Preliminary Testing Results of Sensor for Speciating Benzene, Toluene, and Ethylbenzene/Xylenes in Groundwater

Rachel E. Mohler[1], Florian Bender[2], Antonio J. Ricco[3], Fabien Josse[2], Stephen Fenton[4], Ravi Kolhatkar[5], Edwin E. Yaz[2]

1) Chevron Energy Technology Company, 100 Chevron Way, Richmond, CA 94801
2) Department of Electrical and Computer Engineering, Marquette University, Milwaukee, Wisconsin 53201-1881
3) Department of Electrical Engineering, Center for Integrated Systems, Stanford University, Stanford, California 94305-4075
4) Chevron Energy Technology Company, 6001 Bollinger Canyon Rd, CA 94583
5) Chevron Energy Technology Company, 3901 Briarpark, Houston, TX 77042

Outline

- Background
  - Motivation
  - Composition of groundwater
  - Sensors
- Study
  - Limit of detection
  - Stability
  - Partial selectivity
- Summary
- Questions

Background: Motivation

- Regulators frequently require the monitoring of benzene, toluene, ethylbenzene and xylenes in the groundwater at fuel release sites
- 570,000 federally regulated underground storage tanks exist in the US alone[1]
- Sites can be monitored multiple times a year for many decades
- Monitoring typically involves the following:





[1] U.S. Environmental Protection Agency, Semiannual Report Of UST Performance Measures, End Of Fiscal Year 2014 (www.epa.gov/oust/cat/ca-14-34.pdf)

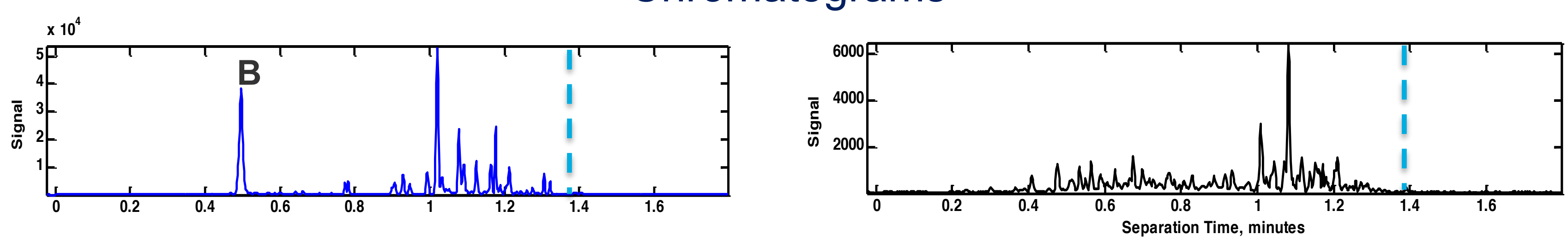
Motivation: In Situ Sensors

- Allow for on demand detection of concentrations of analytes of interest in groundwater monitoring wells
- Minimize travel to the field, since data can be wirelessly transmitted to a remote location
  - Reduced cost due to reduced travel and reduced labor involved
  - Improved safety
- Improved management of hydrocarbon impacted sites
  - Frequent analysis can provide a better understanding of temporal changes in concentrations
  - Real-time assessment of the effectiveness of remediation systems.

Composition of Groundwater at Fuel Release Sites

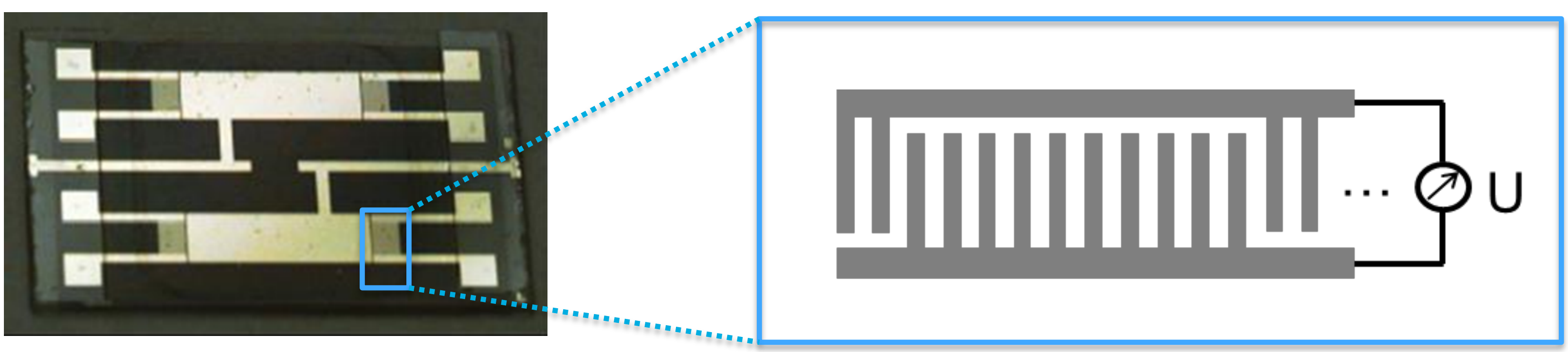
- Varies from site to site, but typically contains aromatic hydrocarbons mostly C15 and lower
- As carbon number increases the number of chemical isomers increase
- Sensing device must be selective enough to differentiate a potentially large number of chemically similar compounds
- Additional interferents might be present (salts, sediment, humic acid, dissolved gases, aliphatic hydrocarbons, ethers, etc.…)

Chromatograms



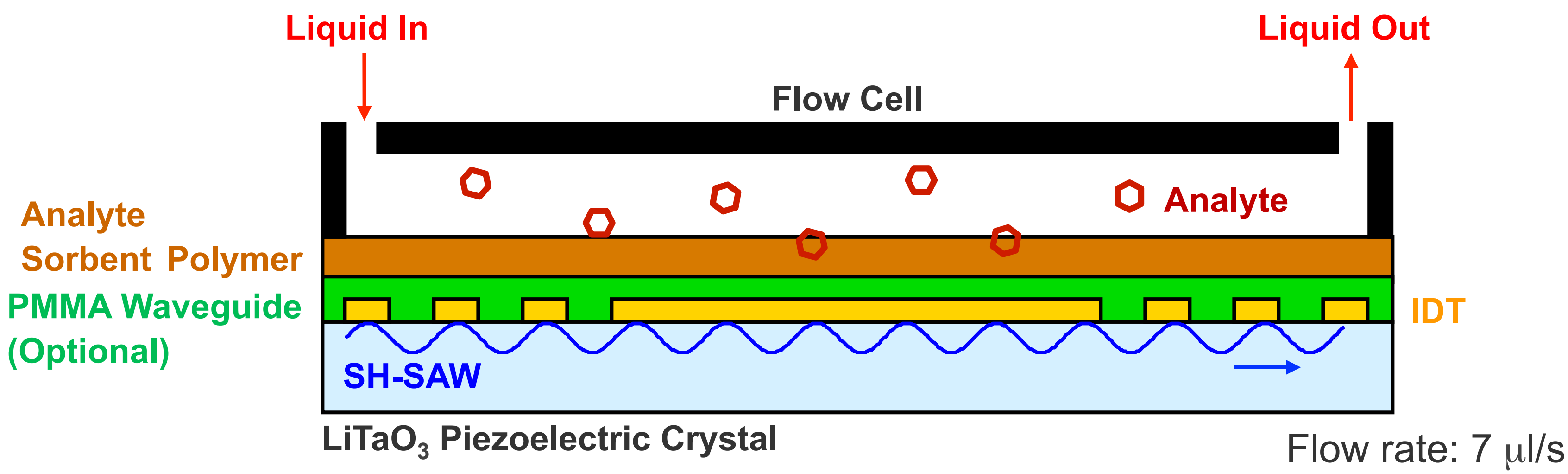
Approach to Sensing: Polymer-coated SH-SAW Sensor Devices

- An acoustic wave sensor device consists of:
  - a piezoelectric crystal supporting an acoustic wave,
  - interdigital transducers (IDTs) that generate and receive the acoustic wave and
  - a partially selective coating that interacts with the analytes of interest.
- Shear-horizontal SAW devices are different from other SAW devices because the acoustic vibration is strictly parallel to the IDT fingers and therefore, no energy is coupled to the liquid in form of compressional waves

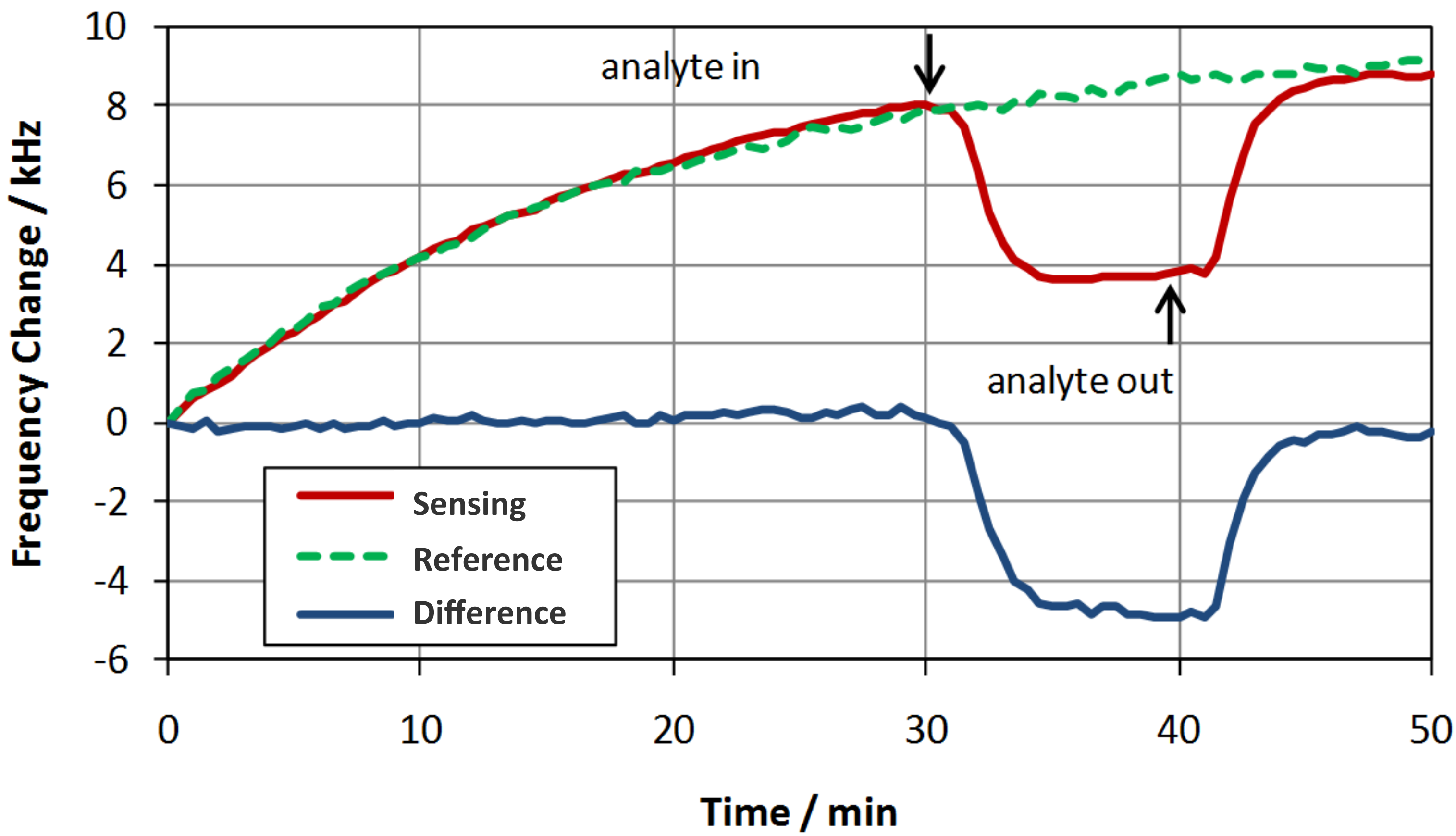


Approach to Sensing: SH-SAW Liquid-Phase Sensor Layout

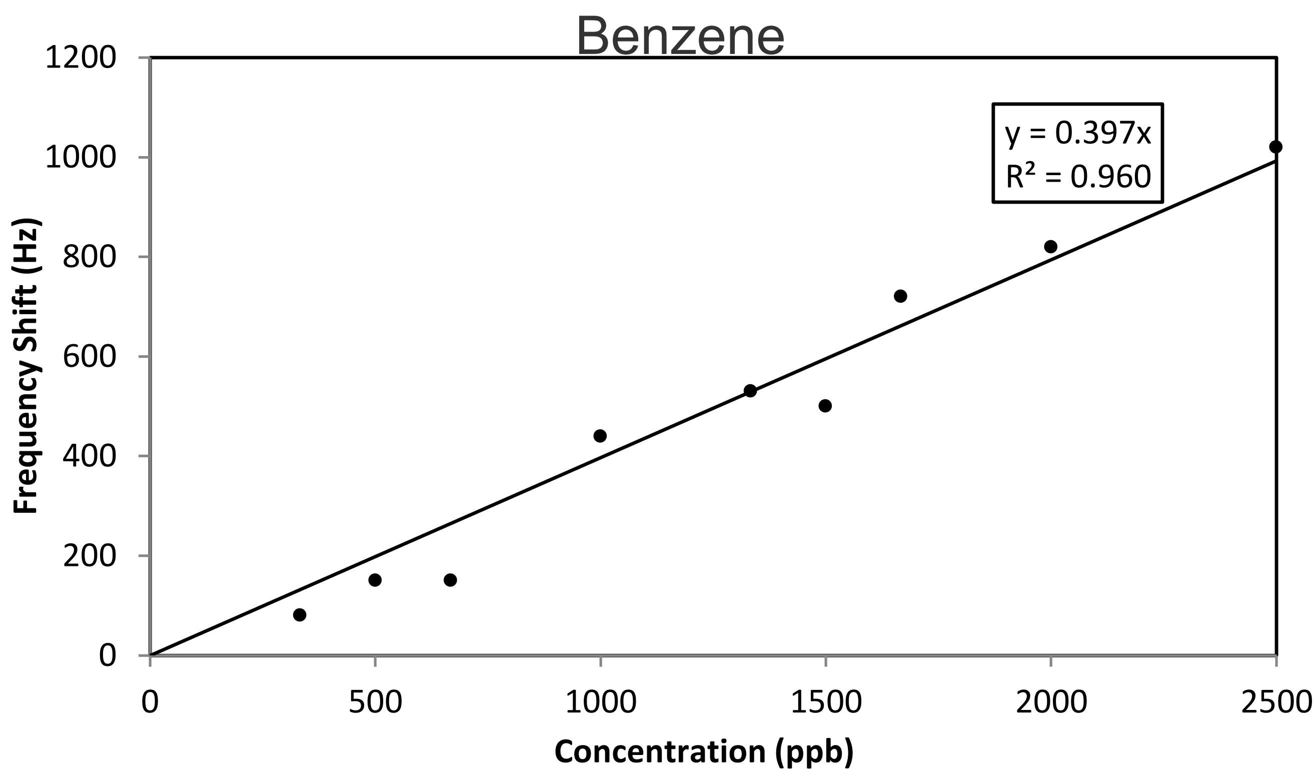
- Sensor device, cross sectional view



Sample Response Curve



Linearity of Sensor Response with Concentration

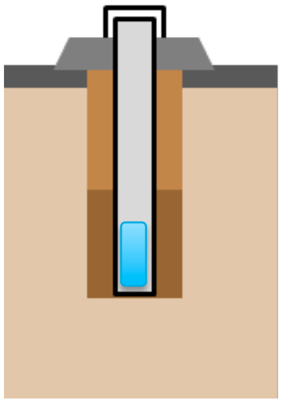


- Linear up to about low ppm (<50ppm) for benzene

Objective of Study

- The goal of the study is to develop a downhole groundwater sensor system that can monitor BTEX and is:
  - Sensitive
  - Robust
  - Selective
  - Efficient

Monitoring Well



Sensor device/system (blue) in downhole groundwater

Experiments: Analytes and Coating materials

- Analytes Quantified: BTEX (benzene, toluene, ethylbenzene and xylenes)
  - dissolved light non-aqueous phase liquid (LNAPL) in DI water and GW
  - Groundwater collected at release sites
- Chemically Sensitive Polymer Coatings:
  - Poly(epichlorohydrin) (PECH)
  - Poly(isobutylene) (PIB)
  - Various other polymers
- The selected polymers show relatively high partition coefficients for BTEX in water[1] and high reproducibility under conditions of changes in ambient temperature, pH, and salinity[2]; coating thickness ranges from 0.5 μm to 1.0 μm

[1] Y.K. Jones et al., *IEEE Sens. J.,* vol. 5, pp. 1175–1184, 2005.
[2] F. Bender et al., *2011 Joint Conf. of the IEEE IFCS and the EFTF,* pp. 422–427, 2011.

Sub-ppm Range BTEX Detection

Single Analyte Detection Limits

Measured and calculated detection limits (defined as 3 × RMS noise / sensitivity) to date for a sensor coated with 0.6 µm PECH (polyepichlorohydrin)

Analyte	Detection Limit (ppb)	Solubility[1] (ppm)	Detection Limit / Solubility ($\times 10^{-6}$)
Benzene	100*	1780	56
Toluene	33 (50*)	531	62
Ethylbenzene[2]	9 (50*)	161	56

[1] Solubility in water, after D.L. Lide, Handbook of Chemistry and Physics, 82nd ed.; CRC Press: Boca Raton, FL, 2001–2002; pp. 8–95
[2] Xylenes are chemical isomers of ethylbenzene and, therefore, they have about the same sensitivity and response time
* Value experimentally verified

Extraction of Sensing Parameters from Single-Analyte Measurements: Calibration of Sensors

Measured average sensitivities, σ (Hz/ppm)[1]

Polymer	$\sigma_{benzene}$	$\sigma_{toluene}$	$\sigma_{ethylbenzene}$
1.0 µm PEA	244 (±27)	690 (±160)	2240 (±460)
0.6 µm PECH	109 (±9)	435 (±25)	1450 (±240)
0.8 µm PIB	63 (±5)	344 (±43)	1670 (±10)

Measured average response times, τ (s)[1]

Polymer	$\tau_{benzene}$	$\tau_{toluene}$	$\tau_{ethylbenzene}$
1.0 µm PEA	36.1 (±10.0)	76.7 (±6.0)	204 (±4.5)
0.6 µm PECH	26.5 (±8.4)	77.6 (±2.8)	175 (±13)
0.8 µm PIB	29.3 (±7.8)	84.2 (±6.5)	245 (±14)

- Extracted average sensitivities and time constants from experiments with single-analyte solutions (DI Water) for the selected polymer coatings[1]:

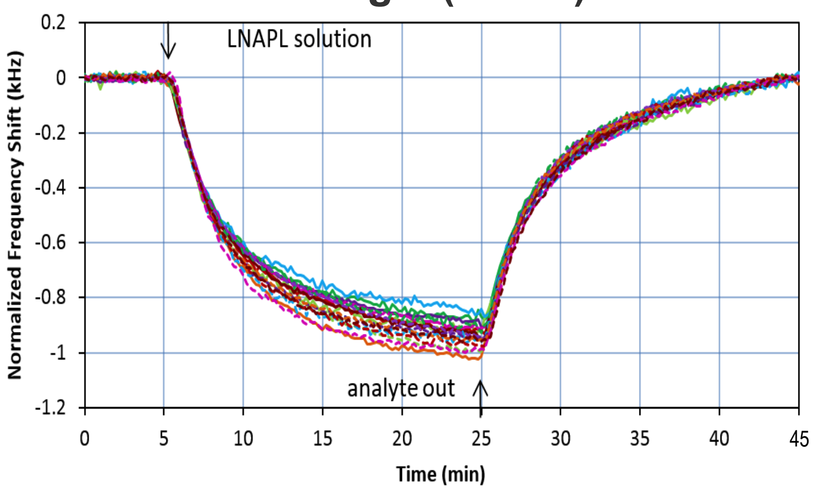
  Note: Xylenes are chemical isomers of ethylbenzene and, therefore, they have about the same sensitivity and response time

[1] F. Bender et al., *Anal. Chem.,* vol. 86, pp. 1794–1799, 2014.

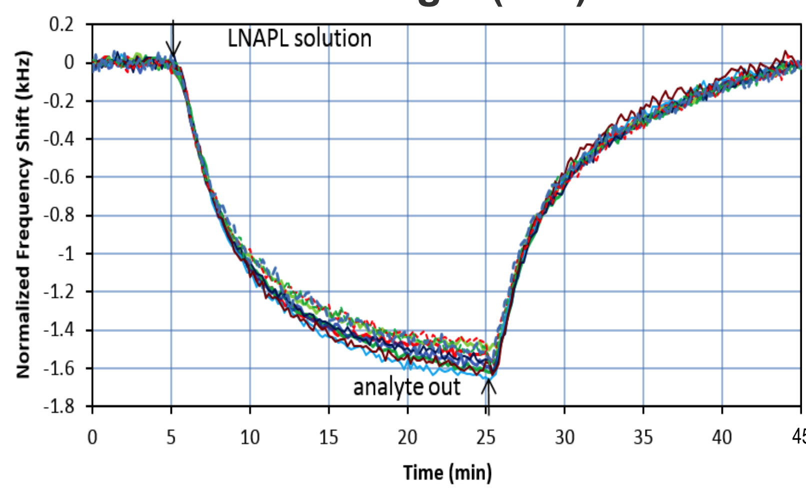
Long-Term Repeatability of Sensor Response

- Prepared a set of samples of aqueous solutions of light non-aqueous phase liquid (LNAPL) from one monitoring well
- Samples were stored at 4°C until used
- Analyzed these samples ***over a three month period***
- Monitored the actual concentration using a portable GC (Defiant Frog 4000) (Error on GC measurement about ±10%[1])
- Normalized the sensor response to toluene concentrations

Coating 1 (PECH)



Coating 2 (PIB)



[1] Defiant Technologies, Inc., 2014 (www.defiant-tech.com/pdfs/Pittcon 2014 A Micro-GC Based Chemical Analysis System.pdf)

Sensor Repeatability over Three Months

- Signal Response Sensitivity:

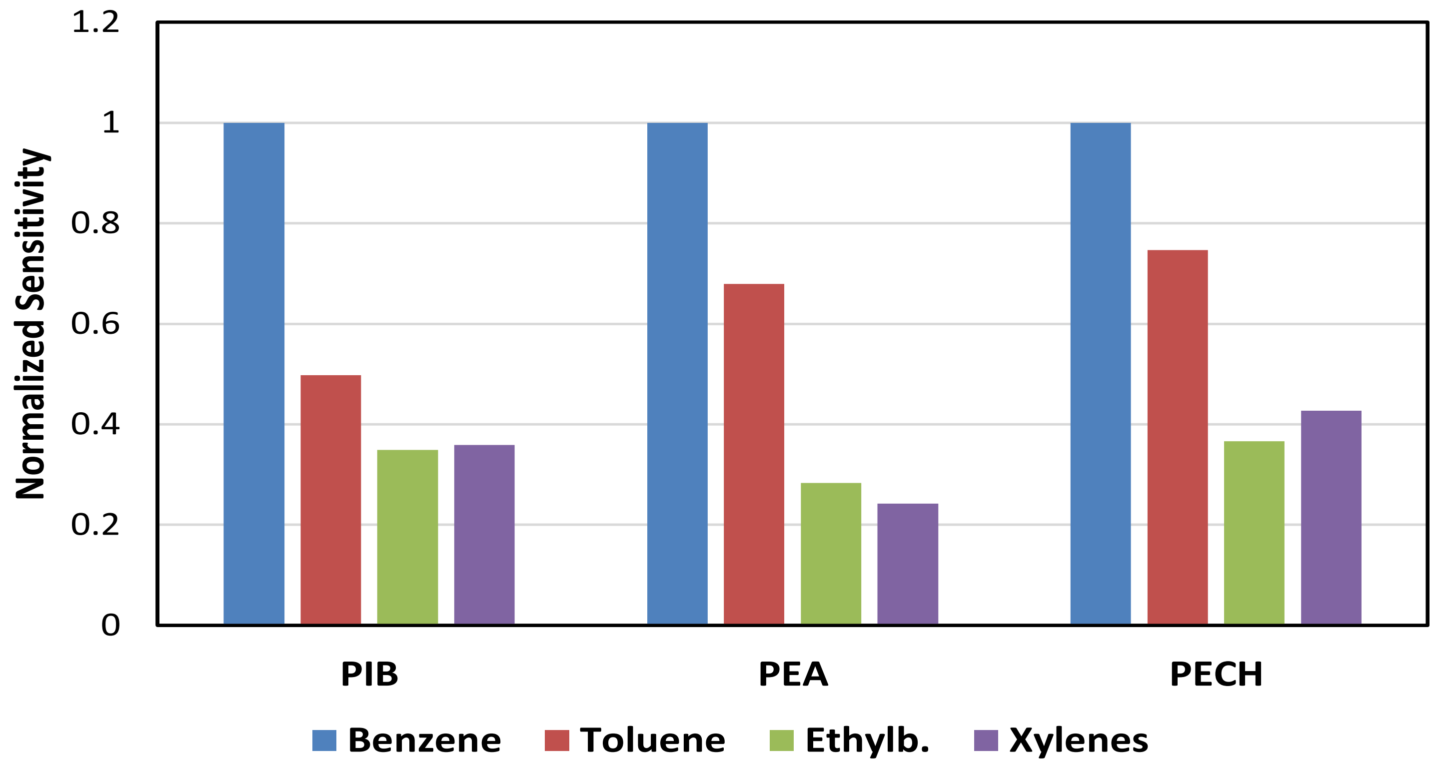
	PIB Signal (kHz)	PECH Signal (kHz)
AVG	-1.40	-1.26
STD	0.19	0.11
RSD %	14	9

- Signal Time Response:

	PIB Time Constant, τ (s)	PECH Time Constant, τ (s)
AVG	263	257
STD	41	23
RSD %	16	9

AVG = average, STD = standard deviation, RSD = relative standard deviation (STD/AVG, in %)

Partial Selectivity: Analyte Response to Each Coating



- Each coating responds to all analytes, but the magnitude of the response varies, indicating partial selectivity.
- Sensitivities are normalized to molecular mass and aqueous solubility of the analyte, and divided by the respective value for benzene

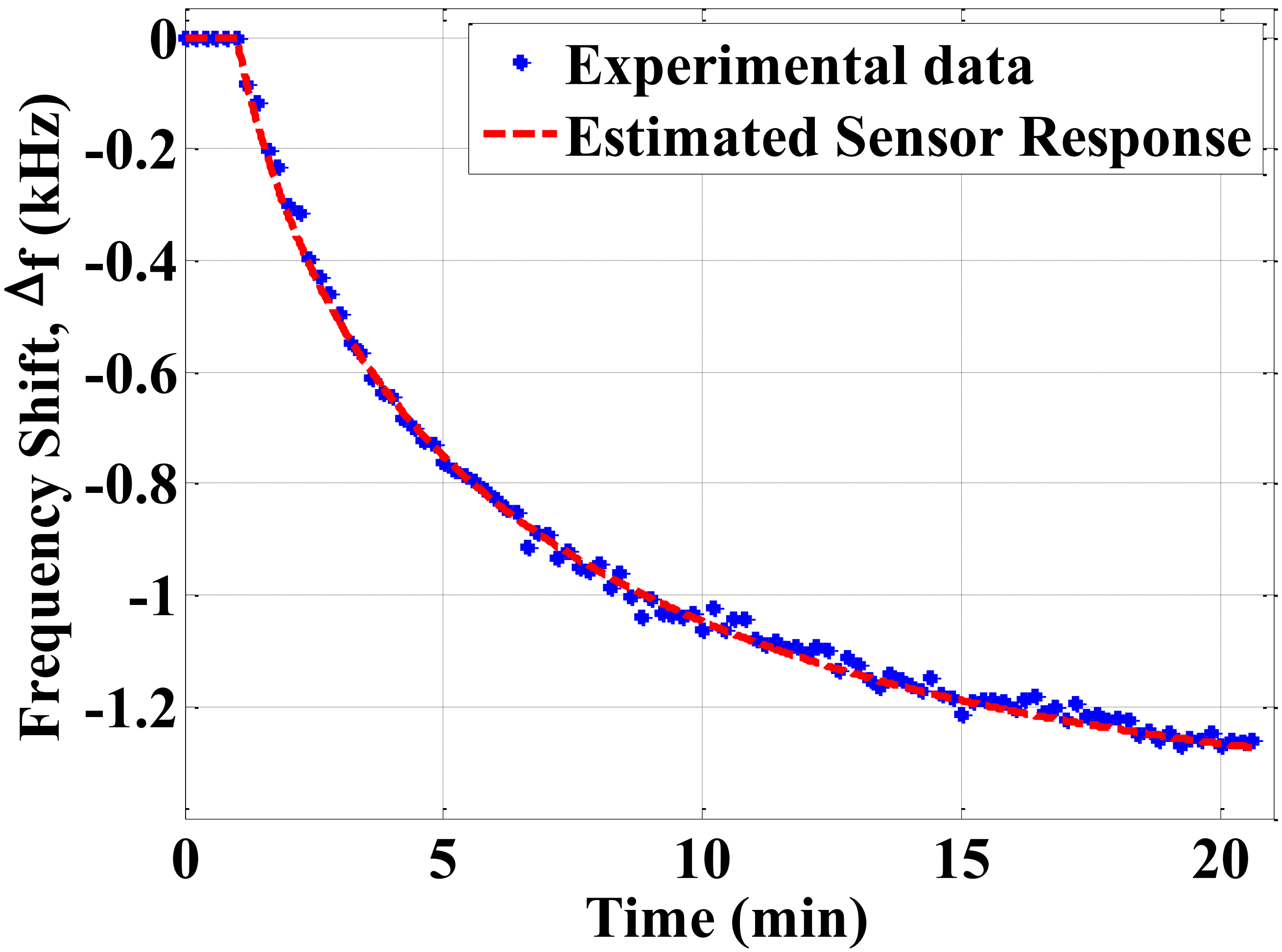
Data Processing Using Estimation Theory: Overview

- Objective: Estimation of BTEX concentrations on-line, extracted from noisy and contaminated sensor responses to samples containing multiple analytes.
- Approach: Use of estimation theory-based sensor signal processing[1]. Assumptions for modeling sensor responses:
  - Experimental observations for small analyte concentrations indicate exponential form for sensor response
  - Response to mixture of analytes given by sum of responses to single analytes (validity of Henry's law)
    - Observed frequency shifts will be additive
  - Analyte sorption is assumed to be reversible (physisorption)
  - Interferents have low sensitivity with coating and/or longer response times

[1] K. Sothivelr et al., *2014 IEEE Sensors,* pp. 578–581, 2014.

Data Processing Using Estimation Theory
Estimation Results: Sample Data

Estimated sensor response obtained for detection of **LNAPL in DI water**, measured using a SH-SAW sensor coated with **0.7 µm PIB**.



Concentrations measured by GC-PID (ppb):

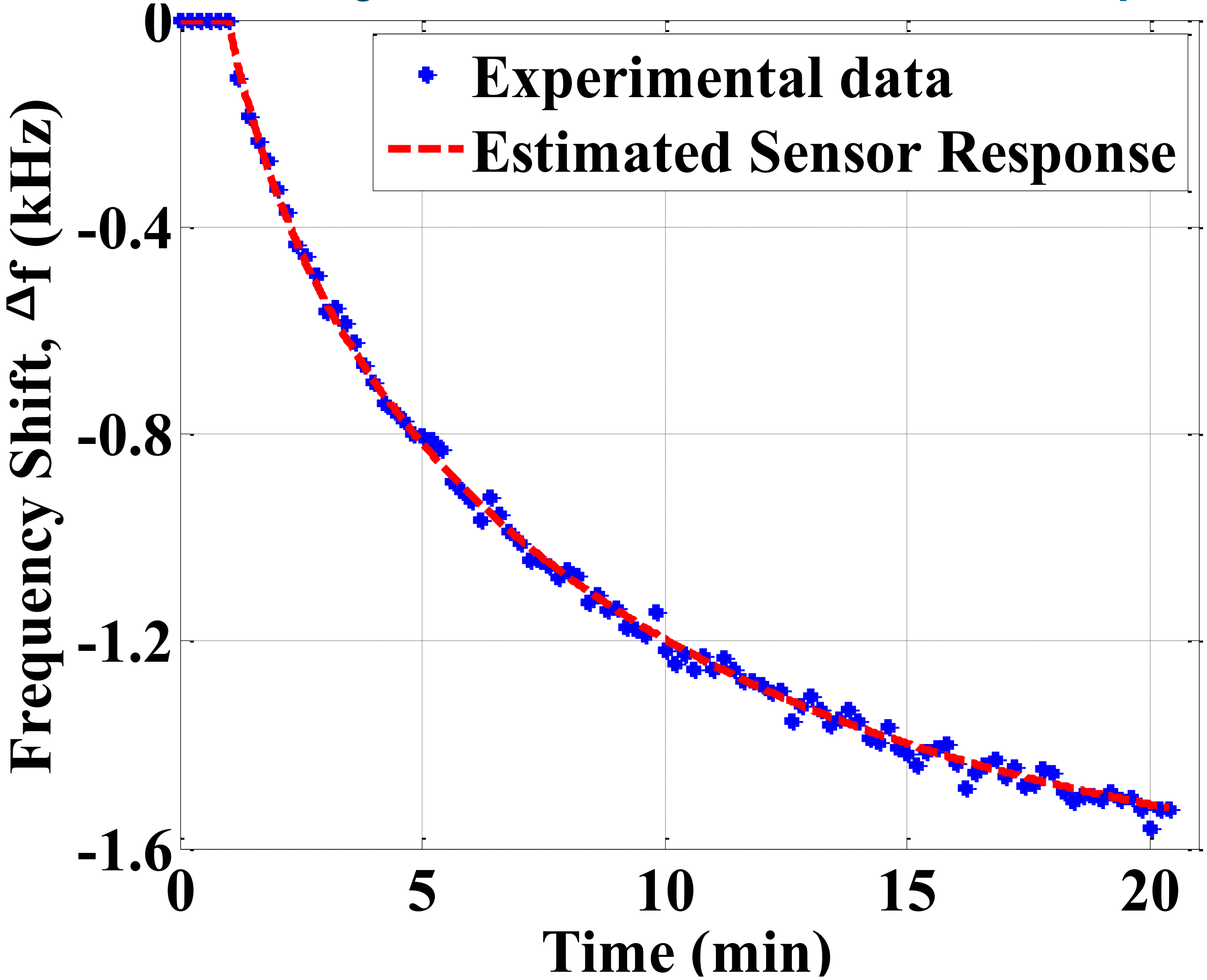
Benzene: 575
Toluene: 910
EX: 224

Estimated concentrations (ppb) (% difference):

Benzene: 478 (17 %)
Toluene: 878 (4 %)
EX: 213 (5 %)

Data Processing Using Estimation Theory
Estimation Results: Sample Data

Estimated sensor response obtained for detection of **LNAPL in groundwater**, measured using a SH-SAW sensor coated with **0.7 µm PIB**.



Concentrations measured by GC-PID (ppb):

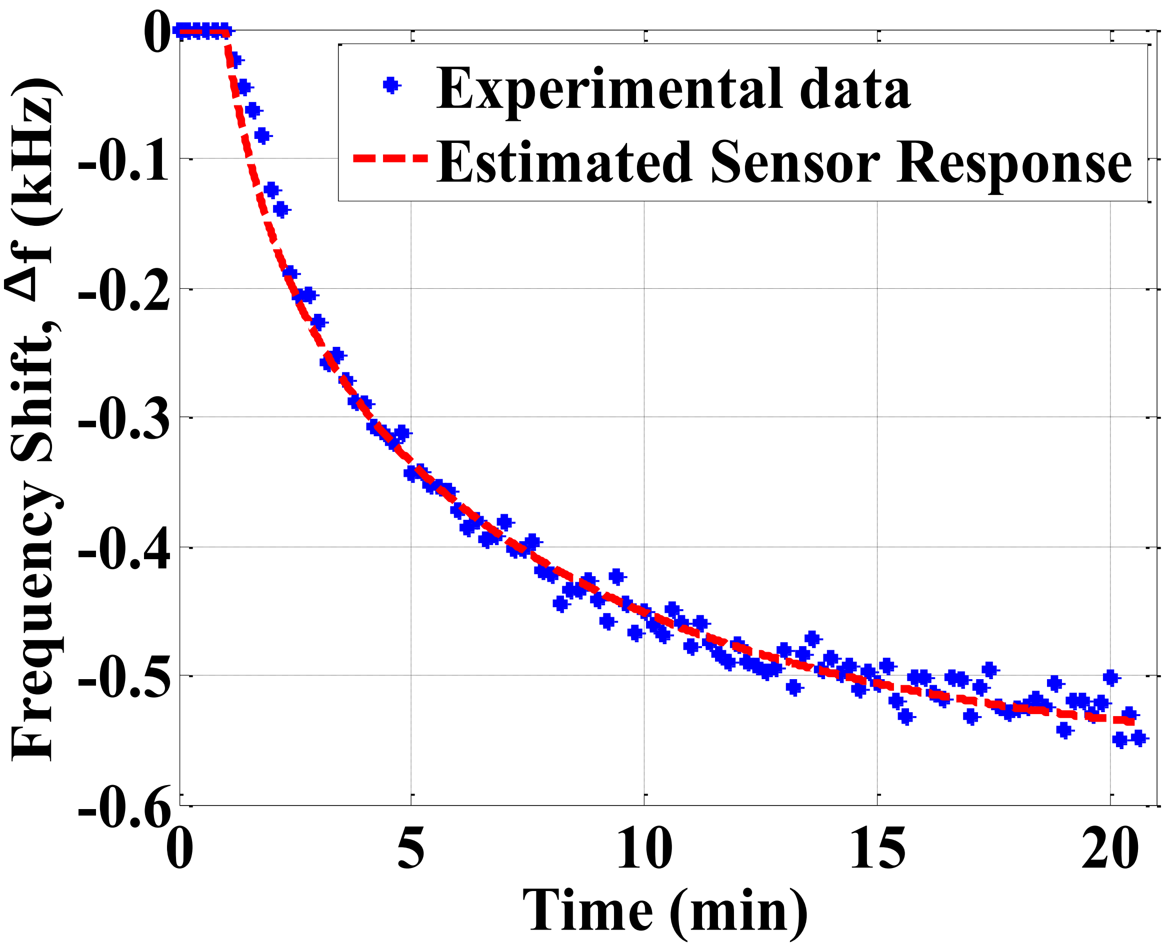
Benzene: 555
Toluene: 827
EX: 118

Estimated Concentrations (ppb) (% difference):

Benzene: 500 (10 %)
Toluene: 894 (8 %)
EX: 134 (14 %)

Data Processing Using Estimation Theory
Estimation Results: Sample Data

Estimated sensor response obtained for detection of **LNAPL in DI water**, measured using a SH-SAW sensor coated with **0.5 µm PECH**.



Concentrations measured by GC-PID (ppb):

Benzene: 219
Toluene: 327
EX: 30

Estimated concentrations (ppb) (% difference):

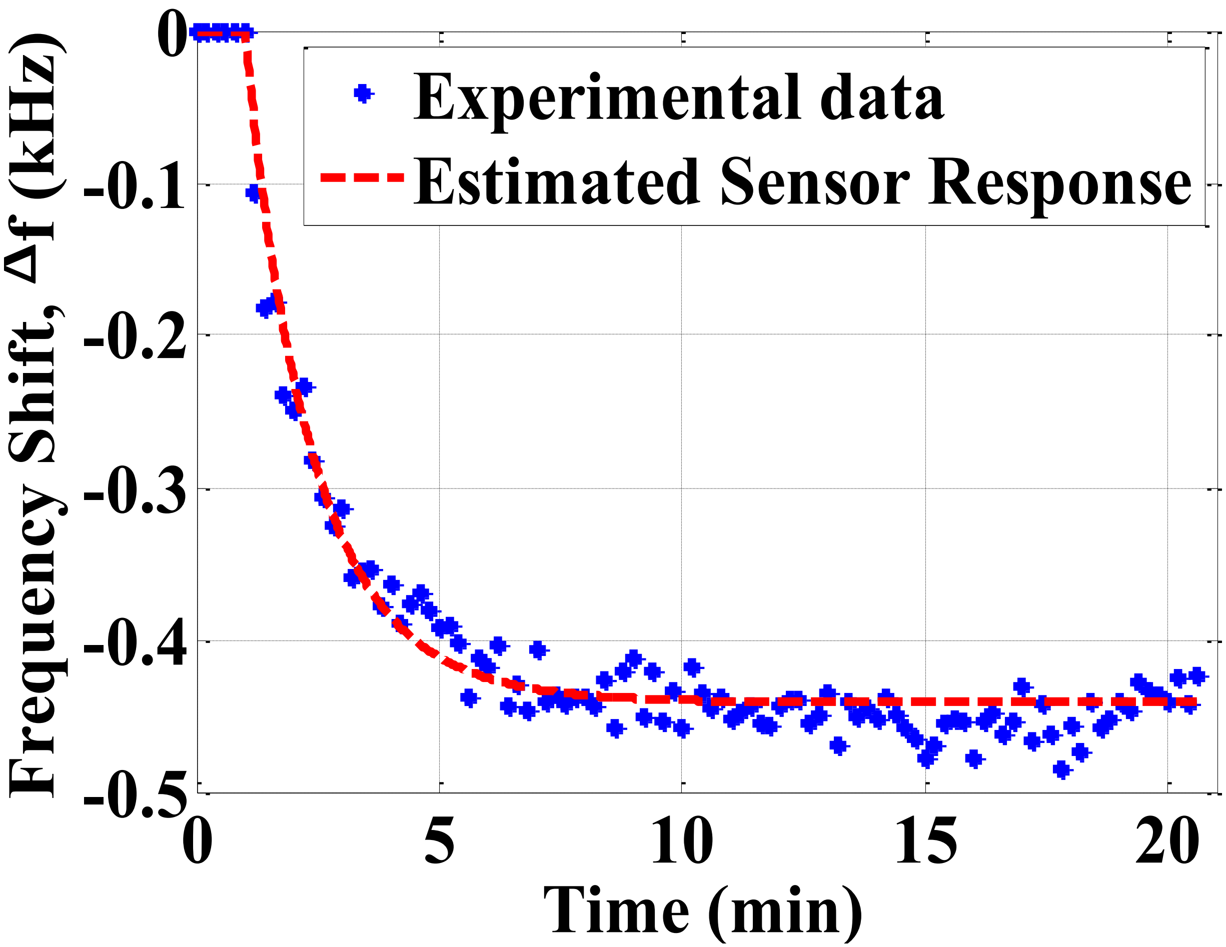
Benzene: 247 (13 %)
Toluene: 284 (13 %)
EX: 49 (64 %)

Marquette University

Data Processing Using Estimation Theory
Estimation Results: Sample Data

Chevron

Estimated sensor response obtained for detection of **LNAPL in groundwater**, measured using a SH-SAW sensor coated with **0.5 µm PECH**.



Concentrations measured by GC-PID (ppb):

Benzene: 197
Toluene: 241
EX: 16

Estimated Concentrations (ppb) (% difference):

Benzene: 225 (14 %)
Toluene: 267 (11 %)
EX: 28 (72 %)

Data Processing Using Estimation Theory
Estimation Results: Summary

- Estimated concentrations obtained from sensor responses to LNAPL in DI water using a SH-SAW sensor coated with 0.7 μm PIB.

Measured Data	Concentrations (ppb)			
	Actual		Estimated	
	Benzene	Toluene	Benzene (% diff.)	Toluene (% diff.)
18-Jul-14	952	1307	**891 (6.4)**	**1418 (8.5)**
22-Jul-14	575	910	**583 (1.4)**	**861 (5.4)**
29-Jul-14	552	877	**555 (0.6)**	**938 (7.0)**
4-Aug-14	553	868	**483 (12.7)**	**974 (12.2)**
11-Aug-14	521	825	**607 (16.5)**	**924 (12.0)**
18-Aug-14	522	807	**578 (10.7)**	**713 (11.7)**
12-Sep-14	618	966	**719 (16.3)**	**848 (12.2)**
22-Sep-14	740	1030	**662 (10.5)**	**1063 (3.2)**
10-Oct-14	464	646	**498 (7.4)**	**580 (10.2)**
20-Oct-14	469	671	**545 (16.2)**	**707 (5.4)**
Average Error (%)			***9.9***	***8.8***

Summary

- Groundwater sensors are an attractive technology for in situ measurements
- A groundwater sensor system is being developed that can detect chemicals of concern down to concentrations in the low ppb range
- The coated sensor has been proven stable over the course of 3 months with % relative standard deviations less than 20%
- Novel sensor data processing methods are being developed that result in errors less than 10% for measurements in DI water and less than 15% for measurements in groundwater

Summary (cont'd)

- A good estimate of the BTEX concentrations can be obtained just by using the data collected in the first few minutes (4 – 7 mins)
- Work is currently in progress to simultaneously process the output of multiple SH-SAW sensors with different polymer coatings to improve accuracy and enhance reliability
- Future development of these devices into downhole sensors capable of detecting and quantifying dissolved BTEX looks promising

Publications

- F. Bender, F. Josse and A.J. Ricco: “Influence of Ambient Parameters on the Response of Polymer-Coated SH-Surface Acoustic Wave Sensors to Aromatic Analytes in Liquid-Phase Detection”, 2011 Joint Conference of the IEEE IFCS and EFTF Proc. 422–427
- F. Bender, R. Mohler, A.J. Ricco and F. Josse: “Quantification of Benzene in Groundwater Using SH-Surface Acoustic Wave Sensors”, IMCS 2012 Proc. 473–476
- F. Bender, F. Josse, R.E. Mohler and A.J. Ricco: “Design of SH-Surface Acoustic Wave Sensors for Detection of ppb Concentrations of BTEX in Water”, Proc. 2013 Joint UFFC, EFTF and PFM Symp. 628–631
- F. Bender, R.E. Mohler, A.J. Ricco and F. Josse: “Identification and Quantification of Aqueous Aromatic Hydrocarbons Using SH-Surface Acoustic Wave Sensors”, Anal. Chem. 86 (2014) 1794–1799
- F. Bender, R.E. Mohler, A.J. Ricco and F. Josse: “Analysis of Binary Mixtures of Aqueous Aromatic Hydrocarbons with Low-Phase-Noise Shear-Horizontal Surface Acoustic Wave Sensors Using Multielectrode Transducer Designs”, Anal. Chem. 86 (2014) 11464–11471
- K. Sothivelr, F. Bender, R.E. Mohler, A.J. Ricco, E.E. Yaz and F. Josse: “Near Real-Time Analysis of Binary Mixtures of Organic Compounds in Water Using SH-SAW Sensors and Estimation Theory”, IEEE Sensors 2014 Proc. 578–581

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Questions

Data Processing Using Estimation Theory: Block Diagram of the Estimation Process