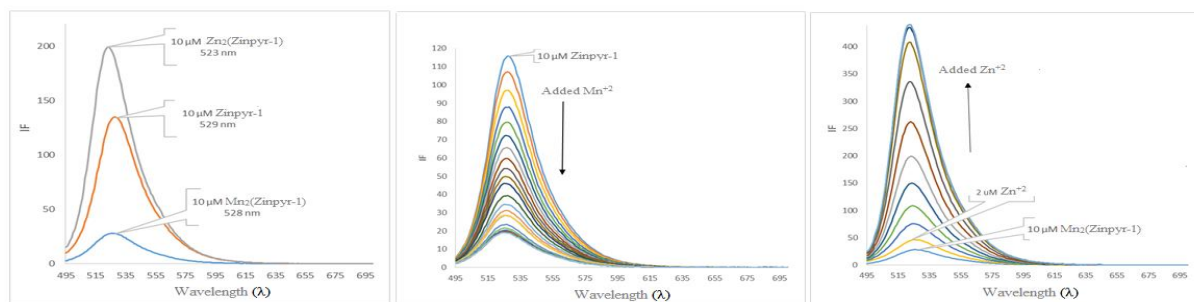
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Zinc ion, as an essential bioelement for the vital functions of the organism, are located in many metabolic processes, such as gene expression, DNA synthesis, enzymatic catalysis, hormonal storage/release, neurotransmission, memory, eyesight, healing and growth. The aim of study was to develop and validate a spectrofluorometric method based on the selective displacement of manganese from $Mn_2(\text{Zinpyr-1})$ nanocomposite by zinc that allows zinc detection has been developed in pharmaceutical products.

9- (o-Carboxyphenyl) -2,7-dichloro-4,5-bis [bis(2-pyridylmethyl) -aminomethyl] -6-hydroxy-3-xanthanone (Zinpyr-1) was synthesized and characterized by ¹H-NMR and ¹³C-NMR and FT-IR analysis. The manganese ion was formed an orange-red colored complex with Zinpyr-1 in the pH:7. The $Mn_2(\text{Zinpyr-1})$ complex was decreased the fluorescence intensity of Zinpyr-1 that shows emission at 529 nm (λ_{ex} :490 nm). The composition of the complex was found 1:2 as revealed by a fluorescence Job's plot and mole ratio plot. K_d values of $Mn_2(\text{Zinpyr-1})$ are greater than $Zn_2(\text{Zinpyr-1})$. So, manganese by zinc ions is displaced thermodynamically.



Different concentration (0–22 μM) of zinc ion at pH 7.0 was added on the $Mn_2(\text{Zinpyr-1})$ (10 μM) and the linear calibration range was in the concentration range of 0–20 μM for zinc ions at 523 nm. The optimized method was successfully applied to the determination of zinc ion in pharmaceutical formulations and obtained results found to be in good agreement with the label claim.

Keywords: Zinc, Zinpyr-1, Manganese-Zinpyr-1 Complex, Pharmaceuticals, Spectrofluorometry

References:

1. [You, Y.](#), [Tomat, E.](#), [Hwang, K.](#), [Atanasijevic, T.](#), [Nam, W.](#), [Jasanoff, A.P.](#), [Lippard, S.J.](#) Chem. Commun (2010) 46(23), 4139–41

Spectroscopic Analyses of $\text{Mg}_2\text{KH}(\text{XO}_4)_2 \cdot 15\text{H}_2\text{O}$ ($\text{X} = \text{P}, \text{As}$): Unusual Spectral Behavior of Symmetric Dimers $[\text{H}(\text{XO}_4)_2]$

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Vibrational spectra of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ and their partially deuterated analogues were recorded and analyzed. Compounds of the type $\text{Mg}_2\text{KH}(\text{XO}_4)_2 \cdot 15\text{H}_2\text{O}$ ($\text{X} = \text{P}, \text{As}$) are a rare case of phosphate and arsenate salts containing dimer $[\text{H}(\text{XO}_4)_2]$ units in the crystal structure. The spectral picture of these compounds very much resembles the one observed for struvite type compounds with the formula $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ($\text{M}^{\text{I}} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$; $\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$), $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{KMgAsO}_4 \cdot 6\text{H}_2\text{O}$. This means that vibrations of the symmetric $[\text{H}(\text{XO}_4)_2]$ dimers have a relatively small part in the general spectral appearance. It was found that in the vibrational spectra of $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ both $\nu_1(\text{AsO}_4)$ and $\nu_3(\text{AsO}_4)$ modes have practically the same wavenumber around 830 cm^{-1} . In the vibrational spectra of the hydrogendiphosphate compound, the band at around 550 cm^{-1} could be attributed to the $\nu_4(\text{PO}_4)$ modes. This band is shifted to lower wavenumber with increasing deuterium content and seems to disappear, similarly as in the case of other phosphates with struvite type of structure. This behaviour could be a result of coupling of the $\nu_4(\text{PO}_4)$ vibrations with some other modes, most probably HDO and/or D_2O librations. Studying this type of compounds is interesting since they belong to the so-called “zero dimensional” hydrogen bonded compounds and may be considered as potential proton conductors.

Keywords: $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$; $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$; Raman; Infrared; Symmetric Dimer Units

Thermal and Spectral Studies of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$

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The thermal hydrolysis of hydrated magnesium salts is an important process which is applied in different industries. Particularly, the thermal hydrolysis of magnesium iodide hydrates is one of the steps of the magnesium-iodine cycle for thermochemical production of hydrogen. In this regard the detailed investigation of the thermal behavior of magnesium iodide hydrates is of great importance. In contrast to other alkaline halogenide hydrates, which have been the subject of thermo-analytical investigations identifying various decomposition products, magnesium iodide hydrates are only briefly studied.

In the present contribution special attention is paid to the thermal and spectroscopic characterization of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ which is the stable hydrate at room temperature. For more precise and deep description of the processes occurring upon heating of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ we have apply simultaneous TG/DTA/Mass spectrometry technique identifying the gases evolved during the thermal decomposition at different heating rates. We have established that the thermal decomposition of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ is a complex process that occurs in two main stages. In the first stage (120 and 275 °C) the salt undergoes a hydrolytic decomposition with the formation of a basic product, magnesium hydroxyiodide. The thermogravimetric data evidence that magnesium hydroxyiodide has non-equimolar ratio of the hydroxyl group and iodine, $\text{Mg}(\text{OH})_{1.44}\text{I}_{0.56}$, in contrast to the well-known $\text{Mg}(\text{OH})\text{Cl}$. According to TG/DTA $\text{Mg}(\text{OH})_{1.44}\text{I}_{0.56}$ is obtained as a result of three-step dehydration process with formation of intermediate lower hydrates: $\text{MgI}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgI}_2 \cdot 2\text{H}_2\text{O}$. Thus obtained $\text{Mg}(\text{OH})_{1.44}\text{I}_{0.56}$ is further decomposed completely to MgO in a single step between 290 and 400 °C (second main stage). This scheme of the thermal decomposition of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ is confirmed by the mass spectrometry data for the gases evolved: H_2O , I_2 , HI and H_2 . Based on TG/DTA/Mass spectrometry data a detailed scheme of thermal decomposition of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ is proposed. The infrared spectra of $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ and deuterated analogues at room and liquid nitrogen temperatures are also presented and interpreted.

Keywords: Magnesium Iodide Octahydrate, Thermal Decomposition, Thermal Hydrolysis, IR Spectra

Fully Substituted Functional Phosphazene Compounds as Selective Anion Probes

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Phosphazene compounds containing $-P(X_2)=N-$ units is interesting class of inorganic compounds. They can be converted to functional materials as a result of the nucleophilic reactions of labile halogen atoms in their structure with the nucleophiles such as alcohol, amines and phenols. In the recent years, cyclotriphosphazene platform has been used as core for the preparation of multi centered probes for ionic species [1-4].

In this study, we synthesized two probe containing cyclotriphosphazene core and six active centers for the anion recognition. For this purpose, hexakis(4-aminophenoxy)cyclotriphosphazene compound was reacted with 4-nitrophenylisocyanate and 4-nitrophenylisothiocyanate. The obtained fully substituted compounds were characterized using spectroscopic techniques such as FT-IR, NMR, Mass and elemental analysis. Then, the sensor properties of compounds for anionic species were investigated using UV-Vis spectrophotometer (Fig. 1).

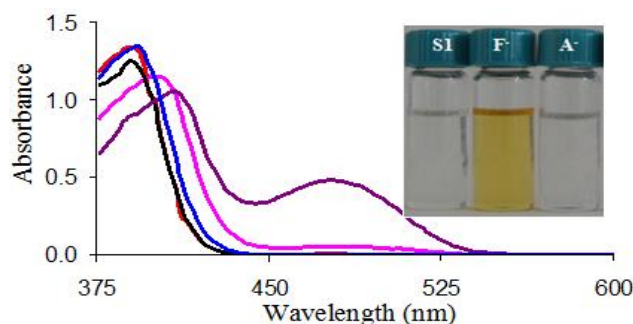


Figure 1. UV-Vis spectra and digital camera image of urea derivative S1 in the presence of different anion

Keywords: Anion Recognition, Sensor, Phosphazene, Urea, Thiourea

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References:

1. Emrah Ozcan, Süreyya O. Tümay, Hüsnüye Ardiç Alıdağı, Bünyemin Çoşut, Serkan Yeşilot, Dyes and Pigments (2016) 132 230-236.
2. Hava Ozay, Mehmet Yildirim, Ozgur Ozay, Phosphorus, Sulfur, and Silicon and the Related Elements (2015) 190 1865–1873.
3. Hava Ozay, Mehmet Yildirim, Ozgur Ozay, Turkish Journal of Chemistry (2015) 39 777-788.
4. Reyhan Kagit, Mehmet Yildirim, Ozgur Ozay, Serkan Yesilot, Hava Ozay, Inorganic Chemistry (2014) 53 2144–2151.

The Synthesis and Application of New Phosphazene Compound as Highly Selective Cyanide Sensor

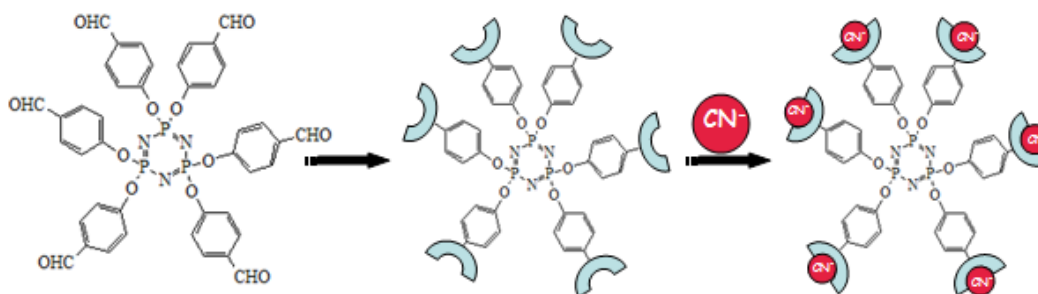
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Biologically and environmentally important anions have played a fundamental role in a wide range of organic and inorganic systems, and their application in sensing and anion transport has gained considerable interest [1]. One of the most interesting anions to monitor the cyanide ion (CN⁻) due to its environmental, biological and industrial importance. Cyanide is one of the most toxic and harmful anions to human health and environmental, since it can suppress the transport of oxygen [2]. Nevertheless, cyanide ion is widely used in many chemical processes such as electroplating, plastics manufacturing, gold and silver extraction, tanning, and metallurgy. Therefore sensitive, selective, simple, and affordable sensors for cyanide ion are in great demand for various applications [3].

In this study, we synthesized a new compound as reaction based selective cyanide sensor using hexakis(4-formylphenoxy)cyclotriphosphazene as starting material. The synthesized compound was structurally characterized using FT-IR, ¹H NMR, ¹³C NMR, ³¹P NMR techniques. Then, sensor behaviors of compound against anionic species were investigated by UV-Vis spectrophotometry in acetonitrile/H₂O solvent mixture. It was determined that compound is an excellent colorimetric and spectrophotometric sensor.



Keywords: Phosphazene, Cyanide, Naked-Eye, Sensor

Acknowledgements: The authors thank the Scientific and Technological Research Council of Turkey (TUBITAK) for the partial financial support (112T278).

References:

1. F. Hu, M. Cao, J. Huang, Z. Chen, D. Wu, Z. Xu, S.H. Liu, *Dyes and Pigments* 119 (2015) 108-115.
2. J.M.M. Rodrigues, A.A.S. Farinha, A.C. Tome, J.A.S. Cavalerio, J.P.C. Tome, *Sensors and Actuators B* 224 (2016) 81-87.
3. P. Zeng, B. Shi, X. You, Y. Zhang, Q. Lin, H. Yao, T. Wei, *Tetrahedron* 70 (2014) 1889-1894.

Molecularly Imprinted Polymer Nanoparticles for Protein Diagnosis

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Many efforts have been made to produce artificial materials with bio-mimetic properties for application to binding assays. Among these efforts, the technique of molecular imprinting has received much attention due to the high selectivity obtainable for molecules of interest, robustness of the produced polymers, simple and short synthesis and excellent cost efficiency [1]. Molecularly imprinted polymer nanoparticles (nanoMIPs) have the potential to be a low-cost and robust alternative to biomolecules such as antibodies, and so are suitable tools for assay and sensor development [2].

In this study, a simple and straightforward technique for coating microplate wells with nanoMIPs to develop assays similar to the enzyme-linked immunosorbent assay (ELISA) is presented. NanoMIPs are considered to be a robust alternative to antibodies that often exhibit batch-to-batch variability, poor performance in non-physiological conditions and, in some cases, short shelf life. NanoMIPs were synthesized by a solid-phase approach with an immobilized horseradish peroxidase (HRP) (template) and characterized using dynamic light scattering, and electron microscopy. Immobilization, blocking, and washing conditions were optimized in microplate format. The detection of horseradish peroxidase was achieved in competitive binding experiments. Immobilized nanoMIPs were stored longer than 1 month at room temperature without any detrimental effects to their binding properties. The high affinity of nanoMIPs and the lack of a requirement for cold chain logistics make them an attractive alternative to traditional antibodies used in ELISA.

Keywords: Molecularly Imprinted Polymer, Nanoparticle, Molecular Recognition, Protein Imprinting

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References:

1. T. S. Bedwell & M. J. Whitcombe, *Anal Bioanal Chem* (2016) 408 1735-1751.
2. A. Poma, A. Guerreiro, M. J. Whitcombe, E. Piletska, A. P. F. Turner, S. Piletsky, *Adv Funct Mater* (2013) 23 2821-2827.

***In vitro* ACE Inhibitory Activity of Beef Dry Muscle (*M. Semimembranosus*)**

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Abstract

Objectives of this study were to *in vitro* determine the antihypertensive activity of peptic hydrolysates of fresh beef and pastirma cuts [*M. semimembranosus* (SEM)]. Antihypertensive activity was determined using (ACE) inhibitory activity assay. As a result of this study, the hydrolysates of pastirma cuts showed a higher ACE inhibitory activity than in fresh meat as indicated by the IC₅₀ value (1.02mg/ml and 1.46mg/ml, respectively). The inhibition ratio against ACE in meat was contradictory to the value exhibited by pastirma, whereas the inhibition ratios of both samples were 85.55 and 77.24%, respectively. However, previously [1] we found contrasting results that meat showed higher ACE inhibitory activity (0.68mg/ml) than pastirma (0.78mg/ml), made from *M. Longissimus lumborum* (LLU). Based on the data of this work and a previous study, it can be suggested that the ACE inhibitory activity of beef is a muscles-based that refers to the differences in structure of muscle protein. Additionally, there might be no need to process meat to enhance its biological activity. Consequently, fresh meat and pastirma proteins might be a good source of ACE inhibitory peptides that serve further nutraceutical purposes.

Keywords: ACE, Hypertension, Pastirma, Hydrolysates.

Introduction

Generally, meat consumption is related to living standards, life quality, diet values, livestock production and consumer ethics, as well as the economy in each country. In 2014, the fresh and processed meat consumption/capita in Turkey was 28.2 kg/person [2]. Almost all meat is processed in some way before it is eaten. Commercially, the main reasons to process meat are to eliminate micro-organisms to extend shelf life and also to improve its organoleptic properties. There is a variety of processing and preservation techniques used in meat industry, whatever the case, the nutrient value of any meat is often altered either positively or negatively by the processing. Some myofibrillar, sarcoplasmic and stroma proteins, enzymes and vitamins (B-group and C) are almost always unstable by the kind of processing they undergo. The purpose of this paper is to discuss whether it is essential to dry-curing the meat in the form of pastirma to enhance its potential lowering blood pressure properties that is measured *in vitro*. In Turkey, pastirma (semi-dry meat product) is most commonly served as thin style slices that are meant to be eaten raw as it contain distinctive aromatic profiles that make its delicacy quite remarkable. There is a little information on Angiotensin I-converting enzyme (ACE) inhibitory activity of its proteins in comparison with fresh meat. ACE is a dipeptidyl-carboxy-peptidase, plays an important physiological role in regulating blood pressure [3]. Hypertension means high blood pressure (HBP), which is a major disease that strikes the public at different ages due to the genetic and or lifestyle related factors. HBP is a serious condition that can lead to coronary heart related diseases and death [4]. The greater the ACE activity, the more angiotensin I is converted to angiotensin II, which induces high blood pressure [5]. Globally, the WHO reported that the

overall prevalence of HBP in adults aged 25 and over was ranged from 30-48% depending on gender [6]. We believe that other methods rather than chemical medication should be identified in the effort to reduce hypertension in individuals [2]. This article compares the antihypertensive activities of both fresh meat and processed meat to determine in which way we should consume meat to take advantage of its nutritional and nutraceutical forces. Additionally, this work attempted to figure out if ACE inhibitory activity is muscles-based.

Materials&Methods

Muscles: *M. semimembranosus* (SEM), (top inside) of fresh and beef pastirma were sourced from the same 30 months old cattle bulls (*Montofon*). SEM muscles were used 48 h *post-mortem* and their pH values before processing was 5.6. Two groups were prepared: one group was analyzed as fresh meat while the other group was processed into pastirma. Cuts of pastirma were manufactured using a traditional method in a local manufacturer in Kayseri city, pastirma making process took one month prior to the experiment, meanwhile the fresh muscles were kept at -80°C . The cuts used for pastirma were covered with a paste of ground spices known as *çemen* during processing [7].

Digestion process: Fifty gram of each minced sample were mixed with 130 ml of distilled water. The mixture was then cooked for 30 min at 70°C . Cooked samples were digested with pepsin and trypsin consecutively for 4 hours after adjustment of pH. The samples were boiled to inactivate the enzymes [1]. Eventually, samples were cooled-down to 20°C and fractionated by centrifugation (5000rpm/10min) and filtration process by a cellulose membrane filter ($0.45\mu\text{m}$) to yield bioactive peptides [4].

SDS-PAGE: Proteins extracted from each sample type were electrophoresed on SDS-PAGE patterns. Proteins were extracted in different buffers such as 1 M sucrose, 2 M urea, low ionic strength buffer (WSP), and high ionic strength buffer (Guba Starub-ATP) [8].

Determination of the antihypertensive activity: *In vitro*, the inhibition ratio and IC_{50} value of fractionated proteins were measured using ACE inhibitory activity assay. The samples were treated with ACE and its substrate (hippuryl-histidyl-leucine), the resultant is hippuric acid that *spectrophotometrically* determined at 280nm, which is released if there is no complete inhibition for ACE [4].

Results and Discussions

As a results, pH value of the pastirma samples have not much changed during the process when compare to fresh meat. Results also indicate that pastirma process along with the enzymatic hydrolysis generated peptides that inhibited ACE activity *in vitro*. SDS-PAGE data indicates major proteins were degraded such as myosin heavy chain (200kDa) and many enzymes including: β -galactosidase, phosphorylase B, trypsinogen lactate dehydrogenase, that was because of the pastirma making process. Generally, the pastirma-making process increased the amounts of proteins extracted by different solutions, implying that the salting and curing process had a beneficial effect on releasing further proteins [8]. Figure 1, shows the protein bands of original and diluted samples derived from fresh beef and pastirma cuts. Apparently, proteins exhibited in meat were not visible in pastirma sample indicating that great degradation occurs on pastirma proteins during processing. They were further split down to small peptides and free amino acids. Hybrid hydrolysates of fresh beef and pastirma showed a remarkable inhibition ratio against ACE [1]. Beef and pastirma showed inhibition rate against ACE activity 85.55 and 77.24%, respectively (Fig. 3). In this study both meat and pastirma were found to have ACE inhibitory activity perhaps due to a generation of substantial number of peptides as a result of protein proteolysis. Hydrolyzed proteins from beef and pastirma showed 1.46 and 1.02mg/ml respectively (Fig. 2). However, a research on another muscle (*M. Longissimus lumborum*) [1] showed dissimilar results, as the IC_{50} value was 0.68 and 0.78mg/ml for fresh meat and pastirma,

respectively (Table 1).

Table 1. Comparison on IC₅₀ and protein concentrations of hydrolysates in Turkish fresh beef and pastirma cuts derived from different muscles (*Montofon*).

Muscle type, B: Beef and P: Pastirma	Protein (mg/ml)	IC ₅₀ (mg/ml)	Source
B: <i>M. Longissimus lumborum</i>	16.68	0.68	[4]
P: <i>M. Longissimus lumborum</i>	18.27	0.78	[4]
B: <i>M. Semimembranosus</i>	15.9	1.46	Current
P: <i>M. Semimembranosus</i>	16.7	1.02	Current

Data suggest that the protein activity is highly related to the muscle type not necessarily to processing method. There might be a slight effect on processing the meat, but still the muscle type largely contributes to the

biological activity of meat protein. The biological activities obtained in this work seemed to be compatible to other studies conducted on different muscles. The current results in agreement with a previous data that it is not necessarily processing the meat to value its biological activities [1]. Apparently, this also demonstrates that meat proteins might lead to better production of peptides that minimize hypertension in patients. A concept can be drawn here meat is a source of peptides that are effective at preventing hypertension and should be considered instead of the chemically based medications. Current food research addresses the extensive links between health and nutrition and other scientific disciplines such as protein-engineering technology (pro-eng), chemistry of food and bioavailability [1]. To understand how to prevent high blood pressure, first it further helps if we know what cause it. Many reasons have been addressed to cause hypertension such as: diet rich in salt and fat, stress, smoking, alcohol consumption, inactivity, obesity and diabetes, etc. There are 3 ways of minimizing the incidence of hypertension disease and they can be split into: medication choice, changing life style option (quite hard) and last to make food as oneself medicine. The first option is the easiest but all medicines have side effects and the problem that many people do not feel the side effects until consequences can be realized. There is only one way to do so that people can prevent any side effects, which can be happened through understanding the bio- activity and -availability of meat to take an advantage of its potential forces. Nowadays people do not really need much advice because they already know basically what they should eat including a variety of foods, whole grains, lean meat, fruits and vegetables. They need more scientific evidences to prove that meat is a great commodity that may contain nutraceuticals to be used efficiently in preventing the incidences of chronic hypertension. This article tries to highlight on meat hybrid proteins as an alternative to prevent and minimize hypertension. Results of the current research suggest that meat contains biologically and nutritionally active peptides that may reduce chronic hypertension in individuals.

Proteins hydrolysates sourced from Montofon beef have remarkable antihypertensive activities. Although many consumers think that pastirma would never be a healthy product due to the high salt level it still can provide peptides with great ACE inhibitory activity. Thus, we would like to disclose that fresh beef and pastirma have a nutraceutical value that effects positively on meat-eating society. Yet, results suggest that fresh beef is richer than pastirma in peptides that may provide physiologically functional peptides, thus lowering blood pressure. Results of this work may considerably bring more beneficial information for the global meat scientists' society and for the Turkish consumer in particular.

Conclusion

We suggest meat might have a nutraceutical value that effects positively on the chronically hypertensive individuals as exhibited *in vitro* a considerable blood pressure-lowering property, which in turns promotes a healthy society. The ACE inhibitory activity exhibited in this study perhaps refer to the coexistence of cyclic, aromatic and sulfur amino acids (Pro, Phe, Try, Tyr, Met and Cys) and also to acidic amino acids such as (Arg and Lys) on the hydrolysate fragments (peptides). We would like to address that dozens of fresh meat peptides do inhibit the

action of angiotensin I-converting enzyme (ACE). Therefore, the ACE inhibitory activity is muscle-based and possibly not related to the processing. The dry-curing process should not be considered to enhance the ACE inhibitory activity. To sum up, manipulation of potential proteins derived from meat as pro-drug nutraceutical using pro-eng system to tackle the chronic hypertension disease can be achieved to minimize the usage of medicines.

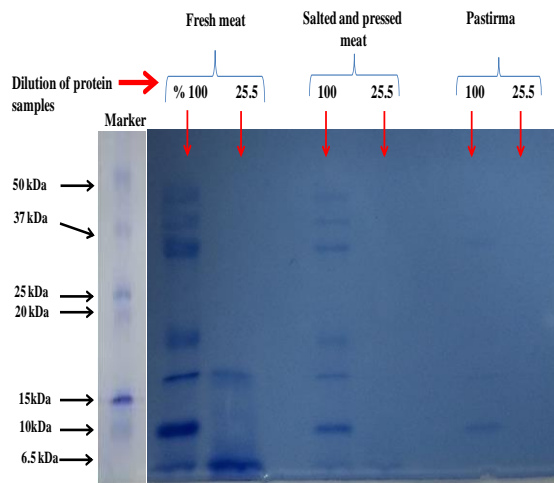


Figure 1. SDS-PAGE pattern of fresh beef and pastirma peptic hydrolysates at three different stages of processing.

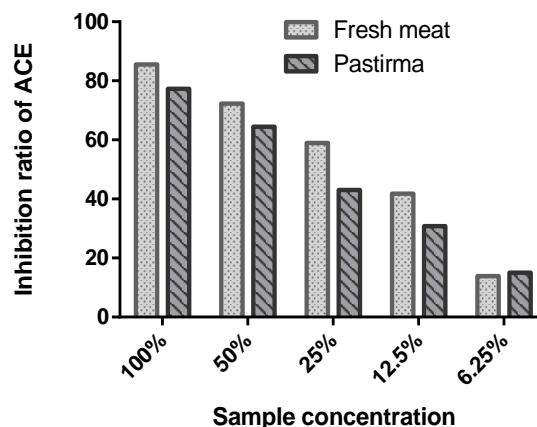


Figure 3. *In vitro* inhibition ratio of ACE as effect of peptide activity from fresh beef and pastirma cuts (*M. Semimembranosus*)

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References:

1. Ahhmed M. A., Ozer, N., Birisik, C., Cam, M., Sakata, R., Muguruma, M., Yetim, H. Meat therapy for hypertension: Hybrid hydrolysates as ACE inhibitory compounds. Proceedings of the 19th International conference, Functional foods, bioactive compounds and biomarkers: Longevity and quality of life 17-18 November 2015 108-111, Kobe, Japan.
2. <https://data.oecd.org/agroutput/meat-consumption.htm> (2014)
3. Skeggs, L., Khan, E. and Shumaay P. The preparation and function of the hypertensin-converting enzyme. Journal of Experimental Medicine (1965) 103 95-299
4. Katayama, K. Henny, E., Mori, T., Ahhmed, A., Kawahara, S., Sugiyama, M., *et al.* Porcine skeletal muscle troponin is a good source of peptides with Angiotensin I-converting enzyme Inhibitory activity and antihypertensive effects in spontaneously hypertensive rats. Journal of Agricultural and Food Chemistry (2008) 56 355-360.
5. Muguruma, M., Ahhmed, M. A., Katayama, K., Kawahara, S., Masugu, M., Nakamura, T. Identification of pro-drug type ACE inhibitory peptide sourced from porcine myosin B: Evaluation of its antihypertensive effects *in vivo*. Food Chemistry (2009) 114 516-522.
6. http://www.who.int/gho/ncd/risk_factors/blood_pressure_prevalence_text/en/ (2013)
7. Kaban, G. Changes in the composition of volatile compounds and in microbiological and physicochemical parameters during pastirma processing, Meat Science (2009) 82 17-23.
8. Ahhmed, M. A. Traditional cured meat-making process degrades the proteins of *M. latissimus dorsi* of bovine. International Food Research Journal (2014) 21 139-148

Synergic and Antagonistic Effects between Boron and Arsenic in Yeast (*Saccharomyces cerevisiae*) Cells

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Doing deep research of application field of boron in Turkey is an important factor due to its rich reserves in our country. While boron can be both essential and toxic depending on its concentration level, arsenic shows toxic properties. The possible correlation between the uptakes of boron and heavy metals by organisms, in particular uptake of boron and arsenic is an important issue to be studied on it when considering high concentrations of these two elements at the same time in some regions of Turkey such as Balıkesir-Bigadiç and Kütahya-Emet [1-2].

In this study, yeast cells (*Saccharomyces cerevisiae*) were used as organisms. As(III) and/or B(III) were spiked to cells grown in liquid growth media including yeast extract peptone dextrose (YPD) to follow arsenic-boron interaction. ICP-OES and ICP-MS results showed that significant percentage of arsenic and boron remained in supernatant solutions compared to cell. Additionally, cell growth was followed in terms of optical density measurements at 600 nm. According to optical density measurements, 9th hour was early logarithmic phase and 24th hour was stationary phase. After 9th hour growth period, B and/or As was added to the growth up to 24th hour. Moreover, yeast cells were exposed to 0.25, 0.50, 1.0 and 5.0 mM B and/or As and only at 5.0 mM, when As together with B resulted in less growth in terms of cell numbers.

Little intake of B and As by cells does not mean that biological damage of cells does not occur. Therefore, as a future work, examination of DNA of yeast cells will be done to observe any possible breaks possibly induced by B and/or As with agarose gel electrophoresis.

Keywords: Arsenic, Boron, *Saccharomyces Cerevisiae*, ICP-MS, ICP-OES.

References:

1. Gemici, Ü., Tarcan, G., Helvacı, C., Somay, A. M. “High arsenic and boron concentrations in groundwaters related to mining activity in the Bigadiç borate deposits (Western Turkey)”, *Applied Geochemistry*, 2008 23 2462-2476.
2. Ünlü, M. İ., Bilen, M., Gürü, M. “Kütahya-Emet bölgesi yer altı sularında bor ve arsenik kirliliğinin araştırılması”, *Gazi Üniversitesi Mühendislik ve Mimarlık Fakültesi Dergisi*, 2011 26 753-760.

Chip-Based Immunomagnetic Separation of Human Chorionic Gonadotropin

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Human chorionic gonadotropin (hCG) is a glycoprotein, and it can be misused by male athletes. This glycoprotein affects testosterone production and release in the human body. Therefore, the use of this hormone as a performance enhancing drug has been prohibited by the World Anti-Doping Agency [1]. In this study, a microchip, which had developed by our group, was used for the detection of hCG using both colorimetric and spectrofluorometric measurements. For this purpose, gold coated magnetic nanoparticles (MNPs) and gold nanorods (AuNRs) were synthesized and modified using different reagents and specific antibody, respectively [2]. Then they were used to form in-chip sandwich immunoassay with the hCG for colorimetric measurement. The developed microchips consist of four micro-chambers connected to each other by microchannels. The first chamber was filled with modified MNPs, the second and third chambers were filled with modified AuNRs and washing buffer, respectively. The last chamber was filled with 3, 3', 5, 5'-tetramethylbenzidine (TMB) and H₂O₂, then used for monitoring the color change. The chip process was performed by moving the MNPs from the first chamber through the microchannels using a magnet. The first step of the process is forming sandwich structure between the MNPs and the horse radish peroxidase (HRP) -labelled AuNRs. The second step includes washing the sandwich structure with the washing buffer. Finally, the enzymatic reaction between the TMB and H₂O₂ occurs in the presence of HRP in the last chamber, then the color change is observed. To get fluorescence signal, this time the second chamber of the microchip was filled with the europium (Eu) labelled-anti hCG, the third and last chamber was filled with the washing buffer. Finally, measurement was performed in the last chamber following same procedure used in colorimetric detection by a spectrofluorometer equipped with a fiber optic prob.

Keywords: AuNRs, Colorimetric Detection, hCG, MNPs, Microchip, Spectrofluorometric Measurement

References:

1. U-H Stenman, K Hotakainen, H Alfthan, British Journal of Pharmacology (2008) 154, 569-583
2. Uğur Tamer, Yusuf Gündoğdu et.al. Journal of Nanoparticle Research (2010) 12:1187-1196

Investigation of Some Heavy Metal Extraction Efficiencies of 1-(2-furoyl)piperazine Substituted Calix[4]arene from Aqueous Solution

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To extract heavy metal from contaminated water is a substantial task when their toxicity and hazardous effects such as lung, dermatological diseases, skin disorder, diarrhea, and immunity depression, and etc. to living life is laid on the table [1-3]. Thus, many researchers have been paid great attention to this matter, and designed effective extractants/adsorbents [1-3].

Calixarenes composed of the condensation of phenol and formaldehyde in basic milieu have been extensively employed in supramolecular chemistry due to the having a unique three-dimensional structure with almost unlimited functionalization [4,5]. In view of their fascinating scaffold properties, calixarenes have become the one of the most preferred supramolecular compounds for removing of toxic and hazardous pollutions from their contaminated sources so far.

In this work, a calix[4]arene derivative was functionalized with 1-(2-furoyl)piperazine groups at its 1,3-distal position. Its structure was characterized using FTIR, ¹H-NMR, ¹³C-NMR and elemental analysis techniques. Moreover, 1-(2-furoyl)piperazine-substituted calixarene derivative was used as an extractant for removing of some heavy metals from aqueous solution.

Keywords: Calixarene, Heavy Metals, Liquid-Liquid Extraction, Host-Guest Interaction.

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References:

1. Elçin S., Karakuş Ö.Ö., Kara İ., Deligöz H. Journal of Molecular Liquids (2015) 202 134-140.
2. Ward J., Li L., Regan F., Deasy M., Kelleher F. Journal of Inclusion Phenomena and Macrocyclic Chemistry (2015) 83 377-386.
3. Deligöz H., Yilmaz M. Solvent Extraction and Ion Exchange (1995) 13 19-26.
4. Sayin S., Azak H., Yildiz H.B., Camurlu P., Akkus G.U., Toppare L., Ersoz M. Physical Chemistry Chemical Physic (2015) 17 19911-19918.
5. Sayin S., Yilmaz M. Desalination (2011) 276 328-335.

Utilization of Enantioselective Behavior of Encapsulated-Lipase Containing a Calixarene Derivative and Fe₃O₄ Nanoparticles Towards Racemic Flurbiprofen Pro-drug

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2-(2-fluoro-4-biphenyl)-propionic acid (flurbiprofen) is a nonsteroidal anti-inflammatory drug when patient is in pain or in tissue injury inflammation, it is necessity to use [1]. However, its enantiomers exhibit different effects, in that case, the enantiomeric resolution of flurbiprofen is required [2].

Lipases are successfully used as catalysts [3] in the hydrolysis of many anti-inflammatory drugs in order to afford optically pure isomer [4]. However, their reusability along with their catalytic as well as enantioselective affinities are quietly low from the aqueous solutions [5]. To dissolve this issue, lipases have been encapsulated in the presence of various additives such as cyclodextrin, Fe₃O₄ nanoparticles, celite, chitosan, amberlite XAD 7, and calixarene etc. via a sol-gel method [6].

Calixarenes synthesized from the condensation reaction of *p*-substituted phenol and formaldehyde have paid a great deal attention in supramolecular chemistry so far [5-7]. Their various derivatives substituted with diverse groups at their both rims “upper and/or lower rims” have caught many occasions [5-7].

In this study, a *p*-nitro aniline-substituted calixarene derivative, bridged with thiourea moieties, was synthesized. Its structure was characterized using FTIR, ¹H-NMR, ¹³C-NMR and elemental analysis techniques. Furthermore, thiourea-bridged calixarene derivative and Fe₃O₄ nanoparticles were employed as additives for the encapsulation of lipase. The encapsulated lipase was then used as a catalyst in the racemic resolution of (*R/S*)-flurbiprofen methyl ester.

Keywords: Calixarene, Enantioselectivity, Fe₃O₄ Nanoparticles, *Candida Rugose* Lipase
Flurbiprofen Pro-Drug

References:

1. Henke E., Schuster S., Yang H., Bornscheuer U.T. *Monatsch Chem* (2000) 131 633–638.
2. Siodmiak T., Mangelings D., Heyden Y.V., Ziegler-Borowska M., Marszall M.P. *Appl Biochem Biotechnol* (2015) 175 2769-2785.
3. Zarei A., Amin N.A.S., Talebian-Kiakalaieh A., Zain N.A.M. *J. Taiwan Inst. Chem. Engrs.* (2014) 45 444-451.
4. Lee E.G., Won H.S., Ro H.S., Ryu Y.W., Chung B.H. *J Mol Catal B: Enzym* (2003) 26 149-156.
5. Sayin S., Akoz E., Yilmaz M. *Org. Biomol. Chem.* (2014) 12 6634-6642.
6. Ozyilmaz E., Sayin S., Arslan M., Yilmaz M. *Colloids and Surfaces B: Biointerfaces* (2014) 113 182–189.
7. Akin S., Gulen M., Sayin S., Azak H., Yildiz H.B., Sonmezoglu S. *Journal of Power Sources* (2016) 307 796-805.

Elemental Analysis of *Chlamydomonas Reinhardtii* Cells exposed to Cd, Ni, and Pb

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Heavy metals are pollutants with increasing impact on the quality of water environments. Excessive concentrations of heavy metals can be detrimental for the biological systems. On the other hand, phytoplankton is the most abundant living species in the water ecosystems and the basis of the food chain. Heavy metals can enter the algae cells, where they induce the synthesis of specific proteins (metallothioneins, phytochelatins, heat shock proteins) which function in several ways to protect the cells from the toxic effects of these pollutants. However, the mechanisms of the protein-metal interactions at the molecular level, as well as the structural implications of these interactions are still unclear (1,2,3).

In this study, three heavy metals, namely cadmium, lead and nickel were added at several sub-lethal concentrations to the nutrient media of the model photosynthetic unicellular alga *Chlamydomonas reinhardtii*. Cells were harvested at the end of the logarithmic phase of their growth, and they were washed with a heavy metal-free buffer before their analysis. The total accumulation of the different heavy metals at the several pollution levels was determined in acid-digested cells by atomic absorption spectroscopy. The amount of the metals which entered the cells through the cell walls was determined by the same technique, after the removal of the cell wall-adsorbed metals by chelation with EDTA. Our data show that the total metal accumulation as well as the percentages of the metals adsorbed on the cell walls and those entered the cells were metal- dependent and concentration- dependent.

Keywords: Heavy Metals; Algae; *Chlamydomonas Reinhardtii*; Pollution Assessment

References:

1. Torres, M.A., Barros, M.P., Campos, S.C.G., Pinto, E., Rajamani, S., Sayre, R.T., Colepicolo, P., , *Ecotoxicol. Environ. Safety* (2008) 71 1-15.
2. Perales-Vela, H.V., Pena-Castro, J.M., Cansares-Villanueva, R.O., *Chemosphere*, (2006) 64 1-10.
3. Jamers, A., Blust, R., De Coen, W., Griffin, J.L., Jones, O.A.H., *Aquatic toxicology*, (2013) 126 355-364.

Simultaneous Detection of Two Different Bacteria Using QDs and MNPs

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The detection of microorganisms has great importance on human life in many fields such as in diagnosis, medicine, pharmacy, food industry etc..[1]. Target bacteria detection is generally done benefiting from plate counting method. However, this is time consuming technique and same procedure should be applied for checking each type of bacteria [2]. In this study, a fast and sensitive sandwich assay has been developed with the combination of immunomagnetic separation (IMS) and fluorescence techniques to enumerate *Escherichia coli* (*E.coli*) and *Salmonella*, simultaneously. Iron oxide core gold shell (Fe₃O₄@Au) magnetic nanoparticles were prepared and modified with biotinylated antibodies specific to *E.coli* and *Salmonella*. Fluorescence labels have been constructed with specific biotinylated antibodies after chitosan coating of CdTe quantum dots (CdTe QDs) and CdTeNi QDs. This novel method is rapid and sensitive for multiplex bacteria detection with a total analysis time less than 60 minutes.

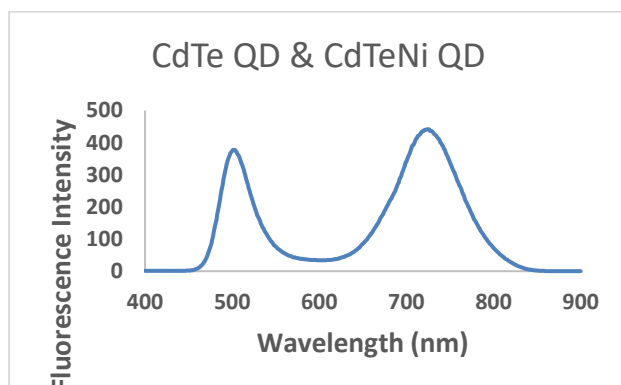


Figure 1. Fluorescence spectrum of CdTe QDs and CdTeNi QDs.

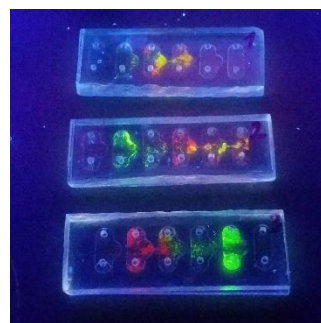


Figure 2. Modified QDs interacted with *E.coli* and *Salmonella*.

Keywords: *Escherichia Coli*, *Salmonella*, Magnetic Separation, Fluorescence Label, Quantum Dot

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References:

1. P. G. Luo and F. J. Stutzenberger, Adv. Appl. Microbiol. (2008) 63 145-181.
2. S. Sandhya, W. Chen and A. Mulchandani, Anal. Chim. Acta (2008) 614 208-212.

Synthesis and Characterization of Ultra-Small Gadolinium Oxide Nanoparticles

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Ultra-small gadolinium oxide nanoparticles (US-Gd₂O₃) have been used as contrast agents for molecular and cellular preclinical magnetic resonance imaging (MRI) procedure, drug targeting, magnetic separation and gene therapy applications. The higher density of magnetic ions per contrast agent unit is the main advantage of using a paramagnetic contrast agent based on oxide nanoparticles. US-Gd₂O₃ nanoparticles generate strong positive contrast enhancement in T₁-weighted MRI. ^[1, 2, 3] There are many techniques that have been introduced to synthesize gadolinium oxide nanoparticles. In this study, we will try to synthesize US-Gd₂O₃ via polyol-like and polyol-free techniques in ultra-small nanosize (<4 nm). Following the synthesis, gadolinium oxide nanoparticles will be characterized utilizing X-ray spectroscopy, scanning electron microscope (SEM), transmission electron microscope (TEM).

Keywords: Magnetic Resonance Imaging MRI, Contrast Agent, Synthesis, Ultra-Small, Gadolinium Oxide, Nanoparticle.

References:

1. Faucher, L., Tremblay, M., Lagueux, J., Fortin, M.-A., 'Rapid synthesis of PEGylated ultrasmall nanoparticles for cell labeling and tracking with MRI', *ACS Appl. Mater. Interfaces*, 2012 4 4506-4515.
2. Park, Y. J., Baek, M. J., Choi, E. S., Woo, S., Kim, J. H., Kim, T. J., Jung, J. C., Chae, K. S., Chang, Y., Lee, G. H., 'Paramagnetic ultrasmall gadolinium oxide nanoparticles as advanced T₁ MRI contrast agent: account for large longitudinal relaxivity, optimal particle diameter, and in vivo T₁ MR images.', *ACS Nano*, 2009 3 3663-3669.
3. Ahrén, M., Selegård, L., Söderlind, F., Linares, M., Kauczor, J., Norman, P., Käll, P.-O., Uvdal K., 'A simple polyol-free synthesis route to Gd₂O₃ nanoparticles for MRI applications: an experimental and theoretical study', *J. Nanopart. Res.*, 2012 14 1006.

***In situ* Formation of Gold Nanostructures on the Graphene-Modified Carbon Surfaces**

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The “nano world” has inspired many applications that make use of the new features and phenomena observed at the nanoscale [1]. Existing and envisioned applications in many areas, including medicine, food, electronics, energy, air pollution, space, and even sports that guides humanity and science have been discovered and have been adapted to our life. From the point of this view, any kind of research based on nanotechnology has a great deal of attention from the scientific community which will present high added value to present situation [2-4].

This research mainly based on the preparation of new surfaces *via in situ* formation of gold nanostructures. Gold nanostructures were synthesized on the graphite rod electrodes decorated with graphene. This synthesis was formed by the reaction between enzyme and substrat that exposes hydrogen peroxide which was effective on H₂AuCl₄. The bare graphite rod and modified surfaces were characterized by scanning electron microscope, atomic force microscope and contact angle measurement. The microscopic characterization results confirmed the formation of gold nanostructures.

The modified surfaces will also be investigated for their applications on the design of glucose sensor.

Keywords: Graphene, Graphit Rod Electrode Modified Electrodes, Gold Nanostructures, *In Situ* Synthesis

Acknowledgement: This work includes the part of MSc Thesis of Orhan Araz managed under Selcuk University, Graduate School of Natural and Applied Sciences.

References

1. M. Loos, Carbon Nanotube Reinforced Composites (2015) Chapter 1 1-36.
2. H. Zhang, Z. Meng, Q. Wang, J. Zheng, Sensors and Actuators B: Chemical (2011) 23-27.
3. S. Sabury, S.H. Kazemi, F. Sharif, Materials Science and Engineering C (2015) 49 297–304.
4. R. Devasenathipathya, V. Mania, S.M. Chena, S.T. Huang, T.T. Huangb, C.M. Lind, K.Y. Hwae, T.Y. Chena, B.J. Chena, Enzyme and Microbial Technology (2015) 78 40–45.

Preparation of Biocompatible Magnetic Nanoparticles for Hyperthermia Treatment

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Cancer is the disease that effect too many people today. Unfortunately, for many case, reason of cancer is still phenomenon and there has not been any efficient therapy for cancer. Now, commonly drug or radiotherapy has been used for cure but their side effect and low effectiveness are serious deficiency for treatments. Nanoscience develops methods to overcome these deficiencies. Hyperthermia treatment is one of them. In this approach, tumor cells goes to apoptosis via heating energy, by helping magnetic nanoparticles [1]. Although functionality of magnetic nanoparticles is suitable for this treatment, the most serious difficulty is their toxic effect. To overcome this problem, magnetic nanoparticles are coated with nontoxic biocompatible materials such as gold, polymer and silica [2]. In this study, different shape magnetic nanoparticles will be synthesized by polyol, thermal decomposition and co-precipitation methods and their surfaces will be coated with chitosan [3], [4], [5], [6]. Characterization studies will be done using Transmission Electron Microscope (TEM), FT-IR Spectrometer, Zeta Potential Measurements Device, Inductive Heating System.

Keywords: Hypertermia, Cancer Treatments, Magnetic Nanoparticles.

References:

- 1.Manuel Bañobre-López, Antonio Teijeiro, Jose Rivas, Reports of Practical Oncology & Radiotherapy, (2013) 8 397–400.
2. Jana Chomouckaa, Jana Drbohlavovaa, Dalibor Huska b, Vojtech Adamb, Rene Kizek b, Jaromir Hubalek, Pharmacological Researc, (2010) 62 144–149.
- 3.Dokyo Kim, Nohyun Lee, Mihyun Park, Byung Hyo Kim, Kwangjin An, and Taeghwan Hyeon, J.Am. Chem. Soc. 2009 131 454–455
- 4.Young Soo Kang, Subhash Risbud, John F. Rabolt, and Pieter Stroeve, Chem. Mater. (1996) 8 2209-2211
- 5.Pierre Hugounenq, Michael Levy, Damien Alloyeau, Lenaïc Lartigue, Emmanuelle Dubois, Valérie Cabuil, Christian Ricolleau, Stéphane Roux, Claire Wilhelm, Florence Gazeau, and Rana Bazzi, J. Phys. Chem. C, (2012) 116 (29), 15702–15712.
- 6.[Marguerite Rinaudo](#), Progress in Polymer Science, (2006) 31 (7) 603–632.

A Green Chemistry Approach for the Synthesis of Gold Nanostructures and Investigations of Their Biological Activities

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Nanotechnology has had a great deal of attention from the scientific community as a result of unique properties compared to their bulk counterparts of nanostructures. Among them, metal nanostructures especially gold and silver have attracted considerable attention in catalysis, optics, sensing and imaging [1]. On the other hand nanostructures exhibit also a common feature that is based on their biological activities [2]. Because of the emergence and increase in the number of multiple antibiotic-resistant microorganisms as bacteria, molds, yeasts, and viruses which are effective on human beings, new effective methods that overcome the resistances of these microorganisms have been developed by many scientists [3]. This work includes the green synthesis of gold nanostructures with different nanoshapes and evaluation of their biological activities such as mutagenicity and antimutagenicity performed by Ames test and antimicrobial activities carried out by broth microdilution method against standard microorganisms which are pathogen for human. Because of having comparison of nanoshapes of gold nanostructure and evaluation of their biological activities, this study is original and different from the other studies performed with nanostructures.

Keywords: Gold Nanostructure, Green Synthesis, Mutagenic Effect, Antimicrobial Activity

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References:

1. M. Loos, Carbon Nanotube Reinforced Composites (2015) 1 1-36
2. A.A. Mostafa, S.R.M. Sayed, E.N. Solkamy, M. Khan, M.R. Shaik, A. Al-Warthan, S.F. Adil, Journal of Nanomaterials (2015) 789178 1-7.
3. R.A.Sperling, P.R. Gil, F. Zhang, M. Zanella, W.J. Parak, Chemical Society Reviews (2008) 37 1896–1908.

Biological Activities of Silver Nanostructures Synthesized *via* Green Chemistry

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In recent years, the development of efficient green chemistry methods for synthesis of metal nanoparticles has become a major focus of researchers and an eco-friendly technique for production of well-characterized nanoparticles has been investigated [1,2]. In this study, as the basic step of this research, a green, simple and low cost synthesis method of silver nanoparticles from walnut was offered. Synthesized silver nanoparticles were characterized by Scanning Electron Microscope and the formation of nanostructures was confirmed by UV-Vis spectroscopy. Biological activities of silver nanoparticles such as mutagenicity and antimutagenicity performed by Ames test and antimicrobial activities carried out by broth microdilution method against standard microorganisms were evaluated. Nanoparticles are important in the point of being antimicrobial agents against drug resistant pathogenic microorganisms. Thus, the development of a reliable green approach for the synthesis of nanoparticles is an important aspect of current nanotechnology research. The results of the study clearly indicate the promising biomedical applications of synthesized silver nanoparticles.

Keywords: Silver Nanostructure, Green Synthesis, Mutagenic Effect, Antimicrobial Activity

Acknowledgement: This study is the part of MSc Thesis of Meric Dogan managed under Selcuk University, Graduate School of Natural and Applied Sciences.

References:

1. S. Iravani, Green Chemistry (2011) 13 2638-2650.
2. N. Alam, N. Roy, D. Mandal, N.A. Begum, **RSC Advances** (2013) **3** 11935-11956.

A Novel Approach to Characterization and Analysis of Cationic Textile Dyes

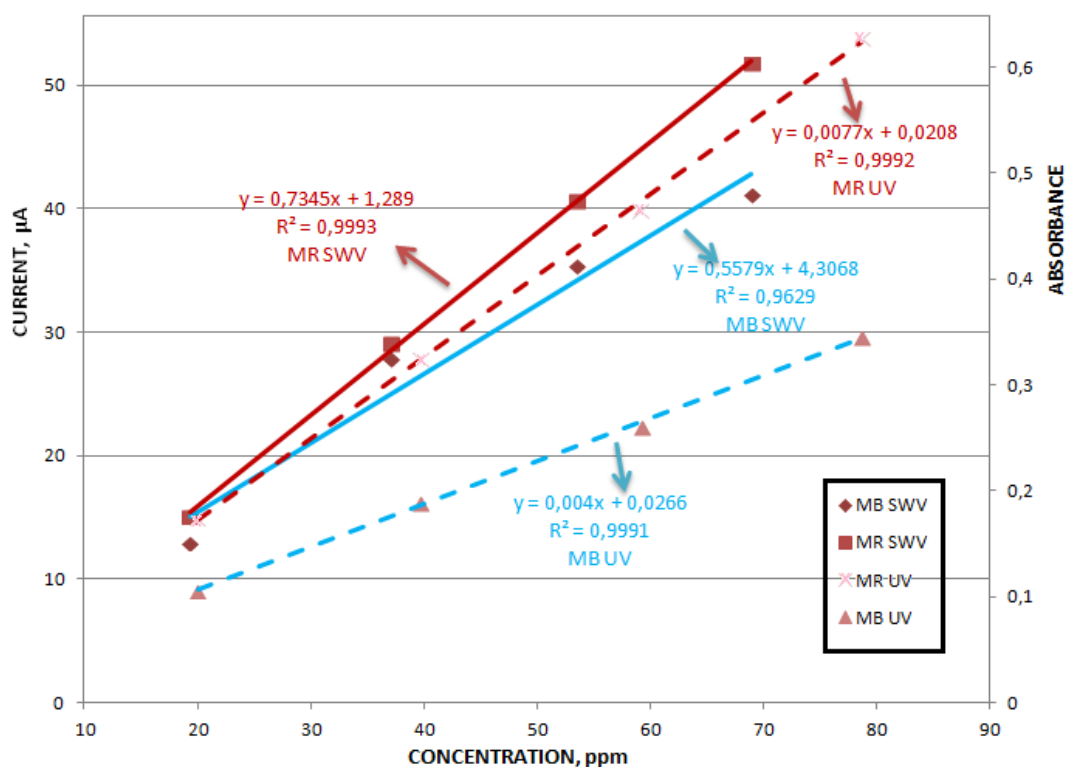
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Cationic dyes are basic nature and widely using in textile industry especially for the anionic modified polyester type of textiles due to higher water solubility. Spectroscopic investigations performed for the analysis and characterization are not specific enough. Because of some cardinal features like as adsorption, fastness, durability and coloration are often based on electron transfer mechanism, voltammetry is an important option to characterize and for specific analysis of these materials.

In our study, randomly selected from commonly used cationic dyes from Maxilon series; red (Basic Red 46), Blue and Yellow (Basic Yellow 28) of paint were investigated. The spectroscopic and voltammetric behaviors of these dyes were evaluated comparatively with using uv-vis spectrophotometry, cyclic voltammetry and square wave voltammetry techniques. In particular, the pH effect was studied and also compared to the calibration graph for making quantitative analysis.



Calibration curves of Maxilon Red and Blue obtained with Uv-Vis and SWV at pH 8

Keywords: Electrochemical Characterization, Redox Behaviour, Cationic Dye, c,d Polyester

References:

1. A.G.Fogg, 'Stripping voltammetry in environmental studies of dyes and thiols', Port. Electrochim. Acta, (1998) 16 5-10.
2. J Zima, J Barek, J C Moreira, V Mejstik and A G Fogg, Polarographic and voltammetric determination of environmentally important dyes, *Crit. Rev. in Analyt. Chem.*,

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Electrochemical Characterization of Cotton Reactive Dyes

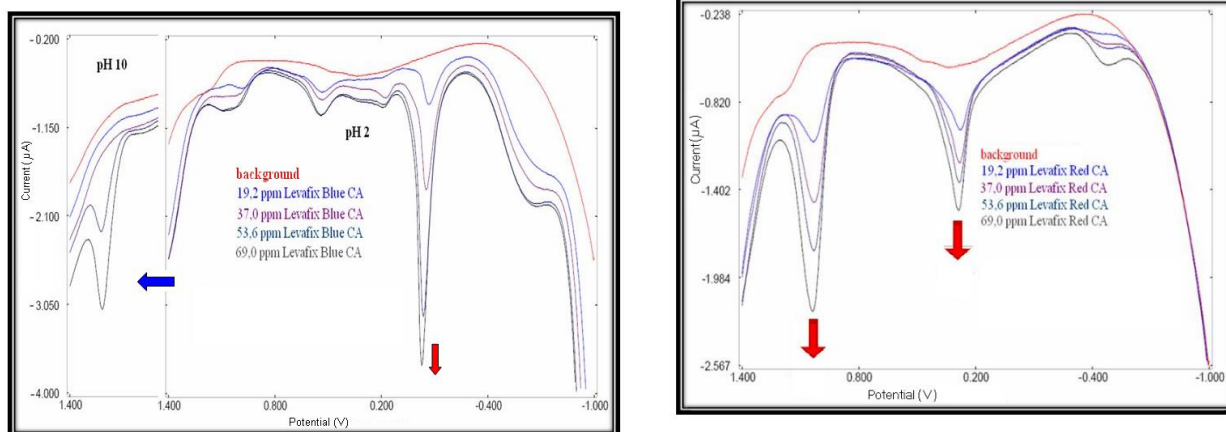
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Many of dyes and auxiliaries used in the textile industry for the same purpose are marketed with different trade names. Qualitative and quantitative characterization of these substances became important because of their unknown content and action mechanisms. Equivalence and characterization testing must be faster, reliably and effortless. Solely spectroscopic investigations remains mostly inadequate for this purpose. Voltammetric experiments which can be characterized to electron exchange of substances using with classical functional and colorimetric assays have a good potential to provide reliable information for comparison and applications of new prescriptions preparing.

For characterization of three cotton reactive dyes, their voltammetric behavior investigated and matched with spectroscopic properties. To determination of oxidation and reduction characteristic and optical specifications of arbitrary choosed amber, blue and yellow dyes in Levafix series studied with square wave voltammetry, cyclic voltammetry and uv-vis spectrophotometry in different pHs and concentrations.



Oxidation peaks of blue cotton dye (left) and red cotton dye (right) obtained with square wave voltammetry.

Keywords: Electrochemical Characterization, Textile Dye Stuff, Redox Behaviour

References:

1. J Barek, A G Fogg, A Muck, J Zima, Polarography and voltammetry at mercury eltrodes. Critical Reviews in Analytical Chemistry, (2001) 31 291-309.
2. C CI Guaratini, A G Fogg, M V B Zanoni, Studies of the voltammetric behaviour and determination of diazo reactive dyes at mercury electrode. Electroanalysis, (2001) 13 1535-1543.

Development of Poly(Pyrrole-3-Carboxylic Acid) Modified Pencil Graphite Electrode for the Voltammetric Determination of Dopamine

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Dopamine (DA), one of the most important catecholamine, plays a significant role in the functioning of the central nervous, renal hormonal and cardiovascular systems [1]. Trace level measurement of DA has been a long-standing goal since the concentration change has been related with various diseases and disorders, such as Parkinson's disease, Alzheimer's disease, HIV infection and Huntington's disease [2-3]. Therefore, several studies have been performed for the determination of DA in biological fluids using different analytical techniques such as high performance liquid chromatography, gas chromatography-mass spectrometry and electrophoresis. Electrochemical methods were also intensively searched for the determination of DA because of its electro-activity [4-5]. Electrochemical methods are most promising ones because of their advantages such as low detection limits and high selectivity according to conventional chromatographic and spectroscopic methods [6-7]. On the other hand, electrochemical methods suffer from the overlapped voltammetric responses, poor selectivity and low reproducibility of the used conventional electrodes. The modification of these electrodes with different substances is a very effective way to overcome these problems.

In this study, the preparation of a modified pencil graphite electrode for the selective determination of DA in human blood serum and pharmaceutical samples have been performed. The modified electrode has been prepared by electropolymerization of pyrrole-3-carboxylic acid on electrochemically treated PGE. It was observed that the prepared modified electrode showed high affinity and selectivity towards DA. The characterizations of the prepared modified electrode were performed by scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. SEM analysis revealed that the prepared poly(pyrrole-3-carboxylic acid) showed cauliflower structure. It was observed that the prepared modified electrode can selectively discriminate the voltammetric response of DA from that of common electroactive interferences. Finally, the analytical application of the prepared modified electrode was tested in real samples (human blood serum and pharmaceuticals).

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Keywords: Dopamine, Pencil Graphite, Poly(Pyrrole-3-Carboxylic Acid), Voltammetry

References:

1. E.R. Kandel, J.H. Schwartz, T.M. Jessell, (2000) Principles of Neural Science, McGraw-hill, New York.
2. P. Damier, E.C. Hirsch, Y. Agid, A.M. Graybiel, Brain, (1999) 122 1437-1448.
3. D. Merims, N. Giladi, Parkinsonism and Related Disorders, (2008) 14 273-280.
4. H.S. Han, H.K. Lee, J.M. You, H. Jeong, S. Jeon, Sens. and Actuat. B: Chem. (2014) 190 886-895.
5. B. Rezaei, M.K. Boroujeni, A.A. Ensafi, Biosens. and Bioelectron. (2015) 66 490-496.
6. X. Weng, Q. Cao, L. Liang, J. Chen, C. You, Y. Ruan, H. Lin, L. Wu, Talanta (2013) 117 359-365.
7. A. Özcan, S. İlkbaş, Anal. Chim. Acta, (2015) 891 312-320.

Novel Electrochemical Sensor Based on Sepiolite Clay Modified Carbon Paste Electrode for Ascorbic Acid Detection

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Ascorbic acid and its sodium, potassium, and calcium salts are commonly used as antioxidant food additives. These compounds are water-soluble and, thus, cannot protect fats from oxidation: For this purpose, the fat-soluble esters of ascorbic acid with long-chain fatty acids (ascorbyl palmitate or ascorbyl stearate) can be used as food antioxidants. Eighty percent of the world's supply of ascorbic acid is produced in China [1]. By virtue of its biological importance, it is vital to develop a sensitive and selective method for quick and reliable determination of AA in various samples like drug, beverage and biological matrices. To meet this need, we have focused on to develop voltammetric method by using novel clay modified carbon paste sensor (SC/CPE). Therefore, differential puls adsorptive stripping voltammetry (AdsDPV) technique was developed for determination of AA on proposed sensor.

Electrochemical stripping methods have some advantages of being relatively less expensive, highly sensitive and they provide low limit of detection (LOD). Therefore, electrochemical stripping methods are becoming more popular as alternative methods in pharmaceutical formulations and biological samples [2-3]. Electrochemical oxidation behavior of AA was examined by using cyclic voltammetry on SC/CPE and other experimental parameters such as pH, composition of sepiolite clay, deposition time and deposition potential were optimized. Under optimized conditions the calibration graph was established and linear working range was identified with in the range of 0.014-0.9 μM and also limit of detection (LOD) and limit of quantification (LOQ) values were calculated as 0.0042 μM and 0.014 μM , respectively. These results are comparable with literature data's. The method was applied successfully to different real samples. The recovery results are very close to 100%.

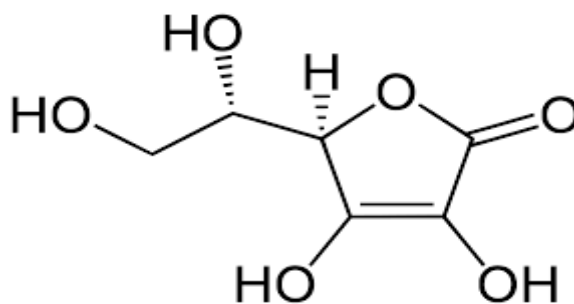


Fig1. Molecular structure of ascorbic acid

Keywords: Ascorbic acid, rosehip, sepiolite clay, carbon paste electrode, voltammetry

References:

1. W. Rick Washington Post, retrieved (2010) 4-25.
2. Farghaly O.A.M. J.Pharm.Biomed.Anal. (2000) 23 783–791.
3. Sagar KA., Smyth M. R., Munden R. J. Pharm. Biomed. Anal. (1993) 11 533–540.

A New Sepiolite Clay/TiO₂/Multiwall Carbon Nanotube Modified Carbon Paste Sensor for the Adsorptive Stripping Square Wave Voltammetric Analysis of Vanillin in Local Food Samples

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Vanilin (4-hydroxy-3-methoxybenzaldehyde) is a phenolic aldehyde. It is produced from three different plant species belonging to the genus *Vanilla*. Vanillin is used in foods, beverages, pharmaceuticals, perfumes and also in the production of derivative chemicals [1]. Vanilin contents of processed food is an important issue because, excess amount of vanillin is known to induce headaches, qualm, retching and adverse effects on liver and kidney functions [2].

Electrochemical techniques for vanillin assay are established and have proven to be cost effective, fast and highly sensitive. Non-destructive nature and extremely low sample consumption is another facet of the techniques making them preferable [3]. Here, we focus on a novel voltammetric sensor, combining sepiolite clay, TiO₂, multiwall carbon nanotube and carbon paste in various proportions and use it for the electrochemical oxidation of vanillin. The anodic signal obtained by adsorptive stripping square wave voltammetry was used as the basis of a sensitive and reliable electroanalytical method for the determination of the compound. The voltammetric method developed was applied to vanillin assay in real samples. The working range, sensitivity, stability, and selectivity against some possible interference were investigated.

A composite electrode comprising sepiolite clay/TiO₂/multiwall carbon nanotube and carbon paste (SC/TiO₂/MWCNT/CPE) was developed and used for the voltammetric quantitative analysis of vanillin (VAN) in processed food. Adsorptive stripping square wave voltammetric (AdsSWV) method was employed. The effects of pH, ratios of electrode ingredients, accumulation potential and accumulation time were investigated. The optimum pH, accumulation potential and accumulation time are 7.0, 0.0 V and 60 s, respectively. The electrode exhibited a linear working range of $3.0 \times 10^{-7} - 9.0 \times 10^{-5}$ mol L⁻¹ and a detection limit of 2.26×10^{-8} mol L⁻¹ for VAN. The sensitivity and selectivity in the presence of glucose, ascorbic acid, citric acid, Na⁺, Ca²⁺, Mg²⁺, Al³⁺, K⁺, Fe²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cl⁻, and NO₃⁻ were found to be satisfactory. The electrode system developed has a lifetime not shorter than 2 months and proved to be practical for the analysis of real samples. The percent repeatability and reproducibility of voltammetric currents are 2.55% and 2.94% respectively at a VAN concentration of 1.0×10^{-5} mol L⁻¹.

Keywords: Vanillin, AdsSWV, Sepiolite Clay, TiO₂, Multiwall Carbon Nanotube

References:

1. P. Barghini, D. Di Gioia, F. Fava and M. Ruzzi, *Microbial Cell Factories*, (2007) 6:13 1-11.
2. L.M. Han, Q.R. Shen, H.Y. Ju, S. Yan and F. Yan, *Acta Ecol. Sin.* (2002) 22:9 1425-14323.
3. S. Erden, Z. Durmus, E. Kılıç, *Electroanal.*, (2011) 23 1967–1974.

Preparation of Graphene-Carbon Nanotube Modified Glassy Carbon Electrode for the Determination of Levofloxacin

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Levofloxacin (LEV) is a third generation broad spectrum synthetic antibiotic which can be used with oral and intravenous ways. It is very effective against gram-positive and gram-negative aerobic bacteria [1]. It has been widely used in human and animals. While LEV is generally tolerated, in some instances it may cause serious side effects like tendon ruptures, heart problems and Stevens-Johnson syndrome [2]. Therefore, the determination of LEV in body fluids and pharmaceutical formulations is very important. Although there are many available methods for the determination of LEV, electrochemical methods can be seen very promising alternatives due to their fast, simple, inexpensive, sensitive and selective characteristics [3-4]. On the other hand, conventional electrodes limits the application of electrochemical methods in analytical chemistry because of their common drawbacks such as high overpotential and low surface area. Different substances were investigated to modify the conventional electrodes. In this frame, graphene and carbon nanotubes are the most widely investigated materials to increase the performance of the electrochemical methods because of their unique properties such as strong electrocatalytic activity, high effective surface area and excellent electrical conductivity [5-6].

In this study, the modification of glassy carbon electrode with graphene and acid treated carbon nanotubes has been investigated for the voltammetric determination of LEV in body fluids and pharmaceutical products. The prepared modified electrode showed electrocatalytic activity towards LEV oxidation. The electrode preparation conditions and parameters related with measurement solution were optimized to increase the efficiency of the modified electrode. The prepared electrode successfully discriminate the voltammetric response of LEV from that of other fluoroquinolone antibiotics (enoxacin, norfloxacin, ciprofloxacin). Finally, the performance of the prepared electrode was tested in the determination of LEV in human blood serum and pharmaceutical samples.

Keywords: Modified Electrode, Carbon Nanotube, Graphene, Levofloxacin, Voltammetry

References:

1. A.P.D. Silva, A.S. Luna, T.M.D.S. Costa, R.Q. Aucelio, J.W.B. Braga, R. Boqué, J. Ferré, *Int. J. Life Sci. & Pharma Res.* (2012) 2 147-158.
2. L. Tang, Y. Tong, R. Zheng, W. Liu, Y. Gu, C. Li, R. Chen, Z. Zhang, *Sens. and Act. B: Chem.* (2014) 203 95-101.
3. A. Özcan, S. İlkbaşı, *Anal. Chim. Acta*, (2015) 891 312-320.
4. A. Özcan, S. İlkbaşı, *Sens. and Act. B: Chem.* (2015) 215 518-524.
5. W. Wen, D.M. Zhao, X.H. Zhang, H.Y. Xiong, S.F. Wang, W. Chen, Y.D. Zhao, *Sens. Actuat. B: Chem.* (2012) 174 202-209.
6. Y.H. Chen, R. Kirankumar, C.L. Kao, P.Y. Chen, *Electrochim. Acta* (2016) 205 124-131.

Differential Pulse Voltammetric Determination of Calcium Dobesilate Using a Pencil Graphite Electrode

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Calcium dobesilate (CD), calcium 2,5-dihydroxy-benzenesulfonate, is a drug with previously demonstrated efficacy in the treatment of diabetic retinopathy and chronic venous insufficiency. These beneficial effects of the drug are related to its ability to decrease capillary permeability, platelet aggregation and blood viscosity and to increase lymphatic transport [1]. Because of the important features of the CD, it is very important to develop rapid, simple, low-cost and practical method of quantitative determination of CD in physiological fluid and pharmaceutical capsule. Among them electroanalytical methods have found great attention for sensitive and selective determination of CD [2-4].

In this study, electrochemical behavior of calcium dobesilate (CD) was investigated by recording its cyclic and differential pulse voltammograms at a disposable and very cheap electrode, pencil graphite electrode (PGE). Cyclic voltammograms recorded in 0.1 M HCl showed that a pair of well-defined redox peaks was observed at the PGE indicating excellent electrochemical activity of CD on the PGE. Oxidation peak current of CD was examined for the determination of CD by recording its differential pulse voltammograms under experimental conditions. The anodic peak current increased linearly with concentration of CD in the range of 1.0×10^{-7} to 1.0×10^{-4} mol L⁻¹ with a detection limit 5.0×10^{-8} mol L⁻¹ (based on 3S_b). Relative standard deviation of 3.0 % was obtained for five successive determinations of 10.0 µM CD, which indicate acceptable repeatability. This voltammetric method was successfully applied to the direct determination of CD in real pharmaceutical samples. The effect of various interfering compounds on the CD peak current was studied. Unmodified PGE provides a new promising and alternative way to sensitive, cheap and selective determination of CD.

Keywords: Calcium Dobesilate, Voltammetry, Pencil Graphite Electrode, Pharmaceutical Analysis.

References:

1. H.D. Patel, A.N. Bhedi, A.P. Chauhan, R.M. Joshi, Nat. J. Med. Res.(2013) 3 42-44
2. G. Hu, Y. Ma, Y. Guo, S. Shao, Talanta (2009) 633 264-267.
3. S. Wang, Q. Xu, X. Zhang, G. Liu, Electrochem. Commun. (2008) 10 411-415.
4. J. Zhenh, Y. Zhang, P. Yang, Talanta (2007) 73 920-925.

Electrochemical Determination of Rosuvastatin

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Rosuvastatin, (ROS, bis((E)-7-(4-(4-fluorophenyl)-6-isopropyl-2-(methyl(methylsulfonyl) amino) pyrimidin-5yl) (3R,5S) -3,5-dihydroxyhept-6-enoic acid) calcium salt), is a cholesterol lowering active pharmaceutical ingredient of statin group. Statins are the most effective cholesterol lowering drug group. By blocking the production of HMG - CoA enzyme used to make the body's cholesterol, statins reduce the synthesis of cholesterol in the liver. Rosuvastatin is one of the most effective drugs in the statin group of drugs. Rosuvastatin lowers total cholesterol, LDL, triglycerides and apolipoprotein B, while raising HDL. Rosuvastatin in the prevention of atherosclerosis, hypercholesterolemia, hyperproteinemia, hypertriglyceridemia and uses of myocardial infarction prophylaxis and stroke prophylaxis. By voltammetry, information obtained from the electrochemical sensor provide opportunity the most appropriate structure for the availability of newly synthesized drug substances and for the predetermination of functional groups and understanding of the in vivo behavior.

In this study, the electrochemical behavior of Rosuvastatin was investigated with in a wide pH range (pH 0,3-7,0) using differential pulse voltammetric technique at glassy carbon electrode. With differential pulse voltammetric techniques, maximum current was observed in the pH 0.3 sulfuric acid medium. As a result of scan rate studies, in the pH 0.3 sulfuric acid medium, the reaction was found diffusion-controlled mechanism. Linear relation range specified in the range of 0,005-0,1 mM and limit of detection calculated as 1,33 nM. In optimized conditions, Rosuvastatin determination was achieved Rosuvastatin containing pharmaceuticals named Rosucor[®] and React[®]. Using proposed method, 10 mg Rosuvastatin was found Rosucor[®] and React[®] as 10,06 mg and 10,02 mg, respectively. By adding pure substance on pharmaceuticals, recovery studies were performed and it was recovered as %100,85 and %100,40 respectively.

Keywords: Rosuvastatin, Electrochemistry, Voltammetry

References:

1. R. Zhang, Y. Li, X. Jiang, L. Wang, Pharmacokinetics and tolerability of multiple-dose rosuvastatin: An open-label, randomized-sequence, three-way crossover trial in healthy Chinese volunteers, *Curr. Ther. Res.* (2009) 70 392–404.
2. S.A., Ozkan, *Electroanalytical Methods in Pharmaceutical Analysis and Their Validation*. HNB Publishing, New York (2012).

Investigation of Electrochemical Behavior of Cefuroxime Axetil Using Hanging Mercury Drop Electrode

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Cefuroxime Axetil (CEFA) is a second-generation cephalosporin and an oral prodrug formulation of the injectable antibiotic cefuroxime (CEF). CEFA is the 1-acetoxyethyl ester of CEF. The electrochemical reduction behaviours of CEFA was investigated by square wave voltammetry in different supporting electrolytes at hanging mercury drop electrode (HMDE). While three peaks (I, II, III) were observed in acidic media (pH 2-5), the highest peak (II), which was a single well-defined peak, was observed at pH 7 phosphate borate (PB) buffer (Fig. 1). Current type, reversibility of electrode reaction and the number of electrons transferred were investigated.

Aleksić et al. investigated the reduction mechanism of the methoxyimino group in the structure of CEFA inside acidic media [1]. There is no literature available about the electro reduction of CEFA in neutral or alkaline media, and there is also no proposed reduction mechanism for C=O group in the structure of axetil. Therefore, the aim of this work was to investigate the electrochemical behaviors of CEFA in neutral media at HMDE, and to propose the mechanism of reduction, by using square wave voltammetry (SWV), cyclic voltammetry (CV), chronoamperometry (CA) and chronocoulometry (CC) methods. Diffusion coefficient (D) and rate constant of electron transfer (kf) were calculated. This is the first study for CEFA about the electroreduction of axetil carbonyl group in neutral media.

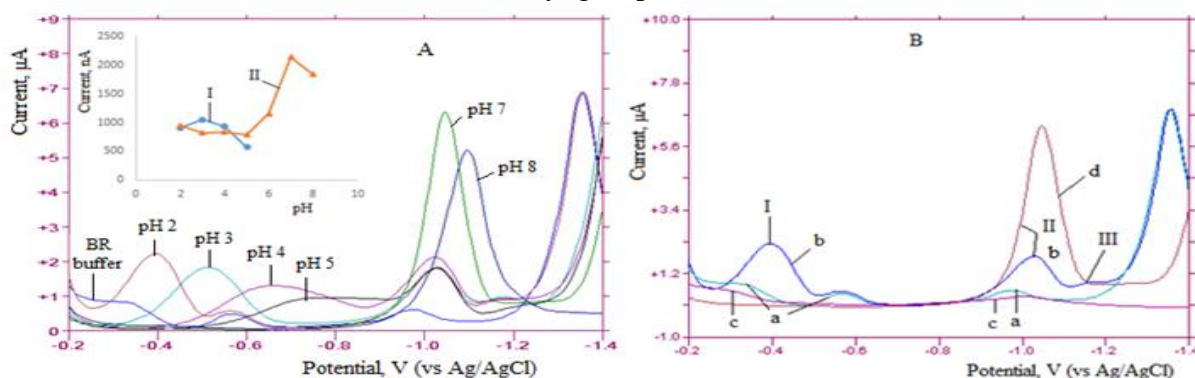


Fig. 1. SWV voltammograms of CEFA using HMDE

A) 8.0 mg L⁻¹ CEFA at different pH in the 0.1 M PB buffer. Inset: The effect of pH on the currents of peak I and peak II for 5.0 mg L⁻¹ CEFA in 0.1 M PB buffer using HMDE

B) a) pH 2 supporting electrolyte b) 8.0 mg L⁻¹ CEFA at pH 2 c) pH 7 supporting electrolyte d) 8.0 mg L⁻¹ CEFA at pH 7

Keywords: Cefuroxime Axetil, Electrochemical Behavior, Voltammetric Methods.

References:

1. K. Nikolić, M.M. Aleksić, V. Kapetanović, D. Agbaba, Journal of the Serbian Chemical Society (2015) 1035-1049.

Validated Square-Wave Voltammetric Determination of Pramipexole in Pharmaceutical Preparations

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Pramipexole (PR), (*S*)-4,5,6,7-tetrahydro-*N*⁶-propyl-2,6-benzothiazolodiamine is a dopaminergic agonist used for the treatment of Parkinson's disease. Few analytical methods have been reported for the determination of PR. Most methods are based on complex, expensive and time consuming steps which include analysis of biological fluids using LC-MS [1], electrophoresis with laser induced fluorescence detection [2] method, spectrophotometric methods and electroanalytical methods related to oxidation [3] for the estimation of PR in pharmaceutical formulations. There is no literature available about the electro reduction of PR. The aim of the present study is to develop and validate simple, sensitive, accurate, precise and reproducible square-wave voltammetry (SWV) method for determination of PR in pharmaceutical dosage forms and to investigate the reduction behavior of PR on hanging mercury drop electrode (HMDE). The experimental and instrumental parameters affecting the peak current were investigated and optimized for the PR determination. Current type and reversibility of the electrode reaction were investigated by using cyclic voltammetry. The relationship between reduction peak current and concentration of pramipexole was investigated by using SWV. A well-defined cathodic peak was observed at -310 mV versus Ag/AgCl reference electrode in phosphate buffer (pH 9.0) (Fig. 1). For SWV method LOD, LOQ and linearity range were found 0.66 $\mu\text{g mL}^{-1}$, 1.32 $\mu\text{g mL}^{-1}$ and 1.32-18.70 $\mu\text{g mL}^{-1}$, respectively. Validation parameters, such as sensitivity, accuracy, precision, ruggedness, robustness and recovery were evaluated. Developed and validated method was employed for quantification of PR in different pharmaceutical formulations.

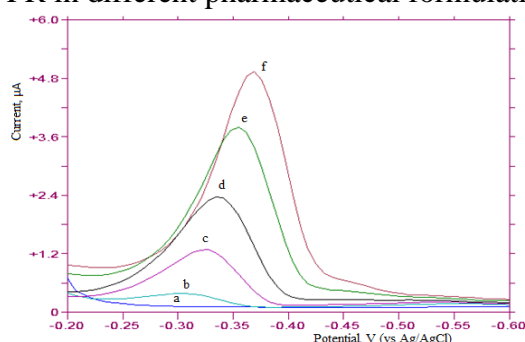


Fig. 1. Square wave voltammograms of PR using HMDE a) pH 9 supporting electrolyte b) 1.32 c) 4.46 d) 8.81 e) 14.04 f) 17.58 $\mu\text{g mL}^{-1}$ PR

Keywords: Pramipexole, Voltammetric Methods, Electrochemical Behaviour, Pharmaceutical Preparations

References:

1. D. V. Bharathi, K. K. Hotha, P. V. Sagar, S. S. Kumar, A. Naidu, and R. Mullangi, Biomed. Chromatogr., (2009) 23 212.
2. A. Musenga, E. Kenndler, E. Morganti, F. Rasi, and M. A. Raggi, Analytica Chimica Acta, (2008) 626 89.
3. R. Jain, R. Sharma, R.K. Yadav, R. Shrivastava, Journal of The Electrochemical Society (2013) 160 (3) H179-H184.

Quantitative Determination of Moxifloxacin Hydrochloride in Drug Dosage Forms by Voltammetric Techniques Using Glassy Carbon and Modified Glassy Carbon Electrodes

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Moxifloxacin hydrochloride (1-cyclopropyl-7-[(S,S)-2,8-diazabicyclo[4.3.0]non-8-yl]-6-fluoro-8-methoxy-1,4-dihydro-4-oxo-3-quinoline carboxylic acid HCl) is drug active material which uses in the treatment of upper respiratory infections (Figure 1) [1,2]. A potentiostat meter (VersaSTAT³, Princeton Applied Research, USA) was used for the voltammetric measurements. A poly (4-aminobenzene sulfonic acid) (4-ABSA) modified glassy carbon electrode (GCE) was prepared for the quantitative determination of moxifloxacin hydrochloride. The 4-ABSA-modified GCE was prepared by electrochemical polymerization method in phosphate buffer solution (PBS) (pH 7.00) The polymer film-modified electrode has high catalytic ability for electrooxidation of moxifloxacin hydrochloride in acetate, phosphate and Britton-Robinson (BR) buffer solutions by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CA) techniques. The best results for the determination of moxifloxacin hydrochloride were obtained in acetate buffer (pH 5.00) by DPV method. Calibration curve was obtained from the various concentration of moxifloxacin hydrochloride by DPV technique. Limit of detection (LOD) and quantification (LOQ) were calculated from equation of calibration curve. The results of experiments indicated that modified electrode have good stability, sensitivity and reproducibility for at least one month if stored dry in air.

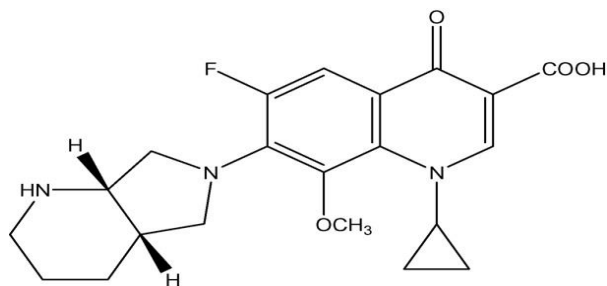


Figure 1. Chemical formule of moxifloxacin hydrochloride

Keywords: Moxifloxacin Hydrochloride, Determination, Differential Pulse Voltammetry, Cyclic Voltammetry, Chronoamperometry, 4-ABSA-Modified Glassy Carbon Electrode

References:

1. A. Laban-Djurdjevic, M. Jelikic-Stankov, P. Djurdjevic, Journal of Chromatography B. (2006) 844 104–111.
2. N. Erk, Anal. Bioanal. Chem., (2004) 378 1351-1356.

Quantitative Determination of Tenoxicam in Drug Dosage Forms by Voltammetric Techniques Using Glassy Carbon and Modified Glassy Carbon Electrodes

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Tenoxicam (4-hydroxy-2-methyl-N-(2-pyridinyl)-2-thieno [2,3-e] -1,2-thiazine-3-carboxamide 1,1-dioxide) is drug active material which uses in the treatment of rheumatic diseases (Figure 1) [1,2]. A potentiostat meter (VersaSTAT³, Princeton Applied Research, USA) was used for the voltammetric measurements. A poly (4-aminobenzene sulfonic acid) (4-ABSA) modified glassy carbon electrode (GCE) was prepared for the quantitative determination of tenoxicam. The 4-ABSA-modified GCE was prepared by electrochemical polymerization method in phosphate buffer solution (PBS) (pH 7.00) The polymer film-modified electrode has high catalytic ability for electroreduction of tenoxicam in acetate, phosphate and Britton-Robinson (BR) buffer solutions by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CA) techniques. The best results for the determination of tenoxicam were obtained in acetate buffer (pH 5.00) by DPV method. Calibration curve was obtained from the various concentration of tenoxicam by DPV technique. Limit of detection (LOD) and quantification (LOQ) were calculated from equation of calibration curve. The results of experiments indicated that modified electrode have good stability, sensitivity and reproducibility for at least one month if stored dry in air.

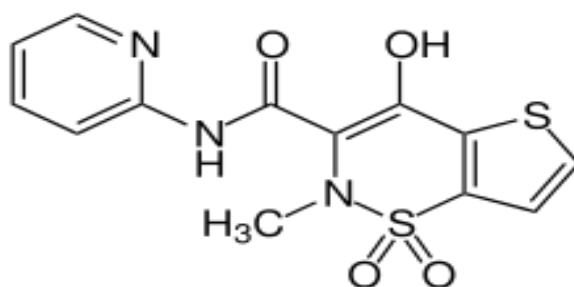


Figure 1. Chemical formule of tenoxicam

Keywords: Tenoxicam, Determination, Differential Pulse Voltammetry, Cyclic Voltammetry , Chronoamperometry, 4-ABSA-Modified Glassy Carbon Electrode

References:

1. K.M. Strub, L. Aeppli, A. Daum, Adv. Inflam. (1986) 10 387
2. S. B. Göksan, A. Atalar, L. Eralp, Acta. Ortop. Traumatol. Turc. (1997) 31, 262-264.

Determination of Nitroaromatic Type Energetic Materials with GC/P(*o*-PDA-co-ANI)-Au_{nano} Electrode

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The detection of explosives and explosive-related compounds has become a priority in recent years for homeland security and counter-terrorism applications. There are many studies on the detection of explosives utilizing a multitude of different analytical techniques. The highly sophisticated current techniques for detecting/quantifying trace explosives include ion mobility spectrometry (IMS) and gas-liquid chromatography (GLC) coupled to mass spectrometry (MS); however, most of these devices are bulky, expensive, and require qualified personnel and time-consuming procedures. In this regard, voltammetric techniques constitute cheaper and portable alternatives if sufficient selectivity is attained with the aid of rapidly growing sensor electrodes [1]. Electrochemical sensors offer good prospects for meeting the growing needs of explosives field detection. The most characteristic redox property of nitro-based explosives, namely the presence of easily reducible nitro-groups, ideally lends itself to electrochemical detection [2]. In this work, a novel electrochemical sensor was developed for the detection of nitroaromatic explosive materials, based on a gold nanoparticle-modified glassy carbon(GC) electrode coated with poly(*o*-phenylenediamine-aniline film) (GC/P(*o*-PDA-co-ANI)-Au_{nano} electrode). Selective determination of nitroaromatic type explosives in the presence of nitramines was enabled by *o*-PDA and reusability of the electrode achieved by AuNPs. Calibration curves of current intensity *versus* concentration were linear in the range of 2.5–40 mg L⁻¹ for 2,4,6-trinitrotoluene (TNT) with a detection limit (LOD) of 2.1 mg L⁻¹, 2–40 mg L⁻¹ for 2,4-dinitrotoluene (DNT) (LOD=1.28 mg L⁻¹), 5–100 mg L⁻¹ for tetryl (LOD=3.8 mg L⁻¹) with the use of the GC/P(*o*-PDA-co-ANI)-Au_{nano} electrode. For sensor measurements, coefficients of variation of intra-and inter-assay measurements were 0.6 % and 1.2 %, respectively (N=5), confirming the high reproducibility of the proposed assay. Determination options for all possible mixture combinations of nitroaromatic explosives are presented in this work. The proposed methods were successfully applied to the analysis of nitroaromatics in military explosives, namely comp B, octol, and tetrytol. Method validation was performed against GC-MS on real post-blast residual samples containing both explosives [3].

Keywords: Cyclic Voltammetry, Nitro-Aromatic Explosives, Gold Nanoparticles, Poly(*o*-Phenylenediamine-Aniline), Modified Electrode.

Acknowledgements:

The authors extend their thanks to Istanbul University Research Fund for the support given to Standard Research Project-14412. Additionally, the authors thank TUBITAK (Turkish Scientific and Technical Research Council) for their support to the Research Project 112T792.

References:

1. L. Senesac, T.G. Thundat, Mater.Today (2008) 11 28–36.
2. J.S. Caygill, F.Davis, S.P.J.Higson, Talanta (2012) 88 14–29.
3. Ş. Sağlam, A. Uzer, Y. Tekdemir, E. Ercag, R.Apak, Talanta (2015) 139 181-188.

Voltammetric Determination of Quercetin with GC/P(*o*-PDA-co-ANI)-Au_{nano} Electrode

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Quercetin belongs to the flavonoid family that is widely distributed in fruits and vegetables. It is reported that quercetin has antiviral, anti-cancer, anti-inflammatory, anti-allergic and antitumor activity, and can protect human colonocyte DNA from oxidative attack in vitro. Hence, it is significant to determine and study it. Until now, many means have been developed for it, such as spectrophotometry, high performance liquid chromatography with UV absorption detector or chemiluminescence detection, and electrophoresis with a diode array detector. The coupling of these techniques may provide high selectivity for the assay, but brings also some disadvantages of operating complexity, time and reagent consumption, high cost, etc [1]. Most flavonoids are electrochemically active at modest oxidation potentials, so electrochemical methods are preferable with advantages of higher sensitivity and less interferences from non-electroactive substances [2].

In this work, an electrochemical sensor (which was previously developed by our research group [3]) was used for the determination of quercetin, based on a gold nanoparticle-modified glassy carbon (GC) electrode coated with poly(*o*-phenylenediamine-aniline film) (GC/P(*o*-PDA-co-ANI)-Au_{nano} electrode). The working principle of the proposed sensor was the electron uptake of ferricyanide ion from an antioxidant to convert into ferrocyanide ($\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-}$) followed by indirect determination of antioxidants *via* ferricyanide consumption, as the decrease of cathodic current due to ferricyanide was proportional to the concentration of antioxidants in the sample. During voltammetric determinations, the surface of the GCE was coated with a copolymer of *o*-phenylenediamine & aniline, and Au-NPs were accumulated on this modified electrode surface so as to increase conductivity. Determination of quercetin was achieved electrochemically by using GC/P(*o*-PDA-co-ANI)-Au_{nano} electrode. Calibration curves of current intensity (*I*) *versus* molar concentration (*c*) were linear in the range of 2×10^{-5} M – 2×10^{-4} M for quercetin and the linear equation was $I = 3.57 \times 10^4 c + 8.94 \times 10^{-1}$ ($r=0.992$).

Keywords: Voltammetry, Quercetin, Gold Nanoparticles, Poly(*o*-phenylenediamine-aniline), Modified Electrode.

Acknowledgement

The authors wish to express their gratitude to Istanbul University – Application and Research Center for the Measurement of Food Antioxidants (Istanbul Universitesi Gıda Antioksidanları Olcumu Uygulama ve Araştırma Merkezi).

References:

1. P. Xiao, F. Zhao, B. Zeng, Microchemical Journal (2007) 85 244-249.
2. X. Q. Lin, J. B. He, Z. G. Zha, Sensors and Actuators B (2006) 119 608-614.
3. Ş. Sağlam, A. Uzer, Y. Tekdemir, E. Ercag, R. Apak, Talanta (2015) 139 181-188.

Electrochemical Determination of Food Preservative Nitrite with Gold Nanoparticles/*p*-Aminothiophenol Modified Gold Electrode

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Nitrite has been used in different meat products mainly to maintain their microbial quality, flavor, color and to prevent or retard lipid oxidation [1]. Another interesting property of nitrite is its capability to retard the development of rancidity during storage, to reduce the thiobarbituric acid (TBA) response (used as a measure of biooxidative status) and the subsequent warmed-over flavors (WOF) developed upon heating of meat [2,3]. Unfortunately, nitrite is an essential precursor in the formation of nitrosamines as a cancer-suspect class of compounds [4]. Due to the above reasons, its determination is important. In this study, the working electrode, *i.e.* *p*-aminothiophenol (*p*-ATP)–modified and gold nanoparticles–derivatized gold electrode (Au/*p*-ATP-Au_{nano}), was manufactured in two steps. In the first step, the surface of the Au working electrode was coated with a polymeric material (polyaminothiophenol (PATP)) *via* electropolymerization. In the second step, Au/*p*-ATP-Au_{nano} working electrode was prepared by coating the surface with the use of HAuCl₄ solution and cyclic voltammetry. Determination of aqueous nitrite samples was performed with the proposed electrode (Au/*p*-ATP-Au_{nano}) using square wave voltammetry (SWV) in pH 4 buffer medium. Characteristic peak potential of nitrite was 0.76 V, and linear calibration curves of current intensity *versus* concentration was linear in the range of 0.5–50 mg L⁻¹ nitrite with a limit of detection (LOD) of 0.12 mg L⁻¹. Alternatively, nitrite in sausage samples could be colorimetrically determined with high sensitivity by means of *p*-ATP–modified gold nanoparticles (AuNPs) and naphthylethylene diamine as coupling agent for azo-dye formation due to enhanced charge-transfer interactions with the AuNPs surface. The slopes of the calibration lines in pure NO₂⁻ solution and in sausage sample solution to which different concentrations of NO₂⁻ standards were added were not significantly different from each other, confirming the robustness and interference tolerance of the method. The proposed voltammetric sensing method was validated against the colorimetric nanosensing method in sausage samples. The method distinguishes itself from similar other methods reported in literature with its effective interference removal technique (*i.e.* removal of ascorbic acid with ascorbate oxidase, and removal of other chemical reductant interferents with Cu(II)-neocuproine extraction into dichloromethane) prior to electrochemical measurement.

Keywords: Nitrite Determination; Gold Electrode; Modified Electrode; Gold Nanoparticles; Square Wave Voltammetry (SWV).

Acknowledgements: The authors thank TUBITAK (Turkish Scientific and Technical Research Council) for their support to the Research Project 112T792. Additionally, thanks are extended to the Scientific Research Projects Coordination Unit of Istanbul University (BAP), who supported this work with the project number: 57182.

References:

1. Alahakoon, A. U.; Jayasena, D. D.; Ramachandra, S.; Jo, C., Trends Food Sci. Technol. (2015) 45 37-49.
2. Parthasarathy, D. K.; Bryan, N. S., Meat Sci. (2012) 92 274-279.
3. Pegg, R. B.; Shahidi, F., Frontmatter. (2008) In Nitrite Curing of Meat, Food & Nutrition Press, Inc.
4. Jo, C.; Ahn, H. J.; Son, J. H.; Lee, J. W.; Byun, M. W., Food Control (2003) 14 7-12.

Applications of Carbon Based Electrode for Voltammetric Determination of Tenofovir in Pharmaceutical Dosage Form

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Tenofovir(TEN) is a type of anti-HIV medicine called a nucleoside reverse transcriptase inhibitor (NRTI). NRTIs work by blocking HIV reverse transcriptase, an HIV enzyme. This prevents HIV from replicating and lowers the amount of HIV in the blood(1).

The voltammetric oxidation of TEN was investigated at a glassy carbon electrode using cyclic and differential pulse voltammetry over a wide pH range. The results revealed that the oxidation of TEN is an irreversible pH-dependent process in an adsorption-controlled mechanism.

For the analytical application, operational parameters have been optimized. The calibration curve was linear in the concentration range of 6.0×10^{-7} – 6.00×10^{-5} M with a detection limit of 8.393×10^{-8} M. The reproducibility of the peak current was found 0.33% (n = 5) in pH 4.7 acetate buffer. The glassy carbon electrode showed good stability and reproducibility, and also it was successfully applied to the sensitive and selective determination of TEN in its dosage forms.

The oxidation mechanism of TEN was try to explained working with some model compounds (adefovir, adenine (ADE)).

The effect of possible interferents on the electrochemical determination of TEN was investigated by adding potential interferents containing compounds to a solution containing 4.0×10^{-6} M TEN in pH4.7 acetate buffer. The tolerance limit for interfering species was considered as the maximum concentration that gave a relative error (%RSD) less than $\pm 10.0\%$. Na^+ , Cl^- , K^+ , ascorbic acid, dopamine and uric acid and glucose solutions were added to the working media, separately (2). According to the obtained results; Na^+ , Cl^- , K^+ , ascorbic acid, dopamine and uric acid and glucose solutions do not interfere with the tenofovir determination with the selectivity ratio of about 1:1.

ICH guidelines recommend performing degradation studies for establishing stability-indicating nature of the assay method. Degradation studies consisted of heat in an oven (at 75 °C), acidic, alkaline hydrolysis and oxidation of the compounds, to evaluate the ability of the proposed method (3). Thermal degradation of TEN was carried out in their solid state. TEN was placed in a controlled-temperature oven at 75 °C, water bath at 100°C and room condition for 24 h.

Keywords: Tenofovir, Voltammetry, Glassy Carbon Electrode, Interference, Degradation.

References:

1. Sanjiv M. B, Rebecca S. AIDS, (2016) 30 4.
2. Burcu D.T, Burçin B.P, Sensors and Actuators B, Multi-walled carbon nanotube modified glassy carbon electrode as a voltammetric nanosensor for the sensitive determination of anti-viral drug valganciclovir in pharmaceuticals (2013) 177 841–8473.
3. Sevinç K., Paula S.M., Chromatographia , Stability-Indicating UPLC Method for the Determination of Bisoprolol Fumarate and Hydrochlorothiazide: Application to Dosage Forms and Biological Sample, (2014) 77 365–371.

Voltammetric Oxidation and Determination of Imatinib in Spiked Human Urine Samples

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One of the representative of cytostatic is a first-generation drug, imatinib (*Ima*), which is the first protein kinase inhibitor endorsed for clinical use, and is a seminal drug for the concept of destined therapy. *Ima* is used in the treatment of chronic myelogenous leukemia.

According to the available literature data, voltammetric studies of *Ima* based on its reduction signal were performed, and hanging mercury drop electrode (HMDE) has been applied till now for the determination of *Ima*. In the published voltammetric assay, *Ima* was investigated by square-wave adsorptive stripping voltammetric (SWAdSV) technique using HMDE in spiked urine samples, and bulk form, pharmaceutical formulation, and human serum. The limits of detection for SWAdSV on HMDE were 5.2×10^{-9} mol L⁻¹ and 2.6×10^{-10} mol L⁻¹. Although the detection limits of the above-mentioned voltammetric works are very low, however, their routine use might be limited due to the toxicity of mercury.

In the present paper, the electrochemical oxidation of a new generation of anticancer drug, imatinib (*Ima*), using differential pulse voltammetry (DPV) on anodically pretreated boron doped diamond electrode has been reported. It was found that *Ima* provided reproducible and well-defined oxidation peak at positive potential of around +1.0 V in the Britton–Robinson buffer at pH 2.0. The experimental conditions, *i.e.* pH, a modulation amplitude, a modulation time, a step potential, and a scan rate, were optimized. A rapid, simple, selective and sensitive DPV procedure for the determination of *Ima* was performed in the concentration range of 3.0×10^{-8} – 2.5×10^{-7} mol L⁻¹ with the limit of detection and the limit of quantification of 6.3×10^{-9} mol L⁻¹ and 2.1×10^{-8} mol L⁻¹, respectively. Additionally, a biological relevance of the developed DPV procedure was demonstrated by quantitative analysis of the spiked human urine samples with satisfactory recoveries (from 102.2% to 105.5%). The influence of some interfering compounds and ions (*Int*) was also evaluated.

Diffusion, Adsorption and Electrode Kinetics of Electro-Oxidations on a Stationary Solid Electrode

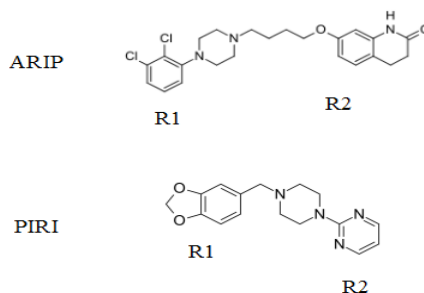
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Schizophrenia is a chronic, debilitating mental illness, which is characterized by both positive and negative symptoms, cognitive dysfunction, and a decline in psycho-social functioning [1, 2]. At least empirically, the ability of aripiprazole (ARIP) and piribedil (PIRI), used as a medication, is able to stabilize dopaminergic and serotonergic systems, may represent a new treatment approach, not only for schizophrenia but it for other mental disorders, when also compared with other classes of drugs than ARIP and PIRI.



The *i*-*E* curves of ARIP and PIRI follow a different pattern. Instead of a peak current formation of a limiting current takes place at a potential that depends on pH, in a steep increase of current and becomes practically potential independent limiting current is observed between +1.0 V and +1.6 V for ARIP and +0.9 V and +1.6 V for PIRI.

The electrochemical measurements were performed using a BAS 100W (Bioanalytical System, USA) electrochemical analyzer. An Ag/AgCl, electrode with 3.0 M NaCl was used as a reference electrode. A 3 mm diameter boron doped diamond electrode (BDDE) (Windsor Scientific Ltd; West Berkshire UK) has been employed as working electrode. An electrolytic glass cell (10 mL) was used. Concentration dependence using LSV of ARIP (0.05 – 0.7 mM) and PIRI (0.1 – 0.7 mM) in pH 4.7 acetate buffer containing 20 % MeCN using BDDE at 100 mV/s scan rate at 25 °C, dependence of *i*₁ on scan rate, dependence of *i*₁ on square root of scan rate for ARIP and PIRI were also performed successfully.

Keywords: Aripiprazole, Piribedil, Boron Doped Diamond Electrode, Mechanism.

References:

1. P. D. Harvey, M. F. Green, R. S. Keefe, D.I. Velligan, J. Clin. Psychiat. (2004) 65 361-372.
2. D. I. Velligan, R. S. Keefe, J. M. Gold, Schizophrenia Bull. (2006) 32 474-485.

Electrochemical Detection of Interaction Between DNA and Leuprolide by Differential Pulse Voltammetry at the Electrode Surface and in Solution Phase

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Leuprolide acetate is a synthetic nonapeptide that is a potent gonadotropin-releasing hormone receptor agonist used for diverse clinical applications, including the treatment of prostate cancer, endometriosis and uterine fibroids.

Electrochemical mechanisms are important to all redox chemistry including biological systems related to electron transport chains. Nucleic acid layers combined with electrochemical transducers produce a kind of biosensor for nanomolecules. Electrochemical approach can provide new insights into rational drug design and the investigation on DNA-antineoplastic drug interactions has a great importance in understanding the mechanism of action of antitumor drugs. Hence, electrochemical biosensors have played an important role in the transition towards point-of-care diagnostic devices.

The electrochemical interaction between leuprolide and ds-DNA was investigated using two different interaction processes, namely interaction on the PGE surface and interaction in the solution phase. The interaction of leuprolide with ds-DNA modified PGE as namely DNA biosensor was studied by differential pulse voltammetry (DPV). The DPV peak currents of guanine were measured before and after the interaction with leuprolide. The linear response was obtained in the range of 0.20 – 6.00 ppm leuprolide concentration with a detection limit of 0.06 ppm on DNA modified PGE. For the confirmation of the interaction between ds-DNA and leuprolide, the interaction in solution phase study was also realized. Linearity of the guanine signals was obtained in response to the range of 0.20 – 1.00 ppm leuprolide. The both proposed methods, ds-DNA modified PGE and interaction with ds-DNA in solution phase, were applied to the direct determination of leuprolide in intravenous injection dosage forms.

Keywords: Leuprolide, Voltammetry, Glassy Carbon Electrode, DNA Biosensor

Sensitive and Selective Voltammetric Approach for Determination of Anti-Cancer Drug Etoposide Based on Sepiolite Clay/TiO₂ Nanoparticles Modified Carbon Paste Sensor and Investigation of Its Interaction with DNA

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Etoposide (ETZ) is used as a form of chemotherapy for cancers such as Kaposi's sarcoma, Ewing's sarcoma, lung cancer, testicular cancer, lymphoma, nonlymphocytic leukemia, and glioblastoma multiforme. It is often given in combination with other drugs (such as bleomycin in treating testicular cancer). It is also sometimes used in a conditioning regimen prior to a bone marrow or blood stem cell transplant [1].

ETZ forms a ternary complex with DNA and the topoisomerase II enzyme (which aids in DNA unwinding), prevents re-ligation of the DNA strands, and by doing so causes DNA strands to break [2]. Cancer cells rely on this enzyme more than healthy cells, since they divide more rapidly. Therefore, this causes errors in DNA synthesis and promotes apoptosis of the cancer cell [1, 3]. Accordingly, it is important to investigate the interaction of drug-DNA by using electrochemical methods so that, new drug design can be provided. Also this phenomenon will lead to understanding of interaction mechanisms of anticancer drugs and DNA.

Electrochemical stripping methods performed by accumulation with an analyte onto the working electrode surface are one of the most suitable methods for the determination of several pharmaceutical compounds. Furthermore, these methods have the advantage of being relatively less expensive, highly sensitive and they provide low limit of detection (LOD). Therefore, electrochemical stripping methods are becoming more and more popular as alternative methods in pharmaceutical formulations and biological samples [4-5].

A simple, sensitive, selective, economical and time-saving square wave adsorptive stripping voltammetric method (AdsSWV) was developed for sensitive and selective determination of ETZ based on a novel Sepiolite clay (SC) and TiO₂ nanoparticles modified carbon paste sensor (CPE). Electrochemical behaviour of ETZ was investigated on newly proposed SC/TiO₂/CPE sensor by using cyclic voltammetry. To develop AdsSWV method, pH, supporting electrolyte, the components of electrode, accumulation potential and accumulation time were optimized. Under these conditions, the oxidation peak was changed linearly with in the range of 8.7 nM to 1000 nM. The limits of detection and quantification values for ETZ were found to be 0.82 nM and 8.7 nM, respectively. The proposed sensor was successfully applied for the determination of ETZ in commercial Etosid vial and the recovery results were calculated in the range of 100.56% to 106.70%. The validation test results (Reproducibility, repeatability and stability) for newly developed sensor are really satisfactory. In addition, interaction studies of ETZ and DNA were examined by using calf-tymus DNA.

Keywords: Etoposide, TiO₂ Nanoparticles, Sepiolite Clay, Carbon Paste Electrode, Voltammetry

References:

1. Hande KR Eur. J. Cancer (1998) 34 1514 –1521.
2. Pommier Y, Leo E, Zhang H, Marchand C Chem. Biol. (2010) 17 421–33.
3. Gordaliza M, García PA, del Corral JM, Castro MA, Gómez-Zurita MA Toxicon (2004) 44 441–459.
4. Farghaly O.A.M. J.Pharm.Biomed.Anal. (2000) 23 783–791.
5. Sagar KA., Smyth M. R., Munden R. J. Pharm. Biomed. Anal. (1993) 11 533–540.

Impedimetric Aptasensor Developed for Thrombin Detection

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The biosensing technology can be combined with aptamers for recognition of nucleic acids, proteins, drugs, and toxins. Thus, there have been many reports in the literature about development of aptamer based sensors (aptasensors) (1-7).

Thrombin (THR) is a serine protease that plays an important role in blood coagulation, thrombosis, inflammation, angiogenesis, tumor growth and metastasis (8,9). Since, the detection of THR in plasma or blood is clinically relevant, various sensing methods have been reported for the detection of thrombin, such as quartz crystal microbalance (QCM), surface plasmon resonance (SPR), and electrochemical analysis (4,6-9).

The impedimetric aptasensor for THR was developed for the first time herein by measuring changes at the charge-transfer resistance, R_{ct} upon to protein-aptamer complex formation. The procedure for impedimetric detection of THR was consist of five steps; pretreatment and covalent activation of pencil graphite electrode (PGE) surface, APT immobilization onto the surface of PGE, surface confined interaction of APT with its cognate protein THR, and finally impedimetric measurement. After the optimization of experimental conditions, the selectivity of impedimetric aptasensor was tested in the presence of other biomolecules: Factor Va (FVa) and bovine serum albumin (BSA).

The study described herein (7) presented a sensitive and selective THR aptasensing protocol resulting in a short time (2.5 hour). Moreover, our impedimetric aptasensor based protocol might be furtherly applied for detection of various proteins and other small molecules.

Keywords: Aptasensor, Thrombin, Pencil Graphite Electrode, Electrochemical Impedance Spectroscopy

Acknowledgements: Arzum Erdem would like to express her gratitude to the Turkish Academy of Sciences (TUBA) as the Principal member for its partial support.

References:

1. Z. Wang, J. Yu, R. Gui, H. Jin, Y. Xia, *Biosens Bioelectron.* (2016) 79 136-149.
2. L. Chen, Z.-N. Chen, *Talanta* (2015) 132 664-668.
3. P. He, L. Liu, W. Qiao, S. Zhang, *Chem. Commun* (2014) 50 1481-1484.
4. A. Erdem, H. Karadeniz, G. Mayer, M. Famulok, A. Caliskan, *Electroanalysis* (2009) 21 1278-1284.
5. E. Eksin, G. Congur, A. Erdem, *Aptasensor Technologies Developed for Detection of Toxins*, In: Ed. D.P. Nikolelis, G-P. Nikoleli (eds.) *Biosensors for Security and Bioterrorism Applications* (2016) pp. 249-259, Springer, Ottawa, ON, Canada.
6. A. Erdem, G. Congur, G. Mayer, *Journal of Electroanalytical Chemistry* (2015) 758 12-19.
7. E. Eksin, A. Erdem, A.B. Kuruc, H. Kayi, A. Ögünç, *Electroanalysis* (2015) 27 2864 – 2871.
8. Z. Suo, B. Citron, B. Festoff, *Curr. Drug Targets-Inflam. Allergy* (2004) 3 105-114.
9. K.A. Tanaka, N.S. Key, J.H. Levy, *Anesth. Analg.* (2009) 108 1433-1446.

The Electrochemical Detection of 6-TG and Its Interaction with DNA Oligonucleotides Using Disposable Pencil Graphite Electrodes

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The interactions of some anticancer drugs with DNA have been widely studied by a variety of techniques such as chromatographic, spectroscopic and electrochemical techniques (1–7).

Electrochemical DNA biosensors attract attention due to their speediness, reproducibility, and reliability. Because of their remarkable characteristics, electrochemical DNA biosensors enable us to perform research in many areas such as clinical diagnosis, environmental monitoring, and drug investigation (8-9). There has been a great attention for electrochemical investigation of the interaction between drugs and DNA since the pre- and post electrochemical signals of the surface confined interaction between DNA and drugs provide good evidence for the interaction mechanism to be elucidated (10-11).

6-Thioguanine (6-TG, 2-amino-7H-purine-6-thiol) as a sulfur derivative of guanine is one of the most important anticancer therapeutic agents used in the clinical treatment of acute childhood lymphoblastic leukemia, AIDS, and some other pathology (6,8,10,12).

The aim of our study is electrochemical detection of 6-TG, and also the interaction between 6-TG and single stranded oligo (A)25 and double stranded oligo (A)25-(T)25 by using disposable pencil graphite electrodes (PGE). Electrochemical measurements were performed by differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) techniques. The interaction between 6-TG and oligo (A)25, or oligo (A)25-(T)25 was explored based on the changes at the oxidation signals of 6-TG and adenine by using DPV. Experimental parameters; such as, 6-TG concentration and its interaction time with oligo (A)25 and oligo (A)25-(T)25 etc. were optimized.

Keywords: 6-Thioguanine, Drug-DNA Interaction, Electrochemical DNA Biosensor, Differential Pulse Voltammetry, Electrochemical Impedance Spectroscopy.

Acknowledgements: Arzum Erdem would like to express her gratitude to the Turkish Academy of Sciences (TUBA) as the Principal member for its partial support.

References:

1. C. Caramelo-Nunes, T. Tente, P. Almeida, J.C. Marcos, C.T. Tomaz, *Analytical Biochemistry* (2011) 412 153–158.
2. Y. Temerk, M. Ibrahim, H. Ibrahim, M. Kotb, *Journal of Electroanalytical Chemistry* (2016) 769 62–64.
3. A. Erdem, M. Ozsoz, *Electroanalysis* (2002) 14 965-974.
4. E. Palecek, M. Fojta, *Analytical Chemistry* (2001) 73 74A-83A.
5. A. Erdem, M. Ozsoz, *Analytica Chimica Acta* (2001) 437 107–114.
6. E. Mirmomtaz, A. A. Ensafi, *Electrochimica Acta* (2009) 54 4353–4358.
7. A. Erdem, M. Muti, P. Papakonstantinou, et al., *Analyst* (2012) 137 2129-2135.
8. E. Eksin, G. Congur, F. Mese, A. Erdem, *Journal of Electroanalytical Chemistry* (2014) 733 33–38.
9. M.C. Vasconcellos, C. Oliveira Costa, E.G Silva Terto, et al., *Journal of Electroanalytical Chemistry* (2016) 765 168-178.
10. W. Wang, S.-F. Wang, F. Xie, *Sensors and Actuators B* (2006) 120 238–244.
11. S. Rauha, J.J. Goodingb, K. Akhtara, M.A. Ghauria, et al., *Journal of Pharmaceutical and Biomedical Analysis* (2005) 37 205–217.
12. P. Qua, H. Lu, X. Ding, Y. Tao, Z. Lu, *Spectrochimica Acta Part A* (2009) 74 1224–1228.

Impedimetric Detection of MicroRNA by Using Graphene Oxide Modified Graphite Electrodes

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Graphene and graphene-based nanomaterials have been attracting great research interest with regard to their unique structural features such as; high surface area, flexibility and chemical stability (1,2). Effective immobilization of nucleic acids onto the surface of analysis platform has been one of the key features for development of advanced biosensor platforms in the field of clinical diagnostics (1-5).

MicroRNAs (miRNA) are small RNA molecules, that contains 19-25 nucleotides. The abnormal expression of miRNA causes different type of cancer, neurodegenerative diseases and metabolic diseases as diabetes (6-9). Therefore, the studies are being performed in order to investigate practical, easy-to-use, miniaturize biosensor platforms which can detect miRNAs rapidly, sensitively and selectively (6-11).

GO modified graphite electrodes were used in our study for sensitive and selective detection of miRNA. Disposable pencil graphite electrode (PGE) surfaces were firstly modified by GO and then they were used for miRNA detection. The microscopic and voltammetric characterization of GO/PGEs was performed by scanning electron microscopy (SEM) and cyclic voltammetry (CV), respectively. The optimization of experimental conditions; such as GO concentration, DNA probe concentration, miRNA concentration were performed by electrochemical impedance spectroscopy (EIS) technique. The selectivity of our assay was also tested in optimum conditions.

GO modified sensor platform presented in our study shows a great promise furtherly in order to develop low-cost and sensitive biosensing protocol for healthcare monitoring, clinical diagnostics, and biomedical devices.

Keywords: Graphene Oxide, miRNA, Nucleic Acid Hybridization, Pencil Graphite Electrode, Electrochemical Impedance Spectroscopy.

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References

1. A.K. Geim, K.S. Novoselov, Nature Materials (2007) 7 6183-6191.
2. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos, A.A. Firsov, Nature (2005) 438 197-200.
3. A. Erdem, Talanta (2007) 74 318-325.
4. W. Ma, B. Situ, W. Ly, et al., Biosensors and Bioelectronics, (2016) 80 344-351.
5. I.B. Olenych, O.I. Aksimentyeva, L.S. Monastyrskii, Y.Y. Horbenko, M.V. Partyka, A.P. Luchechko, L.I. Yarytska, Nanoscale Research Letters, (2016) 11 43-50.
6. R.C. Friedman, K.K. Farh, C.B. Burge, D.P. Bartel, Genome Research (2009) 19 92-105.
7. W.C. Cho, Biochimica Biophysica Acta (2010) 1805 209-217.
8. K. Ruan, X.G. Fang, G.L. Ouyang, Cancer Letters (2009) 285 116-126.
9. S.M. Eacker, T.M. Dawson, V.L. Dawson, National Review of Neuroscience (2009) 10 837-841.
10. A. Erdem, G. Congur, Talanta (2014) 118 7-13.
11. A. Erdem, G. Congur, E. Eksin, Sensors and Actuators B: Chemical (2013) 188 1089-1095.

Electrochemical DNA Nanobiosensor for the Detection of Anticancer Drugs and DNA Interactions

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The design of biological sensors is currently one of the most important field of analytical chemistry and there has still been growing interest in studying DNA-based bio(nano)sensors and their applications related to compound-DNA interactions in the last two decades.

In this study, the interaction of a model anticancer drug and double stranded DNA (dsDNA) / single stranded (ssDNA) was studied by using newly-developed electrochemical DNA (nano)biosensor. The effect of the drug on DNA hybridization was also examined with the biomaterial-containing carbon electrodes and change in oxidation signals of guanine and drug is monitored by using differential pulse voltammetry (DPV). The effect of some nanomaterials on hybridization response was also studied. Thus, obtained results showed that this methodology could be used for the cost effective, sensitive and rapid detection of drug-DNA interactions.

Keywords: Electrochemical DNA Biosensor, DNA, Nanomaterial, Drug-DNA Interactions, Carbon Electrode.

References:

3. I.C. Lopes, S.C. Oliveira, A. Oliveira-Brett, Anal. Bioanal. Chem., (2013) 405 3783–3790.
4. D. Okan, H. Karadeniz, H. Erdem, A. Mascini, M. Ozsoz, M. Journal of Pharmaceutical and Biomedical Analysis (2004) 35 905.
5. Abraham DJ. Antiviral Agents, Burger's Medicinal Chemistry and Drug Discovery. Virginia; Sixth Edition, Volume 5. John Wiley and Sons, Inc. (2003) 293.
6. Wang, J. Anal. Chim. Acta (2002) 469, 63.
7. D. Ozkan-Ariksoysal, B. Tezcanli, B. Kosova, M. Ozsoz, Anal. Chem. (2008) 80 588.
8. S. Aydinlik, D. Ozkan-Ariksoysal, P. Kara, A. A. Sayiner, M. Ozsoz, Analytical Methods. (2011) 3 1607.
9. E. Palecek, M. Bartosik, Chemical Reviews. (2012) 112 3427.
10. F. Lucarelli, G. Marrazza, A. P. F. Turner, M. Mascini, Biosensors & Bioelectronics. (2004) 19 515
11. Y.U. Kayran, D. Ozkan-Ariksoysal, B. Tezcanli, B. Kosova, Mehmet Ozsoz, Electroanalysis (2013) 25 12 2668.

Label Free Aptasensor Designs in Clinical Analysis

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Abstract

Herein we describe label free detection of aptamer / protein and aptamer / cancer cell interactions based on electrochemical impedance spectrometry (EIS) technique. The 5' chemically modified aptamer sequence was immobilized onto carbon based sensor surfaces. The binding of target protein and / or cancer cell onto aptamer sequence were monitored by EIS transduction of the R_{ct} in the presence of 5mM $[Fe(CN)_6]^{3-/4-}$. This study gives a new approach and an overview of alternative electrochemical biosensors for clinical analysis.

Keywords: Electrochemistry, Aptasensor, Electrochemical Impedance Spectrometry

Introduction

Aptamers are short single-stranded DNA or RNA sequences which have high specific affinity in binding protein and several biomolecule targets [1]. Aptamer based studies represent a novel modern and a strategic approach in bioanalytical analysis for specific detection [2-3]. Due to their high stability, chemical simplicity, and easy applicability, they can be used as alternative captures to antibodies. Thereby, aptamer applications hold a great promise for biosensing of proteins, genes, and cells for developing clinical detection arrays [4].

In recent years, there has been a great interest in developing aptamer sensors, thereby different strategies have been developed for aptamer based protein and cell screening. Affinity biosensors have a great promise in aptamer sensing analysis due to their, high sensitivity, selectivity, simple instrumentation, portable and cost effectiveness. Thus a lot of aptamer based sensing interfaces have been developed including optical, piezoelectrical transduction, fluorescence, atomic force microscopy [5-7].

Electrochemical aptasensors provide a unique platform for clinical analysis with the advantages of high selectivity, high sensitivity and low cost detections [8]. In addition Electrochemical Impedance Spectrometry (EIS) based aptasensors also offer label free detection additionally. Electrochemical impedance spectroscopy (EIS) is based on interfacial investigations thus is a unique analytical device for label free diagnostic analysis. EIS measures the response of an electrochemical system to an applied oscillating potential as a function of the frequency. Impedimetric techniques have been developed to characterize the fabrication of the sensors and to monitor the biochemical reaction occurs at the sensor surface [9-10].

Materials & Methods

DNA aptamer that selective bind human IgE with the 5' modified with Biotin and selective sub type non- small cell lung cancer with the 5' amino hexyl modified were used.

The aptamer sequence that specific for Human IgE has a following base composition :

5' Biotin - GCG CGG GGC ACG TTT ATC CGT CCC TCC TAG TGG CGT GCC CCG CGC 3'.

The aptamer sequence that specific for sub type non-small cell lung cancer is as follows:

5' NH₂ (CH₂)₆ GTT GCA TGC CGT GGG GAG GGG GGT GGG TTT TAT AGC GTA CTC AG 3'

Electrochemical impedance spectrometry (EIS) were performed using AUTOLAB PGSTAT-10 –FRA, were performed using an AUTOLAB PGSTAT-30 electrochemical

analysis system.

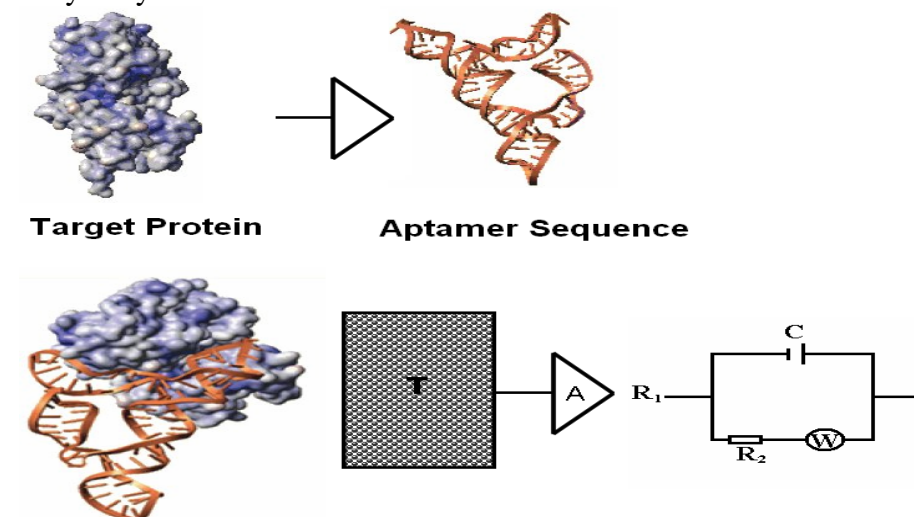


Figure 1: Schematic presentation of study procedure

Results&Discussion

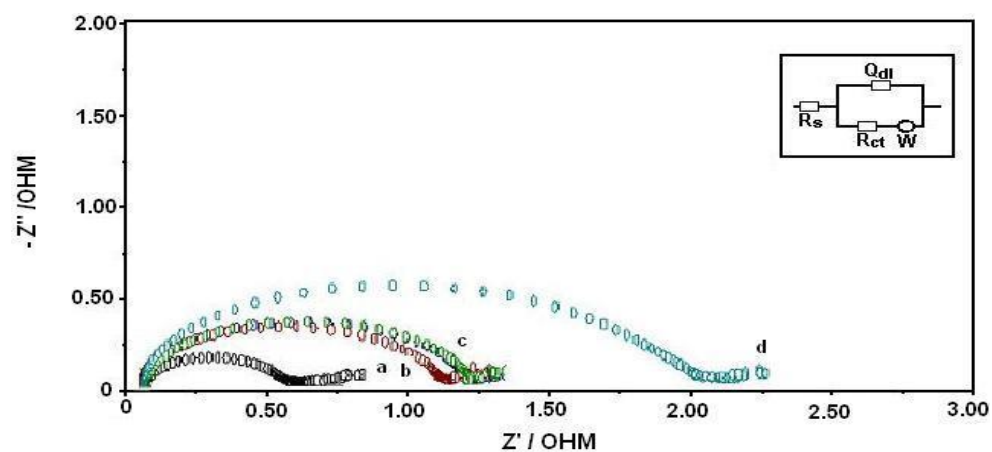


Figure 2: Impedance Spectra of chemically pretreated bare electrode (a), after aptamer immobilization (b), after interaction with non-specific target (c) and IgE (d) targets, at graphite electrode surface. Measurements performed in a 0.05 M phosphate buffer (pH 7.4) in the presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (5×10^{-6} M, 1:1) at +0.24 V.

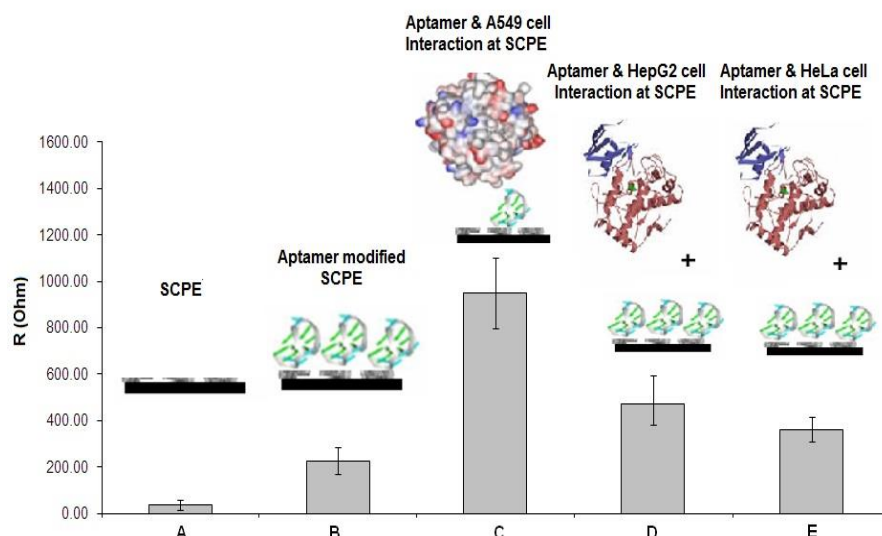


Figure 3: Rct values obtained in 5mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ following the experimental procedure at bare, aptamer modified electrode surfaces, before and after interaction with A549 lung cancer and non-specific HeLa and HepG2 cancer cells.

Conclusion

Here we have described a label free impedimetric aptasensor that provides sensitive detection of specific biomolecules. The selectivity of aptasensor was evaluated by using the EIS response differences between aptamer- target molecule and aptamer non specific targets. Depend on detection limits, such as 0.48 nM of IgE and 163.7 cancer cell /mL; even it is incomparable with previous studies it was shown that the designed aptasensors are capable of label free; low-cost, fast and reliable detection. Furthermore by using different aptamer sequences, more types of biomolecules can be detected.

References:

1. M.Minunni, S. Tombelli, J. Fonti, M. Spiriti, M. Mascini, P. Bogani, M. Bujatti, J. Am. Chem. Soc. (2005) 127 7966–7967.
2. R. Mukhopadhyay, Anal. Chem. , (2005) 77 114A–118A.
3. J. Phills, D. Lopez – Colon, Z. Zhu, Y. Xu, W. Tan, Analytica Chimica Acta, (2008) 621 101 – 108.
4. Z. Zhao, L. Xu, X. Shi, W. Tan, X. Fang, D. Shangguan, Analyst, (2009) 134 1808 – 1814.
5. P. Kara, A. Escosura –Muniz, M. Maltez, M. Guix, M. Ozsoz, A. Merkoçi, Biosensors and Bioelectronics, (2010) 26 1715 – 1718.
6. P. Kara, B. Meric, M. Ozsoz, Combinatorial Chemistry & High Throughput Screening, (2010) 13 578-581.
7. Y. Pu, Z. Zu, H. Liu, Z. Zhang, J. Liu, W. Tan, Anal Bioanal Chem, (2010) 397 3225–323
8. M. Minunni, S. Tombelli, J. Fonti, M. Spiriti, M. Mascini, P. Bogani, M. Buiatti, J. Am. Chem. Soc., (2005) 127 7966 -7967.
9. M. Steichen, Y. Decrem, E. Godfroid, C.B. Herman, Biosens.Bioelectron, (2007) 22 2237- 2243.
10. C. Deng, J. Chen, Z. Nie, M. Wang, X. Chu, X. Chen, X. Xiao, C. Lei, S. Yao Anal. Chem, (2009) 81 739-745.

Electrochemical Study of Cytarabine-Copper (II) Complex: Synthesis, Characterization and Analytical Application

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Cytarabine (Cyt) or cytosine arabinoside (Cytosar-U or Depocyt) is a chemotherapy agent used mainly in the treatment of cancers of white blood cells such as acute myeloid leukemia (AML) and non-Hodgkin lymphoma. [1] It kills cancer cells by interfering with DNA synthesis. It is called cytosine arabinoside because it combines a cytosine base with an arabinose sugar. Cytosine normally combines with a different sugar, deoxyribose, to form deoxycytidine, a component of DNA.

In this study, the copper(II) complex of Cyt has been synthesized. This prepared complex was characterized by physicochemical and spectroscopic methods. Its UV-Vis, IR and mass spectra. The electrochemical behavior of this synthesized complex was studied over glassy carbon electrode in various buffer solutions using cyclic voltammetric technique. Cyt enrichment is observed over Cu(II) complex. The peak current and peak potential of the complex depend on pH, initial potential, and scan rate. Cyclic voltammetric technique was used for the determination of Cyt-Cu(II) complex.

Keywords: Characterized, Electrochemical Properties

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References:

1. Mieszawska, A. J., Mulder, W. J., Fayad, Z. A., & Cormode, D. P. Multifunctional gold nanoparticles for diagnosis and therapy of disease. *Molecular pharmaceutics*, (2013) 10 831-847.

DNA-Functionalized Biosensor for Amisulpride Based Electrochemical Interaction on Pretreated Pencil Graphite Electrode

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The interaction of amisulpride (ASP) with fish sperm double-stranded deoxyribonucleic acid (FSdsDNA) based on the decreasing of the oxidation signal of guanine bases was studied electrochemically with a pencil graphite electrode (PGE) using differential pulse voltammetry. In this work, adsorption method was used for the immobilization of FSdsDNA onto the PGE surface. The decrease in the intensity of the guanine oxidation signals after interaction with ASP was used as an indicator signals for the sensitive determination of ASP. Under the optimum conditions, a linear dependence of the guanine oxidation signals was observed for the ASP concentration in the range of 1–10 $\mu\text{g mL}^{-1}$ with a detection limit of 0.46 $\mu\text{g mL}^{-1}$ at FSdsDNA modified PGE. The reproducibility and applicability of the analysis to pharmaceutical dosage forms were also investigated. These results showed that this DNA biosensor could be used for the sensitive, rapid, simple and cost effective detection and determination of ASP- FSdsDNA interaction.

Keywords: Amisulpride, DNA, Biosensor, Drug, Determination, Adsorptive Stripping Voltammetry

Acknowledgments: The authors wish to thank TUBITAK (Project No: 112T721, COST/CM1105) for the financial supports.

References:

1. Nur Topkaya, Seda Aydinlik, Seyma Aladag, Nilay Ozsoz, Mehmet, Ozkan-Ariksoysal Dilsat, Combinatorial Chemistry & High Throughput Screening, (2010) 13 582-589.

Electroanalysis of Some Pyridine Derivatives in Non-Aqueous Media

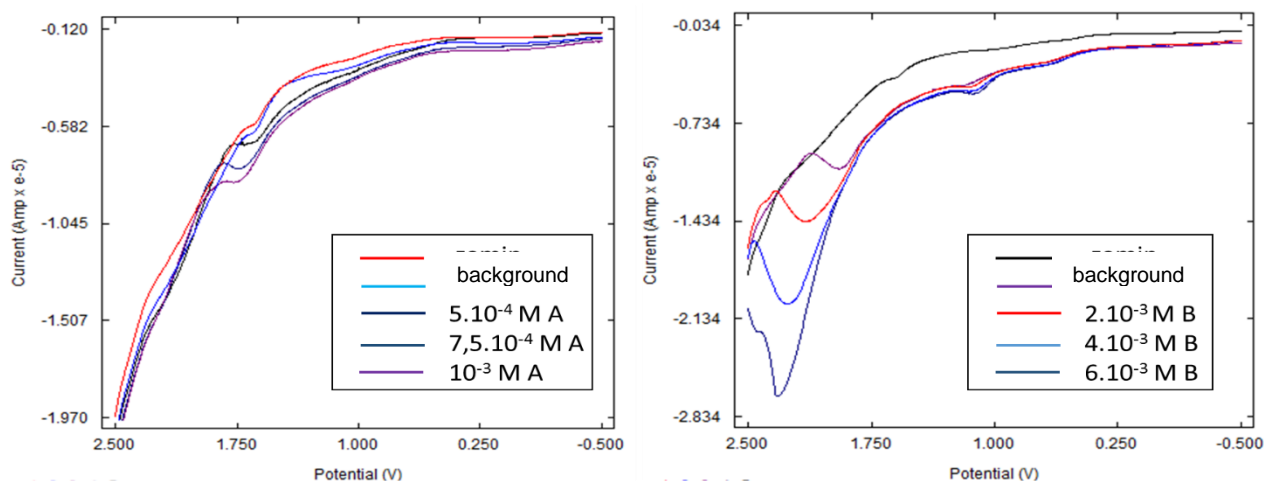
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Some pyridine derivatives and metals such as palladium complexes may show anticancer effect. It requires the development of useful techniques for description of this procedure and characterization of these compounds. This specific analysis of pyridine ligands should be designated for non-aqueous media because of their limited water solubility. Many of these compounds exhibit electroactive behavior and voltammetric techniques are very appropriate for this purpose.

To determination of oxidation and reduction characteristic and optimum analysis conditions of 2-(hydroxymethyl)pyridine and 2-(2-hydroxyethyl)pyridine were studied in DMSO and acetonitrile solvents with using different working electrodes by square wave voltammetry and cyclic voltammetry. A prepared non-aqueous reference electrode and 0,1M tetrabutyl ammonium perchlorate (TBAP) was used as supporting electrolyte in three electrode cell. And also deposition parameters on GCE were investigated with stripping voltammetry.



Oxidation peaks of 2-(hydroxymethyl) pyridine (A) (left) and 2-(2-hydroxyethyl) pyridine (B) (right) were obtained with 100 s deposition on GCE with stripping square wave voltammetry in acetonitrile

Keywords: Non-Aqueous Electrochemistry, Square Wave Voltammetry, 2-(Hydroxymethyl) Pyridine, 2-(2-Hydroxyethyl)Pyridine.

References:

1. M. S. Chenov'yants, I. V. Burykin, and N. E. Erofeev, Electrophoretic Determination of Thioamides, Pyridine and Pyrimidine Derivatives, J of Analytical Chemistry, 2013 68(6) 532.
2. Kosuke Izutsu, Electrochemistry in Nonaqueous Solutions, 2002 Wiley-VCH Verlag GmbH & Co. KGaA ISBNs: 3-527-30516-5.
3. Ferda Ar, et al., Synthesis, structural characterization and cell death-inducing effect of novel palladium(II) and platinum(II) saccharinate complexes with 2-(hydroxymethyl)pyridine and 2-(2-hydroxyethyl)pyridine on cancer cells in vitro. Bioorganic & Medicinal Chemistry (2013) 21 6427–6434.

Production and Certification of Reference pH Buffer Solutions at National Metrology Institute of Turkey

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Determination of pH is essential in both industrial processes and research studies such as biochemistry, food sectors, chemical research and engineering, environmental research, pollution control and pharmaceutical industry. Hence there is a huge demand for traceable measurement results for pH to ensure quality control and comply with the technical requirements [1]. The primary method for measurement of pH is based on the measurement of the potential difference of the electrochemical cell, often referred to as a Harned cell, without a liquid junction, involving a selected buffer solution, a platinum hydrogen gas electrode and a silver/silver chloride reference electrode [2]. pH measurements can be incorporated into the SI as they can be traced to measurements made using a method that fulfills the definition of primary methods of measurement [3]. This study describes procedures for production and certification of reference pH buffers realized at TÜBİTAK UME.

Buffer solutions were prepared and certified according to the instructions given in “IUPAC Recommendation 2002 Measurement of pH - Definition, Standards and Procedures” [4], ISO Guide 34-35 [5,6]. The chemical materials were dissolved in 150 L deionized water and homogenized for 8 hours using a homogenizing equipment and candidate buffer solutions were prepared (300 units each) and transferred into 500 mL HDPE bottles. The buffer solutions were stored at +4 °C. Homogeneity, short term stability, long term stability and characterization studies were performed. In these studies, sample bottles were selected by a special random stratified sample selection software. The measurement results were evaluated using one-way variance analysis (ANOVA) and homogeneity and stability test results showed that the expected criteria according to ISO Guide 35 was obtained. The characterization study was performed by using primary level pH measurement system (Harned Cell). Measurement uncertainty for primary level pH measurements was evaluated according to GUM principles [7]. At the end of the project, the reference pH buffer solutions labeled and will be presented to the users. As a result of this study, the domestic demands for pH buffers will be met as an output and traceability for pH measurements will be also provided over TÜBİTAK UME.

Keywords: pH, pH Buffer, Reference Material, Harned Cell, UME

References:

1. WHO, Trace Elements in Human Nutrition and Health, World Health Organization, Geneva, (1996).
2. Spitzer, Petra, Traceable Measurements of pH, Accred. Qual. Assur. (2001) 6 55-60.
3. Measurement of pH. Definition, Standards and Procedures, Pure Appl. Chem. (2002) 2169-2200.
4. IUPAC Recommendation (2002) Measurement of pH - Definition, Standards and Procedures.
5. ISO Guide 34 Reference materials — General and statistical principles for certification.
6. ISO Guide 35 Reference materials — General requirements for the competence of the reference material procedures.
7. Guide to the Expression of Uncertainty (GUM) BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (1993).

Voltammetric Determination of Boron using p-Xylenol Orange Modified Pencil Graphite Electrode

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This study describes a sensitive and accurate voltammetric determination of boron at p-xylenol orange modified pencil graphite electrode (p-XO/PGE). The oxidation of tiron at 0.86 V in the boron-tiron complex formed in phosphate buffer solution (pH 8) was evaluated as a response. The parameters affecting the peak current such as pH and concentration of supporting electrolyte, concentration of tiron, ionic strength, lead grade, step amplitude, interval time, pulse time and pulse amplitude were optimized. Modified electrode was characterized by Electrochemical Impedance Spectroscopy (EIS) and cyclic voltammetry. The limit of detection (3s) is 28 µg/L and calibration graph is linear between 0.050 mg/L and 10.000 mg/L of boron concentration for p-XO/PGE. The relative standard deviation values and recovery results were satisfactorily obtained for various water samples. The results obtained from the developed method were compared with those obtained from ICP-MS method and no statistically significant difference between the methods was found for 95% confidence level.

Keywords: Boron, Tiron, Pencil Graphite Electrode, Modified Electrode, Xylenol Oange, Voltammetry.

References:

1. Liv, L., Nakiboğlu, N., Turk. J. Chem., (2016).
2. Chandra, U., Swamy, B. E. K., Gilbert, O., Sherigara, B. S., Int. J. Electrochem., (2011) 2011 1-8.
3. Fujimori, T., Akimoto, H., Tsuji, Y., Takehara, K., Yoshimura, K., Electroanal., (2010) 22 1337-1343.

Preparation of Silver-Silver Chloride and Platinized Platinum Electrode for Primary pH Measurements

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Silver/silver chloride electrode (Ag/AgCl) and platinized platinum electrode (Pt/Pt) have been used for precious and accurate pH measurement in Harned Cell. Various electrode preparation procedures for preparation of Ag/AgCl and Pt/Pt electrodes have been used at different National Metrology Institutes. In this study, different electrode preparation procedures for both Ag/AgCl and Pt/Pt electrodes were compared. Ag/AgCl is prepared by spreading silver carbonate paste onto the spiral Pt wire and reduced to silver by heating ca. 400 °C in a quartz tube. This procedure is repeated until the desired cylindrical silver layer is obtained. After that, silver chloride was covered onto metallic silver by using chronopotentiometric and KMnO₄ methods. Chronopotentiometric and classical electrolysis methods were also used for preparation of Pt/Pt electrodes.

Formal electrode potential values of the prepared Ag/AgCl electrodes were determined in six Harned cells. SEM images of the prepared electrodes (Fig. 1) were also evaluated. Chronopotentiometric method was found the better procedure for preparation of both Ag/AgCl and Pt electrodes. Additionally, measurement uncertainty was evaluated for primary pH measurements.

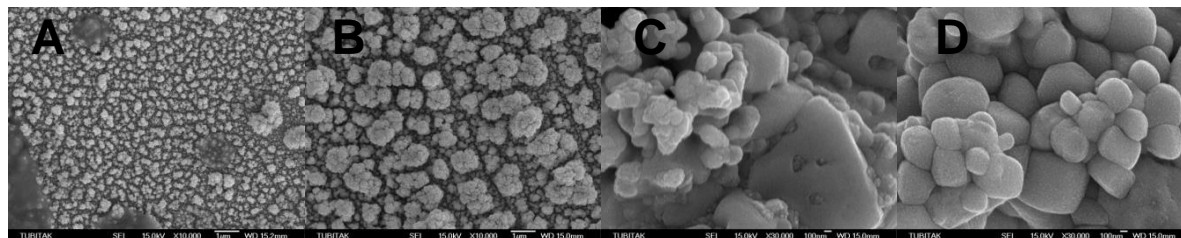


Figure 1. SEM images of Pt/Pt electrodes and Ag/AgCl electrodes made by classical methods (A, C) and chronopotentiometric methods (B, D)

Keywords: pH, Harned Cell, UME, Ag/AgCl Electrode, Platinum Electrode

References:

1. pH measurement and Traceability in Slovakia, Vyskocil, L., Mariashy, M., Mathiasova, A, PTB Report, 166 PTB Seminar, (2001) Braunschweig.
2. VIM International Vocabulary of Metrology, 3rd edition (2008).
3. Metrology in Chemistry at INRIM Workshop, Paola Fisicaro, Enzo Ferrara, “pH measurements of aqueous solutions”, (2005).
4. GUM, Guide to the expression of uncertainty of measurement, Joint Committee for Guides in Metrology (2008) 100.

Fabrication and Characterization of Dual Disc Platinum Nanoelectrodes

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Ultramicroelectrodes are electrodes with characteristic dimensions on the micrometer or sub-micrometer scale. Fast double-layer charging, reduced ohmic loss, and high mass transport rates have allowed them to revolutionize thermodynamic, kinetic, and electroanalytical measurements [1, 2]. These advantages can be expected to be achieved to a greater extent with nanoelectrodes [3].

The small electrode size enables voltammetry in very small spaces, producing important openings to voltammetry close to and even within single biological cells, and giving rise to the new and now widespread form of microscopy called scanning electrochemical microscopy (SECM) [4]. One of the greatest challenges facing nanoelectrode researchers is the preparation and fabrication of devices in order to study and realize some of the benefits discussed above.

Most nanometer-sized electrodes reported to date have been fabricated as single disc-shaped by laser pipette pulling method. In this study the laser pulling method was used for fabricating dual disc-shaped platinum nanoelectrodes. Several dual disc platinum nanoelectrodes have been fabricated. The initial characterization of the electrodes has executed by steady-state voltammetry. The overall radii of nanoelectrodes have calculated from steady-state currents belong to ferrocene solutions. The surface properties like smoothness and the possible gap between the disc and insulator have controlled by the shape of voltammograms.

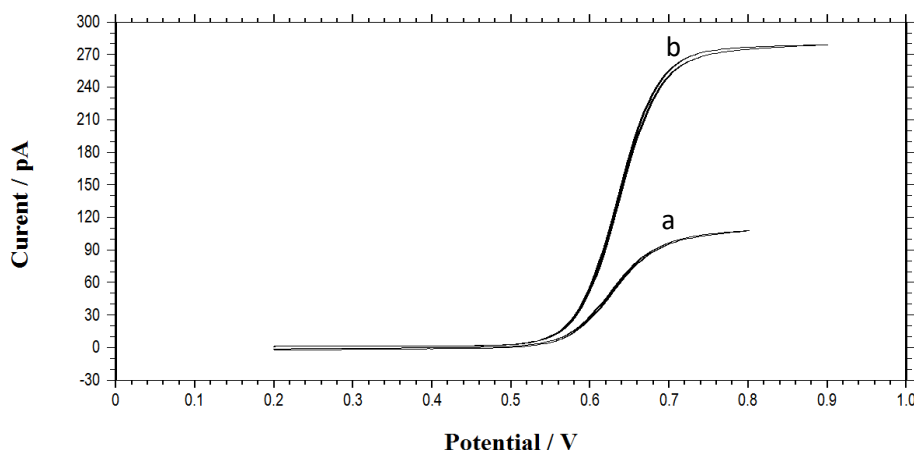


Figure 1. The steady-state voltammograms of single (a) and dual (b) disc platinum nanoelectrodes.

References:

1. Forster, R.J., *Chem. Soc. Rev.*, (1994) 23 289-297.
2. Heinze, J., *Angew. Chem. Int. Ed. Engl.*, (1993) 32 1268-1288.
3. Arrigan, D.W.M., *Analyst*, (2004) 129 1157-1165.
4. Murray, R.W., *Chem. Rev.*, (2008) 108 2688-2720.

Nanoelectrochemistry of Nicotinamide Adenine Dinucleotide

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Nanoelectrodes provide a number of advantages when utilizing in electrochemical studies and practices. The benefits which gain from these can be expected to be achieved to a greater extent with nanoelectrodes. As electrodes decrease in size, three-dimensional diffusion becomes dominant and results in faster mass transport [1]. These kinds of electrodes show steady state voltammograms.

The nanoelectrodes made of gold metal could be potentially useful for a wide range of applications such as sensors, studies of electrocatalysis, kinetic measurements and stripping analysis. Needle-like, polishable nanoelectrodes are suitable for SECM [2].

Nicotinamide adenine dinucleotide (NAD) is a coenzyme in all living cells. The compound is a dinucleotide, because it consists of two nucleotides joined through their phosphate groups. It was shown that the reduction of NAD⁺ is more difficult than the oxidation of NADH [3]. In this study, a new process for fabricating nanometer-sized gold electrodes have been developed using a laser-based micro pipet puller and nano electrochemical behavior of NADH was investigated by cyclic voltammetry and square wave voltammetry on different size gold nanoelectrodes. In phosphate buffer potassium chloride was used as supporting electrolyte, fabricated gold nanoelectrode was used as a working electrode and silver wire was used as both reference and auxiliary electrode. Using two different concentration of potassium chloride, current-concentration relation was determined. In addition, the operational parameters of square wave voltammetry such as amplitude and frequency were optimized.

References:

1. Murray, R., *Chem Rev*, (2008) 108 2688-2720.
2. Arrigan, D., *Analyst*, (2004) 129 1157-1165
3. Katekawa, E., *Anal. Chim. Acta*, (1999) 385 345-352

Low-Cost Diagnostics Based on a Single Responsive Polymer Film Sandwiched Between Two Conductive Tape Strips and Time-Concentration Dependent Acoustic Signalling

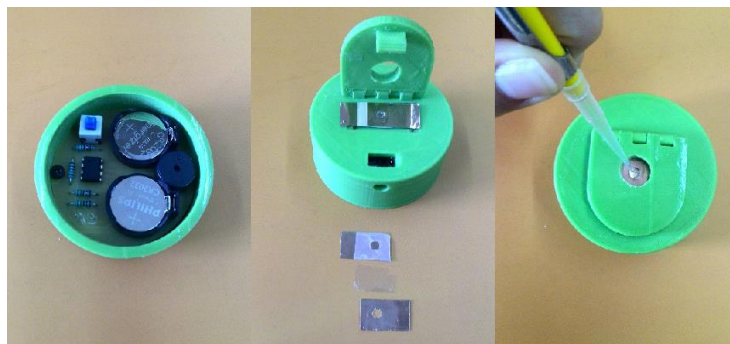
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The ability to perform low-cost and easy-to-perform point-of-use assays, would enable testing, typically reserved for well-equipped laboratories, to be performed in circumstances where resources and expertise are limited.^{1,2} In this work, we describe a novel transduction approach based on a single vertical conduit within a microfluidic device made of a responsive polymer membrane sandwiched between two conductive (copper) tape strips and 3-mm hole patterned double-sided adhesive tape, as illustrated in the (middle) photo below. The microfluidic device is placed over a specially designed holder which, at the bottom (left panel), houses the measuring electronics enabling a blast signal when the electric resistance between the metallic contacts, located on the top, becomes < 20 MOhm. Tight contact between the metallic contacts and the copper strips is provided with the aid of a lid, which also brings an opening to allow the addition of the sample (30 µL). The device was primarily tested using a pH-responsive membrane, a copolymer of methylmethacrylate and methacrylic acid (Eudragit S100), and ammonia solutions over the concentration range 2-100 mM. Results demonstrated that the time required for a sample to degrade the membrane (pH>7) and move downward in the conduit, thus establishing an electrical connection between the copper layers (acoustic signal), is concentration dependent. Using immobilized urease onto 2-mm disks of Biodyne B nylon membrane, the proposed concept was successfully tested for the determination of urea in 1:20 diluted urine samples. In this case, membrane degradation is caused by the enzymatically produced ammonia according to the chemical equation:



Keywords: Microfluidic Device, Diagnostics, Eudragit S100, Responsive Materials, Urea

References:

1. D. Christodouleas, A. Nemiroski, A. Kumar, G. Whitesides, *Anal. Chem.* (2015), 87, 9170.
2. A. Martinez, S. Phillips, G. Whitesides, *Anal. Chem.* (2010), 82, 3.

Low Dimensional Bi₂Te₃-Graphite Oxide Hybrid Film-Modified Electrodes for Ultra-Sensitive Stripping Voltammetric Detection of Pb(II) and Cd(II)

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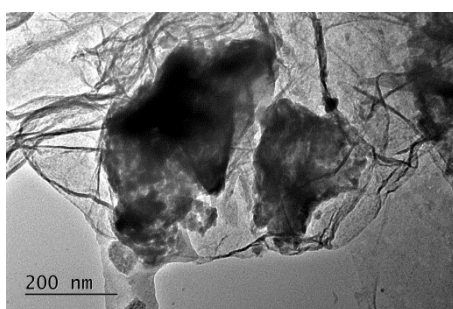
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In recent years there has been an explosion of interest to separate out individual two-dimensional layers in various inorganic materials, similarly to the one-atom thick graphene sheets in graphite. The unique electronic, mechanical and electrochemical properties exhibited by graphene sheets and not by the bulk graphite, has triggered extensive research efforts focusing on a wide spectrum of non-carbon-based layered materials, including transition metal oxides (TMOs), transition metal dichalcogenides (TMDs), layered double hydroxides (LDHs), and other compounds such as boron nitride, bismuth selenide, bismuth telluride (Bi₂Te₃) etc¹.

In this regard, our attempt was focused to Bi₂Te₃. Bi₂Te₃ is a topological insulator, i.e. a material with insulating bulk band gap and metallic surface states. Bismuth is undoubtedly considered to be the most successful electrode material to replace highly toxic mercury in anodic stripping or cathodic voltammetry.

In this work, we propose a simple liquid exfoliation method, using a triple blend of 1-cyclohexyl-2-pyrrolidone (CHP), acetone and water for the exfoliation of Bi₂Te₃ and demonstrate: i) the long term stability of the resulting colloidal suspension, ii) an extended electrode surface coverage with respect to the bulk material, as it was documented by faradic electrochemical impedance spectroscopy comparative measurements, iii) effective mixing of Bi₂Te₃ colloids with aqueous suspensions of graphite oxide (GO), which used as dispersing material of exfoliated Bi₂Te₃ flakes over the electrode surface, iv) significantly enhanced detection capabilities of exfoliated Bi₂Te₃/GO hybrid film-modified glassy carbon (GC) electrodes over bulk Bi₂Te₃/GO hybrid film-modified GCEs towards the stripping voltammetric determination of cadmium and lead at the sub-microgram per liter level, and v) applicability to real samples.



Keywords: Exfoliated Inorganic Layered Materials, Bi₂Te₃, Bi Nanoparticle Modified Electrodes, Ultra Sensitive Anodic Stripping Voltammetric Determination of Cd and Pb.

References:

1.C. N. R. Rao, H. S. S. Ramakrishna Matte, and U. Maitra, Graphene Analogues of Inorganic Layered Materials, *Angew. Chem. Int. Ed.* (2013) 52 13162 – 13185

Development of Sparked-Molybdenum Screen-Printed Graphite Electrodes for the Determination of Synthetic Colorants in Food and Drinks

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Food colorants are categorized into natural and synthetic dyes. Among the synthetic ones, Sunset Yellow FCF (SY) (E110), Tartrazine (Tar) (E102), New Coccine (NC) (E124) and Brilliant Blue (BB) (E124), which belongs to the family of azo dyes, have been widely used in food industry. This work describes the development of an advanced electrocatalytic surface, based on sparked-molybdenum screen-printed graphite electrodes (sparked Mo-SPEs). Sparked Mo-SPEs were produced following a recently devised by our group^{1,2} green (no solutions are required), fast (typically takes 20-30 s) and facile metal-to-SPE electric discharge approach at 1.2 kW under atmospheric conditions. At 0.1 M acetate buffer solution, pH 5 the developed sensors exhibited well-defined oxidation peaks positioned at 0.658 V for NC, 0.730 V for SY, 0.901 V for BB and 0.973 V for TAR. Sparked Mo-SPEs demonstrated 4-fold signal response compared with plain graphite SPEs, thereby enabling the determination of each single colorant or the simultaneous determination of specific pairs of them (SY/TAR, NC/TAR, NC/BB) in the nanomolar range. Based on the importance of the above colorants in the food industry, further studies were focused to the simultaneous determination of SY and TAR. Various experimental variables, such as the composition of the working solution, the pH of the working solution, the preconcentration time and potential, the effect of the initial potential value of the square-wave (SW) voltammograms, the parameters of the SW waveform were investigated and under selected conditions a linear calibration curve over the concentration range from 5 to 250 nM SY/TAR was constructed. The limit of detection (S/N 3) was 1 and 2 nM, respectively. The developed sensors were also successfully applied to the determination of SY and TAR in various real samples. The accuracy of the method was established by recovery studies in spiked samples. Recovery was between 95-106%. Results suggested that the developed sensors are sensitive, rapid and reliable.

Keywords: Sparked Modified Electrodes, Molybdenum Nanoparticles, Screen-Printed Electrodes, Sunset Yellow, Tartrazine, New Coccine, Brilliant Blue, Food Colorants, Electrochemical Sensor.

References:

1. D. Riman, D. Jirovsky, J. Hrbac, M.I. Prodromidis, Green and facile electrode modification by spark discharge: Bismuth oxide-screen printed electrodes for the screening of ultra-trace Cd(II) and Pb(II), *Electrochem Commun*, (2015) 50 20-23.
2. D. Riman, A. Avgeropoulos, J. Hrbac, M.I. Prodromidis, Sparked-bismuth oxide screen-printed electrodes for the determination of riboflavin in the sub-nanomolar range in non-deoxygenated solutions, *Electrochim Acta*, (2015) 165 410-415.

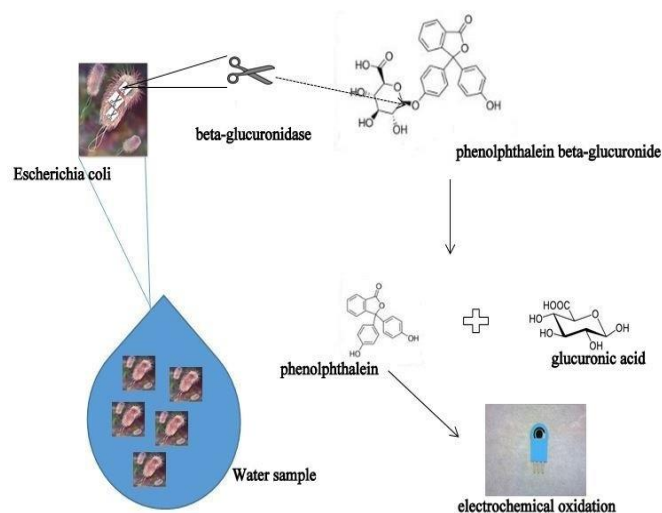
Rapid Detection of *Escherichia Coli* by Measuring Beta-Glucuronidase Activity with Highly Sensitive Screen-Printed, Drop-Volume Electrochemical Cells of Phenolphthalein

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The aim of this study was to develop a compact, low-cost and sensitive electrochemical cell in order to diagnose bacterial infection in water samples. To implement the reporting function for bacterium *Escherichia coli*, we isolated the enzyme beta-glucuronidase, which is excreted by 97% of all *E.coli* strains^{1,2}. Induction of beta-glucuronidase was enforced by methyl-glucuronide, which is then released out of the cells with the aid of lysozyme and ethylenediaminetetraacetic acid. Experiments showed the critical role of dithiothreitol, which was added in both the enzyme induction and permeabilisation steps to preserve the enzyme activity. Under optimized experimental conditions, beta-glucuronidase fractions, as they were isolated by centrifugation of the treated samples through a 200 kDa MWCO Vivaspin concentrator, catalyzed the hydrolysis of the added substrate phenolphthalein beta-glucuronide and the so released phenolphthalein was electrochemically measured in 0.1 M Phosphate buffer pH 7 by employing highly sensitive graphite screen-printed surfaces that allow the determination of phenolphthalein over the concentration range from 50 to 1000 nM with a limit of detection (S/N 3) of 50 nM.



Keywords: Beta-Glucuronidase, *Escherichia Coli*, Electrochemical Cell, Phenolphthalein

References:

1. W Zhang, H. Tang, *Electrochem. Commun.* (2007) 9 833-838.
2. M. Rochelet, S. Solanas, *Anal. Chim. Acta* (2015) 89 260-166.
3. Taegyu Kim, Jong-In Han, *J Environ. Manage.* (2013) 130 267-275.

Development of Chemical Sensors Based on Low Cost Printed Carbon Electrodes Modified with Nafion for Determination of Iron in Drinking Water.

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Iron is the most common element in the earth, which plays an important role in environmental and biological system and therefore, the determination of iron is of major interest. This work investigated the determination of iron in drinking water with square wave voltammetry by using low-cost, disposable and highly reproducible graphite screen-printed electrode (SPE) modified with nafion.

Nafion is a chemically inert polymer and suffixed that the modified electrode displayed a remarkably improved sensitivity and selectivity for Fe (III) through its interaction with the sulfonic groups exist on the polymer surface. The effect of the concentration of Nafion used for the modification of the graphite surface was investigated by comparing the response of 0.1, 0.2, 0.5, 1.0 and 2.0% w/v nafion in ethanol-modified SPEs for a certain concentration of iron. Best results were obtained at 0.2 % w/v nafion in water. The effect of the preconcentration time was also investigated. All experiments were conducted at 0.01 M HCl. Under selected conditions and for a preconcentration time of 60 s, a linear response with respect to the concentration of iron was observed over the concentration range from 0.05 to 5 μ M. The detection limit (S/N 3) was found to be 15 nMiron. The developed electrodes were successfully applied to the determination of iron in tap water. The accuracy of the method was evaluated with recovery experiments in spiked samples. Recovery was 95%. Possible interferences from the coexisting ions were investigated. Results suggested that the proposed sensors are sensitive, rapid and reliable and can be successfully applied to the determination of Iron in water samples.

Keywords: Screen Printed Electrodesn,Nafion Chelating Layers, Modified Electrodes, Fe (III), Square Wave Voltammetric Analysis.

Green and Facile Electrode Modification by Spark Discharge: Sn-Screen Printed Electrodes for the Determination of Trace Cd and Zn

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A graphite screen-printed electrode modified with tin nanoparticles (Sn-SPE) through a green, fast and easy-to-perform sparking process (see Figure below) was used for the square-wave, anodic stripping voltammetric determination of trace cadmium (Cd) and zinc (Zn). Experiments were performed in the presence of bromide ions (Br^-), which thanks to the complex formation with Cd(II) enabled to receive well-resolved stripping peaks for cadmium. In the absence of Br^- , the stripping peak of Cd coalesces with that of Sn. Various experimental variables, such as the number of sparking cycles, the energy of the spark, the pH of the electrolyte, the SW parameters, the concentration of bromide ions, the deposition potential and the deposition time were examined and optimized. Particular attention was paid to alleviate the interference of copper in order to allow the application of the developed sensors in real samples. Copper interference on Cd detection was alleviated by the addition of ferrocyanide ions, while on Zn detection by the addition of gallium ions. Under selected conditions, the limits of detection, for a 2 min preconcentration time, were $0.5 \mu\text{g/L}$ Cd and $0.33 \mu\text{g/L}$ Zn. The developed sensor was also successfully applied to the determination of Cd and Zn in tap water and in bottled water samples suggesting that Sn-SPEs represent a new promising type of low-cost, sensitive and environmentally friendly electrodes for the determination of Cd and Zn in the sub-ppm level.



Keywords: Spark Discharge, Tin Electrode, Screen-Printed Electrodes, Trace Metal Analysis, Anodic Stripping Voltammetry

References:

1. D. Riman, D. Jirovsky, J. Hrbac, M.I. Prodromidis, *Electrochem Commun*, (2015) 50 20-23.
2. D. Riman, A. Avgeropoulos, J. Hrbac, M.I. Prodromidis, *Electrochim Acta*, (2015) 165 410-415.

Sensitive Determination of Iron(II) by Gold Electrode Modified with 1,6-Hexanedithiol and 1-Hexanethiol Self-Assembled Monolayers

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The determination of the form of an element in environmental compartments is important for assessment of its biological activity (bioaccumulation, bioconcentration, bioavailability and toxicity) [1,2]. For essential elements like iron, speciation methods are needed because their bioavailability and metabolism are strongly dependent on the species involved. Particularly the iron uptake is influenced by its oxidation state and complexation by inorganic and organic ligands. Techniques used to determine iron in environmental and geological samples include spectrophotometry, voltammetry, and amperometry [3-5].

In this study, the 1,6-hexanedithiol (Au-HDT) and 1-hexanethiol (Au-HT) SAMs modified electrodes (Au-HTs) were prepared keeping the clean gold electrodes in 10mM HT solutions in ethanol for 3 h. Firstly, oxidation of Fe²⁺ at the Au-HTs electrodes surface was investigated by cycle voltammetry (CV). This process happens diffusion-controlled.

Oxidation of Fe²⁺ was investigated using square wave voltammetry (SWV) and 1,6-hexanedithiol/Au (Au-HDT) and 1-hexanethiol/Au (Au-HT) electrodes. Linear working ranges obtained from calibration graphs of iron by using Au-HDT and Au-HT electrodes were 0.05-38.5 µM and 0.1-25.6 µM, respectively; the limit of detection (LOD) were found to be 0.016 and 0.032 µM. Effect of some anions and cations on the response of Au-HTs SAMs to the Fe²⁺ ions was investigated. Additionally, the suggested method was also applied to the determination of Fe²⁺ various real samples such as drinking water and carob syrup samples. Results compared with the values of producing company.

Keywords: Determination of Iron, Self Assembled Monolayer (SAM), 1,6-Hexanedithiol, 1-Hexanethiol

Acknowledgment:

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References:

1. P. T. Lieu, M. Heiskala, P. A. Peterson, Y. Yang, Mol. Aspects Med. (2000) 22 1.
2. J. L. Breda, H. Dawson, D. J. Pifner, Nutr. Rev. (1996) 54 295.
3. T. H. Bothwell, R. W. Charlton, I. D. Cook, C. A. Finch, Iron Metabolism in Man, Blackwell, Oxford (1979) 576.
4. P. R. Dallman, R. Yip, F. A. Oski, in: Iron Deficiency and Related Nutritional Anemias. Hematology of Infancy and Childhood (Eds: D. G. Nathan, F. A. Oski), Saunders, Philadelphia (1993) 413.
5. A. Cotton, G. Wilkinson, The Biochemistry of Iron in Advanced Inorganic Chemistry, 5th ed., Wiley Interscience, New York (1988) 1336.

Preparation of Polycrystalline Gold Electrode Surface with 1,6-Hexanedithiol and 1-Hexanethiol Self Assembled Monolayers and Their Comparative Characterization

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The 1,6-hexanedithiol (Au-HDT) and 1-hexanethiol (Au-HT) SAMs modified electrodes (Au-HTs) were prepared keeping the clean gold electrodes in 10m MHTs solutions in ethanol for 3 h. Au-HDT and Au-HT monolayer surfaces were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), contact angle measurement (CAM), ellipsometry, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

The XPS obtained for HDT and HT adsorbed on Au surface in the S(2p) region. It shows a peak maximum at binding energies of 161.9 and 162.1 eV, respectively. The detection of sulphur element indicated that the HTs molecules were likely to be chemically adsorbed on the Au surface. The sepeaks indicades that HDT and HT molecules hold on toAu suface [1,2]. Au-HDT showed two S(2p)asymmetric peaks. One of them is free SH grup at binding energy of 164.2eV. The other is at binding energy of 161.9eV, indicative of the formation of a covalent S-Au bond. Au-HT showed one S2p peak at binding energy162.1eV. This peak demonstrates the formation of a covalent S-Au bond on Au surface. The presence of one SH peak in Au-HT proves to be the only one SH group.

The electrocatalytic activity of the catalyst were studied by CV and EIS. The EIS data were approximated by appropriate electronic equivalent circuit models from which kinetic parameters, such as faradaic charge transfer resistance (R_{ct}), double layer capacitance, and potential dependent charge transfer rate constant (k_o) were estimated. The extent of Au-HDT and Au-HT surfaces coverage were evaluated as $9.0 \times 10^{-10} \text{ mol cm}^{-2}$ and $9.6 \times 10^{-10} \text{ mol cm}^{-2}$ based on charged consumed for reductive desorption of the monolayer in the 0.5M NaOH solution, respectively.

Keywords: Self Assembled Monolayer (Sam), 1,6-Hexanedithiol, 1-Hexanethiol, Comparative Chacterization.

Acknowledgment:

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References:

1. D.G. Castner, H. Kenneth, W.G. David, *Langmuir*, (1996) 12 (21) 5083-5086.
2. H. Rieley, G.K. Kendall, F.W. Zemicael, T.L. Smith, S. Yang, *Langmuir*, (1998) 14 (18) 5147-5153.

A Novel Poly-Siloxane Based Polymer as Gel Agent for VRLA Batteries

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Valve-Regulated Lead-Acid (VRLA) battery has been one of the most important energy storage devices since it was introduced in the early 1970s [1]. Two main technologies are used to immobilize of sulfuric acid (electrolyte). One of this technology is called as adsorbed glass mat (AGM) and electrolyte is adsorbed in a kind of separator. The other technology is known as GEL-VRLA battery in which the electrolyte is obtained by the mixing electrolyte and gel agent. Fumed silica and colloidal silica are used as gel agent to prepare three dimensional gel structure [2-4]. However poly-siloxane based gel agent can be an alternative to these gel agents [5, 6].

In this study, a novel poly-siloxane gel agent was synthesized and characterized by FT-IR, Zeta meter, SEM and EDX analysis. Poly-siloxane based gel system was prepared and characterized by electrochemical methods (cyclic voltammetry and electrochemical impedance spectroscopy). Optimum concentration of gel agent was determined as 6 wt% of PSGA to form the best gel structure. The mechanical parameters related forming a suitable gel structure was also investigated. Optimum stirring rate and agitation time were determined as 500 rpm and 2.5 hour, respectively.

Keywords: Poly-Siloxane, Gel Agent, VRLA Batteries, Cyclic Voltammetry

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References:

1. D. John, J. Power Sources (1997) 64 153-156.
2. D. W. H. Lambert, P. H. J. Greenwood, M. C. Reed, J. Power Sources, (2002) 107 173-179.
3. R. D. Prengaman, J. Power Sources, 2005, 144, 426-437.
4. M. Gençten, K. B. Dönmez, Y. Şahin, K. Pekmez, E. Suvacı, J. Solid State Electrochem. (2014) 18 2569-2479.
5. Z. Tang, J. Wang, X. Mao, H. Shao, Q. Chen, Z. Xu, J. Zhang, J. Power Sources (2007) 168 49-57.
6. Z. Tang, J. Wang, X. Mao, Q. Chen, C. Shen, J. Zhang, J. Appl. Electrochem. (2007) 37 1163-1169.

The Protective Silicate Film on Positive and Negative Electrodes For Gel-Valve Regulated Lead-Acid Battery

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Valve Regulated Lead-Acid (VRLA) batteries have common use in all around the world due to their lower cost, availability and low temperature performance, either with gel or absorptive glass mat technology.¹ Two different immobilization methods have widespread use on VRLA batteries. These are known as absorptive glass mat (AGM) and gel electrolyte. Gel-VRLA batteries have many advantages when gel and absorptive glass mat technologies compared. Gel-VRLA batteries experience less electrolyte stratification then AGM type VRLA batteries either with partial and deep discharge condition.^{2,3}

In the present work, sodium silicate based corrosion protective film was generated on positive and negative electrodes by aqueous sodium silicate solution. Then electrochemical behaviors of the coated Pb electrodes were investigated in various electrolyte solutions by cyclic voltammetry and electrochemical impedance spectroscopy. Charge-discharge behavior and discharge capacities were obtained by battery tests. Finally, sodium silicate based gelled electrolyte and fumed silica based gelled electrolyte were compared by electrochemical methods and battery tests. Silicate coated electrode surface was characterized by SEM analysis.

Keywords: Cyclic voltammetry, EIS, sodium silicate film, GEL-VRLA

*This work was supported by SAN-TEZ program (Project Code: 00897.STZ.2011-1) of T.C. Ministry of Science, Industry and Technology, with Ericsson Turkey and Anadolu University.

References:

1. J.C. Hern'andez, M.L. Soria, M. Gonz'alez, E. Garc'ia-Quismondo, A. Mu~noz, F. Trinidad Journal of Power Sources (2006) 162 851–863.
2. D.W.H. Lambert, P.H.J. Greenwood, M.C. Reed, Journal of Power Sources (2002) 107 173–179.
3. M. Gençten, K. B. Dönmez, Y. Şahin, K. Pekmez, E. Suvacı, J. Solid State Electrochem. 2014, 18 2569-2479.

Determination of Antimony(III) with Rivastigmine by Adsorptive Stripping Voltammetry on a Glassy Carbon Electrode

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Antimony exists in two common oxidation states, antimony(III) and (V). Sb(III) is generally accepted to be more toxic than Sb(V). Antimony and its compounds are listed as pollutants by the Council of the European Communities and the Environmental Protection Agency of the United States [1,2]. Therefore, sensitive and selective methods for the determination of antimony have attracted considerable attention.

Among the developed methods in the literature, voltammetric methods offer advantages of cost effectiveness, ease and speed of analysis, and high sensitivity. Many voltammetric studies, including stripping methods for determination of antimony, have focused on the modification of the electrode surface or use of a chelating/complexing agent to increase the detection limit. Electrodes based on mercury have been widely used for this purpose [3,4]. However it is not preferred to use due to its toxicity. Recently, the use of environmentally friendly electrodes is preferred to use instead of mercury electrodes [5,6].

A very simple and sensitive adsorptive anodic stripping voltammetric method was developed for Sb(III) determination using rivastigmine (RIV) on a glassy carbon electrode (GCE). RIV is an active pharmaceutical ingredient for the treatment of Alzheimer and Parkinson's disease. In this study, RIV was used as the chemical receptor for the first time. The calibration graph was constructed under the optimized conditions consisted of two linear segments of 5.0×10^{-4} – $0.5 \mu\text{M}$ ($R^2 = 0.9974$) and 0.5 – $2.5 \mu\text{M}$ ($R^2 = 0.9959$). The detection limit for Sb(III) was calculated as 7.1×10^{-11} M Sb(III) for the accumulation time of 120 s. The RSD (n = 5, intra-day) for 1.0×10^{-6} M Sb(III) and 5.0×10^{-7} M Sb(III) were calculated as 1.53% and 2.62%, respectively.

The developed methods were successfully applied to determination of antimony in drinking water, natural spring water (bottled water) and Glucantime[®] ampoules by using the standard addition.

Keywords: Rivastigmine, antimony(III) determination, adsorptive anodic stripping voltammetry, glassy carbon electrode

References:

1. Council of the European Union, (1998) Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Official J. L330, 32.
2. United States Environmental Protection Agency, (1999) National Primary Drinking Water Standards, USEPA Office of Water, Washington, DC, USA, Doc. 810-F-94-001.
3. Rojas-Romo, C., Arancibia, V., *Electroanalysis* (2015) 27 1262-1267.
4. El-Shahawi, M.S., Bashammakh, A.S., Al-Sibaai, A.A., Bahaffi, S.O., Al-Gohani, E.H., *Electroanalysis* (2011) 23 747-754.
5. Rojas-Romo, C., Serrano, N., Ariño, C., Arancibia, V., Díaz-Cruz, J.M., Esteban M., *Talanta* (2016) 155 21-27.
6. Su, J., Zhong, S., Li, X., Zou, H., *Journal of The Electrochemical Society*, (2014) 161 512-516.

Flow Injection Analysis of Sulfide at Calmagite (CLM) Modified Pencil Graphite Electrode

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Sulfide species have many toxic effects to environment and living organisms. Sulfide species are largely found in industrial waste waters. It gives great attention in many fields like analytical chemistry, environmental chemistry, food science, and quality control. Also gas form of the sulfide (H_2S) has negative effects on human health and the other living organisms. Therefore, fast, sensitive and selective determination of sulfide species or total sulfide in lake, river and industrial waste waters has gained a big importance for analytical and environmental chemists [1]. Several methods are available to measure sulfide and its species in aqueous medium. Among these methods, the electrochemical techniques have some advantages such as easy application, low cost, providing direct, sensitive and fast detection of lower concentrations of H_2S [1, 2].

Recently, modified electrodes have been prepared from various organic mediators for the electrocatalytic oxidation of sulfide. One of the important redox mediators is Calmagite [3]. However it has not been used for the electrocatalytic oxidation of sulfide. In this study, a new modified electrode has been proposed for electrocatalytic oxidation and determination of sulfide. For this, a Calmagite modified pencil graphite electrode (PGE) was prepared by electropolymerization of calmagite using cyclic voltammetry (CV). Electropolymerization parameters (monomer concentration, pH, scan rate, cycle number) were optimized. Cyclic voltammograms of bare PGE and modified PGE were recorded in the absence and presence of sulfide in Britton Robinson Buffer solution (pH 9.0) at scan rate of 20 mV/s. Cyclic voltammetric studies show that the peak potential of sulfide oxidation shifts from +400 mV at bare PGE to +200 mV vs. Ag/AgCl /KCl (sat) at modified PGE. This result showed that Calmagite modified PGE exhibit a good electrocatalytic activity towards oxidation of sulfide. Then, a homemade electrochemical flow cell was used to perform the electrocatalytic determination of sulfide in Flow Injection Analysis (FIA) system. The electrocatalytic currents obtained from amperometric measurements in FIA at +250 mV vs. Ag/AgCl /KCl (1.0 M) and at pH 9.0 BRBS containing 1.0 M KCl were linearly related to the concentration of sulfide. As a result, the development of a simple and highly sensitive electrochemical detection of sulfide based on a new modified electrode, Calmagite modified PGE, was described for the first time in FIA system using new home made electrochemical flow cell.

This work supported from TUBİTAK (115Z235).

Keywords: Sulfide, Redox Mediator, Calmagite, Pencil Graphite Electrode, Flow Injection Analysis.

References:

1. N. S. Lawrence, J. Davis, R. G. Compton, Talanta (2000) 52 771-784
2. Y. Dilgin, B. Kızılkaya, B. Ertek, F. Işık, D. G. Dilgin Sensors and Actuators B: Chemical (2012) 171 223-229
3. U. Chandra, K. Swamy, O. Gilbert, B. S. Sherigara, Electrochimica Acta (2010) 55 7166-7174

Electrocatalytic Oxidation of Hydrazine in Flow Injection Analysis System using Pyrocatechol Violet (PCV) Modified Pencil Graphite Electrode

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Hydrazine (N₂H₄) is a toxic substance. Also it is known with its carcinogenic, neurotoxin and mutagenic effects to living organisms and environment [1]. Hydrazine is widely used in industry and agriculture as a reactant in fuel cells, a corrosion inhibitor in boilers, a rocket propellant, an antioxidant, a catalyst and a pesticide [1, 2, 3]. Because of its all properties, sensitive, selective, fast determination of hydrazine has a critical importance in many fields like environmental science and chemistry. Redox mediators are significant molecules in electrochemistry because they transfer electrons between substrate and electrode surface. From these mediators, organic dyes have been widely used in preparing modified electrodes for high catalytic activity to many molecules. Among organic dyes, Pyrocatechol violet (PCV) which contains hydroxyl groups bonded to carbon atoms of the aromatic ring have also been used as a redox mediator for electrocatalytic oxidation of some compounds [4].

In this work, electrocatalytic oxidation of hydrazine has been described using PCV modified pencil graphite electrode (PGE) for the first time. Modified PGE was prepared through immersion of PGE into 10⁻² M PVC solution in water for 10 min. Cyclic voltammograms of bare PGE and modified PGE were recorded in the absence and presence of hydrazine in Britton Robinson Buffer solution (pH 9.0) at scan rate of 20 mV/s. Cyclic voltammetric studies show that the peak potential of hydrazine oxidation shifts from +600 mV at bare PGE to +200 mV vs. Ag/AgCl /KCl (sat) at PVC/PGE. This result showed that PVC modified PGE exhibit a good electrocatalytic activity towards oxidation of hydrazine. Then, a homemade flow cell, which was constructed from Teflon for PGE for the first time, was used to perform the electrocatalytic determination of hydrazine in Flow Injection Analysis (FIA) system. The electrocatalytic currents obtained from amperometric measurements in FIA at +100 mV vs. Ag/AgCl /KCl (1.0 M) and at pH 9.0 BRBS containing 1.0 M KCl were linearly related to the concentration of hydrazine. As a result, the development of a simple and highly sensitive electrochemical Hydrazine sensor based on a new modified electrode, PVC modified PGE, was described for the first time in FIA system using new home made electrochemical flow cell.

Keywords: Hydrazine, Pyrocatechol Violet, Pencil Graphite Electrode, Flow Injection Analysis.

The authors are grateful to TUBİTAK (Project Number: 115Z235) for financial support.

References:

1. S.M. Golabi, H.R. Zare, J. Electroanal.Chem. (1999) 465 168-176.
2. K. Yamada, K. Yasuda, N. Fujiwara, Z. Siroma, H. Tanaka, Y. Miyazaki T. Kobayashi , Electrochem. Commun. (2003) 5 892-896.
3. E.R. Riegel, Richel's Handbook of Industrial Chemistry (1992), Kluwer Academic/Plenum, New York, (2003).
4. Jun Zhu, Xiao-Yan Wu, Dan Shan, Pei-Xin Yuan, Xue-Ji Zhang, Talanta (2014) 130 96-102.

Palladium/ Electrochemical Reduced Graphene Oxide (Pd-ERGO) Nanocomposite Electrocatalysts for Alcohol Electro-oxidation and Biosensor Applications

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Future energy concerns demand a transition from fossil fuels to new energy sources that are more environmentally benign and renewable. Direct alcohol fuel cells (DAFCs) are considered an attractive power source with potential applications due to their ease of handling, high energy density, and low operation temperatures [1]. Due to its high conductivity, huge theoretical surface area, unique graphitized basal plane structure, efficient electrocatalytic activity, good stability and potentially low manufacturing costs, graphene and graphene-based metal nanocomposite electrocatalysts have been widely used as anode and cathode electrocatalysts in DAFCs for the respective methanol oxidation and oxygen reduction reactions [2]. Graphene exhibits excellent electron transfer promoting ability for some enzymes and excellent catalytic behavior toward small biomolecules such as H₂O₂, dopamine, ascorbic acid and glucose. In this study, we used a simple electrochemical method to fabricate the palladium-electrochemical reduced graphene oxide (Pd-ERGO) layered nanocomposites by electrochemical reduction of graphene oxide and Pd on Au(111) electrode. Then Pd-ERGO electrode used as electrocatalyst for alcohol electro-oxidation and biosensors. Pd-ERGO composite modified Au electrode exhibited lower oxidation potential than naked Au electrode (Figure 1). Results show that Pd-ERGO hybrid has potential application as a heterogeneous catalyst support in alcohol electro-oxidation and biosensors.

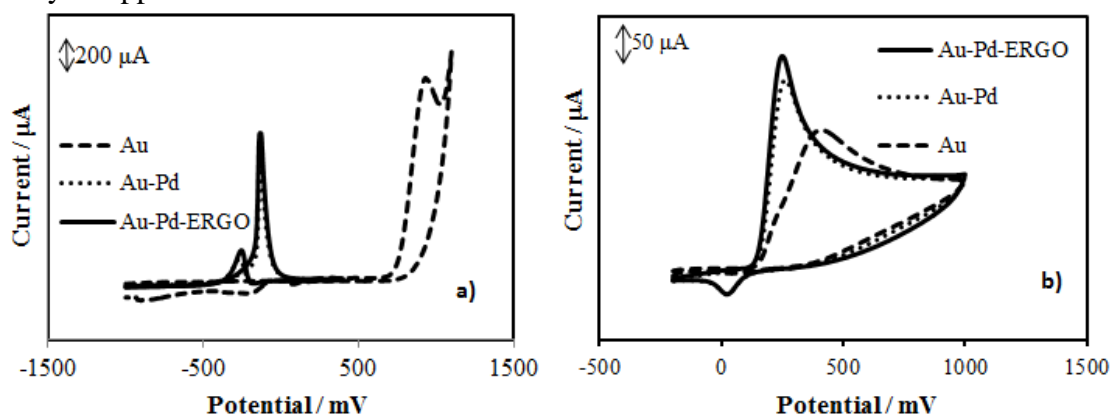


Figure 1. Cyclic voltammogram of Pd-ERGO nanocomposite modified Au electrode in solutions containing a) 1 M methanol b) 10 mM dopamine.

Keywords: Graphene Nanocomposite, Palladium, Electrochemical Reduction, Ethanol, Biosensor.

References:

1. Hu Y., Zhang H., Wu P., Zhang H., Zhou B., Cai C., Phys. Chem. Chem. Phys. (2011) 13 4083–4094.
2. Qiu J., Wang G., Liang R., Xia X., Yu H., J. Phys. Chem. C, (2011) 115 15639–15645.

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Ni/Electrochemical Reduced Graphene Oxide (Ni-ERGO) Nanocomposite Electrocatalysts for Direct Alcohol Electrooxidation

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The electrochemical oxidation of alcohols is an important process with regard to direct alcohol fuel cells, alcohol sensing, and the electrochemical conversion of alcohols to aldehydes and ketones. Many electrocatalysts have been employed to oxidize alcohol, however, the highest electrocatalytic activity is gained at Pt and Pt-based alloys [1]. The strong adsorption of carbon monoxide on Pt tends to slow down the kinetics of methanol oxidation reaction, in addition to the high cost of precious Pt metal as a catalyst. As an alternative to Pt metal, recently as catalyst for alcohol oxidation reaction have been studied relatively less expensive noble metals such as Pd, Cu, Ni, etc. As catalysis is a surface effect, the catalyst needs to have the highest possible surface area. Therefore, carbon-supported electrodes are generally used as catalyst, such as graphene, glassy carbon, graphite electrodes [2]. In the present work, Ni-electrochemical reduced graphene oxide (ERGO) nanocomposite was synthesized on gold electrode surface by electrochemical method and then used for the electrochemical oxidation of methanol and ethanol in 1 M NaOH. This prepared Ni-ERGO nanocatalysts were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDX). The SEM image of Ni-ERGO nanocomposite was shown in Figure 1.

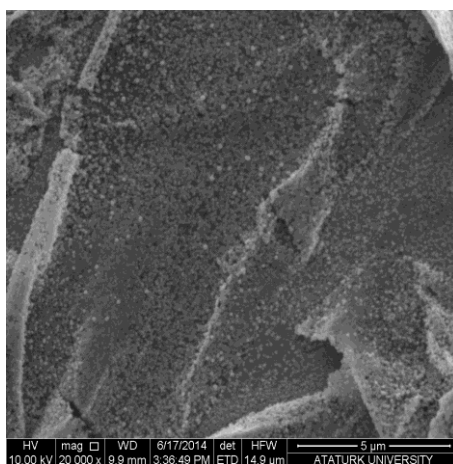


Figure 1. The SEM image of Ni-ERGO nanocomposite.

Keywords: Graphene Nanocomposite, Palladium, Electrochemical Reduction, Ethanol, Biosensor.

References:

1. Wen, Z. H.; Liu, J.; Li, J. H., *Adv. Mater.*, (2008) 20 743–747.
2. Gao L., Yue W., Tao S., Fan L., *Langmuir*, (2013) 29 957–964.

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Preparation and Characterization of Carbon Nanotubes/Conducting Polymer Nanocomposites Coated Surfaces

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Nanostructured materials including carbon nanotubes, graphene, nanoparticles, nanowires and nanostructured polymers are widely used in biological, pharmaceutical, clinical, forensic, food safety, energy storage and environmental applications due to their good chemical, mechanical, electrical, structural, optical and thermal properties [1-3]. In this study, preparation of single-walled carbon nanotubes/conducting polymer nanocomposites coated electrodes were carried out using cyclic voltammetry (CV) and constant-potential electrolysis. For the electropolymerization process, pyrrole and 3,4-ethylenedioxythiophene monomers were used. Thus, single-walled carbon nanotubes/polypyrrole and single-walled carbon nanotubes/poly(3,4-ethylenedioxythiophene) coated gold electrode (AuE), platinum electrode (PtE) and glassy carbon electrode (GCE) were obtained during the study. The electrochemical behaviors of the coated surfaces were examined with cyclic voltammetry and electrochemical impedance spectroscopy (EIS). Various cyclic scans and electropolymerization times were used in order to investigate the changes in the electrochemical behaviors of the coated electrodes. We believe that the coated electrodes later on can be used for different applications such as biosensing applications.

Keywords: Electrochemistry, Electropolymerization, Conducting Polymers, Carbon Nanotubes

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References:

1. M. Pumera The Chemical Record (2009) 9 211-223.
2. [B. Pérez-López](#), [A. Merkoçi](#) Microchimica Acta (2012) 179 1-16.
3. F. Kuralay, A. Erdem Analyst (2015) 140 2876-2880.

Detection of Mitomycin C-DNA Interaction with Carbon Nanotubes/Polymer Modified Electrodes

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Interaction of anticancer drugs with DNA is an important topic for understanding the nature of binding mechanism of these drugs to DNA and for studies in drug discovery and pharmaceutical development processes [1,2]. Mitomycin C is a widely used chemotherapeutic agent which is generally effective for upper gastro-intestinal, breast and anal cancers [3]. In this study, we have prepared a sensing platform for Mitomycin C-DNA interaction based on single-walled carbon nanotubes/poly(3,4-ethylenedioxythiophene) nanocomposite modified disposable pencil graphite electrode. The interaction between Mitomycin C and DNA on the prepared electrode was investigated using differential pulse voltammetry (DPV). The performance of the electrodes prepared in the presence and absence of carbon nanotubes was compared and discussed. The changes in the peak currents of guanine and adenine were used as the indicators of drug-DNA interactions.

Keywords: Electrochemistry, Conducting Polymers, Carbon Nanotubes, Mitomycin C, DNA, DNA-Anticancer Drug Interaction

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References:

1. S. Rauf, J.J. Gooding, K. Akhtar, M.A. Ghauri, M. Rahman, M.A. Anwar, A.M. Khalid J. Phar. Biomed. Anal. (2005) 37 205-217.
2. E. Canavar, F. Kuralay, A. Erdem, Electroanal. (2011) 23 2343-2349.
3. F. Kuralay, A. Erdem Analyst (2015) 140 2876-2880.

Electrooxidation of Poly(vinylferrocene) In the Presence of Acetaminophen

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Acetaminophen is a pain killer and fever reducer. It is generally used to treat headache, backache, muscle aches, toothaches, colds and fevers. Thus, it is an attractive alternative drug for people who are sensitive to aspirin [1]. Conducting polymers are widely used materials with various applications. they are permeable to electroactive species, they can be easily- modified by various methods, they are efficient coatings for many surfaces. These polymers have high conductivities, porous structures and high surface areas [2,3]. The aim of this work is to investigate electrooxidation of poly(vinylferrocene) on platinum (Pt) electrode, gold (Au) electrode and glassy carbon electrode (GCE) in the presence of drug molecule, acetaminophen. Two different polymerization techniques were studied for a polymerization solution containing poly(vinylferrocene), tetrabutylammonium perchlorate and acetaminophen: constant-potential electrolysis and cyclic voltammetry. The electrochemical behavior of the oxidized form of the polymer (poly(vinylferrocenium)) modified electrodes were investigated in phosphate buffer solution containing NaCl. The electrochemical behavior of the electrodes prepared in the presence and absence of acetaminophen were compared and discussed.. The prepared electrode could be very helpful in future biomedical applications such as drug delivery.

Keywords: Electrochemistry, Conducting Polymers, Poly(vinylferrocenium), Acetaminophen

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References:

1. M. Zhou, N. Zhou, F. Kuralay, J.R. Windmiller, S. Parkhomovsky, G. Valdés-Ramírez, E. Katz, J. Wang *Angew. Chem. Int. Ed.* (2012) 51 2686-2689.
2. F. Kuralay, H. Özyörük, A. Yıldız *Sensors and Actuators B: Chemical* (2006) 114 5000-506.
3. M.R. Abidian, D.-H. Kim, D.C. Martin *Advanced Materials* (2006) 18 405-409.

Poly(3,4-ethylenedioxythiophene) Surfaces for Controlled Drug Release

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The application of polymeric substances widely increased in recent years since they exhibit similar properties to the natural biological systems. Among various polymeric materials, conducting polymers are of quite importance for the development of drug release/delivery systems [1-3]. The aim of this work is to prepare poly(3,4-ethylenedioxythiophene) (PEDOT) coated surfaces in the presence of anticancer drug, Mitomycin C and to investigate the release behavior of the drug using electrical stimuli. Electropolymerization of 3,4-ethylenedioxythiophene was performed in the presence of Mitomycin C using cyclic voltammetry and constant-potential electrolysis. The controlled release behavior of the drug from the polymeric structure was achieved applying -0.2 V vs. Ag/AgCl to the system. Characterization of the polymer coated surfaces was performed with cyclic voltammetry (CV).

Keywords: Electrochemistry, Conducting Polymers, Poly(3,4-ethylenedioxythiophene), Mitomycin C Controlled Drug Release

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References:

1. M.R. Abidian, D.-H. Kim, D.C. Martin *Advanced Materials* (2006) 18 405-409.
2. D. Svirakis, J. Travas-Sejdic, A. Rodgers, S. Garg *Journal of Controlled Release* (2010) 17 6-15.
3. X. Luo, X.T. Cui *Electrochemistry Communications* (2009) 11 1956-1959.

DNA Damage Detection using Carbon Nanotubes Modified Electrodes

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Deoxyribonucleic acid (DNA) is the largest, welldefined and the most important molecule of life. DNA damage results in critical disturbances of the cell life. Damage to the DNA can cause serious negative effects on human's health. Thus, there is a considerable interest in the development of highly sensitive and accurate sensing platforms for the detection of DNA damage [1,2]. Electrochemical techniques are well suited for rapid and direct detection of DNA damage since DNA bases are electroactive. In addition, electrochemistry have attracted great attention for the construction of sensitive, selective, low-cost, rapid and simple sensing platforms [3,4]. In this work, we present a single-walled carbon nanotubes modified disposable pencil graphite electrode for the detection of DNA damage. DNA damage was investigated in the presence and absence of Fenton reagents ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) according to the changes in the oxidation signals of DNA bases (Guanine and Adenine). Electrochemical detection of the damage was carried out with differential pulse voltammetry (DPV).

Keywords: DNA, DNA Damage, Electrochemistry, Carbon Nanotubes

Acknowledgments: F. Kuralay acknowledges Turkish Academy of Sciences (TÜBA) as an associate member and TÜBA-GEBİP programme.

References:

1. M. Fojta *Electroanalysis* (2002) 14 1449-1463.
2. E. Palecek, M. Fojta *Analytical Chemistry* (2001) 73 74A-83A.
3. F. Kuralay, A. Erdem *Analyst* (2015) 140 2876-2880.
4. F. Kuralay, S. Campuzano, J. Wang *Talanta* (2012) 99 155-160.

Probing The Effect of Antioxidants on DNA Damage

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The reactive oxygen species produced in cells include hydrogen peroxide (H_2O_2) and free radicals such as the hydroxyl radical ($\cdot\text{OH}$) and the superoxide anion (O_2^-). The hydroxyl radical is particularly unstable and reacts rapidly with most biological molecules. This species is produced from hydrogen peroxide in metal catalyzed redox reactions such as the Fenton reaction. These oxidants can induce cells damage by starting chemical chain reactions by oxidizing DNA [1,2]. This damage to DNA can cause mutations and possibly cancer. Researches have been confirmed that antioxidant molecules can inhibit this DNA damage [3]. In the present work, we investigate the effect of ascorbic acid and uric acid on the DNA damage, produced by Fenton reagents ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$). A single-walled carbon nanotubes modified disposable pencil graphite electrode was used for the construction of the biosensing platform for the investigation of the effect of antioxidants on DNA damage. Electrochemical detection of the effect of antioxidants was carried out with differential pulse voltammetry (DPV) using different concentrations of ascorbic acid and uric acid. It was found that the studied molecules are able to inhibit the DNA damage. The effect of different interaction times of antioxidants on the inhibition of DNA damage was also examined in the present study.

Keywords: DNA damage, Antioxidants, Electrochemistry, Carbon Nanotubes

References:

1. A. Sancar *Chemical Reviews* (2003) 103 2203-2238.
2. K. [Cahová-Kuchařiková](#)-, [M. Fojta](#), T. [Mozga](#), E. Palecek *Analytical Chemistry* (2005) 77 2920-2927.
3. M. Fojta *Electroanalysis* (2002) 14 1449-1463.

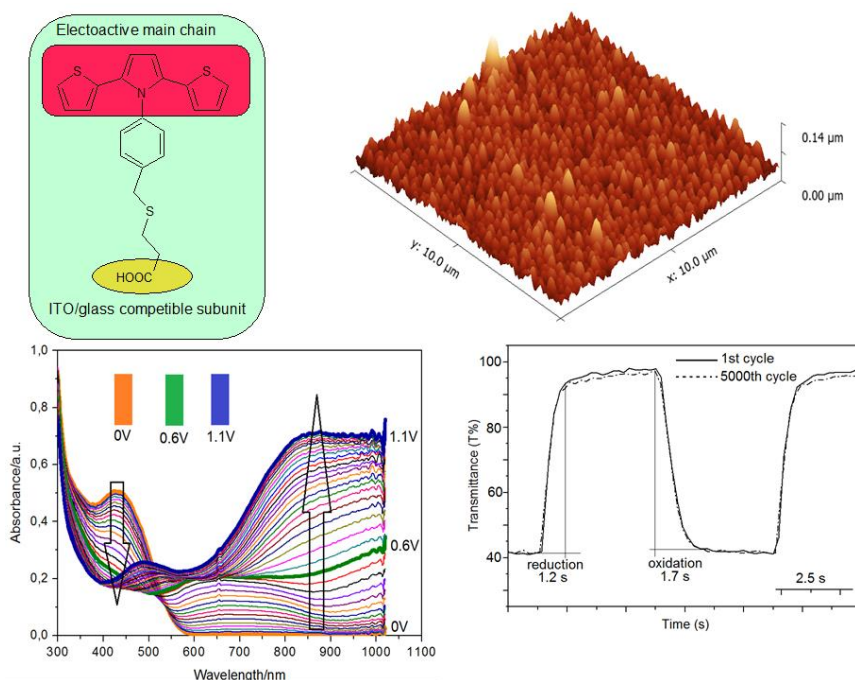
A New Side Group Functionalized Electroactive Polymer and Its Electrochromic Application

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Electrochromics are materials that can induce a reversible change in the absorption, reflection, or transmission of optical radiation when the material is involved in an electrochemical reductive or oxidative process in the visible, ultraviolet (UV), infrared (IR), and also microwave regimes of the electromagnetic spectrum. [1]. Long term stability problem is the most important factor in front of the commercialization of electrochromic material [2,3]. To overcome of this problem, ITO/glass surface compatible electrochromic materials are important.



In this work, we synthesized a 2,5-dithienyl-1H-pyrrole based monomer containing allyl subunit (EA1) and then this allyl subunit have functionalized with carboxyl groups which will be compatible with ITO / glass surface. After that, synthesized monomer directly polymerized on to ITO/glass surface via electrochemical process. AFM images reveal that electrochemically deposited **poly-EA-a** has a self-organized surface due to ITO compatible-COOH subunit. The results clearly indicate that ITO/glass compatible side chain has a major impact on electrochromic performance of the polymer. Poly-EA1 with ITO/glass compatible side chain exhibits a high contrast ratio ($\Delta T\% = 58\%$ at 850 nm), a response time of about 1.5 s, high coloration efficiency ($382 \text{ cm}^2 \text{ C}^{-1}$) and retained its performance by 98.3% even after 5000 cycles.

References:

1. C.G. Granqvist, Progress in electrochromics: tungsten oxide revisited, *Electrochim. Acta* (1999) 44 3005–3015.
2. Mortimer R. J., *Electrochromic materials*, Chemical Society Reviews (1997) 26 147–156.
3. Rosseinsky D. R., Mortimer R. J., *Electrochromic systems and the prospects for devices*, *Advanced Materials* (2001) 13 783–793.

A New Highly Stable Electrochromic Material from 2,5-Di-(2-Thienyl)-1H-Pyrrole (SNS) Polymer Based on Schiff Base-Metal Complexes

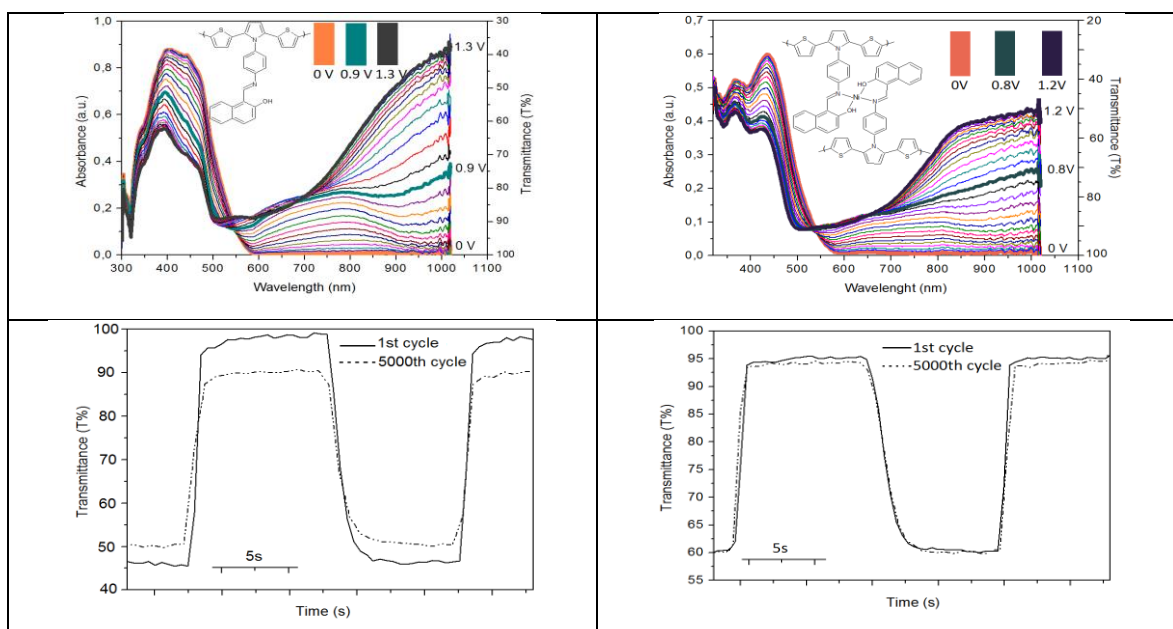
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Imine or Schiff Base polymers containing $-\text{CH}=\text{N}-$ bound have been used in optoelectronic materials such as light emitting diodes, thin film transistors, electrochromic devices and photovoltaic cells [1]. Owing to the preparation of Schiff base-metal complexes on the polymer structure, the materials gain some useful properties. Schiff base-metal complexes have important roles both in chemistry as intermediates of many enzymatic reactions, and applications in chemistry and biology [2]. On the other hand, 2,5-di-(2-thienyl)-1H-pyrrole (SNS) derivatives have outstanding properties for electrochromic applications. Moreover, the attachment of another electroactive or a photoactive moiety into SNS backbone can provide the band gap tunability and valuable properties.



In this work, A new 2,5-di-(2-thienyl)-1H-pyrrole (SNS) moiety containing naphthalene based imine side chain (GL-1) and its Ni complex (GL-2) has been synthesized for an electroactive monomers and then directly deposited onto ITO/glass surface via electrochemical polymerization process. Thin films of the GL-1 and GL-2 polymers electrodeposited onto transparent electrode showed ambipolar multi-electrochromic behavior in anodic regime between 0-1.3 V. We further demonstrated that the electrochromic switching stability can be improved after attaching the Ni^{+2} metal ion on the Schiff Base metal complex structure. Besides, GL-2 polymer film has a reasonable contrast ratio ($\Delta T = 35\%$ at 950 nm), a fast response (0.8 s), high coloration efficiency ($216 \text{ cm}^2 \text{ C}^{-1}$) and retained its performance over 98% even after 5000 cycles.

References:

1. C.J. Yang, S.A. Jenekhe, *Conjugated Aromatic Polyimines. 2. Synthesis, Structure, and Properties of New Aromatic Polyazomethines*, *Macromolecules*, (1995) 28 1180-1196.
2. T. Kaliyappan, S. Rajagopan, P. Kannan, *New Polymeric Schiff Base and Its Metal Complexes*, *Journal of Applied Polymer Science*, (2004) 91 494–500.
3. P.E. Just, K.I. Chane-Ching, P.C. Lacaze, *Synthesis of 2,5-di(2-thienyl)-1H-pyrrole N-linked with conjugated bridges*, *Tetrahedron*, (2002) 58 3467–3472.

Application of Bipolar Membrane Electrodialysis (BMED) for Separation of Lithium and Boron from Aqueous Solution

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Electrodialysis (ED) is an electromembrane separation process in which ions are separated, concentrated and purified from aqueous feed solutions under the influence of the applied electrical potential gradient as a driving force. The ED process in combination with bipolar membranes (BMED) was developed to split an aqueous saline solution into its corresponding acid and base without addition of any chemicals. In this study, BMED was applied to a solution containing both lithium and boron. The effects of electrical potential applied and initial compositions of acid base compartments were investigated. Lithium was separated and recovered as LiOH while boron as B(OH)₃ (Figure 1). According to the results obtained, the efficiencies of separation and recovery for lithium and boron increased with increasing the electrical potential applied. However, after the maximum optimum voltage, no improvement in process performance was observed. The performance of BMED system was also influenced by the initial compositions of acid and base compartments. Thus, it was concluded that BMED is a successful electromembrane process for separation of boron and lithium simultaneously and their recovery from a mixture.

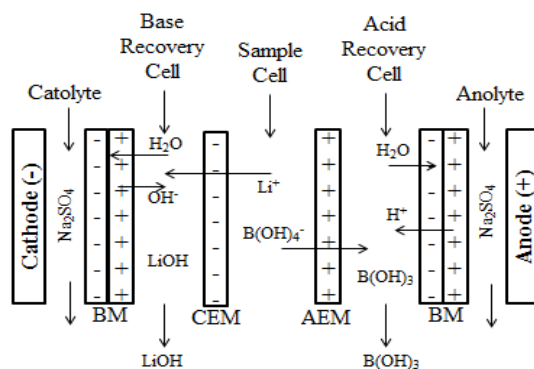


Figure 1: Flow sheet for separation and recovery of boron and lithium

Keywords: Bipolar Membrane Electrodialysis (BMED), Boron, Lithium, Separation, Recovery

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References:

1. Bazinet, L., Lamarchey, F., and Ippersiel D., Trends in Food Science & Technology (1998) 9 107-113.
2. Mani, K.N., J. Membrane Sci. (1991) 58 117-138.
3. Hiroki, N., Atsushi, I., Akihiro, Y. and Yukio, Y., Ind. Eng. Chem. Res. (2011) 50 6325-6330.
4. Parsa, N., Moheb, A., Mehrabani-Zeinabad, A. and Masigol, M. A, Chemical Engineering Research and Design (2015) 98 81-88.

Development of an SPE-UPLC-MS/MS Method for the Determination of 13 Cytostatics in Water

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Anticancer drugs are classed into various categories, mainly including cytotoxic, cytostatic and hormonally active compounds. Cytostatics may present secondary side effects and considerable health risks mainly cytotoxic, genotoxic (mutagenic), carcinogenic, embryotoxic and/or teratogenic effects. Cytostatics and their human metabolites enter the environment through discharge of untreated or partly degraded wastewater/hospital effluents, eventually reaching surface or groundwater resources.

In this study, a fast, sensitive and robust analytical method was developed and optimized, for the simultaneous determination of 13 cytostatics (5-fluorouracil, methotrexate, paclitaxel, irinotecan, doxorubicin, epirubicin, etoposide, oxaliplatin, temozolomide, capecitabine, gemcitabine, cyclophosphamide and docetaxel) with various physicochemical properties, in aqueous matrix, using LC-ESI-MS/MS. Chromatographic separation was performed on an Acquity UPLC BEH C18 column (2.1mm * 100mm, 1.7µm) by Waters maintained at 30 °C. The mobile phase composition consisted of binary mixtures with 0.1% of formic acid in ultrapure water (A) and 0.1% formic acid in methanol (B) using a gradient elution. Identification was achieved with a triple quadrupole detector (TqDetector, Acquity Waters, USA). MS operating parameters (ESI mode) were selected for optimum and unambiguous identification of analytes, using multiple reaction monitoring (MRM) mode. For isolation and preconcentration of the selected compounds, several SPE materials (PCX, C18, graphitized carbon and HLB) were tested in an off-line solid-phase extraction assembly.

The two optimum selected ion transitions as well as the retention time for each compound are given as follows: 5-fluorouracil (negative mode) 129>42, 86; 1.3 min, gemcitabine 264>122, 95; 1.6 min, temozolomide 195>138; 2.3 min, methotrexate 455>308, 175; 6.1 min, cyclophosphamide 261>140, 106; 8.8min, irinotecan 587>124, 167; 9.2 min, etoposide 589>229, 185; 9.9 min, doxorubicin 544>130, 361; 10.6 min, capecitabine 360>224, 174; 10.7 min, epirubicin 544>361, 397; 10.8 min, paclitaxel 854>105, 286; 13.4min, docetaxel 808>226, 282; 13.8 min, oxaliplatin 396>134, 162; 18.7 min.

The efficiency of the extraction process was tested using different cartridge materials, sample volume, pH of initial sample and different elution solvents. HLB cartridges have achieved increased recoveries for methotrexate (84%), etoposide (83%) and oxaliplatin (82%) at pH 5, whereas C18 cartridges for capecitabine (81%) and docetaxel (91%) at the same pH. Graphitized carbon cartridges were efficient for gemcitabine (78%) and cyclophosphamide (82%) at pH 3, while PCX cartridges were proven suitable for methotrexate (95%) at pH 5. The next step is the development of a combined extraction process for the simultaneous analysis of 13 cytostatics in drinking and surface waters using different SPE material and the application in real samples.

Keywords: LC-MS/MS, SPE, Cytostatics, Pharmaceuticals

References:

1. Noelia Negreira, Miren López de Alda, Damió Barcelo, Journal of Chromatography A, (2013) 1280 64–74.

N-Glycan Analysis of Human Placental Alkaline Phosphatase (PLAP) by HILIC-FT-MS

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Alkaline phosphatase (AP) is a membrane-bound glycoprotein that is widely distributed in the plasma membrane of cells of various organs and also found in many organisms from bacteria to humans¹. The complete amino acid sequence and three-dimensional structure of human placenta alkaline phosphatase has been reported. Based on the literature data, this protein contains two putative glycosylation sites, at A sn-144 and A sn-271². However, it only contains a single occupied *N*-linked glycosylation site and no occupied *O*-linked glycosylation sites. Glycosylation is one of the most important and most complex post translational modifications (PTMs) of proteins and plays a significant role in many biological processes, including protein stability, cellular adhesion, signaling and most importantly diseases. More than half of the human proteins are glycosylated and their function depends on particular glycoforms. *N*-linked glycans are complicated by their monosaccharide compositions, branching and glycosidic linkages. They can be divided into three main groups based on their monosaccharide composition and branching: 1) highmannose, 2) complex; and 3) hybrid types. Mass spectrometry (MS) combined with a variety of separation techniques such as capillary electrophoresis (CE), liquid chromatography (LC), and hydrophilic interaction chromatography (HILIC) has been widely employed for the characterization of the glycan structures derived from glycoproteins³. HILIC is widely used for the analysis of glycans from glycoproteins. In this chapter, we investigated *N*-glycan structures from human placenta alkaline phosphatase (PLAP). First, we used in-gel tryptic digestion of PLAP to determine the glycosylation site within the peptide sequence of the glycoprotein. Second, *N*-linked glycans were released and purified from PLAP glycoprotein by in-gel PNGase F digestion. Third, purified *N*-glycans were analyzed by HILIC-ESI-FT-MS to determine the structures and finally, the PLAP *N*-glycans were identified by data processing and glycan assignment software based on their mass composition and established biological rules.

Keywords: Glycosylation, HILIC, Mass Spectrometry, *N*-linked glycans

References:

1. Endo, T., Ohbayashi, H., Hayashi, Y. *et al.* Journal of Biochemistry, (1988) 103 182-187.
2. Millan, J.L. Purinergic Signaling, (2006) 2 335-341.
3. North, S.J., Hitchen, P.G. *et al.* Current Opinion in Structural Biology, (2009) 19 498-506.

Application of Simulated Annealing Support Vector Machine as a Novel Chemometrics Tool to Support Non-target Screening in liquid Chromatography High Resolution Mass Spectrometry

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Liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS) has been used widely due to its high sensitivity, selectivity and accuracy for identification purposes. One of the bottlenecks in non-target analysis of any sample by LC-HRMS is the identification of suspected and unknown compounds with high confidence. Mass accuracy and isotopic pattern of the precursor ions, MS/MS spectra interpretation and retention time (t_R) information are needed to reach a high level of identification confidence. However, the identification procedure through non-target workflow requires of great effort and can be time consuming due to existence of false positive and less important features. For that purpose, we have developed an algorithm to rank the importance of features and decrease the number of features (MZ). Simulated Annealing (SA) [1] starts to rank the features, generated by peak picking algorithms, such as XCMS or MZ mine, based on their contributions on overall accuracy of increasing the net similarities between the samples. The net similarity function can be then coupled to either supervised or unsupervised techniques to derive the important MZ and map their effects on grouping of similar samples. Support Vector Machine (SVM) has been widely used to study the correlation of certain number of features with related properties [2], but have not been applied so far in non-target screening workflow. In this contribution, we successfully coupled a features selection algorithm with SVM to distinguish between most and least important features to enhance the identification procedure. For a case study, the proposed method was successfully applied in real olive oil samples for the identification of markers responsible for sensory profile. Out of 771 features, created using XCMS, 11 features found to be the most important compounds that can be used to differentiate extra virgin olive oil from defective oils.

Keywords: Chemometrics, Simulated Annealing, Non-Target, LC-HRMS, Olive Oil

References:

1. Kirkpatrick S, Gelatt CD, Vecchi MP Science (1983) 220 671-680.
2. Thissen U, Üstün B, Melssen WJ, Buydens LMC, Analytical Chemistry (2004) 76 3099–3105.

Development of Target, Suspect and Non-Target High Resolution Mass Spectrometry Screening Strategies Coupled with Advanced Chemometric Tools for the Evaluation of Extra Virgin Olive Oil's Sensory Profile

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Currently, there is emerging concern for the substantiation of olive oil's authenticity, due to its economic importance, no less than it is considered a prime component due to its nutritional, sensory and therapeutic properties [1, 2]. In this respect, an RP-UHPLC-ESI-QTOFMS analytical method was developed employing target, suspect and non-target screening strategies coupled to advanced chemometric tools for the investigation of authenticity of extra virgin olive oil (EVOO). The proposed method was successfully applied in real olive oil samples for the identification of markers responsible for its sensory profile. The proposed target analytical method includes the determination of 14 phenolic compounds and demonstrated low limits of detection (LODs) over the range of 0.015 (apigenin) - 0.039 (vanillin) $\mu\text{g mL}^{-1}$ and adequate recoveries (96-107%). A suspect list of 60 relevant compounds was compiled and suspect screening was then applied to all the samples. Semi-quantitation of the suspect compounds was performed using the calibration curves of the target compounds having similar structures. Then, a non-target screening workflow was applied with the aim to identify additional compounds, responsible to differentiate EVOOs from defective oils. Robust classification-based models were built using supervised discrimination techniques, PLS-DA and CP-ANNs, for the classification of olive oils into EVOOs or defectives. Variance in Projection (VIP) was calculated to select the most significant features that affect the discrimination. Overall, 51 compounds were identified and suggested as markers. 14, 26 and 11 compounds were identified using target, suspect and non-target screening, respectively.

Keywords: Authenticity, Olive Oil, Non-Target Analysis, Chemometrics, Markers

References:

1. Sánchez de Medina V, Priego-Capote F, de Castro MDL Talanta (2015) 132 424-432.
2. Ballus CA, Quirantes-Piné R, Bakhouché A, de Oliveira da Silva LF, Coutinho EF et al. Food Chemistry (2015) 170 366-377.

A Novel UPLC-MS/MS Method for Quantitative Determination of Etodolac in Human Plasma

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Etodolac (ETO), 1,8-diethyl-1,3,4,9-tetrahydropyrano-[3,4-b]indole-1-acetic acid, is a non-steroidal antiinflammatory antirheumatic drug widely using as a painkiller (Figure 1). Several analytical methods have been reported in literature for the determination of ETO [1-3]. It's aimed in our study to develop an accurate, sensitive and rapid method for determination of etodolac in human plasma samples. This method includes a very simple liquid-liquid extraction procedure consisted precipitation with methanol.

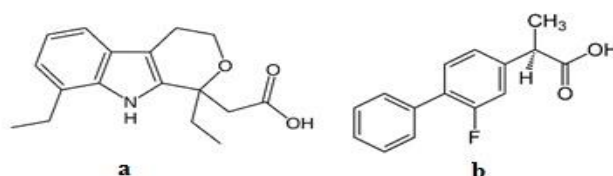


Figure 1. Chemical structure of etodolac (a) and flurbiprofen (b)

In this study, a rapid and sensitive ultra performance liquid chromatographic tandem mass spectrometric (UPLC-MS/MS) method was developed and validated for quantitative assay of etodolac (ETO) in human plasma. Flurbiprofen (FLU) was used as internal standard. (Figure 1).

Measurement were performed on an UPLC system (Agilent 1260 series) consisting of a quaternary pump, degasser and autosampler. A gradient elution was performed with the mixture of methanol/water (5 mM AMNF). For mass spectrometric detection, an Agilent 6460 triple quadrupole equipped with a Jet Stream electrospray ion source operating in negative-ion mode was used. Selected precursor and product ions for ETO and FLU were 286.2 \rightarrow 212.1 and 243.2 \rightarrow 199.1, respectively. The LLOQ was established at 1 ng/mL, and the LLOD was calculated as 0.2 ng/mL (S/N =3). The method was linear in the range of 1-5000 ng/mL. Developed method is sufficiently sensitive to permit determination of ETO even down to 1 ng/mL in plasma samples. Hence, we can conclude that the proposed method is suitable for routine determination of ETO in real plasma samples obtained from patients who used ETO medications.

Keywords: Etodolac, UPLC-MS/MS, Validation, Plasma

References:

1. Leea, H-S., Kanga, I-M, Leea, H-W, Seoa, Ji-H., Ryua, Ju-H., Choia, S-J., Leea, M-J., Jeonga, S-Y., Chob, Y-W., Leea, K-T., Journal of Chromatography B (2008) 863, 158-162.
2. Giachetti, C., Assandri, A., Zanol, G., Brembilla, E., Biomedical Chromatography (1994) 8 180-183.
3. Jin, Y-X., Y-H. Tang, S. Zeng, Journal of Pharmaceutical and Biomedical Analysis (2008) 46 953-958.

Rapid and Sensitive UPLC-MS/MS Method for Determination of Flurbiprofen in Pharmaceutical Formulations

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Flurbiprofen (FBP), 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid, is a member of non-steroidal anti-inflammatory drug (NSAID) group, mainly used in surgery and cancer pain management (Figure 1). Several analytical methods have been presented for FLP in pharmaceutical formulations [1-3]. The aim of this study was to develop a simple, precise, accurate and specific UPLC-MS/MS method for determination of FBP from pharmaceutical formulations. The working standard solutions of FBP and internal standard (IS) (etodolac) were prepared from the stock solution (1 mg/mL) in methanol and they were prepared in the range of 5-5000 ng/mL. All samples were included 100 ng/mL IS. Chromatographic separation was carried out a mobile phase consisting of methanol and water (5 mM AMNF) with a gradient program. Flow rate was 0.4 mL/min. Mass spectrometric detections were carried out in negative-ion mode. Selected precursor and product ions for FBP and IS were 243.2→199.1 and 286.2→212.1, respectively. The LLOQ was established at 1 ng/mL, and the LLOD was found as 0.2 ng/mL (S/N =3).

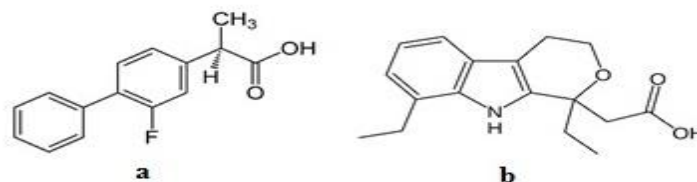


Figure 1. Chemical structure of flurbiprofen (a) and etodolac (IS) (b).

The method was linear in the range of 1-5000 ng/mL. Developed and validated method was successfully applied to three different pharmaceutical formulations of FBP in Turkish drug market.

Keyword: Flurbiprofen, UPLC-MS/MS, Pharmaceutical Formulations

References:

1. Sajeev, C., *Analytica Chimica Acta* (2002) 463 207-217.
2. Hamoudová, R. and M. Pospíšilová, *Journal of Pharmaceutical and Biomedical Analysis* (2006) 41 1463-1467.
3. Santoro, M.I.R., Singh, A.K., Kedor-Hackmann, E.R. *Journal of Liquid Chromatography & Related Technologies* (2003) 26 517-527.

Determination of PFOS and PFOA in Environmental Media

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PFOS (Perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid) are fluorinated manmade organic chemicals that have been used in cleaning products; paper packaging for food; stain and water resistant carpets, clothing, upholstering etc.

PFOA and PFOS are stable in environmental media. Because they are resistant to environmental degradation processes, such as biodegradation, photolysis, and hydrolysis. In water, no natural degradation has been demonstrated. They can be transported long distances in air or water as a result of being persistent. These compounds have been detected even in Arctic media and biota, including in polar bears, birds, and fish.

Water resources have been contaminated by PFOA and PFOS mainly releases from manufacturing sites, industrial sites, fire training areas, and industrial or municipal waste sites.

Water contamination by these chemicals became an interest among scientists throughout the world. However, in Turkey, no study about this subject has been reported yet. There is a need for data to analyze occurrence of these compounds in water and data on health effects.

In this study, liquid chromatography tandem mass spectrometry (LC-MS/MS) method for the determination of PFOS and PFOA in drinking, ground and surface water is going to be experienced. Analyses will be carried out based upon the EPA Method 537. In this method solid phase extraction (SPE) cartridges are used to extract the analytes and the compounds are eluted from the solid phase with a small volume of methanol. An injection are going to be made into an LC equipped with a C18 column that is interfaced to an MS/MS.

Keywords: LC-MS/MS, PFOS, PFOA

References:

- 1.EPA (2014), Emerging contaminants fact sheet – PFOS and PFOA
- 2.EPA (2009), *Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and LC/MS/MS*

Developing the Method for the Antibiotic Analyses Held in the Water Matrice

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It has been known that 7 of the each 10 drug prescriptions written in Turkey contain antibiotics and the resistance of many bacteria species against antibiotic is very high throughout our country. Antibiotics have taken place on the top among all the drug consumption for 6 years in our country. Human induced antibiotic consumptions in Turkey have been increasing a little more with each passing year. This makes think that the setopic groups carry potential risks in terms of environment. Although the excess consumption of antibiotics was emphasized many times in the last years, unfortunately, there are no studies about determination of antibiotic rate and composing the analysing method intended the determination of antibiotics.

Antibiotics will be analysed by LC-MS/MS. The composite samples will be taken from the water matrice seasonally. These lected antibiotics will be determined by SPE (solidphaseextraction) using LC-MS/MS and afterwards, the emission rate of antibiotic will be calculated.

A standard measuring method is not available for the antibiotic analyses in the water matrice. As seen from the literature, analyzing methods can be different according to the antibiotic group and the analyzes of the antibiotics belonging to the same group draw attention. The most commonly use dantibiotics in Turkey have been specified as 5 different groups and the analyzes of these antibiotics will be realized by selecting only the optimum method after experiencing different methods. The antibiotics which have been parted according to m/z (mass/charge) ratio by LC-MS/MS, the highest technology of HPLC, for carrying out the analyzing method more sensitevely are subjected to degradation using a high-purity special gas named as collision gas. For this reason, LC-MS/MS makes the quantitation of the low-concentrated material possible. Besides, verification of the results is not needed.

Keywords: Antibiotics, SPE, LC-MS/MS, Water Matrice

Stir Bar Sorptive Extraction Techniques For PAHs Analysis In Water Samples

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Sample preparation is one of the most important stages of the analytical process. This step becomes more important as the complexity of the samples increases and when the concentration levels to be detected are minimal. In fact, selecting the detection technique for an analysis is currently considered easier than choosing the sample treatment technique.

Preparation of samples involves clean-up and pre-concentration procedures aimed to improve the sensitivity, specificity and selectivity of the analytical methods. Current trends in analytical chemistry focus on miniaturization of these steps. For aqueous samples, conventional extractions require 1 to 2 L of water to obtain sufficient micropollutant residues for analysis. Extraction and enrichment steps in these traditional sample preparation techniques are tedious, time consuming, labor intensive and use large of organic solvents.

The application of a efficient extraction technique which is known as stir bar sorptive extraction (SBSE), followed by gas chromatography (GC) and triple quadrupole mass spectrometry, was assessed for determining a lot of pollutants in water samples.

The extraction conditions such as methanol addition (2, 5, 10, 20 %), extraction time (1, 2, 5, 10 hours), length of bar (1 and 2 cm) and sample volume (50, 100, 250 mL) profiles were studied.

The individual quantification of Polyaromatic Hydrocarbons (PAHs), in different water samples (tap water, drinking water and wastewater) were analyzed. The full analytical protocol including Stir Bar Sorptive Extraction (SBSE) and tandem mass spectrometry detection allowed the detection limit in the range of 0.1–5 ng L⁻¹. PAHs quantification is achieved using a five point calibration plot with internal calibration. Real sample analysis proved that the procedure is convenient for PAHs determination in environmental water.

Once SBSE parameters were optimized, the method presented good linearity, good precision and sensitivity. This method can be considered as an alternative to other analytical methods, which used SPE and SPME, for determining PAHs in waters. The main advantages of the SBSE method are: its simplicity without any preliminary sample preparation step and the reduced volume of organic solvents used.

Keywords: Polyaromatic Hydrocarbons, Stir Bar Sorptive Extraction, SBSE, PAHs, GC-MS/MS

References:

1. P. Sandra, E. Baltussen, F. David, A. Hoffmann, GERSTEL AppNote 1 2000.
2. N. Ochiai, K. Sasamoto, H. Kanda, E. Pfannkoch, Gerstell AppNote 12 2008.
3. M. Shamsipur and B. Hashemi, Rsc Advances (2015) 5 20339-20345

Determination of Some Additives in Polymeric Materials by Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS)

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The using of laser ablation in combination with ICP–MS for the determination of major, minor and trace elements as well as isotopic ratios in solids and liquids has grown over the past decade. There are several advantages using laser ablation as a sampling technique: Almost no sample preparation and no contamination from solvents and acids, less interferences due to the absence of solvents and acids, spatial resolution to as low as few μm (1-2 μm) are possible, elemental and isotopic information are obtainable, limits of detection are superior to other solid sampling techniques and the speed of data acquisition allows large quantities of samples to be analyzed within reasonable time. Although laser ablation has many advantages, the biggest disadvantages of this technique is quantitative analysis. Quantitative analysis by laser ablation ICP-MS is difficult to achieve for many sample types. This reflects a lack of suitable standards which ideally, though unobtainably, need to be identical to the sample both chemically and physically on all relevant spatial scales. Accurate results are generally obtained only when the sample and the standard are prepared in the same matrix. In this study, fusion discs are used as calibration standards. The prepared fusion discs were checked in terms of the homogeneity and some important laser parameters; laser energy, laser frequency, scan rate, carrier gas flow and aperture size were optimized. The method has linear working ranges of 30-1000 mg/kg for Br and 120-1600 mg/kg for Sn. Method's precision values were calculated as 6 % for Br and 12 % for Sn. The uncertainties of method were estimated as 20% for Br and 28% for Sn and then for 95% confidence interval, the reliability ranges of the method were found as 408-612 mg/kg for BFRs interms of Br concentration and 720-1280 mg/kg for OTCs interms of Sn concentration.

The results obtained have shown that this technique can be used for screening of plastics materials in terms of polybrominated flame retardants and organotin compounds which are under regulation by most of the countries especially in EU countries. Besides the LA-ICP-MS method can be used for heavy metals (Cr,Cd, Pb and Hg) analysis in plastics with optimization of some laser.

Keywords: Plastics, Laser Ablation Inductively Coupled Mass Spectrometry, Polybrominated Diphenyl Ethers, Organo-Tin Compounds, Heavy Metals.

References:

1. İzgi, B., Kayar, M., Determination of bromine and tin compounds in plastics using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) *Talanta* (2015) 139 117–122.
2. Kayar, M., İzgi, B., Çimenoglu, M. A, Multi-element analysis in plastics by laser ablation inductively coupled plasma mass spectrometry *International Journal of Mass Spectrometry*, (2016) 399–400 10-16.

Enrichment of VEGF Protein on the Aptamer Bind Surfaces and Detection via Mass Spectrometry

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Aptamer whose archaic meaning is ‘suited’ or ‘adapted’ is RNA or DNA oligonucleotide that can bind to their targets with high affinity and specificity[1]. Thanks to the unique characteristic and chemical structure, aptamers offer themselves as ideal candidates for use in analytical devices and techniques[2]. They are [synthesized](#) via in vitro selection process called SELEX (systematic evolution of ligands by exponential enrichment) and they have a wide range of target molecules such as organic-inorganic molecules, drugs, proteins because of their unique three-dimensional structure. Aptamer-target interaction is so specific that aptamer which is generated by SELEX according to target only binds to their target even if other protein structures are found in the solutions. Despite a wide range of targets, aptamer-protein interaction is remarkable. In our study, Vascular Endothelial Growth Factor (VEGF) is an important protein in order to check aptamer-protein interactions. VEGF is in charge of growing of the endothelial cells and creating new blood vessels during [embryonic development](#)[3]. Besides these features, VEGF is found in not only physical processes but also [pathogenic](#) illnesses like tumor growth in the body. As a result, the amount of VEGF in the blood is so important that the detection of the low concentration VEGF has attracted in the science world for a long time[4]. During our study, firstly, aptamers were bound to the polymeric surface via amine-to-sulfhydryl crosslinker then the low concentration VEGF was preconcentrated with aptamers on the surface. VEGF which was bound to aptamers on the polymeric surface was digested via trypsin enzyme and then peptide fragments were analyzed by using MALDI-MS. Besides low concentration study of VEGF, it was succeeded that VEGF was analyzed specifically in the solution which consists of other proteins such as lysozyme and cytochrome c. Finally, aptamer-VEGF interaction was checked in the blood plasma sample and VEGF peptide fragments were observed thanks to MALDI-MS.

Keywords: Aptamer, VEGF, Mass Spectrometry, MALDI-MS

References:

1. D. Proske, M. Blank, R. Buhmann, and A. Resch, “Aptamers - Basic research, drug development, and clinical applications,” *Appl. Microbiol. Biotechnol.*, (2005) 69 367–374.
2. T. Mairal, V. Cengiz Özalp, P. Lozano Sánchez, M. Mir, I. Katakis, and C. K. O’Sullivan, “Aptamers: Molecular tools for analytical applications,” *Anal. Bioanal. Chem.*, (2008) 390 989–1007.
3. L. S. Green, D. Jellinek, C. Bell, L. A. Beebe, B. D. Feistner, S. C. Gill, F. M. Jucker, and N. Janjić, “Nuclease-resistant nucleic acid ligands to vascular permeability factor/vascular endothelial growth factor,” *Chem. Biol.*, (1995) 2 683–95.
4. G. Neufeld, T. Cohen, S. Gengrinovitch, and Z. Poltorak, “Vascular endothelial growth factor (VEGF) and its receptors,” *FASEB J.*, (1999) 13 9–22.

Optimization of Chromatographic Conditions with Solvato Chromic Parameter Values for the Separation of Some Selective Serotonin Re-Uptake Inhibitors by RPLC Method

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Selective serotonin reuptake inhibitors (SSRIs) are the most commonly prescribed antidepressants. They can ease symptoms of moderate to severe depression, are relatively safe and typically cause fewer side effects than other types of antidepressants. SSRIs ease depression by increasing levels of serotonin in the brain. SSRIs are called selective because they seem to primarily affect serotonin, not other neurotransmitters. SSRIs also may be used to treat conditions other than depression, such as anxiety disorders [1]. In this study, sertraline, fluvoxamine and citalopram were chosen as investigated drugs.

In the HPLC method optimization, the most important aim is to provide the best separation conditions. Several approaches have been investigated to estimate the solute retention behavior as a function of chromatographic conditions. The factors generally selected to optimize the chromatographic separation of ionisable compounds are the pH of the mobile phase and content of organic solvent of the eluent. As well as this optimization, the solvatochromic linear solvation energy relationships (LSER) approach of Kamlet and Taft allows us to predict the chromatographic retention of drugs studied for any composition of the mobile phases by using relationship obtained between the chromatographic parameter $\log k$ and solvatochromic parameters of mobile phases (π^* , α , β). At the same time, chromatographic behaviour of compounds can be predicted with linear relationships between the solute logarithm of retention factor and solvent polarity parameter (E_T^N) [2].

The aim of this study is to select the optimum chromatographic condition to separation of citalopram, fluvoxamine and sertraline by using these approaches. The optimized chromatographic condition was applied to quantitative determination of investigated drugs in pharmaceutical dosage forms.

Keywords: LSER, Kamlet and Taft, Chromatographic Optimization, Method Validation

References:

1. Depression (major depressive disorder), Selective serotonin reuptake inhibitors (SSRIs), <http://www.mayoclinic.org/diseases-conditions/depression/in-depth/ssris/art-20044825>, (2016)
2. J.G.Dorsey, B.P.Johnson, J. Liq. Chromatogr.Rel.Tech. (1987) 10 2695-2706.

New Method for the Simultaneous Determination of Two Multicomponent Mixtures Containing Etodolac and Thiocolchicoside in Combined Pharmaceutical Preparation by Using Chemometric Calibration Methods

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Etodolac is a nonsteroidal anti-inflammatory drug (NSAID) that exhibits antiinflammatory, analgesic, and antipyretic activities. Various NSAID's have been demonstrated to enhance analgesia such as thiocolchicoside which is also an anti-inflammatory analgesic with muscle relaxant action. Recently, several multivariate methods such as PLS (partial least squares), PCR (principal component regression) and ILS (Inverse Least Squares) have been applied to mixtures of drugs in pharmaceutical formulations in the presence of a variety of excipients.

In this study, it is aimed to develop and validate simultaneous quantitative analysis of etodolac and thiocolchicoside in combined pharmaceutical preparation by the UV-Visible spectrophotometric method without any separation process by using the data obtained from chemometric calibration methods (PLS, PCR and ILS).

The calibration (25 samples) and validation (8 samples) concentration data matrices were prepared by using the mixtures containing etodolac (15-75 µg/mL) and thiocolchicoside (1-10 µg/mL) by using a factorial design method. The absorbance data in UV spectra were measured in the 241-440 nm spectral regions ($\Delta\lambda = 1$ nm intervals). After that PLS, PCR and ILS calibrations were plotted by concentration and absorbance data matrix. The validations of the developed multivariate methods were performed. Recovery values of PLS, PCR and ILS methods were calculated to be 102.5%, 100.6% and 103.5 % for etodolac while these values were calculated to be 102.0 %, 100.3 % and 101.7% for thiocolchicoside.

The optimized models were successfully applied to the simultaneous assay of the two mentioned drugs in combined pharmaceutical formulation and obtained results found to be in good agreement with the label claim. In conclusion, it is claimed that these methods are simple, rapid and can be easily used in the quality control of drugs as alternative analysis tools.

Keywords: Etodolac, Thiocolchicoside, Chemometric Calibration Methods, Experimental Design

References:

1. Pandey R, Patil P.O., Bari S.B., Dhumal D.M., Chem. Ind. Chem. Eng. Q. (2014) 20 (1) 9–17.
2. Kelani K.M., Shalaby A.A., Elmaamly M.Y., Halim K.M., Pharm. Anal. Acta (2015) 6(1) 2-11.

Simultaneous Determination of Anions and Orotate in Milk Samples by Ion Chromatography

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Abstract

We describe a simple method for simultaneous determination of chloride, nitrate, sulfate, iodide, phosphate, thiocyanate, perchlorate, and orotic acid in milk samples. The method involves the use of dialysis cassettes for matrix elimination, followed by ion chromatography on a high capacity anion exchange column with suppressed conductivity detection. The proposed method was successfully applied to milk samples collected from İstanbul markets. The advantages of the method described herein are reagent-free, simple, and reliable.

Keywords: Milk, Dialysis, Anions, Orotic Acid, Ion Chromatography

Introduction

Thyroid hormones are necessary for brain and neural development in fetuses and infants [1]. In the cellular membrane of the cells from thyroid follicles, the protein responsible for iodide capture from the bloodstream was identified as Na⁺I⁻ symporter (NIS). Sodium-iodide symporter is present in the thyroid gland and also in the mammary glands. Iodide is an important trace element used by the thyroid gland to make thyroid functioning in human beings [2]. A number of inorganic anions can block iodide (I⁻) uptake at the thyroidal sodium iodide symporter (NIS) in a competitive manner. Among these, nitrate (NO₃⁻), thiocyanate (SCN⁻), and perchlorate (ClO₄⁻) are of particular dietary and/or environmental importance [3]. Sufficient inhibition of iodide uptake can lead to decreased thyroid hormone production and, ultimately, result in adverse health effects secondary to hypothyroxinemia. Chloride (Cl⁻) is one of the typical anions which its determination in milk has a great interest. The chloride determination in milk is a useful parameter to understand the degree of subclinical mastitis that may occur in the cattle [4]. It is important to determine phosphate and sulfate concentrations in milk because they are naturally present in the crude matter and may also be introduced during the industrial manipulations [5]. Orotic acid (1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid; uracil-6-carboxylic acid) is found in milk. The biological effects of orotic acid have been focused on considerable attention, because recent experimental studies have demonstrated that it is involved in carcinogenesis, hepatic lipid storage and renal toxicity [6]. Several studies have shown that repeated dosing of orotic acid promotes the formation of tumours initiated by various known carcinogenic substances [7].

Sample preparation is an important part of an analysis in a complex matrix especially for milk so as to manage a good analytic procedure. Because milk has high molecular mass compounds such as fats, proteins, and carbohydrates that can interfere with the analysis, some

initial cleanup procedures are required before analysis of anions. A wide range of techniques have been employed for the determination of anions and organic acids in milk, including voltammetry [8], flow injection methods [9], X- ray fluorescence spectroscopy [10], and neutron activation analysis[11]. In a representative report, anions, including iodide, nitrate and nitrite in biological samples were analyzed by micellar electrokinetic capillary chromatography [12]. In another study, determination of iodine species in milk was done with using epithermal neutron activation analysis. In this method, preconcentration of iodine anion was achieved by using polymer inclusion sorbent [13]. Another study showed that benzoic acid and sorbic acid in food products were analyzed by using electrokinetic flow injection analysis [14].

The aim of this work is to present a simple and accurate procedure for milk pre-treatment. The sample's matrix elimination is done by using dialysis method with dialysis cassette. The method takes advantage of following; (a) no chemicals are needed (b) proteins and lipids can be removed easily.

Materials & Methods

Instrumentation

Dionex ICS-3000 (Sunnyvale, CA, USA) ion chromatograph equipped with a suppressed conductivity detector (ASRS ULTRA II-2mm suppressor and conductivity cell) was used for analyses of anions in milk samples. Chromatographic separations were performed at 25°C with a Dionex IonPac® AS20 analytical column (2x250mm) equipped with a Dionex IonPac® AG20 guard column (2x50mm).

Preparation of milk samples for anions and orotic acid analysis

Milk samples from different brands were purchased from local markets on different dates in İstanbul. 5 mL milk sample dialysis to 400 mL ultrapure water in a dialysis cassette in order to remove macromolecules such as milk fat, carbohydrates and proteins etc. After 45 hours in sample processing method dialysis filtrate was analyzed with ion chromatography with conductivity detector by using gradient elution program.

Chromatographic conditions

The conditions of the suitable program was: the concentration of NaOH; 0-1 min 3 mM isocratic, 1.1-13 min 3-20 mM gradient, 13.1-20 min 20 mM isocratic, 20.1-21 min 20-50 mM gradient, 21.1-24 min 50 mM isocratic, 24.1-25 min 50-3 mM gradient, 25.1-30 min 3 mM isocratic column temperature was 25°C, cell temperature was 30 °C; current of the suppressor was 31 mA and injection volume was 10 µL.

Results & Discussion

Validation of the method

To validate the proposed method, numerous analytical parameters such as linearity, limits of detection (LOD) and quantitation (LOQ), with-in run precision, intermediate precision, and accuracy have been evaluated. Linear concentration range, linear regression equations, correlation coefficients, LOD and LOQ values are given in Table 1.

Table 1. Linear concentration range, regression equation, retention time, r^2 , LOD and LOQ values

Analyte	Linear Range (mg L ⁻¹)	Regression Equation	t _R (min)	r ²	LOD* (mg L ⁻¹)	LOQ* (mg L ⁻¹)
Chloride	0.01 - 9.0	$y = 0.2131x - 0.017$	7.76	0.9989	0.012	0.040
Nitrate	0.05 - 9.0	$y = 0.0791x - 0.0067$	10.01	0.9985	0.516	1.720
Sulfate	0.05 - 9.0	$y = 0.0989x - 0.009$	11.71	0.9999	0.520	1.733
Iodide	0.03 - 9.0	$y = 0.0437x + 0.003$	13.76	0.9989	0.312	1.040
Phosphate	0.01 - 9.0	$y = 0.154x - 0.0219$	14.29	0.9968	0.112	0.373
Thiocyanate	0.01 - 9.0	$y = 0.123x - 0.0058$	16.13	0.9968	0.140	0.467
Perchlorate	0.03 - 9.0	$y = 0.0716x - 0.0114$	16.87	0.9975	0.280	0.933
Orotate	0.07 - 9.0	$y = 0.0661x - 0.0026$	19.08	0.9953	0.840	2.800

*LOD and LOQ values were corrected with dilution factor of sample.

Analysis of milk samples

Figure 1 presents the chromatogram for the milk sample 3. The ion chromatographic results of the anions in milk samples are given in Table 2. The milk samples between number 1–4 in Table 2 were different brands purchased from local markets on different dates in İstanbul. Sample number 5 was a raw milk sample. The raw milk sample was also boiled and it was analyzed in same conditions as sample 6. It has been observed that the concentrations of anions in raw milk were dramatically changed after boiling. Concentrations of chloride, nitrate, sulfate and orotic acid was increased whereas phosphate was decreased and thiocyanate peak disappeared in boiled milk. Moreover, a bottled daily milk sample (number 7) was analyzed. Chloride, sulfate, phosphate, and orotate were observed in all of the samples. Iodide and thiocyanate were detected in some samples. Perchlorate was not observed in the samples according to the present method. Nitrate was not measured in only one sample.

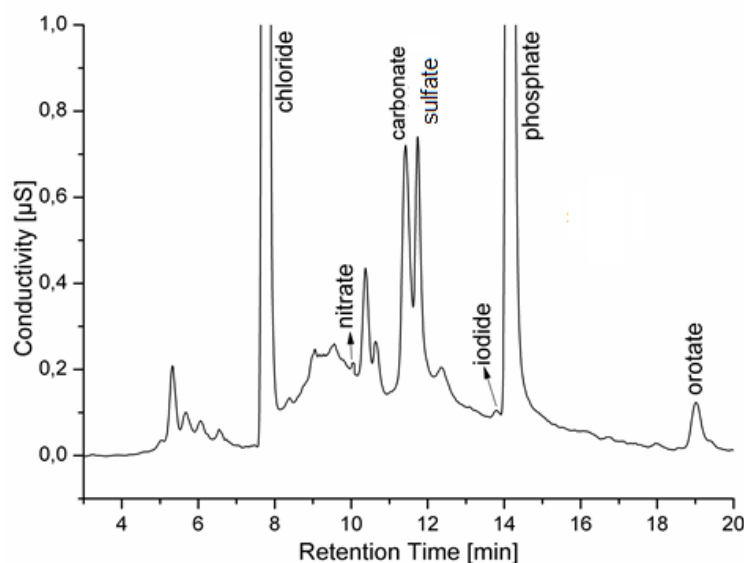


Figure 1. Chromatogram of milk sample 3.

Table 2. Concentration results of chloride, nitrate, sulphate, iodide, phosphate, thiocyanate, perchlorate, and orotate in real milk samples (n=5).

Sample ^a	Chloride		Nitrate		Sulfate		Iodide		Phosphate		Thiocyanate		Perchlorate		Orotate	
	C (mg L ⁻¹)	RS D (%)	C (mg L ⁻¹)	RS D (%)	C (mg L ⁻¹)	RS D (%)	C (mg L ⁻¹)	RS D (%)	C (mg L ⁻¹)	RS D (%)	C (mg L ⁻¹)	RS D (%)	C (mg L ⁻¹)	RS D (%)	C (mg L ⁻¹)	RS D (%)
Sample 1	99	11	42	34	96	4	ND	-	16	2	ND	-	N.D.	-	746	8
Sample 2	95	8	67	124	1565	48	ND	-	9	0	ND	-	N.D.	-	526	43
Sample 3	82	01	85	19	79	8	77	2.29	8	6	ND	-	N.D.	-	627	34
Sample 4	96	07	90	22	801	5	75	3.76	6	0	ND	-	N.D.	-	581	10
Sample 5	117	05	36	29	484	22	ND	-	12	4	8	07	N.D.	-	521	15
Sample 6	147	01	48	24	857	8	ND	-	9	4	ND	-	N.D.	-	674	18
Sample 7	105	07	ND	-	560	30	ND	-	11	4	ND	-	N.D.	-	491	36

Conclusion

The most important advantage of this study is that this is the first study in the literature for the simultaneous determination of chloride, nitrate, sulfate, iodide, phosphate, thiocyanate, perchlorate, and orotate in milk by using dialysis technique for matrix elimination. This study may be a good alternative for studies related to needed difficult matrix elimination before analysis. The proposed method possesses many advantages which included easy preparation, the absence of chemicals, simple sample pretreatment procedure even if the dialysis time is long. The method was validated in terms of linearity, limits of detection and quantitation, intra-/inter-day accuracy, precision, and recovery. After hundreds of injections, no significant changes were observed on retention times. Very stable retention time values indicated that not only our method had good precision, but the life time of analytical column has also been prolonged as well. LOQ values were adequately small even though the analytes were diluted to 400 mL of water.

References:

1. Martinelango, P. K.; Gümü; G., Dasgupta, P.K. *Analytica Chimica Acta* (2006) 567 79-86.
2. Leung, A.M.; Pearce, E.N.; Braverman, L.E. (2010) 24 133–141.
3. Tonacchera, M.; Pinchera, A.; Dimida, A.; et.al. *J. Thyroid* (2004) 14 1012- 1019.
4. Silva, F.V.; Souza, G.B.; Ferraz, L.F.M.; Nogueira, A.R.A. *Food Chemistry* (1999) 67 317-322.
5. Licata, P.; Naccari, F.; et.al. *Food Additives & Contaminants: Part A* (2010) 30 (3) 458–465.
6. Cataldi, T.R.; Nardiello, D.; et.al. *Journal of Chromatography A* (2006) 1107 130–138.
7. Manjeshwar, S.; Rao, P.M.; et.al. *Molecular Carcinogenesis* (1999) 24 188-196
8. Shukla, J.; Pitre, K. S. *Reviews in Analytical Chemistry*, DeGruyter: Ettenheim, (2013) 265.
9. Trajonowicz, M. *Instrumentation and Application*; World Scientific: London, (2000) 344.
10. Sam, A. K.; Osman, M. M.; El-Khang, F. A. *Journal of Radioanalytical* (1998) 231 (1-2) 21-23.
11. Cunha, I.I.L.; De Oliveria R. M. *Jof Radioanal. and Nuclear Chemistry* (1996) 213 (3) 185- 192.
12. Bjergegaard, C.; Moller, P.; Sorenson, H. *Journal of Chromatography A* (1995) 717 409-414.
13. Bhagat, P.R.; Pandey, A.K.; Acharya, R.; et.al. *A.V.R. Talanta* (2007) 71 1226-1232.
14. Han, F.; He, Y.-Z.; Li, L.; Fu, G.-N.; et.al. *Analytical Chemical Acta* (2008) 618 79-85.

Simultaneous Determination of Cyanide and Hexavalent Chromium by Ion Chromatography with Conductivity Detection

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Abstract

In this work, we presented a new method for simultaneous determination of cyanide and hexavalent chromium by ion chromatography with conductivity detection. Cyanide ions were converted into cyanate with chloramine-T at alkaline pH to make measurable with conductivity detector. The chromatographic separations on anion exchange column were accomplished by optimized multi-step gradient eluent program using NaOH as the eluent. Proposed method was applied to artificial electroplating wastewater solution, electroplating bath solutions and in industrial wastewater.

Keywords: Cyanide, Hexavalent Chromium, Ion Chromatography, Conductivity Detection

Introduction

Since cyanide compounds can form stable complexes with metals in a wide spectrum, they are used in mining, metallurgy, manufacture, photography, etc. The most harmful cyanide species to the environment are shown to be free and WAD cyanides [1]. Inhalation of hydrocyanic acid (prussic acid (HCN)) or digestion of cyanide salts causes fast-appearing symptoms. HCN vapors are formed by mixing the salts with acids or in the stomach following oral ingestion. The lethal dose is probably 100 mg for hydrocyanic acid while it is 300 mg for potassium cyanide [2].

Chromium is generally used as an additive for alloys or materials to donate some properties such as strength, hardness, permanence, hygiene, color and resistance to temperature, wear and corrosion [3]. Chromium species can be released into environment through industrial activities such as textile dyeing, preservation of wood, tanning, paint and pigment production, electroplating and metallurgy. Cr(VI) can be toxic, mutagenic, and carcinogenic. Cr(VI) damages to the skin, the respiratory tract, the kidneys and augments risk of lung cancer depending on exposure type. The US EPA has set the maximum contaminant level for Cr(VI) in drinking water and inland surface waters as 0.05 and 0.1 mg L⁻¹, respectively. Industrial wastewaters containing chromium have to be refined prior to discharging into the environment because Cr(VI) concentration must be lower than the permitted limits [4]. Therefore, the control of these compounds in electroplating baths and wastewater is crucial issue.

Cyanide ion (CN⁻) and hexavalent chromium (Cr(VI)), which are highly toxic compounds, are extensively used in electroplating industry. Though many different methods have been described in literature for the determination of cyanide and Cr(VI) individually, no study has focused on simultaneous analysis. It is clear that simultaneous determination of Cr(VI) and cyanides in wastewaters is challenging task.

In the present study, we developed a new method for simultaneous determination of cyanide and Cr(VI) by ion chromatography with suppressed conductivity detector. Cyanide was

converted to cyanate for being measurable with a conductivity detector, because the dissociation constant of hydrogen cyanate (HCNO) is highly sufficient ($pK_a = 3.66$) to give a reasonable response [5-8]. Proposed method was applied to electroplating bath solutions and wastewater.

Materials & Methods

Instrumentation

The ion chromatographic analysis was performed on an ICS-3000 (Thermo Scientific, Waltham, MA, USA) equipped with a suppressed conductivity detector (ASRS ULTRA II-2mm suppressor and conductivity cell). An IonPac AG20 guard column (50 mm \times 2 mm, I.D., Thermo Scientific, Waltham, MA, USA) and an IonPac AS20 separation column (250 mm \times 2 mm) were used as the analytical columns. The mobile phase gradients were generated on-line from ultra-pure water using the Reagent-Free (RF) EGC-NaOH EluGen II cartridge and then polished off from the contaminants using Continuously Regenerating Trap Column (CR-ATC). Data acquisition and instrumental control were performed via a Chromeleon Client (6.80) software (Thermo Scientific, Waltham, MA, USA). The RFIC system provides avoiding potential contamination compared to systems with manually prepared eluents. The instrument was also equipped with a pump attached to an AS autosampler. ICP-MS (Perkin Elmer ELAN DRC-E) analyses were conducted for determination of elemental content of samples.

Optimum IC conditions

Several IC parameters were exercised in order to separate the unidentified peaks, cyanate peak, thiocyanate peak, and Cr(IV) peak through the analytical column, and the resulting conditions were as follows:

The optimized chromatographic conditions: the eluent gradient was 0-15 min 2 mmol L⁻¹ NaOH isocratic, 15-25min gradient from 2 to 30 mmol L⁻¹ NaOH, 25-30 min 30 mmol L⁻¹ NaOH isocratic, 30-31min gradient from 30 to 2 mmol L⁻¹ NaOH, 31-35 min 2 mmol L⁻¹ NaOH isocratic (recondition step). The suppressor current was 19 mA. Column compartment temperature and detector cell temperature were kept constant with a thermostat at 35 °C and 40 °C, respectively. The flow rate was 0.250 mL min⁻¹ and the sample loop was 10 μ L.

Sample collection

Electroplating bath solutions, effluent and refined wastewaters from industrial estate were collected from the İstanbul, İkitelli region. The samples were tightly stoppered and immediately transferred to the laboratory to keep at + 4 °C. The samples were pretreated as soon as taking out of the refrigerator and analyzed with IC.

Conversion cyanide into cyanate

Free cyanides react with chloramine-T to form an intermediate cyanogen chloride (CNCl), which is hydrolyzed to cyanate at alkaline pH when heated. 2-mL sample solution was mixed with 20 μ L 5% chloramine-T solution, stoppered, and kept in a hot water bath (80°C) for 20 minutes in order to convert cyanide to cyanate.

Results & Discussion

Simultaneous determination of cyanide and Cr(VI)

A standard mix solution of $61.5 \mu\text{mol L}^{-1}$ cyanide and $7.4 \mu\text{mol L}^{-1}$ Cr(VI) was added to 30-40 μL of 10 M NaOH, thus the pH value adjusted to ≥ 12 , then 20.0 μL of 5% chloramine-T solution was added, vortexed for 1 minute, then kept in a water bath at 80°C for 20 minutes. The solution was allowed to reach room temperature, than loaded into IC autosampler vials. Figure 1 shows the chromatogram of a standard solution of cyanide and Cr(VI).

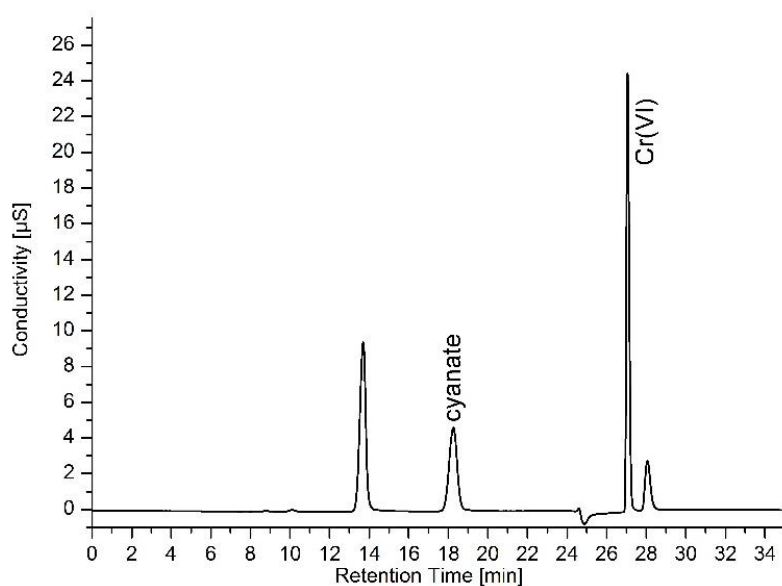


Figure 1. Standard mix solution containing $61.5 \mu\text{mol L}^{-1}$ cyanide and $7.4 \mu\text{mol L}^{-1}$ Cr(VI)

Method Validation

Linearity, limit of detection (LOD), limit of quantification (LOQ), and repeatability for the peak area and retention time parameters are given in Table 1. External calibration method was used for quantification analytes in the samples. Linearity was evaluated by linear regression with R^2 . LOD and LOQ were calculated from the peak height as the average concentration corresponding to the signal-to-noise ratio equal to 3 and 10, respectively.

Table 1. Linear calibration curve parameters, RSD of the retention time, and area for 0.23 mmol L^{-1} cyanide and 0.03 mmol L^{-1} Cr(VI), LOD ($S / N = 3$) and LOQ ($S / N = 10$). All the measurements have been performed by repeating six time injections.

Analytes	Linear Range		r^2	t_R (min)	Area ($\mu\text{S min}$)	RSD% (n=6)		LOD ($\mu\text{mol L}^{-1}$)	LOQ ($\mu\text{mol L}^{-1}$)
	($\mu\text{mol L}^{-1}$)	Regression equation				t_R	Area		
Cyanide	0.6 – 961.5	$Y = 0.0097x - 0.0539$	0.999	18.31	2.21	0.34	0.91	0.18	0.61
Cr(VI)	0.9 – 118.5	$Y = 0.0038x - 0.001$	0.999	27.05	0.11	0.04	1.46	0.26	0.86

Analysis of artificial electroplating wastewater solution

10 mL of the synthetically prepared electroplating wastewater was adjusted to $\text{pH} \geq 12$ and 20 μL of 5% chloramine-T solution was added. Then, this solution was kept in a water bath at 80 $^{\circ}\text{C}$ for 20 minutes. After the temperature of the solution reached to room temperature, it was injected repeated five times into IC system under the optimum chromatographic conditions. Recovery values of cyanide and Cr(VI) were found $99.96 \pm 0.15 \%$ and 99.61 ± 0.31 , respectively. Figure 2 presents the chromatogram of synthetic plating wastewater solution.

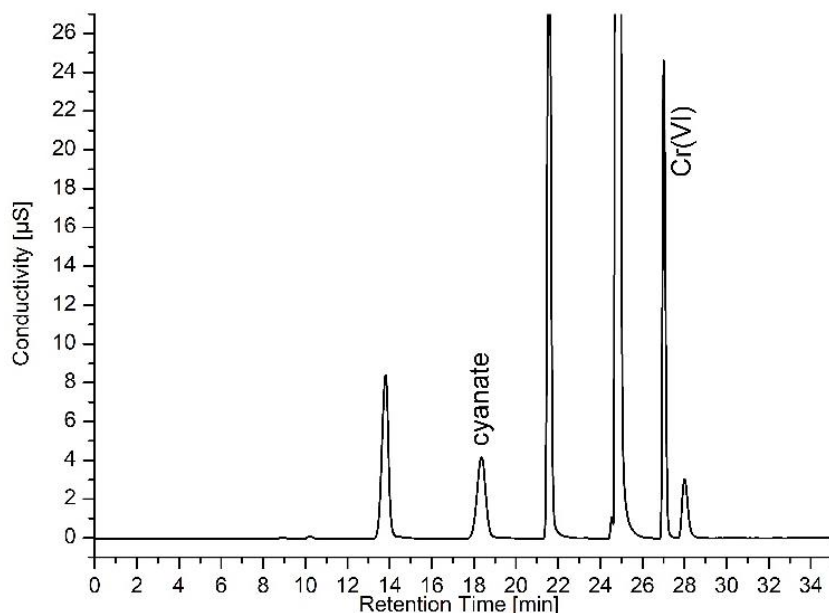


Figure 2. Synthetic Plating Rinse Wastewater Solution

Conclusion

In conclusion, we proposed a new method for simultaneous determination of cyanide and Cr(VI) by ion chromatography with suppressed conductivity detector. The procedure is reliable, precise, selective, sensitive and suitable for routine analysis. The presented method is suitable for controlling cyanide and Cr(VI) concentrations in wastewater samples which has a great importance for environmental health.

References:

1. A. Zheng, D.A. Dzombak, R.G. Luthy, B. Sawyer, W. Lazouskas, P. Tata, et al., *Environ. Sci. Technol.* (2003) 37 107–15.
2. S. Jickells, A. Negrusz, *Clarke's Analytical Forensic Toxicology*; Vol 1, p 111-112, published by the Pharmaceutical Press, London UK, IL USA, 2008.
3. R. Cornelis, H. Crews, J. Caruso, K.G. Heumann, *Handbook of Elemental Speciation II: Species in the Environment, Food, Medicine & Occupational Health*, John Wiley & Sons, Ltd. 2005.
4. S. Yalçın, R. Apak, *Anal. Chim. Acta.* (2004) 505 25–35.
5. O. Destanoğlu, G. Gümüş Yılmaz, R. Apak, *J. Liq. Chromatogr. Relat. Technol.* (2015) 38 1537–1545.
6. J.S. Fritz, D.T. Gjerde, *Ion Chromatography*, p61, WILEY-VCH Verlag GmbH, 2000.
7. M. Nonomura, *Anal. Chem.* (1987) 59 2073-2076.
8. M. Nonomura, T. Hobo, *J. of chromatogr. A* (1989) 465 395-401.

Chromatographic and Spectroscopic Determination of Oxidation Intermediates of a Fluoroquinolone Antibiotic (Levofloxacin)

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Levofloxacin (LEV) is a more recently developed fluoroquinolone antibiotic that has been widely used to cure infectious diseases, such as community-acquired pneumonia and the acute exacerbation of chronic bronchitis. While antibiotics are very effective substances against some diseases, they show resistance to biodegradation, which increases the accumulation of these substances in the environment. This situation leads to the promotion of antibiotic resistance within the native bacterial populations [1-3], which is considered to be one of the greatest threats to human health by the World Health Organization [4]. Therefore, oxidation and elimination of these substances are very important objectives for human healthy and environment. In this frame, advanced oxidation processes (AOP) are very promising because of their high oxidation abilities [5-6]. In these methods, organic substances are oxidized up to carbon dioxide and water by radicalic species. The oxidation of organics leads to the formation of different intermediate species such as aromatic intermediates, short-chain carboxylic acids and inorganic ions. The determination of these intermediates is also a very important phenomena from environmental points.

In this study, we have investigated the identification and quantification of oxidation intermediates of LEV formed during the electro-Fenton treatment, which is a most widely used AOP. The reaction between LEV and hydroxyl radical led to formation of different aromatic intermediates. Three of them were identified by liquid chromatography-mass spectrometry (LC-MS) analysis. Gas chromatography-mass spectrometry (GC-MS) analysis allowed the determination of eight aliphatic oxidation intermediates. High performance liquid chromatography (HPLC) analysis using an ion-exclusion column revealed the formation of six different short-chain carboxylic acids. Finally, the formation of inorganic ions (nitrate, ammonium and fluoride) was verified by ion-exchange chromatography analysis.

Keywords: Antibiotics, Levofloxacin, Oxidation, Chromatography,

Financial support of Anadolu University Scientific Research Projects Commission (Project No: 1401F009) is gratefully acknowledged.

References:

1. M.M. Huber, A. Göbel, A. Joss, N. Hermann, M. Kampmann, D. Löffler, C.S. McArdell, A. Ried, *Environ. Sci. Technol.* (2005) 39 4290-4299.
2. J.E. Moore, P.J.A. Moore, B.C. Millar, C.E. Goldsmith, A. Loughrey, P.J. Rooney, J.R. Rao, *Agric. Water Manage.* (2010) 98 217-221.
3. I. Sirés, E. Brillas, *Environ. Int.* (2012) 40 212-219.
4. M. Chen, W. Chu, *Appl. Catal. B: Environ.* (2015) 168-169 175-182.
5. A. Dirany, I. Sirés, N. Oturan, A. Özcan, M.A. Oturan, *Environ. Sci. Technol.* (2012) 46 4074–4082.
6. M. Gençten, A. Özcan, *Chemosphere* (2015) 136 167–73.

Characterization of Urethane-Modified Polyester in the Coating System with FTIR and Pyrolyser-GCMS

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Polyesters are widely used in one or two components coating systems. Most coating polyesters which are made by diols and dibasic acids have amorphous and branched structure. Polyesters have the advantages for coating systems in terms of physical and chemical properties such as adhesion, toughness, abrasion resistance, durability, dispersibility, flexibility, stress release. They can be designed with combination and modification of different materials such as urethane, acrylic, silicone, polyamide to improve the mechanical properties (1). One of these well-designed types is urethane modification. The coating including the urethane-modified polyester resin composition has improved exceptional mechanical strength and adhesion between the basecoat and a substrate or topcoat film and has enhanced processibility, impact resistance and flexibility. Urethane-modified polyester can be designed by reacting a polyester resin with an isocyanate compound. Types of diols, dibasic acids and isocyanates which are used in polyester resin have great importance in respect to variety properties given to coating systems (2). In this study, we aim to determine qualitatively the monomer composition of the polyester system which can be cross-linked melamine formaldehyde resins by FT-IR and Pyrolyser-GCMS. Initially, we have obtained whether or not there is urethane modification in polyester resin by using FT-IR. After then, diols, dibasic acids monomers and isocyanate types have been identified by Pyrolyser-GCMS. This research improves the characterization of polyester monomers and urethane types with different analytical method.

Keywords: Polyester Resin, Urethane modification, Pyrolyser-GCMS, Characterization, Coating

References:

1. Zeno W. Wicks (2007) Organic Coatings: Science and Technology, Wiley, USA.
2. Chapman & Hall (1993) Surface Coatings, Tafe Educational Books, New South Wales University Press, Australia.

Determination of pK_a Value of Tyrosine Kinase Inhibitors in 50% Acetonitrile-Water Binary Mixtures by Reversed Phase Chromatographic Method

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Protein kinases form an important part of these signal pathways which take part in issues that are of vital importance for the cells. Activation of receptors by growth factors is an important step for the proliferation of tumor cells. Epidermal growth factor receptor inhibitors (EGFR) are highly effective agents which are improved in the treatment of metastatic epithelial cancer. EGFRs are expressed too much in many tumor types. As a result of EGFR inhibitor's usage in the treatment of many cancer types such as colorectal cancer, head-neck cancer, lung cancer and breast cancer, these inhibitors are accepted as successful agents that take part in the treatment of cancer.

In the present work, ionization constants of several tyrosine kinase inhibitors named erlotinib, canertinib and bosutinib that are used for the treatment of cancer (especially leukemia, breast and lung cancer) determined by the reverse-phase liquid chromatographic (HPLC) method in 50% ACN- water binary mixture. The pK_a values of studied compounds were determined from k/pH data pairs by means of the non-linear regression program NLREG [1].

Keywords: Erlotinib, Canertinib, Bosutinib, HPLC, Dissociation Constants

Acknowledgments: This work was supported by Usak University BAP (project2014MF-008)

References:

1. Sherrod P.H., NLREG Version 4.0. www.sandh.com/Sherrod

Determination of pK_a Value of Roxithromycin in Tetrahydrofuran- Water Binary Mixtures by Reversed Phase Liquid Chromatography

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Macrolide antibiotics consist of 12-16 carbon atom lactone ring to which one or more sugar moieties are substituted (1). They have been widely used in human and veterinary medicine to prevent and treat microbial infections (2). Roxithromycin (ROX) is a semi-synthetic macrolide antibiotic derived from erythromycin, consist of 14 carbon atom lactone ring (3).

pK_a values are important parameters in absorption, distribution, metabolism, excretion and toxicity researches because it governs solubility, absorption, distribution and elimination of substances (4). There has not been reported for determination of pK_a value of roxithromycin, including the use of liquid chromatography.

In this study pK_a value of roxithromycin was determined and the effect of the mobile phase composition on the ionization constant was studied by measuring the pK_a at different tetrahydrofuran (THF)- water mixtures 35, 40 and 45% (v/v) using LC-UV method. Determination of pK_a values were carried out by using the software NLREG 4.0 (6). This a non-linear regression program specifically developed to calculate pK_a values from capacity factors and pH.

	<i>pK_a Value</i>
35% THF	9.245±0.126
40% THF	8.839±0.040
45% THF	8.536±0.050

Table 1. The pK_a values and the capacity factors of ROX in THF-water mixture

Keywords: Roxithromycin, RP-HPLC, pK_a, Macrolide antibiotics

References:

1. Kim Y.H., Pothuluri J.V., Cerniglia C.E. Journal of Pharmaceutical and Biomedical Analysis (2005) 38 390–396.
2. Sanlı S., Altun Y., Alsancak G. Journal of Solution Chemistry (2012) 41 1352–1363.
3. Głowska F.K., Karázniewicz-Łada M. Journal of Chromatography B, (2007) 852 669–673.
4. Martell A.E., Motekaitis R.J. (1992) Determination and Use of Stability Constants, 2nd ed. pp. 75-85 VCH Publishers. New York.
5. Sanlı S., Sanlı N., Alsancak G. Acta Chimica Slovenica (2010) 57 980–987.
6. Sherrod P.H., NLREG Version 4.0. www.sandh.com/Sherrod

Determination of Dissociation Constants of Some Anti-diabetic Drugs in Water by Capillary Electrophoresis Method

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Glibenclamide, gliclazide (second generation sulfonylurea) and glimepiride (third generation sulfonylurea) are oral blood sugar-lowering drugs. They are oral hypoglycemic ([anti-diabetic drug](#)) and is classified as a [sulfonylurea](#). Sulfonylureas are used to treat Type II diabetes. They inhibit ATPase-dependent sodium channels in pancreatic beta cells.

Capillary electrophoresis has been introduced as a convenient method for the separation of different substances. In the case of ionizable compounds, their electrophoretic behavior is established from the relationships between the electrophoretic mobility of each species, the dissociation constants of the substances, and the pH of the buffer solution. This allows the acidity constants of the substances by measuring the electrophoretic mobility as a function of pH.^{1,2}

In this work, capillary electrophoresis method have been used for the determination of the dissociation constants of some sulfonyl ureas namely glipizide, glibenclamide, gliclazide.

Keywords: Dissociation Constants, Sulfonylurea, Capillary Electrophoresis

Acknowledgments: This work was supported by Usak University BAP (project 2014MF-008)

References:

1. Janos P. J. Chromatogr., A (2004) 1037 15–28.
2. Poole SK, Patel S, Dehring K, Workman H, Poole CF. J. Chromatogr., A (2004) 1037 445–454.

Temperature-dependent Determination of Dissociation Constants of Three ACE Inhibitors with Reversed Phase Liquid Chromatography

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Angiotensin converting enzyme (ACE) inhibitors are widely used in the treatment of hypertension. They have also been effective in a number of other disorders, prolonging survival in patients with heart failure, coronary heart disease, and acute myocardial infarction, and slowing the rate of progression in chronic renal failure, particularly diabetic nephropathy [1]. In addition to the role these group plays in constricting arteries and raising blood pressure, in that it causes increases in size or thickness of several cardiovascular structures. Therefore, determinations of clinical and physicochemical properties of these drugs are very significant in order to drug discovery, development and manufacturing.

Dissociation constants (pK_a) are fundamental to the variability of the biopharmaceutical characteristics of drugs. pK_a values affect physicochemical properties such as aqueous solubility, which in turn influences drug formulation approaches. More importantly, absorption, distribution, metabolism, excretion and toxicity (ADMET) are profoundly affected by the charge state of compounds under varying pH conditions. Consideration of pK_a values in conjunction with other molecular properties are great significance and have the potential to be used to further improve the efficiency of drug discovery [2].

There are several different methods that can be employed to determine the pK_a values of the drugs, such as: chromatographic, spectrophotometric, potentiometric and electrophoretic. This study demonstrated that determined the dissociation constants of studied ACE inhibitors (benazepril, cilazapril and quinapril) in various acetonitrile-water mixtures to show how the temperature and solvent properties affect the dissociation of such compounds. In existing study, chromatographic pK_a determinations were performed at two different temperature (25°C and 37°C). A YMC Triart C₁₈ column (150 x 4.6 mm ID, 3 µm) was used for all separations. The effect of the mobile phase composition on the pK_a values was studied at four acetonitrile concentrations, 40%, 45%, 50% and 55% (v/v). In result, estimated pK_a values of investigated drugs were assessed by comparing them with literature data.

Keywords: ACE Inhibitors, Temperature Effect, pK_a Determination, Chromatographic Behaviour.

References:

1. Smith T.W., Morgan J.P. www.uptodate.com (2015).
2. Manallack D.T., Prankerd R.J., Yuriev E., Oprea T.I., Chalmers D.K. Chemical Society Reviews (2013) 42 (2) 485-496.

Prediction of Retention Behaviour of Some Quinolones; Their Dissociation Constants and Lipophilicity Parameters

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Quinolones are a class of synthetic antimicrobial agents widely used against a variety of bacterial infections. Its molecular structure confers the characteristic of being zwitterionic drugs[1]. As zwitterionic substances, they may exist in four different species (cation, neutral, anion and zwitterion) in solution depending on the pH of the medium and their dissociation constants[2]. A simple rule in reversed phase HPLC is that the more hydrophobic an analyte is the more it will be retained. Of course this observation is valid when the mobile phase consists of solvents that cannot induce ion formation of the analyte molecules. However, it is common place that using mobile phases adjusted different pH values, compounds bearing acidic or basic groups will ionize to a different extent. Therefore, depending on the eluent pH, analytes will be found partially or fully ionized form and their retention might have a considerable shift. A realistic approach of the retention mechanism should include the study of all interaction taking place. For these purpose quantitative structure retention relationships models are employed[3].

In the present study the dissociation constant and lipophilicity of anti-diabetic drugs have been determined by reverse phase HPLC in isocratic mode. The influences of pH of the mobile phase and the organic modifier content (Acetonitrile) on the retention times were investigated. The theoretical models for the dependence of retention time on pH of the mobile phase were tested. Inclusion of the acid dissociation constant (pK_a) and f parameters in the calculation makes it possible to predict the retention behavior of these compounds. pK_a values are discussed in terms of solvatochromic parameters (π^* , α , β), of the mixed solvent. The relationships obtained allow the calculation of the aqueous pK_a values of the studied substances. Moreover, tr_{HA} and tr_A calculated from the measured data in order to calculate log P parameters of these substances. The distribution coefficient graphs were constructed by using mathematically derived theoretical equations (for neutral, P and ionic, P_i) to show the change in lipophilicity with respect to pH.

Keywords: Quinolones, RP-HPLC, Kamlet Taft solvatochromic parameters

References:

1. Cárdenas-Youngs G, Beltrán J Journal of Chemical and Engineering Data (2015) 60 3327–3332.
2. Mazák K, Kökösi J, Noszál B European Journal of Pharmaceutical Sciences (2011) 44 68–73.
3. Roses M, Bolliet D, Poole CF Journal of Chromatography A (1998) 829 29–40.

Experimental Determination for Thermodynamic Protonation Constant of Three Selective Serotonin Reuptake Inhibitors

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The selective serotonin reuptake inhibitors (SSRIs) are antidepressant that used as a major alternative to tricyclic antidepressants in the treatment of depression as well as other psychiatric disorders such as mood, anxiety, some personality and eating disorders. The advantages of SSRIs over the tricyclic antidepressants are their less pronounced anticholinergic adverse effects and lack of severe cardiotoxicity [1]. Commonly used SSRIs include fluoxetine, sertraline, paroxetine, fluvoxamine, citalopram, and escitalopram.

In the present work, thermodynamic protonation constant of SSRIs group drugs (fluvoxamine, citalopram and sertraline) using chromatographic data in acetonitrile-water binary mixtures with acetonitrile percentages of 40, 45, 50 and 55% (v/v) were determined with reversed phase liquid chromatography method (RPLC). pH values were measured in the hydroorganic mixture, which was used as the mobile phase, taking into account the effect of the activity coefficients. The combined effect of the two factors (solvent percentage and pH of the mobile phase) on the chromatographic behavior of these compounds was investigated. The sigmoidal relationship between mobile phase pH and experimental retention factor values of fluvoxamine, citalopram and sertraline at each mobile phase composition were given Fig 1.

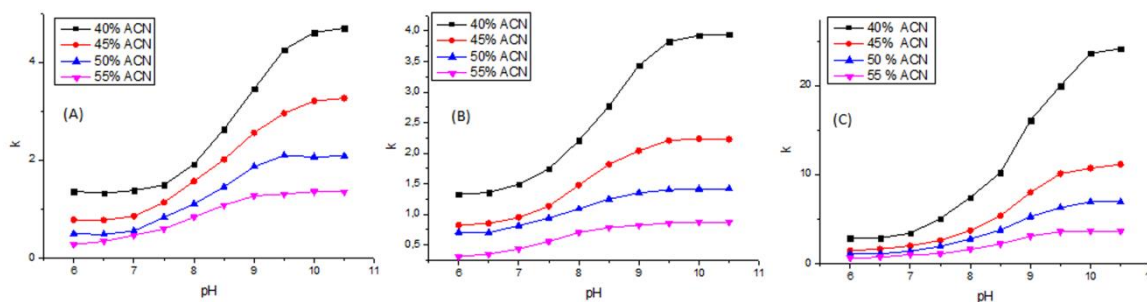


Fig.1. Plots of the calculated retention factors vs. the pH of the mobile phase for (A) citalopram (B) fluvoxamine (C) sertraline in several acetonitrile-water mobile phases.

The thermodynamic aqueous protonation constant was also calculated from mobile phase pK_a values determined by means of the Yasuda-Shedlovsky equation [2,3] and linear relationships between the mole fraction of acetonitrile and mobile phase pK_a values.

Keywords: Antidepressant, Combined Chromatographic Effect, Aqueous Pk_a Value

References:

1. P. Baumann, Clinical Pharmacokinetics (1996) 31 444-469.
2. M. Yasuda, Bull. Chem. Soc. Jpn. (1959) 32 429-432.
3. T. Shedlovsky, B (1962). Electrolytes, Pergamon Press, New York,

Prediction of Retention Behaviour of Selected NSAIDs and Zofenopril; Their Dissociation Constants and Lipophilicity Parameters

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Most pharmaceutical compounds contain ionisable functionalities. The retention of an ionisable compound in RP-LC is different from the retention of a neutral one. An ionizable compound presents equilibrium between its acidic (HA) and its basic (A) forms related by the dissociation constant where the concentration each form depends on factor that effect the extent of the dissociation. In addition the hydrophobic interaction the secondary interactions between the species of ionisable compounds and stationary phase are important. The observed retention time (t_r) is an average of the retention time of the neutral ($t_{r,HA}$) and anionic forms ($t_{r,A}$). It has been demonstrated that reversed phase liquid chromatography (RPLC) can be used to determine the dissociation constants of weak acids from the measurement of the retention factor of the solute as a function of the mobile phase composition [1]. The simultaneous determination of pK_a values together with the k_{HA} and k_A from k/pH data requires the application of non-linear curve-fitting. Recently linear equation between $\log t_r$ and molecular parameter, $\log [1-D(1-f)]$, was preferred. Inclusion of the acid dissociation constant (pK_a) and f parameters in the calculation makes it possible to predict the retention behavior of ionisable compounds [2]. In current study, the pH dependencies of the retention times of eight non-steroidal anti-inflammatory drugs (NSAIDs) etodolac, diclofenac, acetaminophen, aceclofenac, diflunisal, dexketoprofen, ketorolac, tolmetin and zofenopril were investigated. The data obtained are also evaluated for the calculation of the lipophilicity parameter. The results obtained revealed the chromatographic method can be used for pK_a and $\log P/\log D$ determination.

Keywords: Ionisable Compounds, Solute Descriptors, Dissociation Constant

References:

1. Horvath, C. Analytical Chemistry (1977) 49 142-154.
2. M. Roses, D. Bolliet, C. F. Poole, Journal of Chromatography A (1998) 829 29-40.

Prediction of Retention Behaviour of Diabetic Drugs and Investigation of Their Dissociation Constants and Lipophilicity Parameters

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Diabetes mellitus is a heterogeneous group of disorders characterized by abnormalities in carbohydrate, protein, and lipid metabolism. Drugs belonging to classes such as sulfonyl ureas (glipizide, glibenclamide, glimepiride) and thiazolidinedione group derivatives (pioglitazone, rosiglitazone), are the commonly prescribed hypoglycemic drugs for the treatment of non-insulin dependent type II diabetes mellitus [1,2]. In the present study the dissociation constant and lipophilicity of anti-diabetic drugs have been determined by reverse phase HPLC in isocratic mode. The influences of pH of the mobile phase and the organic modifier content(THF) on the retention times were investigated. The theoretical models for the dependence of retention time on pH of the mobile phase were tested. Aqueous pK_a values; t_{r,HA} and t_{r,A} calculated from the measured pK_a in order to calculate log P parameters of sulfonyl ureas. The distribution coefficients graph were constructed by using mathematically derived theoretical equations(for neutral, P and ionic, P_i) to show the change in lipophilicity with respect to pH. Similar approach was also applied thiazolidinedione derivatives. In this study, sulfonyl ureas and thiazolidinedione group drugs were determined by the reverse-phase liquid chromatographic (RP-HPLC) method with UV detection in 40, 45, 50, 55% (v/v) acetonitrile-water binary mixtures. Chromatographic separation was performed using YMC J'Sphere ODS-H80 column (150 mm × 4.6 mm, 4.0 μm).

Keywords: Sulfonyl Ureas, Diabetes Mellitus, RP-HPLC, Acetonitrile-Water Binary Mixtures

References:

1. L. Narasimham, V. D. Barhate, European Journal of Chemistry (2011) 2 36-46.
2. Roses M, Bolliet D, Poole CF Journal of Chromatography A (1998) 829 29–40.

Factor-Analysis Applied to the Study of the Effects of Solvent Composition on the Protonation Constants of Aliphatic Diamines in Ethanol-Water Mixtures within the Kamlet-Taft formalism

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Amino functionalized organic compounds are ubiquitous in nature. Their biological importance [1] has led to extensive studies of their structural and physicochemical properties. In addition to their relevance in biochemistry and pharmaceutical chemistry, amines are attractive building blocks in supramolecular chemistry [2]. Depending on solution pH, amine-based ligands can act as both cation and anion chelators. In order to make reliable predictions of the acid-base properties of macroligands with a large number of ionizable sites such as dendrimers, one needs to develop and validate computational methods that accurately estimate the acidity constants (pKa) of their chemical building blocks.

In this study, the stoichiometric protonation constants ($\log K_1$ and $\log K_2$) of nine aliphatic diamines have been determined in 10–80% (v/v) ethanol-water mixtures at 25 °C and constant ionic strength (0.1 mol.L⁻¹ sodium perchlorate), by potentiometric technique and calculated using a suitable computer program, which employs a nonlinear leastsquares method.

It is very difficult to interpret the $\log K$ variations of aliphatic diamines studied by only macroscopic parameters of the ethanol-water mixtures. It is known that one of the most important factors determining the equilibrium constants is the reaction medium, so, the solvent effect on protonation constants could be explained on the basis of dielectric constant of the medium, solvent structure, preferential solvation, and microscopic parameters (as Kamlet-Taft solvatochromic parameters) [3, 4].

The effect of solvent properties on pK values was studied for water-ethanol mixtures covering a wide range of solvent compositions, from data sets on aliphatic diamines. The establishment of the model was carried out using different approaches: the use of a classical procedure, where the best multiparametric fit to the Kamlet and Taft equation [5, 6] was evaluated for each substance; and the application of combined factor analysis and target factor analysis to quantify and identify the factors affecting the variation of the whole data sets, without the need to postulate any a priori hypothetical model.

Kamlet and Taft's general equation was reduced to two terms by combined factor analysis and target factor analysis in these mixtures: the independent term and polarity/polarizability π , which are solvatochromic parameters. Further, an overview of the effect of preferential solvation and solvent structure of electrolytes in ethanol-water mixtures on the values of the protonation constants in these media were also discussed.

References:

1. Lehninger, A. L.; Nelson, D. L.; Cox, M. M. Principles of Biochemistry, 2nd ed.; Worth Publishers: New York, (1993)
2. Steed, J.; Atwood, J. Supramolecular Chemistry; John Wiley and Sons, LTD: Chichester, (2000)
3. C. Reichardt, Chem. Rev. (1994) 94, 2319–2358
4. Y. Marcus, Solvent Mixtures Properties and Selective Solvation, Marcell Dekker, Inc., New York, (2002)
5. M. J. Kamlet, R. W. Taft, J. Am. Chem. Soc. (1976) 98 377–383.
6. M. J. Kamlet, J. L. Abboud, R. W. Taft, J. Am. Chem. Soc. (1976) 99 6027–6038. M. J. Kamlet, J. L. Abboud, M. H. Abraham, R. W. Taft, J. Org. Chem. (1983) 48 2877–2887.

Acidity Constant Determination of Tadalafil: Potentiometry and Spectrophotometry

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Acidic dissociation constant (pK_a) is an important physicochemical parameter in drug absorption, dissociation and elimination mechanisms. Ionization degrees of drugs at different pH values effects crossing capability through biological membranes, thus determine their pharmacodynamics/pharmacokinetic properties and application routes [1]. Tadalafil (Figure 1) is specific to cyclic guanosine monophosphate (cGMP), which is reversible and selective inhibitor of phosphodiesterize type 5 (PDE5). PDE5 inhibition of Tadalafil leads an increase in the level of Corpus cavernosum cGMP during emission of nitric oxide in consequence of sexual arousal.

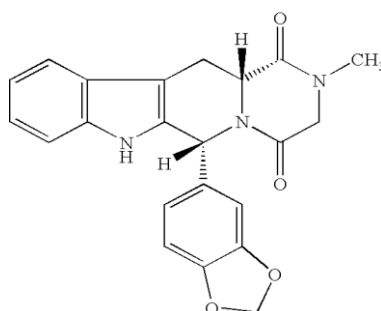


Figure 1. Tadalafil

To the authors' knowledge, experimental pK_a value for Tadalafil is not reported in the literature. In this study, pK_a of Tadalafil by using spectroscopic and potentiometric methods were optimized. The RSD for methods were not higher than 2%. The pK_a of Tadalafil was found to be 3.44 ± 0.02 by spectrophotometry and 3.52 ± 0.01 by potentiometry. Difference between the pK_a values determined by potentiometry and spectrophotometry was not statistically significant ($p < 0.05$). Moreover, experimental values were far from predicted or estimated pK_a values.

Keywords: Acidity Constant, pK_a , Tadalafil, Spectroscopic, Potentiometric

References:

1. Forgue, S.T., Patterson, B.E., Bedding, A.W., Payne, C.D., Phillips, D.L., Wrishko, R.E. et al
Tadalafil pharmacokinetics in healthy subjects. *British journal of clinical pharmacology*, (2006) 61
280-288.

Prediction of the Retention Behaviour on Butyl Column of Six NSAIDs and Zofenopril: Relation of Chromatographic Data and Eluent pH

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Non-steroidal anti-inflammatory drugs (NSAIDs) are widely used for the treatment of several rheumatic and inflammatory diseases. These drugs have the same weak monoprotic acid functionality and practically insoluble in water. Zofenopril is an ACE inhibitor drug which has carboxylic functional group. A common approach for the pK_a measurements of aqueous insoluble compounds involves the use of hydro-organic mixtures [1,2]. RPLC of lipophilic, highly retained compounds require the use of high organic modifier content. In some cases column packing with an intermediate polarity such as butyl is considered as the first choice for the investigation of retention behaviour both neutral and ionisable pharmaceuticals. These columns are capable of providing the information necessary concerning the mechanism on reversed phase chromatography with relatively low retention times for the analytes.

In the present study, the dissociation constant of etodolac, diclofenac, acetaminophen, aceclofenac, diflunisal, dexketoprofen and zofenopril were determined in acetonitrile-water binary mixtures at three different percentages (30, 35, and 40, v/v %) using RP-HPLC method. The pK_a values are calculated by fitting the molecular descriptor model to a series of retention time measurements collected at different pH values. The correlation between the theoretical and the experimental retention times of the compounds studied over the whole experimental pH range was good. In this way, a complete description of the retention behavior of each solute in the space defined by the pH of the mobile phase and degree of ionisation was obtained. The retention behavior of these compounds was accurately modeled as a function of pH of the mobile phase and f parameter.

Keywords: NSAIDs, N-Octanol: Water Partition Coefficient, RP-HPLC

References

1. M. Roses, D. Bolliet, C. F. Poole, Journal of Chromatography A, (1998) 829 29-40
2. Stareka M, Komstab L, Krzek J, Journal of Pharmaceutical and Biomedical Analysis (2013) 85 132-137.

Separation, Preconcentration and Recovery of Au (III) Ions Using Bis(3-aminopropyl)amine Bonded Silica Gel

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Bis(3-aminopropyl)amine bonded silica gel (BAPA-SG) was synthesized [1] and used as an adsorbent for recovery, preconcentration and adsorption of Au (III) ions. The effective factors on the preconcentration of Au (III) ions such as pH, volume, and flow rate of the Au (III) solution, and the type and volume of the eluent solution, and also matrix ions such as alkaline and heavy metals were investigated and optimized by solid phase extraction method. The modified silica gel could adsorb Au (III) ions quantitatively from the solutions up to 500 mL at pH 2.0 by the flow rate of 5 mL/min. The retained Au (III) ions could be easily eluted by using 5 mL of 1% (m/v) thiourea in 0.1 M HCl solution. In batch adsorption studies, the effect of contact time and initial Au (III) concentration on the adsorption were also investigated and optimized. Au (III) adsorption was found to be favoured at pH values of 2.0 and pCl of 1.0. The Au (III) adsorption was reached to equilibrium in 4 hours. Flame atomic absorption spectrometry was used for the determination of Au (III) ion concentrations through the study.

Keywords: Solid Phase Extraction, Preconcentration, Adsorption, Modified Silica Gel, Bis(3-Aminopropyl) Amine (BAPA)

References:

1. S.Sivrikaya, H.Altundağ, M.Zengin, M.İmamoğlu, Separ. Sci. Technol. (2011) 46 2032-2040.

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