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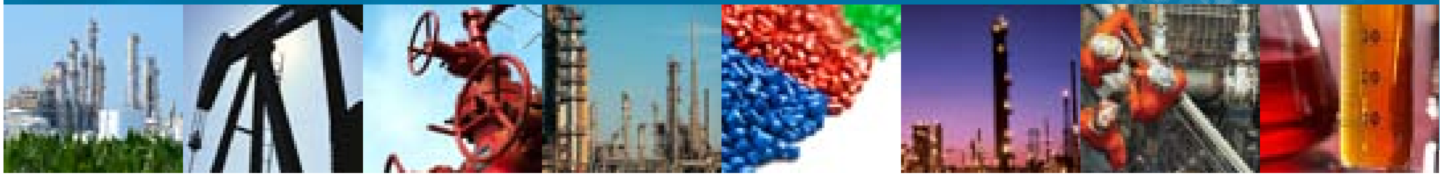

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Agilent 6850 Sub-Ambient Oven Performance for ASTM D3710 Simulated Distillation of Gasoline

Application

Gas Chromatography

September 2000

Authors

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Abstract

The Agilent 6850 gas chromatograph is now offered with sub-ambient column oven capabilities using liquid carbon dioxide as the cryogenic gas. This extends the 6850 oven temperature from -20 °C to 350 °C. The sub-ambient oven performance of the 6850 was tested using the ASTM D3710 method for simulated distillation of gasoline range materials. This method requires starting oven temperatures of -20 °C followed by programming to 180 °C. Four chromatogaphic performance tests required by the ASTM method were used to evaluate 6850 system performance. The same tests were also run on the Agilent 6890 GC to offer a comparison with an industry standard system. Both the 6850 and the 6890 results exceeded the specifications for peak shape, resolution, and retention time repeatability and area percent repeatability. In most cases both GCs showed performance that was 10 times better than the ASTM requirements. The 6850 and the 6890 also showed nearly identical performance when compared to each other. Additionally, the 6850 used about one-half of the CO_2 cryogenic gas compared to the 6890 when running this method.

Introduction

Most gas chromatographic separations can be performed with GC oven temperatures starting above ambient conditions. However, there are some instances that require GC oven temperatures that are below ambient. For example, separation of gases, low boiling components, and solvent focusing are all examples where the chromatographer needs to use cold oven temperatures. For modern instruments, sub-ambient temperatures are achieved by controlled introduction of a cryogenic gas into the oven. Typically, liquid carbon dioxide (CO_2) or liquid nitrogen are used as the cryogenic gas.

The Agilent 6850 gas chromatograph is a rugged, easy-to-use, single channel instrument especially suited for production laboratories where space is a premium. The 6850 occupies 50% of the linear bench space compared to the Agilent 6890, while still providing the same chromatographic performance. For applications requiring sub-ambient oven temperatures down to -20 °C, the 6850 now offers a CO_2 cryogenic cooling option.

The 6850 cryogenic oven performance was evaluated using the ASTM D3710 Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography[1]. This simulated distillation method was slightly modified by using a fused silica capillary column in place of a packed column. Instrument conditions for this method are listed in table 1. The sample run on these instruments was a D3710 Qualitative Calibration Mix (part # 506427, Supelco, Bellefonte, PA, USA) which contains the nineteen compounds required for system performance evaluation. Five consecutive runs of this mix were made on each GC. The quantity of CO_2 cryogenic gas used for each run was also measured to compare consumption differences between the 6850 and 6890.

Table 1. Instrument conditions for ASTM D3710 Simulated Distillation

Autoinjector	Agilent 7683 ALS 10 µL Teflon-tipped plunger syringe
Inlet	Split/splitless operated in split mode Temperature: 200 °C Liner part # 5183-4647
Column	HP-1, 3.0 µm film thickness, 15 m × 530 µm (part # 19095Z-421E)
Oven	-20 °C for 2 min, 20 °C/min to 180 °C, hold 2 min
Detector	Flame ionization detector (FID) Temperature: 300 °C FID hydrogen flow rate: 40 mL/min FID air flow rate: 450 mL/min FID make-up flow rate: 45 mL/min nitrogen Data acquisition rate: 10 Hz
Data system	Agilent Chemstation

This ASTM D3710 method is useful for evaluating GC cryogenic oven performance. It is a widely used application and is familiar to many GC analysts. D3710 also has stringent chromatographic performance specifications that can be used to assess the sub-ambient oven performance. These requirements are listed below:

1. *Resolution* - compounds lighter than isopentane must be separated such that the valley above the baseline is less than 5% of the height of the smaller peak.
2. *Peak Shape* (Skew) - peak skew must be not less than 0.5 and not more than 2.0.
3. *Retention Time Repeatability* - the retention time difference between consecutive runs must not be not more than 3 seconds for isopentane and lighter compounds. For compounds heavier than n-pentane, the maximum difference in retention time between successive runs must not be greater than the time equivalent of 3 °C. Additionally, the minimum retention time of the propane must be greater than 15 seconds.
4. *Area Percent Repeatability* - duplicate area percent results for each compound from consecutive runs must not differ by more than 0.1 area percent.

Results

Resolution. Figure 1 shows the chromatograms of the D3710 qualitative calibration sample run on both the 6850 and 6890 GCs. The nineteen compounds in this sample are baseline resolved on both GCs in approximately 12 minutes. Figure 2 shows the resolution of the compounds that are lighter than isopentane. For all four peaks, the valley above the baseline is much less than 5% of the height of the smaller peak.

Peak Shape. Table 2 lists the symmetry of each peak in the chromatograms shown in figure 1. A skew value of 1.0 would indicate perfectly symmetrical peaks. Skews of less than 0.5 would indicate tailing, and values greater than 2.0 would indicate fronting (overload). Both the 6850 and 6890 show peaks that are almost all perfectly symmetrical.

Retention Time Repeatability. Both the 6850 and 6890 show excellent retention time repeatability as shown in table 3. For isopentane and lighter compounds, the retention time repeatability on both GCs is about ten times better than the ASTM specification. For compounds heavier than n-pentane, the ASTM specification calls for repeatability of less than the time equivalent of 3 °C. For this method, that translates into a value of ≤ 2.0 seconds. Both the 6850 and the 6890 show retention time repeatability that is 20 times better. Additionally, the retention time of the propane on each GC is greater than 15 seconds (figure 2).

Area Percent Repeatability. Table 4 shows the area percent repeatability of the 6850 and 6890. Both instruments show 5-10 times better performance than what is required by the ASTM specification.

CO_2 Cryogenic Gas Usage. The 6850 required about 1.5 lbs. of CO_2 cryogen for each run of D3710. The 6890 GC used about 3 lbs. of carbon dioxide. The smaller oven design of the 6850 makes it easier to cool below ambient conditions and hold that temperature. Oven cycle times after temperature programming were approximately the same for both instruments (10 minutes).

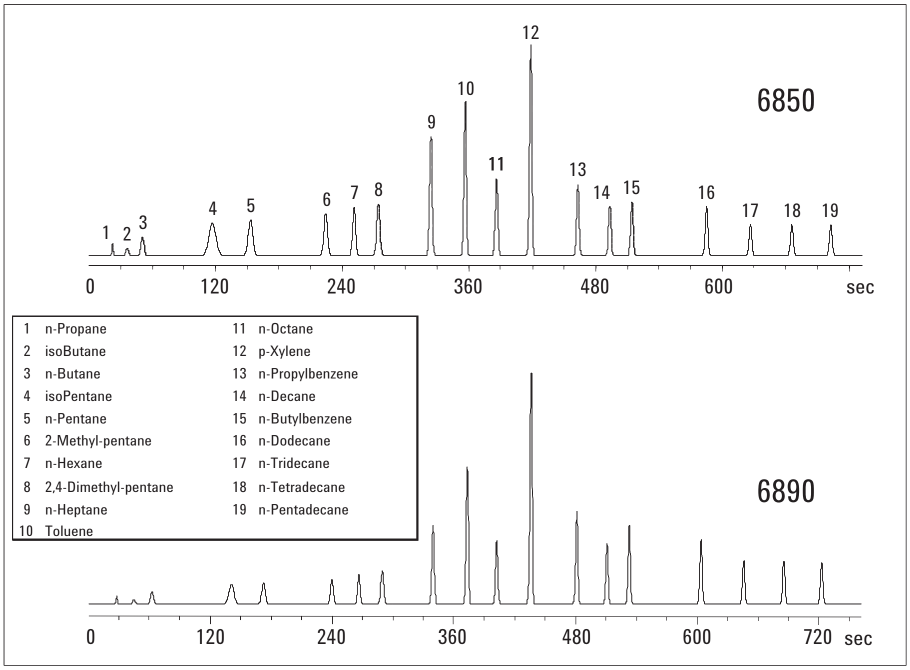

Figure 1. Separation of nineteen compounds used to evaluate GC system performance of the ASTM D3710 method for the simulated distillation of gasoline. Each run was made using CO_2 as the cryogenic gas for sub-ambient oven temperatures on both the 6850 and 6890.

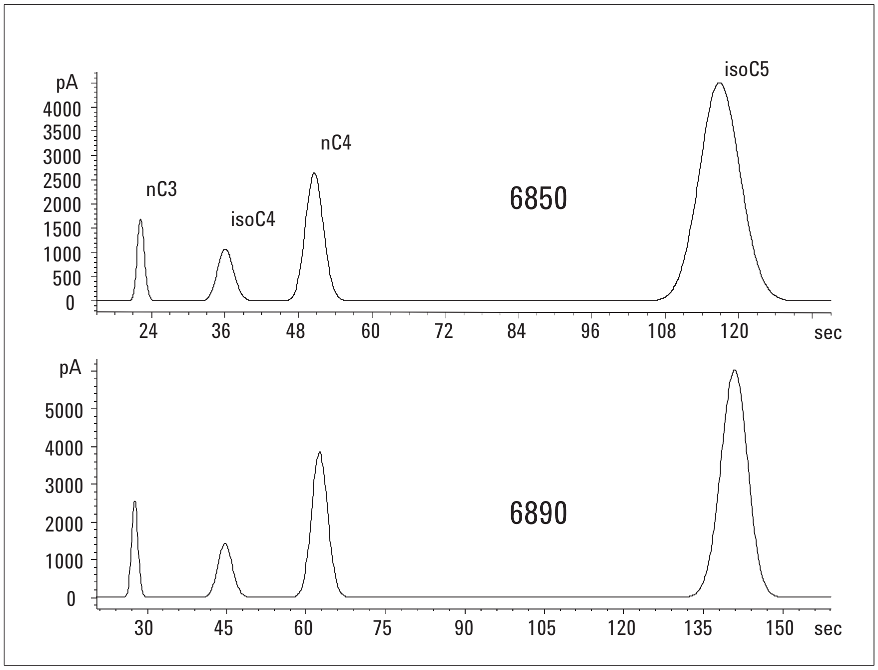

Figure 2. Baseline resolution is achieved for isopentane and lighter compounds on both the 6850 and 6890.

Table 2. ASTM D3710 Peak Symmetry Test (Skew)

Compound	ASTM Specification	Observed* 6890	Observed* 6850
n-Propane	0.5-2.0	0.9	0.9
IsoButane	0.5-2.0	0.9	0.9
n-Butane	0.5-2.0	1.0	0.9
isoPentane	0.5-2.0	1.0	1.0
n-Pentane	0.5-2.0	1.0	1.0
2-Methyl-pentane	0.5-2.0	1.0	1.0
n-Hexane	0.5-2.0	1.0	1.0
2,4-Dimethyl-pentane	0.5-2.0	1.0	1.0
n-Heptane	0.5-2.0	1.1	1.1
Toluene	0.5-2.0	1.2	1.1
n-Octane	0.5-2.0	1.1	1.1
p-Xylene	0.5-2.0	1.5	1.2
n-Propylbenzene	0.5-2.0	1.2	1.1
n-Decane	0.5-2.0	1.1	1.0
n-Butylbenzene	0.5-2.0	1.2	1.1
n-Dodecane	0.5-2.0	1.2	1.1
n-Tridecane	0.5-2.0	1.1	1.0
n-Tetradecane	0.5-2.0	1.1	1.0
n-Pentadecane	0.5-2.0	1.1	1.0

*Average from 5 consecutive runs

Table 3. ASTM D3710 Retention Time Repeatability Test

Compound	ASTM Specification	Observed (sec)* 6890	Observed (sec)* 6850
n-Propane	≤ 3.0s	0.1	0.1
isoButane	≤ 3.0s	0.1	0.1
n-Butane	≤ 3.0s	0.1	0.0
isoPentane	≤ 3.0s	0.2	0.3
n-Pentane	≤ 2.0s	0.2	0.2
2-Methyl-pentane	≤ 2.0s	0.2	0.1
n-Hexane	≤ 2.0s	0.2	0.1
2,4-Dimethyl-pentane	≤ 2.0s	0.1	0.1
n-Heptane	≤ 2.0s	0.1	0.1
Toluene	≤ 2.0s	0.1	0.1
n-Octane	≤ 2.0s	0.1	0.1
p-Xylene	≤ 2.0s	0.1	0.1
n-Propylbenzene	≤ 2.0s	0.1	0.1
n-Decane	≤ 2.0s	0.1	0.1
n-Butylbenzene	≤ 2.0s	0.1	0.1
n-Dodecane	≤ 2.0s	0.1	0.1
n-Tridecane	≤ 2.0s	0.1	0.1
n-Tetradecane	≤ 2.0s	0.1	0.1
n- Pentadecane	≤ 2.0s	0.1	0.1

*Average from 5 consecutive runs

Table 4. ASTM D3710 Area Percent Repeatability Test

Compound	ASTM Specification	Observed (area%)* 6890	6850
n-Propane	≤ 0.10%	<0.01	<0.01
isoButane	≤ 0.10%	<0.01	<0.01
n-Butane	≤ 0.10%	0.01	<0.01
isoPentane	≤ 0.10%	0.02	<0.01
n-Pentane	≤ 0.10%	0.01	<0.01
2-Methyl-pentane	≤ 0.10%	0.01	<0.01
n-Hexane	≤ 0.10%	0.01	<0.01
2,4-Dimethyl-pentane	≤ 0.10%	0.01	<0.01
n-Heptane	≤ 0.10%	0.02	<0.01
Toluene	≤ 0.10%	<0.01	0.01
n-Octane	≤ 0.10%	<0.01	<0.01
p-Xylene	≤ 0.10%	0.03	0.01
n-Propylbenzene	≤ 0.10%	0.02	<0.01
n-Decane	≤ 0.10%	0.01	<0.01
n-Butylbenzene	≤ 0.10%	0.02	<0.01
n-Dodecane	≤ 0.10%	0.02	<0.01
n-Tridecane	≤ 0.10%	0.01	<0.01
n-Tetradecane	≤ 0.10%	0.02	<0.01
n- Pentadecane	≤ 0.10%	0.02	<0.01

*Average from 5 consecutive runs

Summary

The Agilent 6850 gas chromatograph can now use liquid carbon dioxide to achieve sub-ambient column oven temperatures down to -20 °C. The CO_2 cryogenic performance characteristics of the 6850 were tested using the ASTM D3710 method for simulated distillation of gasoline. The 6850 showed ten-times better chromatographic performance. These results were also identical to the Agilent 6890 equipped with CO_2 cryogenic oven cooling. The 6850 also used 50% less CO_2 for each run of D3710 when compared to the 6890.

References

1. ASTM Method D3710, "Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography", ASTM Book of Standards, Volume 5.02, ASTM, 500 Barr Harbor Drive, West Conshohocken, PA 19428, USA.

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A Unified Gas Chromatography Method for Aromatic Solvent Analysis

Application

Gas Chromatography

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Abstract

A single, easy-to-use GC method for aromatic solvent purity analysis is described that meets the chromatographic requirements of ten separate ASTM methods. This method can be used to obtain identical results on both the Agilent 6890 and 6850 Series Gas Chromatographs designed for the method development lab and the routine production lab respectively. Reproducibility of results between instruments, between labs, and over time are further improved by applying the technique of retention time locking to this unified method.

Introduction

The producers and users of many aromatic hydrocarbons evaluate the product quality by measuring the purity of the material along with specific contaminants. For these types of measurements the most commonly used analysis technique is gas chromatography (GC). In an effort to standardize analysis procedures, the American Society of Testing and Materials (ASTM) has developed and published a number of GC methods specific to an aromatic compound or class of compounds.[1] These methods have evolved over time to meet the requirements of new materials specifications or to incorporate new GC technologies (i.e. capillary columns replacing packed columns). The result of this evolution is a large number of methods that are remarkably alike. In practice, many QA laboratories that support a variety of chemical processes typically devote one GC instrument to each ASTM method they must run.

Recently, there has been a move by many chemical companies to consolidate lab facilities, simplify measurements, and reduce the costs that chemical measurements add to production. Laboratory space is expensive and is becoming limited. Where three or four GCs were operating in the past, there is now only space and budget for one or two. Another part of this trend is to have non-traditional personnel such as plant operators; technicians and engineers perform chemical analyses. Since these personnel are not trained as analytical chemists, simpler methods are needed to perform the analyses without losing measurement performance.

Accommodating these changes in the lab environment makes it necessary to explore alternative approaches to performing GC analyses. One approach is to develop a method that combines the elements of several separate ASTM methods.

A single method has a number of advantages over multiple methods. Fewer GCs could be used in place of a larger number of instruments previously dedicated to individual methods; thus reducing required lab space. By running one method, any GC could also serve as a backup for instruments that are undergoing maintenance or repair. This would result in shorter down times and better utilization of lab space. A single method would also eliminate the need to stock multiple columns and supplies. Plant operators would also find it easier to use since they would only need to be trained once on a single procedure.

Another important advantage to a single aromatics method lies in the use of retention time locking (RTL). RTL is a technique that allows any Agilent 6890 or 6850 GC systems running the same method to obtain nearly identical retention times. Comparing data between instruments, between laboratories, or over time can be difficult due to variations in retention times. This is further complicated when using multiple methods since the different columns and operating conditions result in different retention times for the same compound. For instance, there are eight ASTM methods that measure p-xylene; however, p-xylene retention times range from 6 to 16 minutes depending on the method's operating conditions (column, flow, temperature). By using one method for all aromatic samples, retention time variations can be reduced to less than 0.5 minutes. Then by applying RTL to this method, system-to-system retention time variations can be further reduced to less than 0.03 minutes. Retention time precision on this order greatly simplifies comparison of data between systems, between laboratories, and over time.

This application note describes a GC method that is chromatographically suitable for a wide range of samples typically analyzed by ten different ASTM methods. Table 1 lists these ten methods along with the ASTM recommended columns and reporting specifications.

Table 1. Ten ASTM Methods for the GC Analysis of Aromatic Solvents

ASTM Method	Title	Liquid phase	Column type	Report specifications
D2306	Std Test for C8 Aromatic Hydrocarbons	0.25 µm Carbowax	Capillary 50 m × 0.25 mm	wt% of individual C8 HC
D2360	Std Test for Trace Impurities in Monocyclic Hydrocarbons	0.32 µm Carbowax	Capillary 60 m × 0.32 mm	wt% of individual aromatic impurities, total impurities, purity
D3760	Std Test for Cumene	0.25 µm Carbowax	Capillary 50 m × 0.32 mm	wt% of individual impurities, cumene purity (wt%)
D3797	Std Test for o-Xylene	0.5 µm Carbowax	Capillary 60 m × 0.32 mm	wt% of individual impurities, o-xylene purity (wt%)
D3798	Std Test for p-Xylene	0.25 µm Carbowax	Capillary 50 m × 0.32 mm	wt% of individual impurities, total impurities, p-xylene purity (wt%)
D4492	Std Test for Benzene	0.25 µm Carbowax	Capillary 50 m × 0.32 mm	wt% of individual impurities, benzene purity(wt%)
D4534	Std Test for Benzene in Cyclic Products	10%TCEPE on Chromasorb P	Packed 3.7 m × 3.175 mm	wt% of benzene
D5060	Std Test for Impurities in Ethylbenzene	0.5 µm Carbowax	Capillary 60 m × 0.32 mm	wt% of individual impurities, ethylbenzene purity
D5135	Std Test for Styrene	0.5 µm Carbowax	Capillary 60 m × 0.32 mm	wt% of individual impurities, styrene purity
D5917	Std Test for Trace Impurities in Monocyclic Hydrocarbons (ESTD Cal)	0.25 µm Carbowax	Capillary 60 m × 0.32 mm	wt% individual impurities, wt% total non-aromatics, wt% total C9 aromatics, purity of main component

Experimental

Two Agilent 6890 Plus Series gas chromatographs and four Agilent 6850 gas chromatographs were used for this work. Each GC was equipped with a split/splitless capillary inlet, a flame ionization detector (FID) and an Agilent 7683 Automatic Liquid Sampler (ALS). The split/splitless inlets were fitted with high-pressure Merlin Microseal Septa (Agilent Part no. 5182-3442) and spilt-optimized liners (Agilent Part no. 5183-4647). Injections were made using 10 µL gas-tight syringes (Agilent Part no. 5181-8809) designed for use with the Merlin Microseal. Table 2 lists the instrument conditions used for this method. An Agilent Chemstation was used for all instrument control, data acquisition and data analysis.

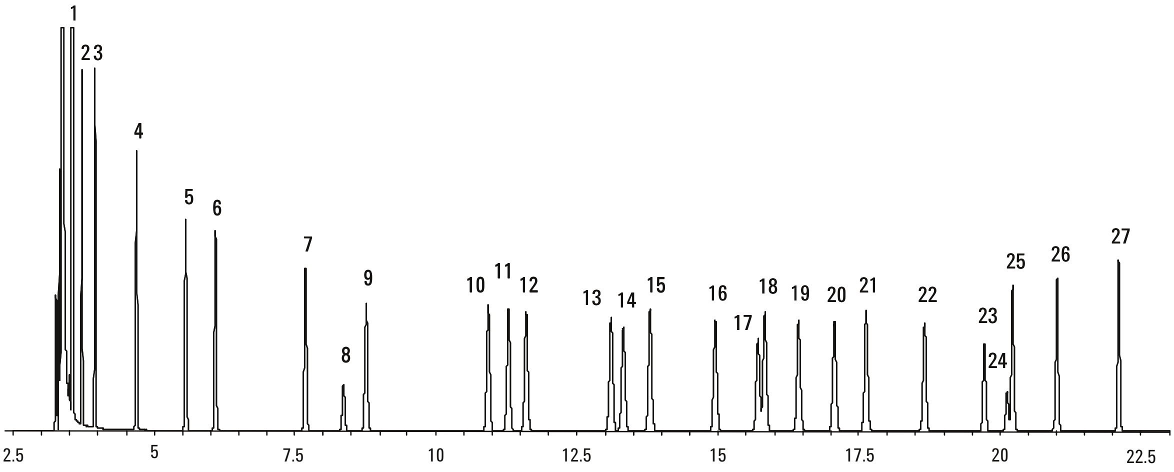
Table 2. Conditions for Unified Aromatic Solvents Method

Column	HP-Innowax, 60 m × 0.32 mm × 0.5 µm Agilent Part no.19091N-216
Carrier Gas	Helium @ 20.00 psi constant pressure mode
Inlet	Split/Splitless @ 250 °C 100:1 to 400:1 split ratio
Oven Temp	75 °C (10 min); 3 °C/min to 100 °C (0 min) 10 °C/min to 145 °C (0 min)
Detector	FID @ 250 °C Data acquisition rate @ 20 Hz
Injection Size	0.1 to 1.0 µL

An n-hexane solution was prepared containing 0.1 wt% of all the aromatic solvents and impurities specified for analysis by the ten ASTM methods listed in Table 1. This standard was used to develop the RTL calibration and to assess the separation of each compound. Final evaluation of this unified method was done by running the recommended standards specified in each of the ten ASTM methods.

Results and Discussion

Figure 1 shows a chromatogram of the hexane solution containing an aggregate of aromatic solvents and impurities. For most compounds, baseline resolution was achieved. There are two pairs that are only partially resolved. The first pair, p-ethyltoluene and m-ethyltoluene, are also not resolved in the original ASTM method (D-5060 Impurities in ethylbenzene) and, along with o-ethyltoluene, are reported as total ethyltoluene. Therefore, the results presented here represent the same result obtained with the original ASTM method. A second pair, diethylbenzene and n-butylbenzene are also only partially resolved. Again, this does not present a problem since these two components are not typically found together in the same material. Diethylbenzene is sometimes found as a contaminant in ethylbenzene (ASTM D-5060) while n-butylbenzene is used as the internal standard for cumene analysis (ASTM D3760).



1	heptane	8	1,4-dioxane	15	o-xylene	22	tridecane
2	cycohexane	9	undecane	16	proplybenzene	23	diethylbenzene isomer
3	octane	10	ethylbenzene	17	p-ethyltoluene	24	diethylbenzene isomer
4	nonane	11	p-xylene	18	m-ethyltoluene	25	n-butylbenzene
5	benzene	12	m-xylene	19	t-butylbenzene	26	α-methylstyrene
6	decane	13	cumene	20	s-butylbenzene	27	phenylacetylene
7	toluene	14	dodecane	21	styrene		

Figure 1. Separation of the 27 compounds analyzed by the ten ASTM aromatics methods listed in Table 1.

Retention Time Locking (RTL)

Retention time locking calibration was performed using t-butylbenzene as the target peak. Figure 2 shows the five RTL calibration runs with the retention times of t-butylbenzene indicated and Figure 3 shows the RTL calibration. These calibration runs do not have to be repeated by anyone wishing to lock this method on their Agilent 6890 or 6850 GC systems. To use this RTL calibration, simply create a new method with conditions outlined in Table 2, then use the Chemstation RTL software to create a new RTL calibration and enter the data shown in Figure 3. The GC can then be locked by running a sample containing t-butylbenzene and using the RTL software to re-lock the method. The general theory and use of RTL is detailed in previous publications.[2]

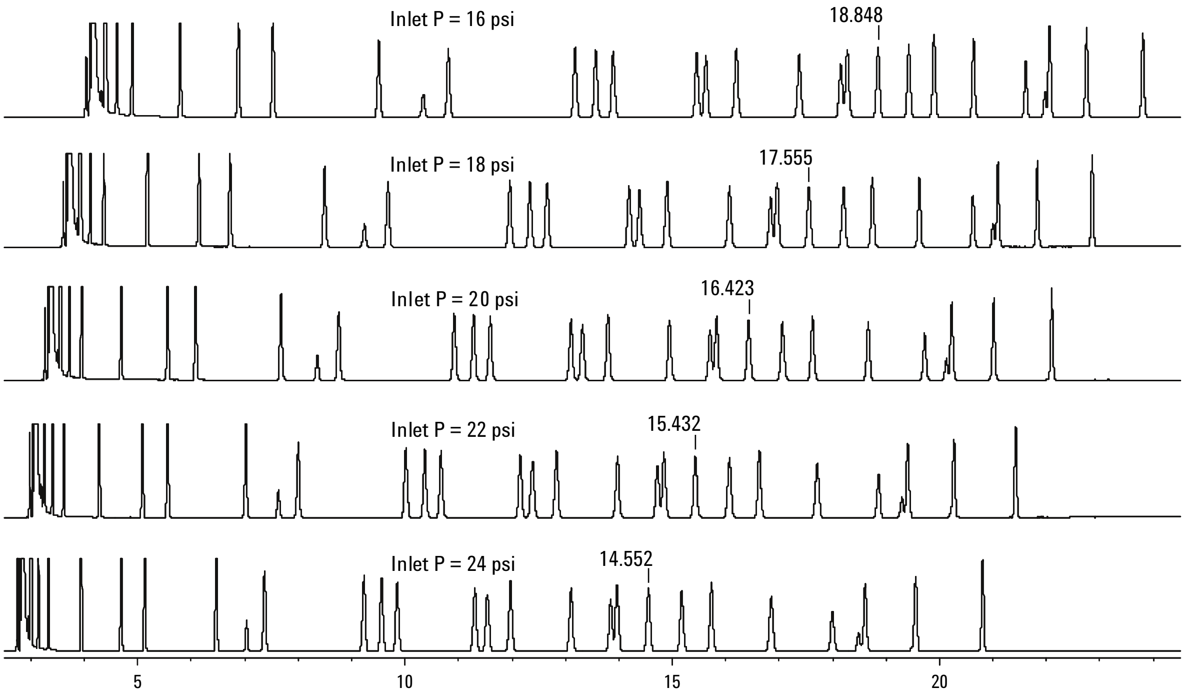
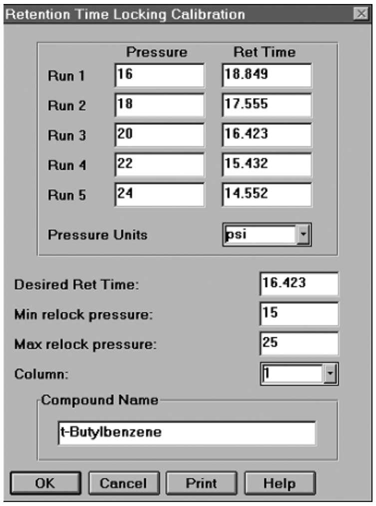


Figure 2. **Retention time locking calibration runs using t-butylbenzene as the RTL target peak.**



	Pressure	Ret Time
Run 1	16	18.849
Run 2	18	17.555
Run 3	20	16.423
Run 4	22	15.432
Run 5	24	14.552

Pressure Units: psi

Desired Ret Time: 16.423

Min relock pressure: 15

Max relock pressure: 25

Column: 1

Compound Name: t-Butylbenzene

Figure 3. **Retention time locking calibration using t-butylbenzene as the RTL target peak.**

A total of six GC systems, two 6890s and four 6850s, were configured to run this unified method. Each GC was retention time locked using a t-butylbenzene target retention time of 16.423 minutes. Figure 4 shows an overlay of the locked chromatograms from each of the six GCs. Table 3 lists the retention times and precision of each compound in the standard mix. Excellent retention time precision was observed for the 6890 and 6850 instruments across the entire time range of the chromatographic run. Peaks falling within the initial 10-minute isothermal time had a standard deviation of about 0.02 minutes. Those peaks eluting during the 3 °C/min program ramp had a standard deviation of 0.01 minutes and those eluting in the 10 °C/min ramp showed a standard deviation of 0.03 minutes

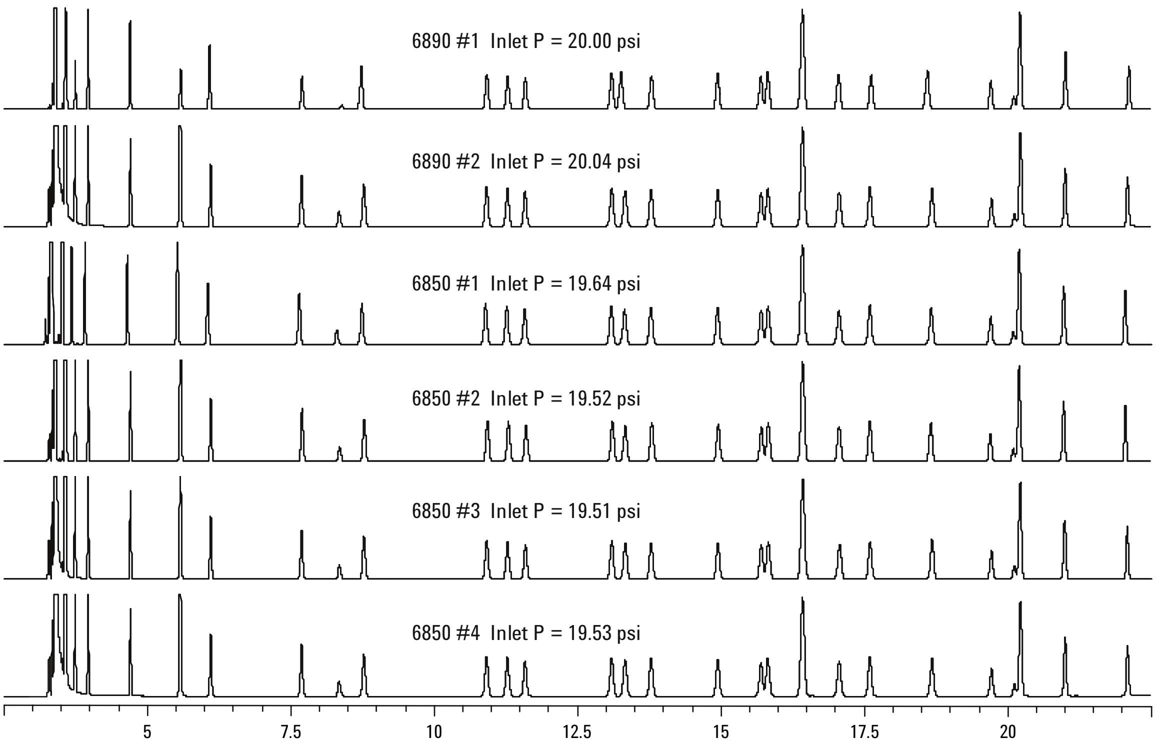


Figure 4. Using RTL, excellent retention time precision was observed for all 27 compounds analyzed using the unified aromatics method. Details of retention time precision are listed in Table 3.

Table 3. Retention Time Precision for Each Compound Analyzed by the Unified Method

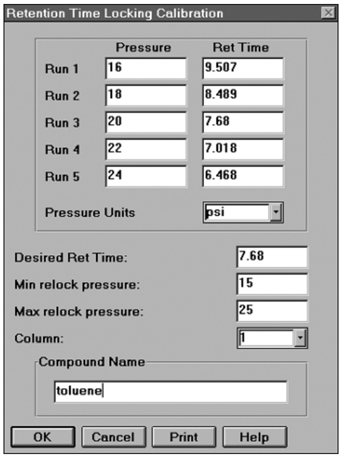
	Retention time (min)							
Compound	**6890 #1**	**6890 #2**	**6850 #1**	**6850 #2**	**6850 #3**	**6850 #4**	**Std Dev**	**Range**
heptane	3.572	3.568	3.508	3.569	3.566	3.568	0.025	0.064
cyclohexane	3.745	3.742	3.682	3.743	3.741	3.742	0.025	0.063
octane	3.969	3.971	3.911	3.972	3.970	3.971	0.024	0.061
nonane	4.696	4.704	4.646	4.705	4.703	4.704	0.023	0.059
benzene	5.581	5.572	5.518	5.576	5.572	5.572	0.023	0.063
decane	6.084	6.105	6.053	6.106	6.104	6.105	0.021	0.053
toluene	7.694	7.686	7.646	7.695	7.687	7.686	0.018	0.049
1,4-dioxane	8.386	8.342	8.306	8.350	8.346	8.342	0.025	0.080
undecane	8.732	8.776	8.741	8.782	8.777	8.776	0.022	0.050
ethylbenzene	10.922	10.915	10.899	10.932	10.918	10.915	0.011	0.033
p-xylene	11.282	11.278	11.267	11.295	11.280	11.278	0.009	0.028
m-xylene	11.592	11.587	11.577	11.604	11.589	11.587	0.009	0.027
cumene	13.097	13.097	13.089	13.110	13.098	13.097	0.007	0.021
dodecane	13.264	13.334	13.323	13.337	13.333	13.334	0.028	0.073
o-xylene	13.790	13.781	13.778	13.795	13.782	13.781	0.007	0.017
propybenzene	14.940	14.943	14.939	14.951	14.945	14.943	0.004	0.012
p-ethyltoluene	15.696	15.699	15.699	15.706	15.702	15.699	0.003	0.010
m-ethyltoluene	15.819	15.820	15.820	15.827	15.823	15.820	0.003	0.008
t-butylbenzene	16.423	16.424	16.420	16.426	16.426	16.424	0.002	0.006
s-butylbenzene	17.049	17.060	17.053	17.059	17.063	17.060	0.005	0.014
styrene	17.623	17.600	17.600	17.600	17.603	17.600	0.009	0.023
tridecane	18.602	18.683	18.665	18.661	18.681	18.683	0.031	0.081
diethylbenzene	19.707	19.718	19.701	19.700	19.713	19.718	0.008	0.018
diethylbenzene	20.111	20.123	20.101	20.101	20.116	20.123	0.010	0.022
n-butylbenzene	20.217	20.225	20.201	20.203	20.219	20.225	0.011	0.024
α-methylstyrene	21.011	21.003	20.976	20.975	20.994	21.003	0.015	0.036
phenyacetylene	22.115	22.090	22.050	22.050	22.081	22.090	0.025	0.065
						Avg	***0.015***	***0.039***

For this method it is not always necessary to use t-butylbenzene to perform retention time locking. Analysts who want to use this method for samples not containing t-butylbenzene can select another compound as the RTL target peak. Compounds that do not elute near temperature program transitions can serve as RTL target peaks. Table 4 lists the other suitable RTL target compounds along with the retention time data for constructing alternate RTL calibrations for this method. For instance, if one were preparing the benzene standard prescribed by ASTM method D4492, the toluene in that standard could serve as the RTL target compound. It is not necessary to perform the five RTL calibration runs. Simply create a new RTL calibration using the inlet pressures and toluene retention times from Table 4. This example of an RTL calibration using toluene is shown in Figure 5.

Table 4. Retention Time Locking Calibration Data for Unified Aromatics Method

	Retention time (min) at each inlet pressure				
Compound	**16.00 psi**	**18.00 psi**	**20.00 psi**	**22.00 psi**	**24.00 psi**
nonane	5.794	5.174	4.682	4.279	3.943
benzene	6.880	6.143	5.558	5.080	4.681
toluene	9.507	8.489	7.680	7.018	6.468
cumene	15.460	14.188	13.100	12.148	11.305
o-xylene	16.189	14.897	13.791	12.825	11.969
propylbenzene	17.370	16.064	14.646	13.968	13.100
t-butylbenzene*	18.849	17.555	16.423	15.432	14.552
s-butylbenzene	19.424	18.201	17.061	16.063	15.176
n-butylbenzene	22.054	21.090	20.220	19.404	18.607
styrene	19.891	18.743	17.620	16.621	15.733
α-methylstyrene	22.745	21.824	21.010	20.261	19.552
phenylacetylene	23.795	22.852	22.097	21.421	20.800

*t-butylbenzene used as RTL target peak for this publication (target RT = 16.423 min).



	Pressure	Ret Time
Run 1	16	9.507
Run 2	18	8.489
Run 3	20	7.68
Run 4	22	7.018
Run 5	24	6.468

Pressure Units: psi

Desired Ret Time: 7.68

Min relock pressure: 15

Max relock pressure: 25

Column: 1

Compound Name: toluene

Figure 5. Alternate retention time locking calibration for the unified aromatics method that uses toluene as the locking target compound.

Evaluation of Calibration Standards

The calibration standards specified by each of the ten ASTM methods were prepared and run using this unified method. Each standard was run with Agilent 6890 and Agilent 6850 series gas chromatographs that were retention time locked using t-butylbenzene as the target peak (RT = 16.423 min.).

D2306 - Standard Test for C8 Aromatic Hydrocarbons

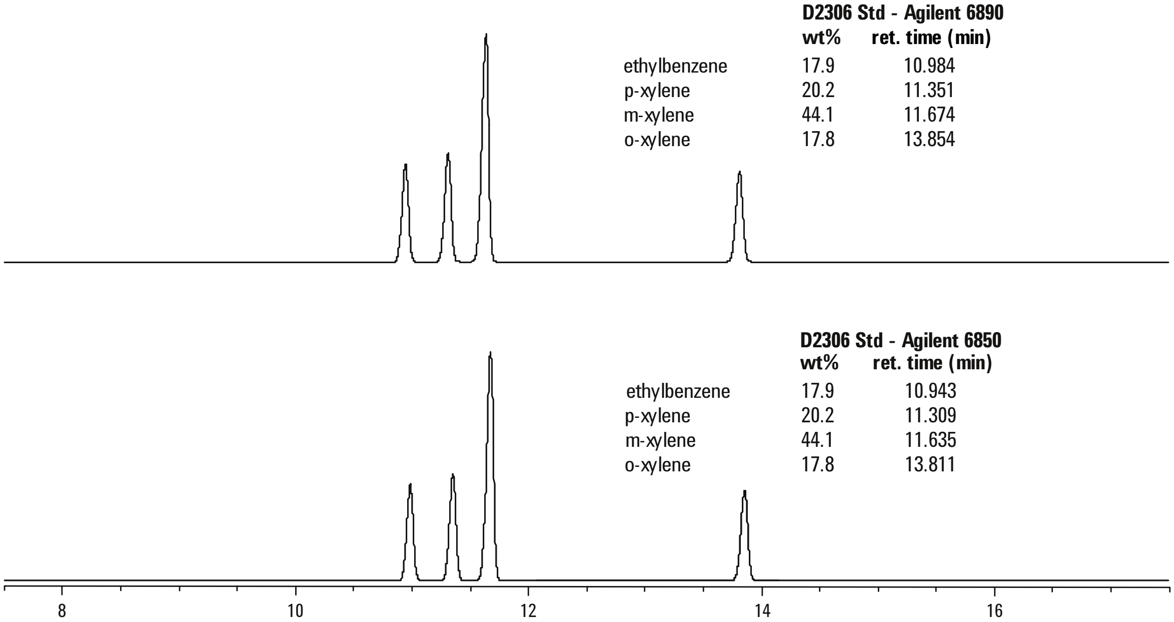
Figure 6 shows the chromatograms of the D2306 calibration standard run on Agilent 6890 and 6850 gas chromatographs. The injection size for both runs was 0.1 µL and the split ratio was 400:1.

D2360 - Standard Test for Trace Impurities in Monocyclic Hydrocarbons

The standard calibration mix specified by D2360 was prepared in p-xylene. Figure 7 shows the chromatograms of the D2360 calibration standard. Injection size was 1.0 µL and the split ratio was 100:1. The ethylbenzene peak (RT = 10.98 min) elutes just before p-xylene and was much broader than the other contaminants. This peak shape was due to a reverse solvent effect caused by the overloaded p-xylene along with an oven starting temperature (75 °C) that was much lower than the p-xylene boiling point (138 °C). A broad ethylbenzene peak was also observed in the original ASTM D2360 method.[3]

D3760 - Standard Test for Analysis of Isopropylbenzene (Cumene)

Figure 8 shows the chromatograms of the D3760 calibration standard. The injection size for both runs was 1.0 µL and the split ratio was 100:1. The xylene isomers' concentrations were not listed because they were not added to the standard, but were present as trace contaminants in the cumene used to prepare the standard. Since both GCs are retention time locked, the identification of each xylene isomer could be easily made.

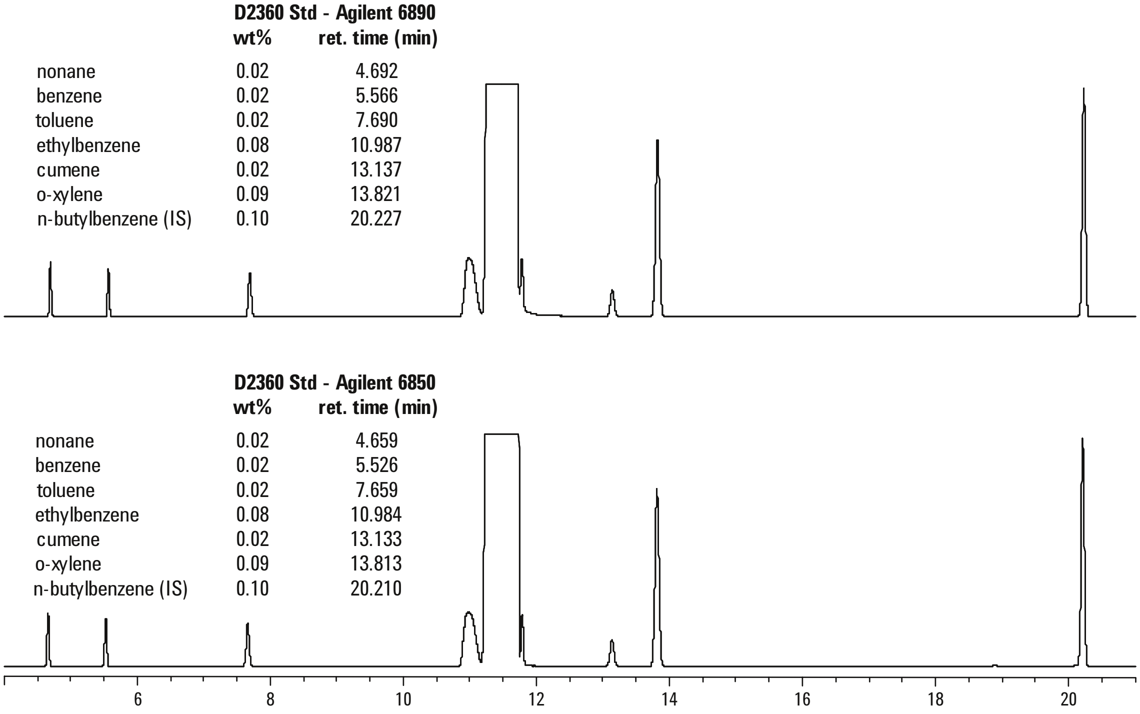

D2306 Std - Agilent 6890

	wt%	ret. time (min)
ethylbenzene	17.9	10.984
p-xylene	20.2	11.351
m-xylene	44.1	11.674
o-xylene	17.8	13.854

D2306 Std - Agilent 6850

	wt%	ret. time (min)
ethylbenzene	17.9	10.943
p-xylene	20.2	11.309
m-xylene	44.1	11.635
o-xylene	17.8	13.811

Figure 6. ASTM D2306 C8 aromatic hydrocarbon quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.

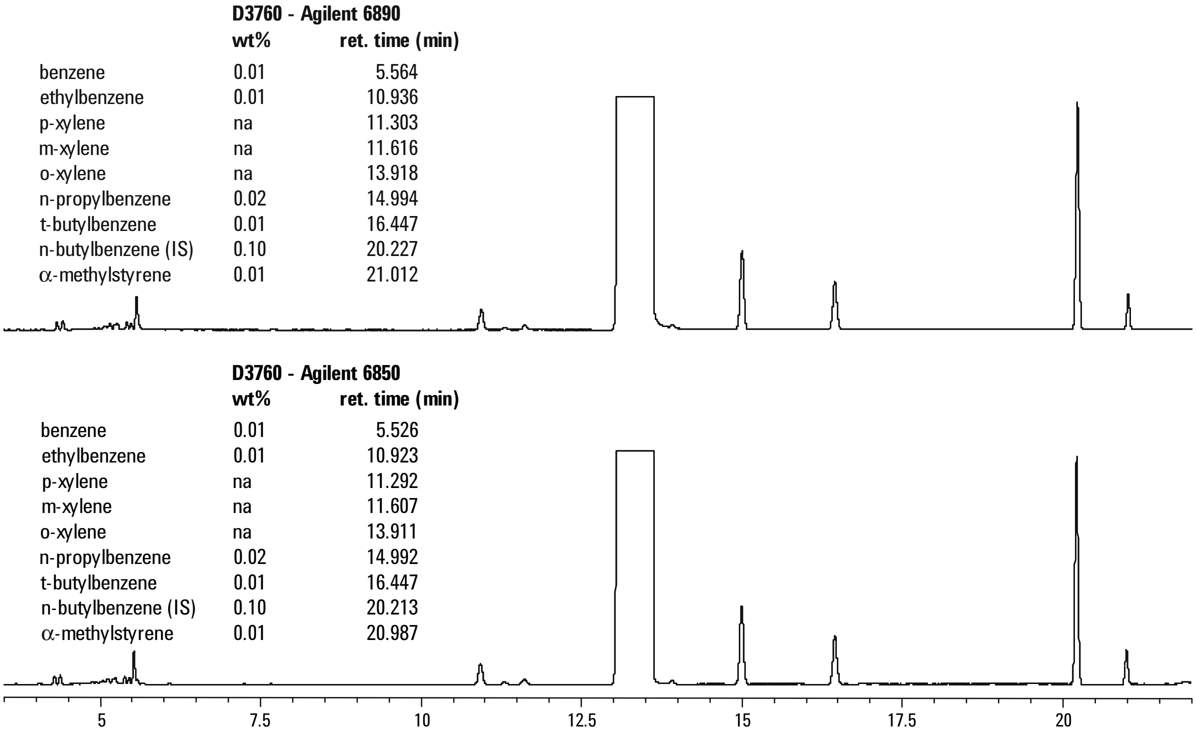

D2360 Std - Agilent 6890

	wt%	ret. time (min)
nonane	0.02	4.692
benzene	0.02	5.566
toluene	0.02	7.690
ethylbenzene	0.08	10.987
cumene	0.02	13.137
o-xylene	0.09	13.821
n-butylbenzene (IS)	0.10	20.227

D2360 Std - Agilent 6850

	wt%	ret. time (min)
nonane	0.02	4.659
benzene	0.02	5.526
toluene	0.02	7.659
ethylbenzene	0.08	10.984
cumene	0.02	13.133
o-xylene	0.09	13.813
n-butylbenzene (IS)	0.10	20.210

Figure 7. ASTM D2360 monocyclic hydrocarbon quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.



D3760 - Agilent 6890

	wt%	ret. time (min)
benzene	0.01	5.564
ethylbenzene	0.01	10.936
p-xylene	na	11.303
m-xylene	na	11.616
o-xylene	na	13.918
n-propylbenzene	0.02	14.994
t-butylbenzene	0.01	16.447
n-butylbenzene (IS)	0.10	20.227
α-methylstyrene	0.01	21.012

D3760 - Agilent 6850

	wt%	ret. time (min)
benzene	0.01	5.526
ethylbenzene	0.01	10.923
p-xylene	na	11.292
m-xylene	na	11.607
o-xylene	na	13.911
n-propylbenzene	0.02	14.992
t-butylbenzene	0.01	16.447
n-butylbenzene (IS)	0.10	20.213
α-methylstyrene	0.01	20.987

Figure 8. **ASTM D3760 isopropylbenzene (cumene) quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.**

D3797 - Standard Test Method for Analysis of o-Xylene

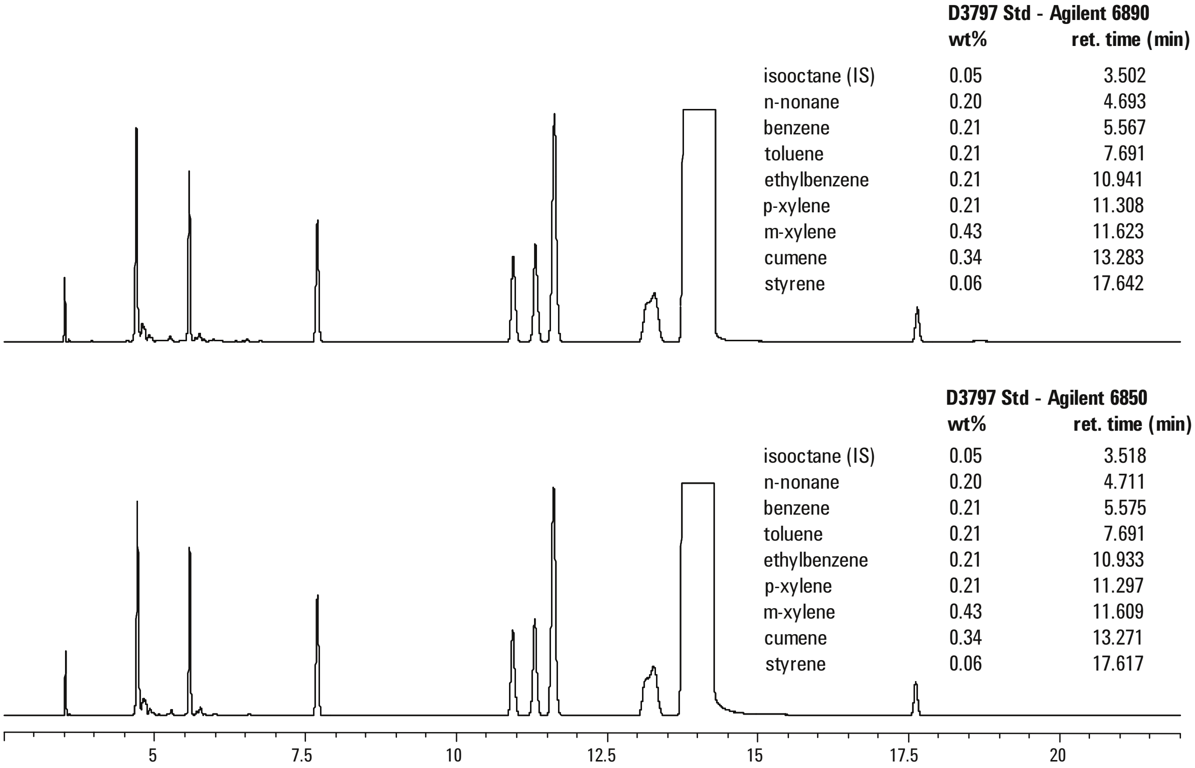
Figure 9 shows the chromatograms of the D3797 calibration standard. The injection size was 1.0 µL and the split ratio was 100:1. The broadening of the cumene peak (RT = 13.28 min) was due to the reverse solvent effect of the overloaded o-xylene peak. This was also observed in the original ASTM D3797 method.

D3798 - Standard Test Method for Analysis of p-Xylene

Figure 10 shows the chromatograms of the D3798 calibration standard. The injection size was 1.0 µL and the split ratio was 100:1. The ethylbenzene peak shows the same broadening observed in the D2360 standard. The original ASTM D3798 method specifies that the valley points between the large p-xylene peak and the ethylbenzene and m-xylene contaminants should be less than 50% of the contaminants' peak height. Figure 11 shows the details of this separation using the unified method. For each GC this requirement was met for both the ethylbenzene and the m-xylene.

D4492 - Standard Test for Analysis of Benzene

Figure 12 shows the chromatograms of the D4492 calibration standard. The injection size was 1.0 µL and the split ratio was 100:1.



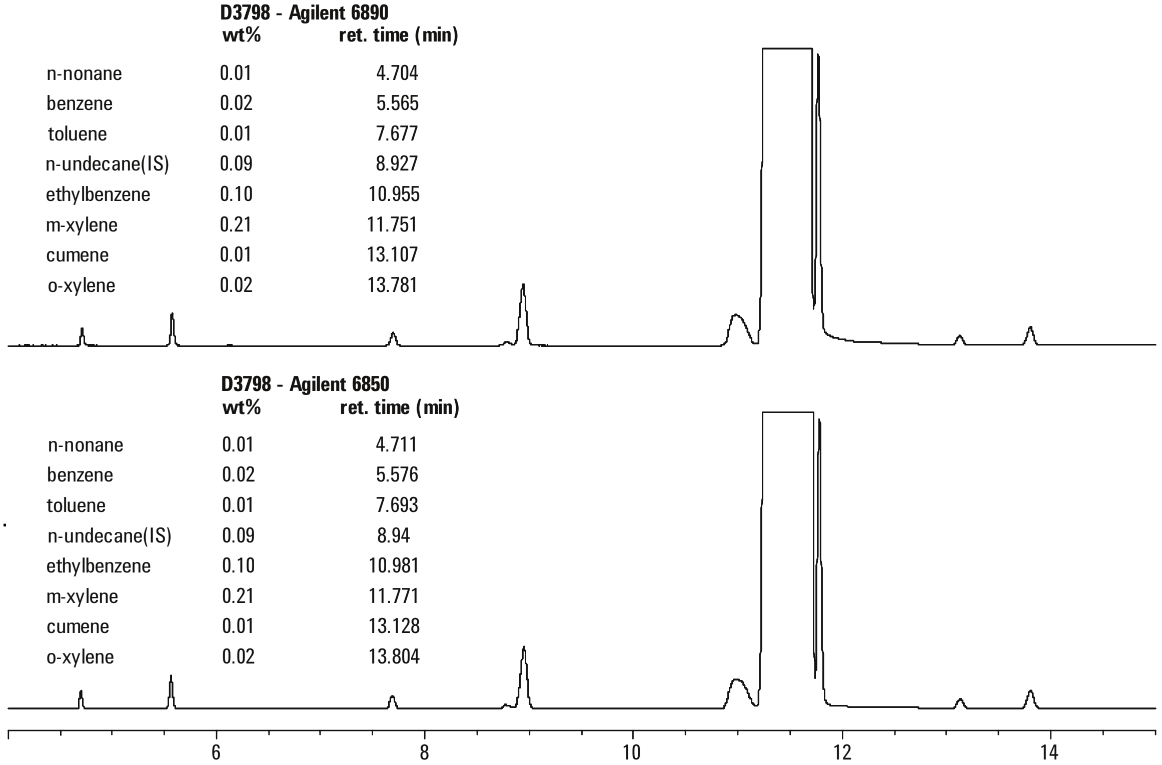
D3797 Std - Agilent 6890

	wt%	ret. time (min)
isooctane (IS)	0.05	3.502
n-nonane	0.20	4.693
benzene	0.21	5.567
toluene	0.21	7.691
ethylbenzene	0.21	10.941
p-xylene	0.21	11.308
m-xylene	0.43	11.623
cumene	0.34	13.283
styrene	0.06	17.642

D3797 Std - Agilent 6850

	wt%	ret. time (min)
isooctane (IS)	0.05	3.518
n-nonane	0.20	4.711
benzene	0.21	5.575
toluene	0.21	7.691
ethylbenzene	0.21	10.933
p-xylene	0.21	11.297
m-xylene	0.43	11.609
cumene	0.34	13.271
styrene	0.06	17.617

Figure 9. ASTM D3797 o-xylene quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.



D3798 - Agilent 6890

	wt%	ret. time (min)
n-nonane	0.01	4.704
benzene	0.02	5.565
toluene	0.01	7.677
n-undecane(IS)	0.09	8.927
ethylbenzene	0.10	10.955
m-xylene	0.21	11.751
cumene	0.01	13.107
o-xylene	0.02	13.781

D3798 - Agilent 6850

	wt%	ret. time (min)
n-nonane	0.01	4.711
benzene	0.02	5.576
toluene	0.01	7.693
n-undecane(IS)	0.09	8.94
ethylbenzene	0.10	10.981
m-xylene	0.21	11.771
cumene	0.01	13.128
o-xylene	0.02	13.804

Figure 10. ASTM D3798 p-xylene quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.

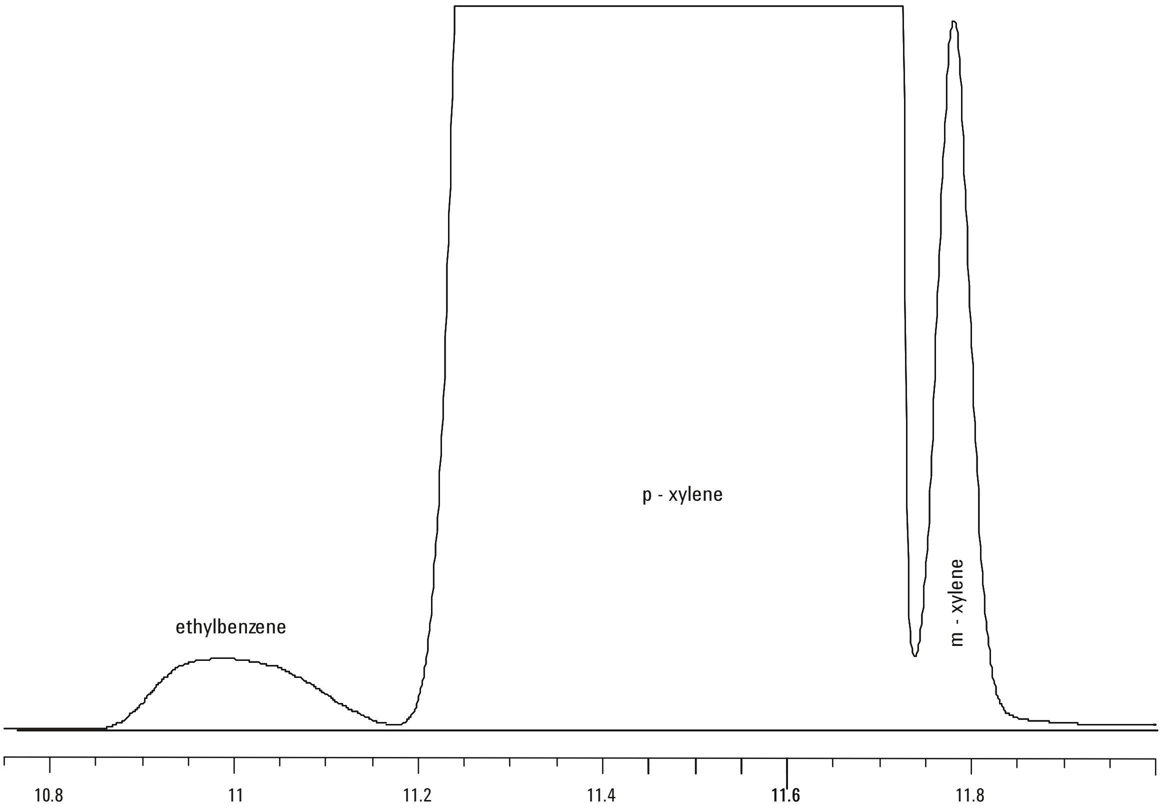
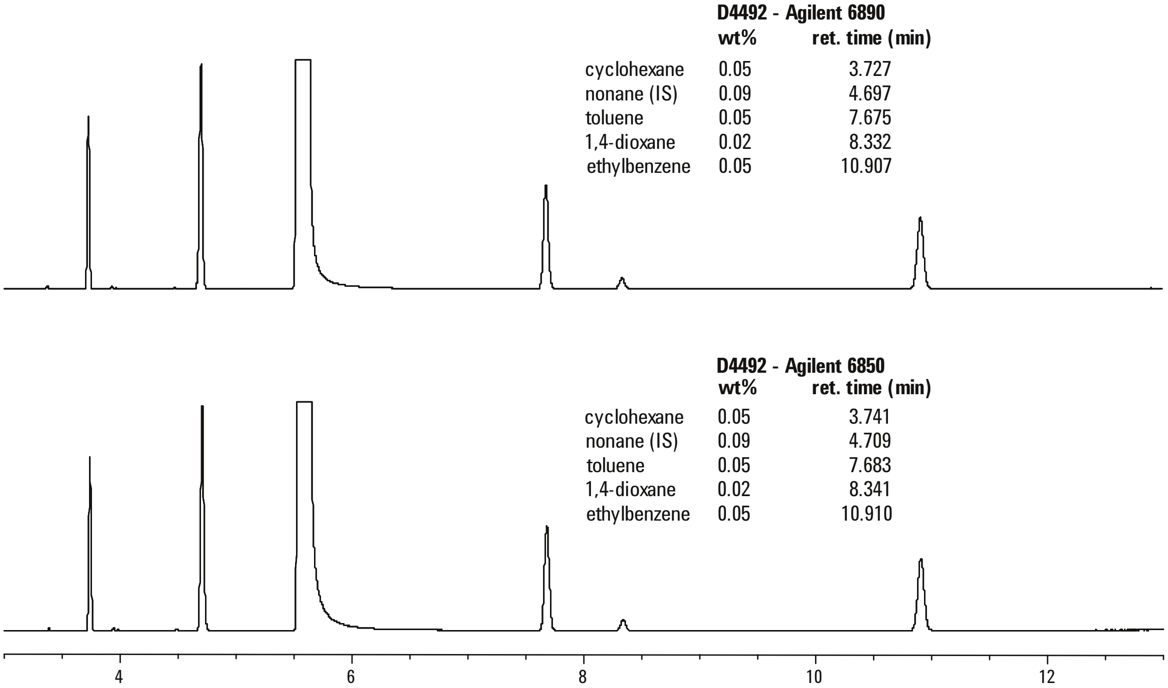


Figure 11. Expanded view from Figure 10 shows excellent separation of m-xylene from p-xylene peak using the unified aromatics method.



D4492 - Agilent 6890

	wt%	ret. time (min)
cyclohexane	0.05	3.727
nonane (IS)	0.09	4.697
toluene	0.05	7.675
1,4-dioxane	0.02	8.332
ethylbenzene	0.05	10.907

D4492 - Agilent 6850

	wt%	ret. time (min)
cyclohexane	0.05	3.741
nonane (IS)	0.09	4.709
toluene	0.05	7.683
1,4-dioxane	0.02	8.341
ethylbenzene	0.05	10.910

Figure 12. ASTM D4492 benzene quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.

D4534 Standard Test Method of Benzene Content of Cyclic Products - Cyclohexane

Figure 13 shows the chromatograms of the D4534 calibration standard containing 8 mg/kg (ppm) benzene in cyclohexane. The injection size was 1.0 µL and the split ratio was 100:1.

D4534 Standard Test Method of Benzene Content of Cyclic Products - Toluene

Figure 14 shows the chromatograms of the D4534 calibration standard containing 9 mg/kg (ppm) benzene in toluene. The injection size was 1.0 µL and the split ratio was 100:1. Several contaminants were found in the toluene used to prepare this standard. Most of these contaminants were identified, but the peak at 15.3 minutes did not correspond to the retention times of those listed in Table 3. If the GC systems were not retention time locked, one might assume that this contaminant could be n-propylbenzene or p-ethyltoluene. However, given the retention time precision expected with RTL, it is clear that this contaminant is an unknown.

GC/MS is the best approach to identify this unknown, but under the same GC conditions, GC/MS retention times are often considerably faster than those obtained using atmospheric detectors. However, by combining retention time locking with a technique called method translation, one can obtain GC/MS retention times nearly identical to those found with conventional GC.[4] This makes identifying unknown peaks much easier. Figure 15 shows the D4534 toluene standard run on both the Agilent 6850 and the Agilent 5973 GC/MS. A mass spectral library search of the unknown peak at 15.320 minutes identifies this compound as chlorobenzene. The source of the chlorobenzene was found to be the toluene used to prepare the standard.

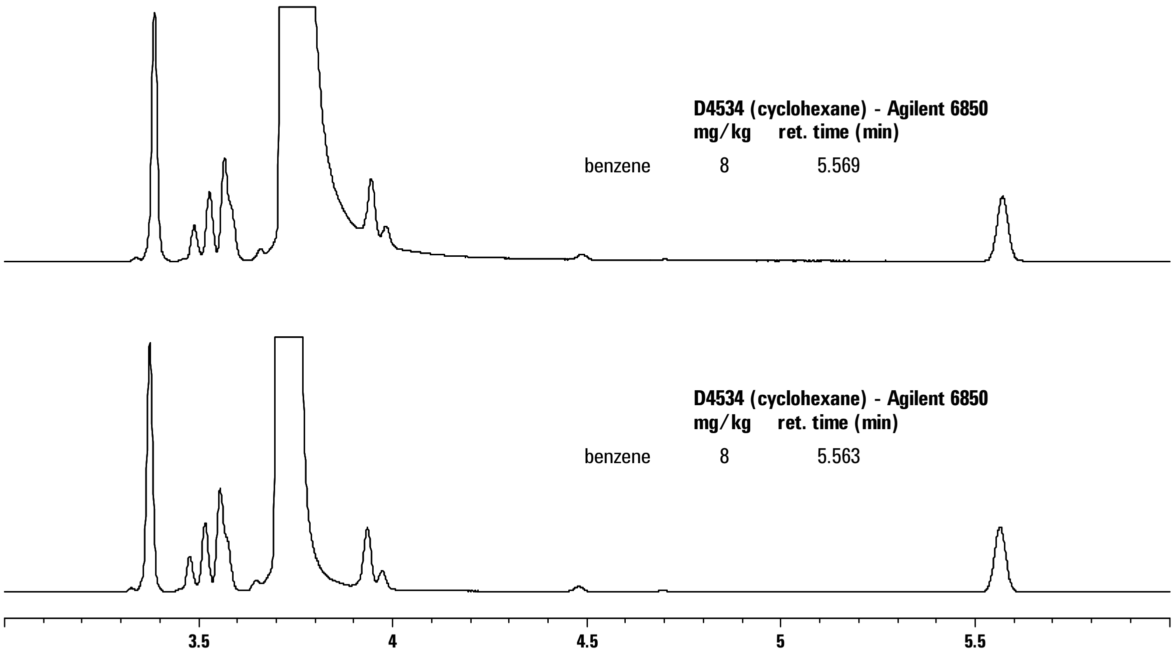
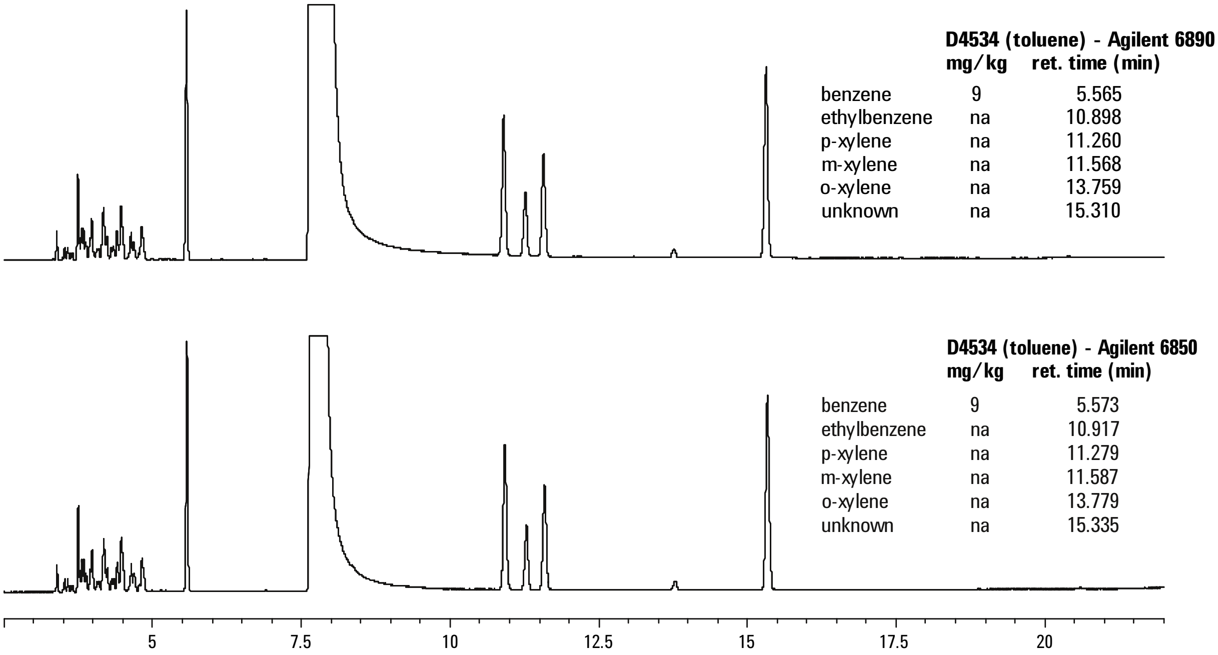


Figure 13. ASTM 4534 cyclohexane quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.



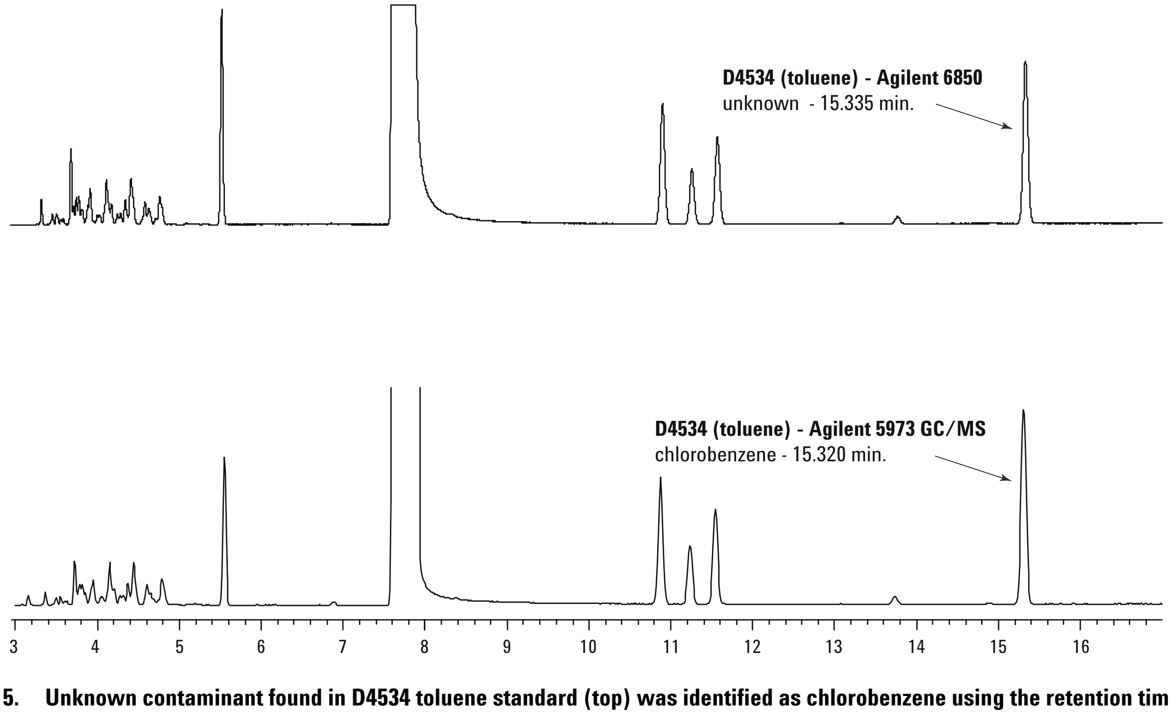
D4534 (toluene) - Agilent 6890

	mg/kg	ret. time (min)
benzene	9	5.565
ethylbenzene	na	10.898
p-xylene	na	11.260
m-xylene	na	11.568
o-xylene	na	13.759
unknown	na	15.310

D4534 (toluene) - Agilent 6850

	mg/kg	ret. time (min)
benzene	9	5.573
ethylbenzene	na	10.917
p-xylene	na	11.279
m-xylene	na	11.587
o-xylene	na	13.779
unknown	na	15.335

Figure 14. **ASTM D4534 toluene quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.**



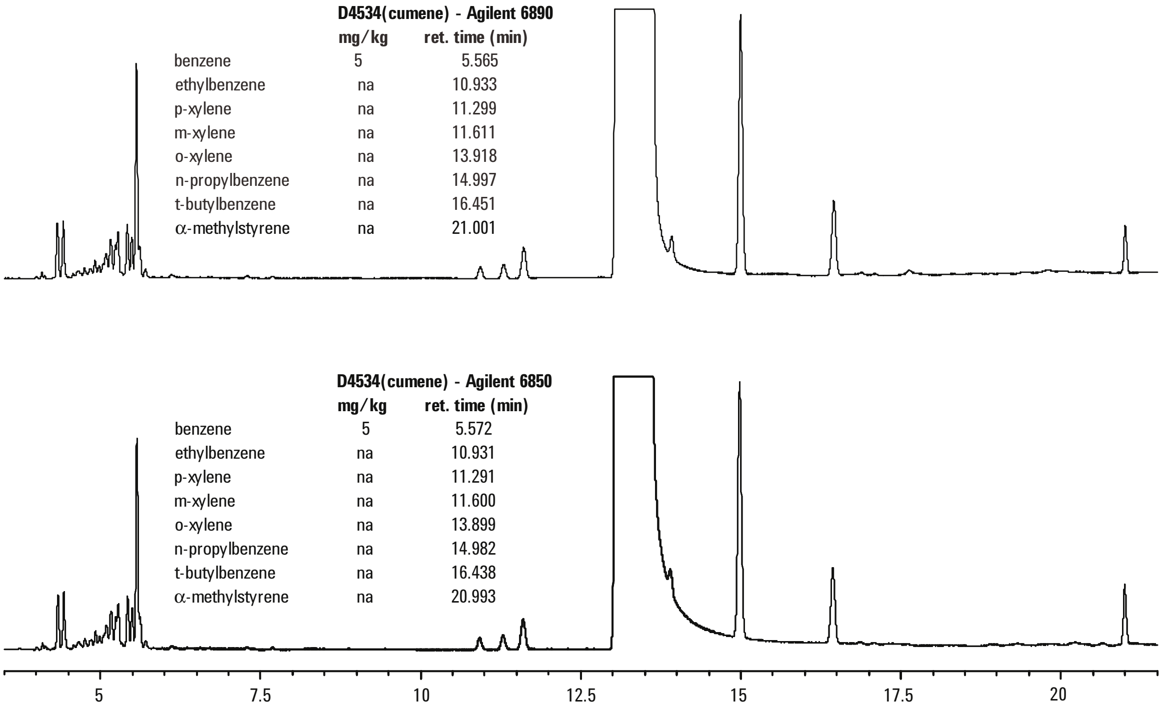
D4534 (toluene) - Agilent 6850
unknown - 15.335 min.

D4534 (toluene) - Agilent 5973 GC/MS
chlorobenzene - 15.320 min.

Figure 15. **Unknown contaminant found in D4534 toluene standard (top) was identified as chlorobenzene using the retention time locked unified aromatics method run on the Agilent 5973 GC/MS (bottom).**

D4534 Standard Test Method of Benzene Content of Cyclic Products - Cumene

Figure 16 shows the chromatograms of the D4535 calibration standard containing 5 mg/kg (ppm) of benzene in cumene. The injection size was 1.0 µL and the split ratio was 100:1. Details of these chromatograms are shown in Figure 17. Although benzene is well resolved, there are still some C9 hydrocarbons that elute near benzene. These compounds represent a potential source of interference when measuring small amounts of benzene (less than 5 mg/kg) in cumene.



D4534(cumene) - Agilent 6890

	mg/kg	ret. time (min)
benzene	5	5.565
ethylbenzene	na	10.933
p-xylene	na	11.299
m-xylene	na	11.611
o-xylene	na	13.918
n-propylbenzene	na	14.997
t-butylbenzene	na	16.451
α-methylstyrene	na	21.001

D4534(cumene) - Agilent 6850

	mg/kg	ret. time (min)
benzene	5	5.572
ethylbenzene	na	10.931
p-xylene	na	11.291
m-xylene	na	11.600
o-xylene	na	13.899
n-propylbenzene	na	14.982
t-butylbenzene	na	16.438
α-methylstyrene	na	20.993

Figure 16. **ASTM D4534 cumene quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.**

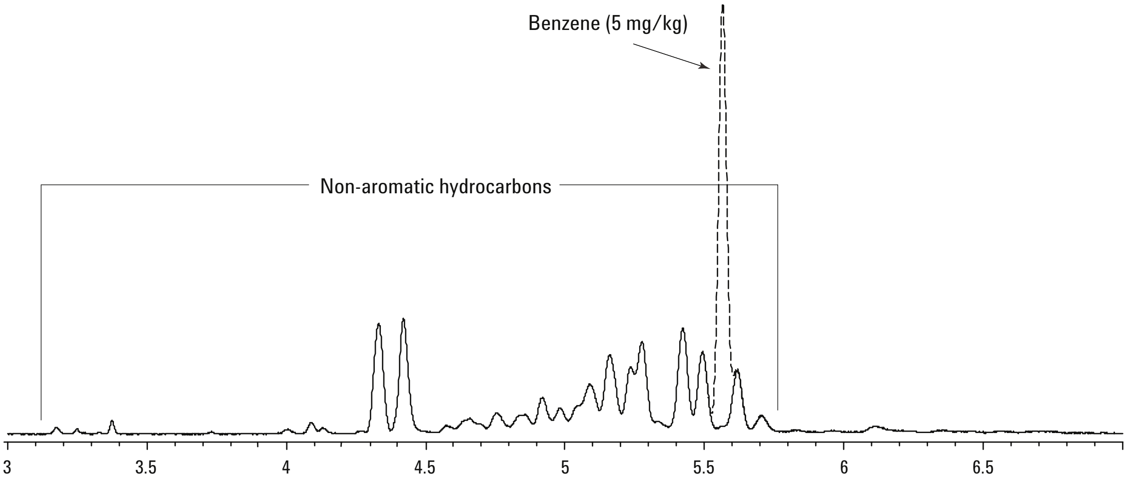


Figure 17. **Details of the D4534 cumene standard showing the separation of 5 mg/kg of benzene from non-aromatic hydrocarbons typically found in cumene.**

D5060 Standard Test Method for Determining Impurities in High-Purity Ethylbenzene

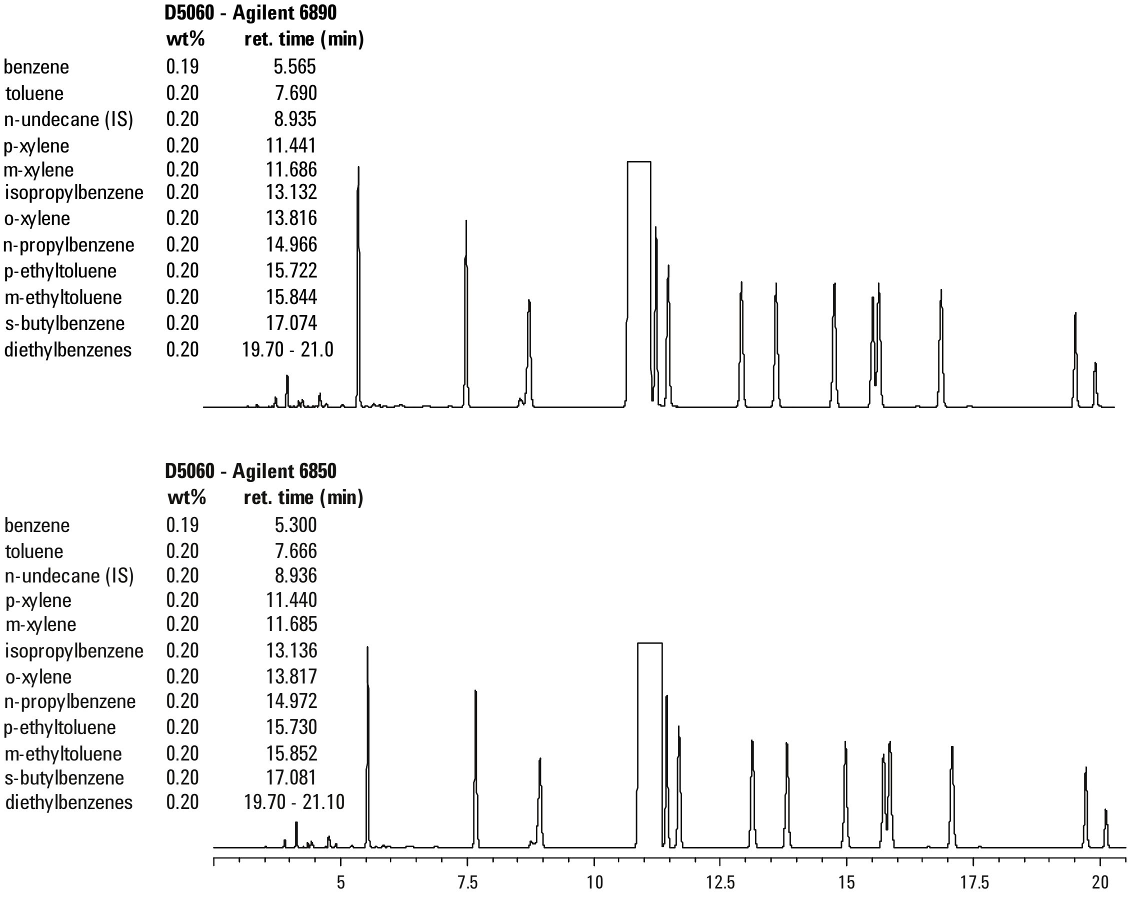
Figure 18 shows the chromatograms of the D5060 calibration standard. The injection size was 1.0 µL and the split ratio was 100:1.

D5135 Standard Test Method for Analysis of Styrene by Capillary Gas Chromatography

Figure 19 shows the chromatograms of the D5135 calibration standard. The injection size was 1.0 µL and the split ratio was 100:1.

D5917 Standard Test for Trace Impurities in Monocyclic Hydrocarbons (ESTD Cal)

This method is identical to D2360 without the addition of the internal standard, n-butylbenzene, so that the chromatogram shown in Figure 7 is a good representation of an expected result. However, since n-butylbenzene is not included in the standard or samples for D5917, the run time of the unified method can be reduced to approximately 15 minutes.



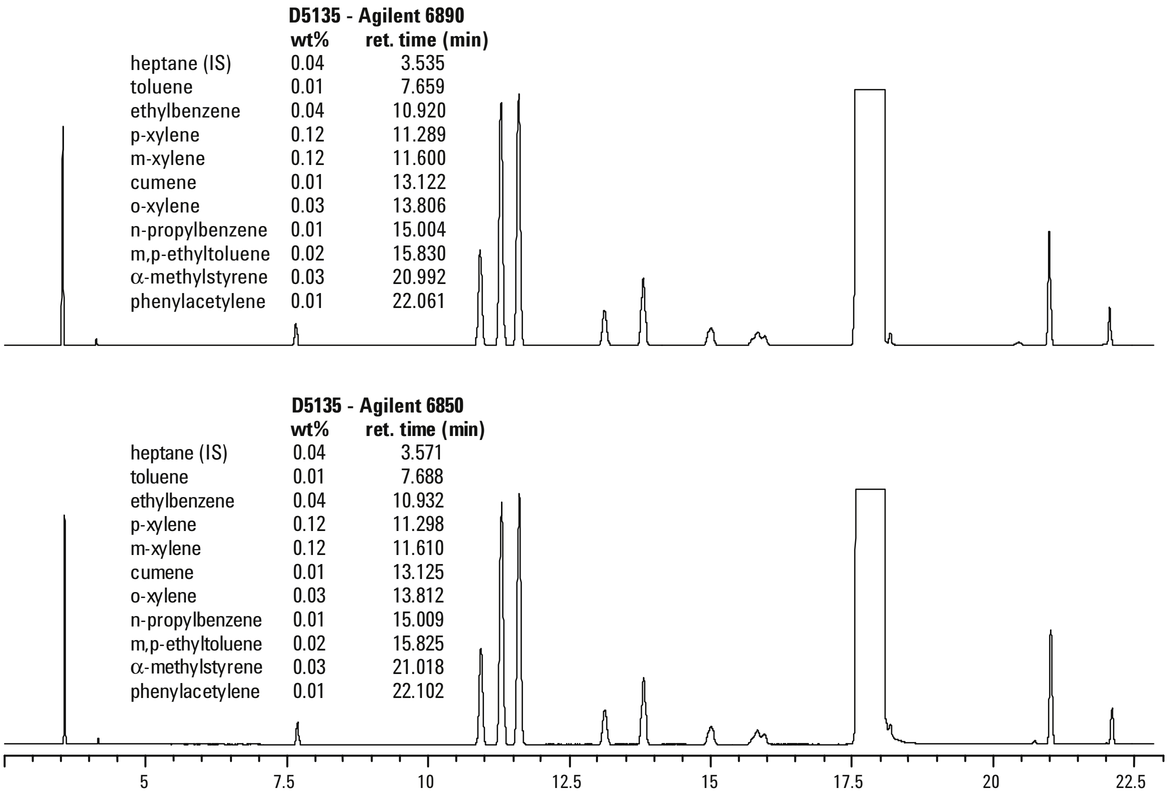
D5060 - Agilent 6890

	wt%	ret. time (min)
benzene	0.19	5.565
toluene	0.20	7.690
n-undecane (IS)	0.20	8.935
p-xylene	0.20	11.441
m-xylene	0.20	11.686
isopropylbenzene	0.20	13.132
o-xylene	0.20	13.816
n-propylbenzene	0.20	14.966
p-ethyltoluene	0.20	15.722
m-ethyltoluene	0.20	15.844
s-butylbenzene	0.20	17.074
diethylbenzenes	0.20	19.70 - 21.0

D5060 - Agilent 6850

	wt%	ret. time (min)
benzene	0.19	5.300
toluene	0.20	7.666
n-undecane (IS)	0.20	8.936
p-xylene	0.20	11.440
m-xylene	0.20	11.685
isopropylbenzene	0.20	13.136
o-xylene	0.20	13.817
n-propylbenzene	0.20	14.972
p-ethyltoluene	0.20	15.730
m-ethyltoluene	0.20	15.852
s-butylbenzene	0.20	17.081
diethylbenzenes	0.20	19.70 - 21.10

Figure 18. ASTM D5060 ethylbenzene quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.



D5135 - Agilent 6890

	wt%	ret. time (min)
heptane (IS)	0.04	3.535
toluene	0.01	7.659
ethylbenzene	0.04	10.920
p-xylene	0.12	11.289
m-xylene	0.12	11.600
cumene	0.01	13.122
o-xylene	0.03	13.806
n-propylbenzene	0.01	15.004
m,p-ethyltoluene	0.02	15.830
α-methylstyrene	0.03	20.992
phenylacetylene	0.01	22.061

D5135 - Agilent 6850

	wt%	ret. time (min)
heptane (IS)	0.04	3.571
toluene	0.01	7.688
ethylbenzene	0.04	10.932
p-xylene	0.12	11.298
m-xylene	0.12	11.610
cumene	0.01	13.125
o-xylene	0.03	13.812
n-propylbenzene	0.01	15.009
m,p-ethyltoluene	0.02	15.825
α-methylstyrene	0.03	21.018
phenylacetylene	0.01	22.102

Figure 19. **ASTM D5135 quantitative calibration standard run on Agilent 6890 (top) and 6850 (bottom) using the retention time locked unified aromatics method.**

Conclusions

The analysis of many different bulk aromatic solvents in the QA/QC laboratory presents the analyst with an array of ASTM methods specific to each material. In an effort to simplify these measurements for today's laboratory environment, the chromatographies of ten ASTM methods were consolidated into one method. This unified method can resolve the 27 compounds found in aromatic materials and can successfully run the calibration standards used by each ASTM method to determine solvent purity. This versatile method can be run on both the Agilent 6890 and 6850 GC to yield consistent results between the method development lab and the plant production lab. To further improve performance, retention time locking (RTL) was applied to the unified method so that retention time standard deviation for each compound in any sample is less than 0.03 minutes. This allows easy comparison of results between instruments, laboratories and over time. The retention time locked unified method meets the need for a fast, simple method that can be run in today's production laboratories.

References

1. Annual Book of ASTM Standards, Vol. 6.04 *Paint - Solvents; Aromatic Hydrocarbons*, ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
2. V. Giarrocco, B.D. Quimby, and M.S. Klee, *Retention Time Locking: Concepts and Applications*, Agilent Technologies, Application Note 228-392, Publication number 5966-2469E, December 1997.
3. ASTM Method D2360, *Standard Test for Trace Impurities in Monocyclic Hydrocarbons*, Annual Book of ASTM Standards, Vol. 6.04, ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
4. B.D. Quimby, L.M. Blumberg, M.S. Klee, and P.L. Wylie, *Precise Time-scaling of Gas Chromatographic Methods Using Method Translation and Retention Time Locking*, Agilent Technologies, Publication number 5967-5820E, May 1998.

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Agilent Technologies

Increasing Sample Throughput with High-Speed Megabore Columns

Application

Greater than 20% More Plates Per Meter

Improved Resolution and/or Faster Run Times Compared to 0.53-mm ID Columns

No Special Hardware Required

Decreasing the diameter of a capillary column is an effective way of increasing column efficiency. This increase in the number of theoretical plates per meter (N/m) can be utilized to improve compound resolution. A significant decrease in analysis time can also be achieved by adjusting the analysis conditions or shortening the column length.

For the chromatographer using Megabore (that is, 0.53-mm ID) columns, going to smaller internal diameter columns has not always been an option, due in part to capacity issues and injector and/or detector hardware incompatibilities. The 0.45-mm ID, High-Speed Megabore column introduces the traditional Megabore chromatographer to a column that can increase the resolution of analytes and/or reduce some analysis times by as much as 45%. Because Agilent's High-Speed Megabore columns retain the same outer diameter as 0.53-mm ID columns, no special ferrules or adaptors are required.

High-Speed Megabore columns also have the same phase ratio (ß) as 0.53-mm ID columns, making it very easy to translate the method conditions. Methods can easily be optimized for speed or resolution using free method translation software available from the Agilent Web site or by speaking with our Technical Support Department (call 800-227-9770 in the U.S. or Canada or visit www.agilent.com/chem).

On average, the High-Speed Megabore provides 24% more theoretical plates per meter than the comparable 0.53-mm ID column (Table 1). At some point, increasing a column's length can begin to work against chromatographic efficiency gain due to high carrier gas pressure drop in long capillaries. This is exemplified with the 105 m, DB-502.2. Figure 1 compares the two DB-502.2 columns for the analysis of volatile organics by purge and trap (for example, EPA Method 502.2). Most notable in these chromatograms are the essentially identical resolution of analytes and the 23-minute decrease in run time with the High-Speed Megabore column.

High-Speed Megabore columns are ideally suited to applications where dual 0.53-mm columns are currently being used. Figure 2a and 2b show one such application.

Table 1. Column Efficiencies

Column phase	Column length	Internal diameter	Film thickness [1]	Plates/meter (% increase) [2]
DB-VRX	75 meters	0.449 mm	2.55 µm	1997 (28)
	75 meters	0.540 mm	3.00 µm	1447
DB-624	75 meters	0.446 mm	2.55 µm	1402 (22)
	75 meters	0.546 mm	3.00 µm	1090
DB-502.2	75 meters	0.453 mm	2.55 µm	1526 (20)
	105 meters	0.544 mm	3.00 µm	873
DB-WAX	30 meters	0.447 mm	0.85 µm	1656 (25)
	30 meters	0.544 mm	1.00 µm	1357
DB-1	30 meters	0.455 mm	1.30 µm	1477 (27)
	30 meters	0.551 mm	1.50 µm	1357
DB-5	30 meters	0.446 mm	1.30 µm	1895 (23)
	30 meters	0.540 mm	1.50 µm	1454
DB-608	30 meters	0.450 mm	0.71 µm	1477 (23)
	30 meters	0.535 mm	0.83 µm	1134

[1] Phase ratio (ß) held constant for all columns

[2] Average 24%

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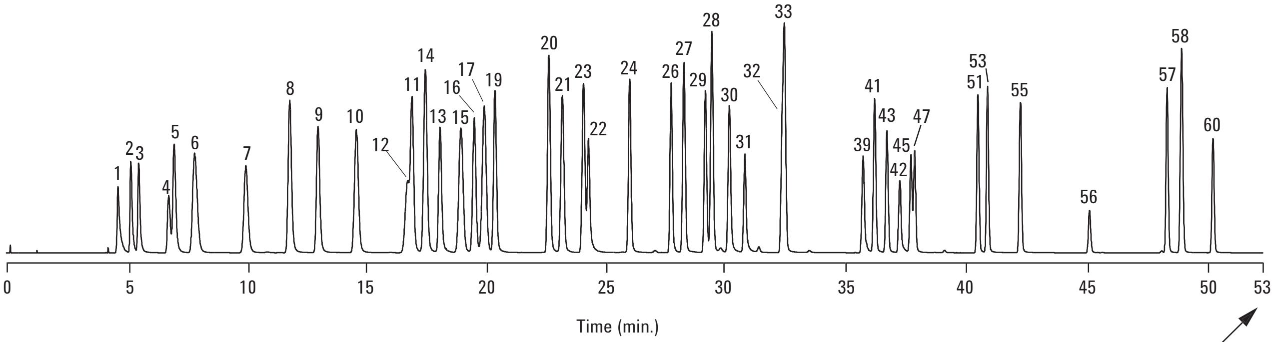
Compound List for all Chromatograms

1. Dichlorodifluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane
7. 1,1-Dichloroethene
8. Methylene chloride
9. trans-1,2-Dichloroethene
10. 1,1-Dichloroethane
11. cis-1,2-Dichlorethene
12. 2,2-Dichloropropane
13. Bromochloromethane
14. Chloroform
15. 1,1,1-Trichloroethane
16. 1,1-Dichloropropene
17. Carbon Tetrachloride
18. Benzene
19. 1,2-Dichloroethane
20. Silica trichloroethene
21. 1,2-Dichloropropane
22. Dibromomethane
23. Bromodichloromethane
24. cis-1,3-Dichloropropene
25. Toluene
26. trans-1,3-Dichloropropene
27. 1,1,2-Trichloroethane
28. Tetrachloroethene
29. 1,3-Dichloropropane
30. Dibromochloromethane
31. 1,2-Dibromomethane
32. Chlorobenzene
33. 1,1,1,2-Tetrachloroethane
34. Ethylbenzene
35. meta-Xylene
36. para-Xylene
37. ortho-Xylene
38. Styrene
39. Bromoform
40. Isopropylbenzene
41. 1,1,2,2-Tetrachloroethane
42. Bromobenzene
43. 1,2,3-Trichloropropane
44. n-Propylbenzene
45. 2-Chlorotoluene
46. 1,2,3-Trimethylbenzene
47. 4-Chlorotoluene
48. tert-Butylbenzene
49. 1,2,4-Trimethylbenzene
50. sec-Butylbenzene
51. 1,3-Dichlorobenzene
52. para-Isopropyltoluene
53. 1,4-Dichlorobenzene
54. n-Butylbenzene
55. 1,2-Dichlorobenzene
56. 1,2-Dibromo-3-chloropropane
57. 1,2,4-Trichlorobenzene
58. Hexachlorobutadiene
59. Naphthalene
60. 1,2,3-Trichlorobenzene

Conditions

Column: DB-502.2, 105 m x 0.53-mm ID, 3.0 µm
Part no.: 125-14A4
Carrier: Helium at 10 mL/min, measured at 35 °C
Oven: 35 °C for 10 min
35 °C - 200 °C at 4 °C/min
200 °C for 5 min

Injector: Purge and trap (OIA 4560)
40 ppb per component in 5 mL water
Trap: Tenax™/Silica gel/Charcoal
Detector: Electrolytic conductivity detector (ELCD) (OIA 4420) with NiCat™ reaction tube in the halogen mode



Conditions

Column: DB-502.2, 75 m x 0.45-mm ID, 2.55 µm
Part no.: 124-1474
Carrier: Helium at 9 mL/min, measured at 35 °C
Oven: 35 °C for 6 min
35 °C - 200 °C at 8 °C/min
200 °C for 3.5 min

Injector: Purge and trap (OIA 4560)
40 ppb per component in 5 mL water
Trap: Tenax/Silica gel/Charcoal
Detector: ELCD (OIA 4420) with NiCat reaction tube in the halogen mode

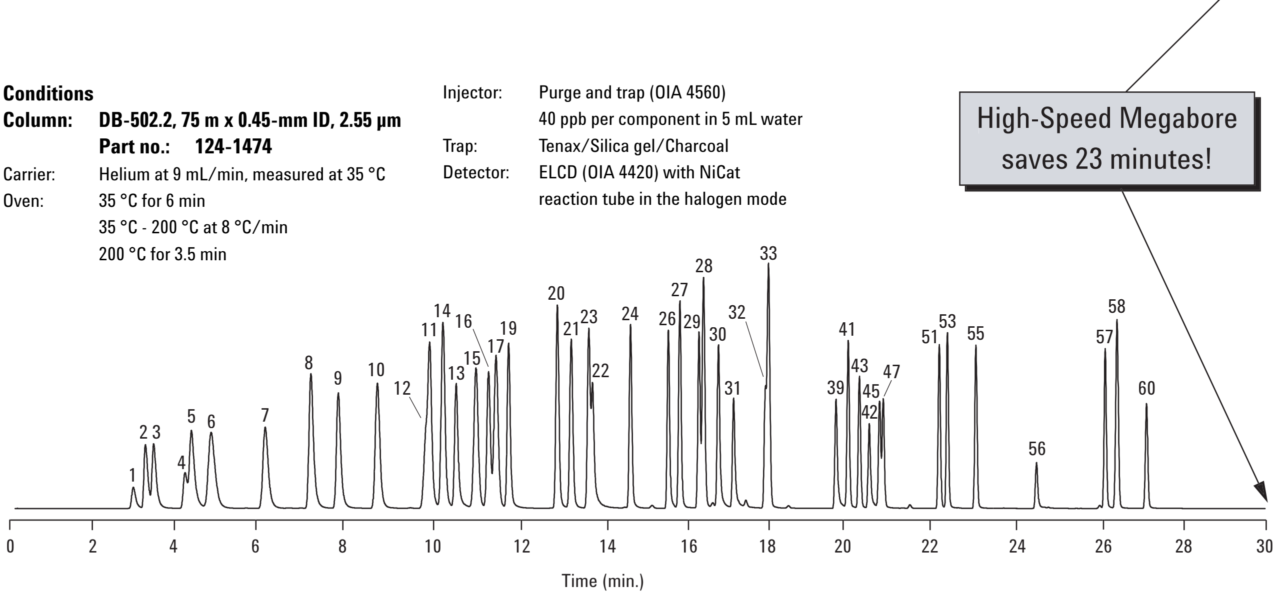


Figure 1. Analysis time comparison

Conditions
Figure 2a and 2b

Columns:	**DB-624** 75m x 0.45-mm ID, 2.55 µm Part no.: 124-1374 **DB-VRX** 75m x 0.45-mm ID, 2.55 µm Part no.: 124-1574
Guard Column:	5m x 0.53-mm ID deactivated fused silica tubing 3-way universal glass union
Carrier:	Helium at 9 mL/min (18 mL/min total), measured at 35 °C
Oven:	35 °C for 12 min 35 °C - 60 °C at 5 °C/min 60 °C for 1 min 60 °C - 200 °C at 17 °C/min 200 °C for 4 min
Injector:	Purge and trap (OIA 4560) 40 ppb per component in 5 mL water
Trap:	Tenax/Silica gel/Charcoal
Detector A:	Photoionization detector (PID) (OIA 4430) at 220 °C
Detector B:	Electrolytic conductivity detector (ELCD) (OIA 4420) with NiCat reaction tube in the halogen mode

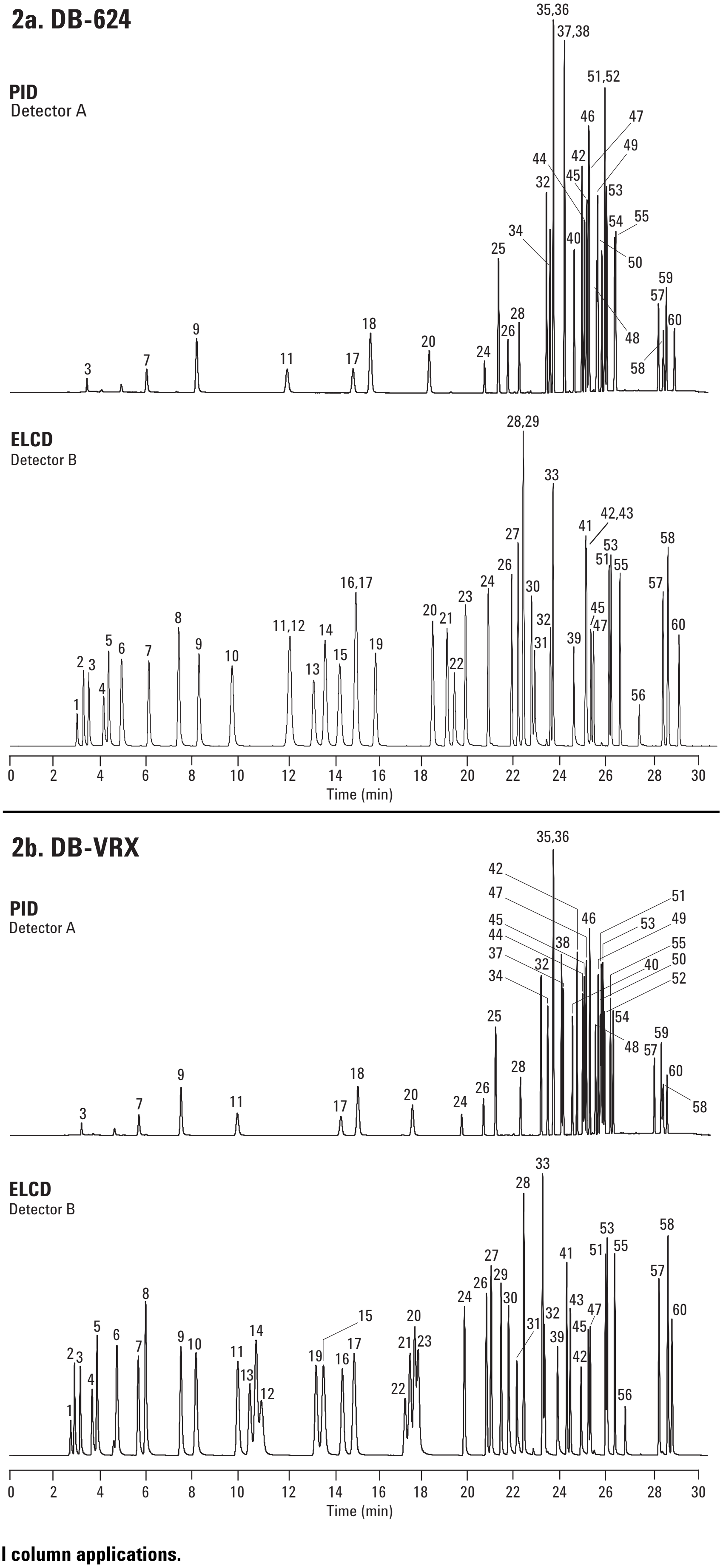


Figure 2a and 2b. High-Speed Megabore dual column applications.

0.45-mm ID High-Speed Megabore Column Order Guide

Phase[1]	Inner diameter (mm)	Length (meter)	Film thickness (µm)	Temperature limits (°C)	Part number
DB-1	0.45	15	1.27	-60 to 300/320	124-1012
DB-1	0.45	15	2.55	-60 to 260/280	124-1014
DB-1	0.45	30	0.42	-60 to 300/320	124-1037
DB-1	0.45	30	1.27	-60 to 300/320	124-1032
DB-1	0.45	30	2.55	-60 to 260/280	124-1034
DB-1	0.45	30	4.25	-60 to 260/280	124-1005
DB-1	0.45	60	1.27	-60 to 300/320	124-1062
DB-5	0.45	15	1.27	-60 to 300/320	124-5012
DB-5	0.45	30	0.42	-60 to 300/320	124-5037
DB-5	0.45	30	1.27	-60 to 300/320	124-5032
DB-5	0.45	30	4.25	-60 to 260/280	124-5035
DB-17	0.45	15	0.85	40 to 260/280	124-1712
DB-17	0.45	30	0.85	40 to 260/280	124-1732
DB-1701	0.45	30	0.42	-20 to 260/280	124-0737
DB-1701	0.45	30	0.85	-20 to 260/280	124-0732
DB-200	0.45	30	0.85	30 to 280/300	124-2032
DB-210	0.45	30	0.85	45 to 220/240	124-0232
DB-2887	0.45	10	2.55	-60 to 350	124-2814
DB-502.2	0.45	75	2.55	0 to 260/280	124-1474
DB-502.2	0.45	105	2.55	0 to 260/280	124-14A4
DB-608	0.45	30	0.42	40 to 260/280	124-6837
DB-608	0.45	30	0.70	40 to 260/280	124-1730
DB-624	0.45	30	2.55	-20 to 260	124-1334
DB-624	0.45	75	2.55	-20 to 260	124-1374
DB-FFAP	0.45	15	0.85	40 to 250/250	124-3212
DB-FFAP	0.45	30	0.85	40 to 250	124-3232
DB-MTBE	0.45	30	2.55	35 to 260/280	124-0034
DB-TPH	0.45	30	1.00	-10 to 290/290	124-1632
DB-VRX	0.45	30	2.55	-10 to 260	124-1534
DB-VRX	0.45	75	2.55	-10 to 260	124-1574
DB-WAX	0.45	60	0.85	20 to 230/240	124-7062
DB-WAX	0.45	15	0.85	20 to 230/240	124-7012
DB-WAX	0.45	30	0.85	20 to 230/240	124-7032
DB-WAXetr	0.45	5	1.70	50 to 230/250	124-7304
DB-XLB	0.45	30	1.27	30 to 320/340	124-1232

[1] Additional phases, lengths, and film thickness can be made with a 0.45-mm ID High-Speed Megabore column. If you do not find the column you are looking for, ask for a custom column quote (order part number 100-2000 and specify the phase, ID, length, and film thickness).

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Agilent Technologies

DuraGuard Columns: GC Columns with Built-In Protection

Application

Guard columns/retention gaps without the use of unions

- **Minimize front-end contamination of the column and increase column lifetime**
- **Aid in focusing sample onto the front end of the column for excellent peak shape**
- **Minimize the amount of mass selective detector (MSD) source contamination originating from the column**

All this with no leaks, no added activity, and no hassle

Deactivated fused silica tubing is commonly added to the front of an analytical column to act as a guard column or retention gap. It can also be added to the back of the analytical column as a transfer line into the MSD to minimize the amount of source contamination originating from the column.

Historically, deactivated tubing has been connected to the analytical column by using a union. These are difficult to install requiring a great deal of care and skill to ensure they will work properly. With incorrect installation unions can cause leaks resulting in column degradation, dead volume resulting in peak shape problems, or activity problems resulting in peak shape problems and/or response loss. Leaks are especially a problem when the union is located close to the MSD when using deactivated fused silica for the transfer line.

DuraGuard columns, with a built in length of deactivated fused silica tubing, avoid these potential problems. The deactivated fused silica and the analytical column are made with a single, continuous piece of fused silica tubing, thus eliminating the need for the union. Installation hassles, peak shape problems and leaks associated with unions are history. Samples containing difficult analytes such as pesticides or drugs can be chromatographed without any undesirable contributions from the union.

Guard Columns

DuraGuard columns are especially beneficial as guard columns when analyzing samples containing low levels of chemically active compounds. Unions can be active towards these analytes and can cause peak-shape problems, which in turn result in poor detection limits. DuraGuard columns eliminate the potentially active union by using a single piece of fused silica tubing. Agilent Technologies' special deactivation process results in extremely inert columns and tubing for a broad range of analyte types.

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Guard columns are used when samples contain nonvolatile residues that contaminate the column. The nonvolatile residues deposit in the guard column and not in the analytical column. This greatly reduces the interaction between the residues and the sample since the guard column does not retain the solutes (because it contains no stationary phase). Also, the residues do not coat the stationary phase which often results in poor peak shapes. Periodic cutting or trimming of the guard column is usually required upon a build-up of residues. Guard columns 5–10 meters in length allow for substantial trimming before the entire guard column requires replacement. The onset of peak shape problems is the usual indicator that the guard column needs trimming or changing.

Retention Gaps

DuraGuard columns offer the user the benefits of a retention gap without the hassle of making critical clean column cuts and installing the fused silica tubing to the front of their analytical column with a union. By avoiding the union there are no additional sources of leaks or activity. The only difference is the improved peak shape of the analytes.

Retention gaps are used to improve peak shape for some types of samples, columns and GC conditions. Use of 3–5 meters of tubing is required to obtain the benefits of a retention gap. The situations that benefit the most from retention gaps are large volume injections (>2 µL) and solvent-stationary phase polarity mismatches for splitless, Megabore direct and on-column injections. Peak shapes are sometimes distorted when using combinations of these conditions. Polarity mismatches occur when the sample solvent and column stationary phase are very different in polarity. The greatest improvement is seen for the peaks eluting closest to the solvent front or solutes very similar to the solvent in polarity. The benefits of a retention gap are often unintentionally obtained when using a guard column.

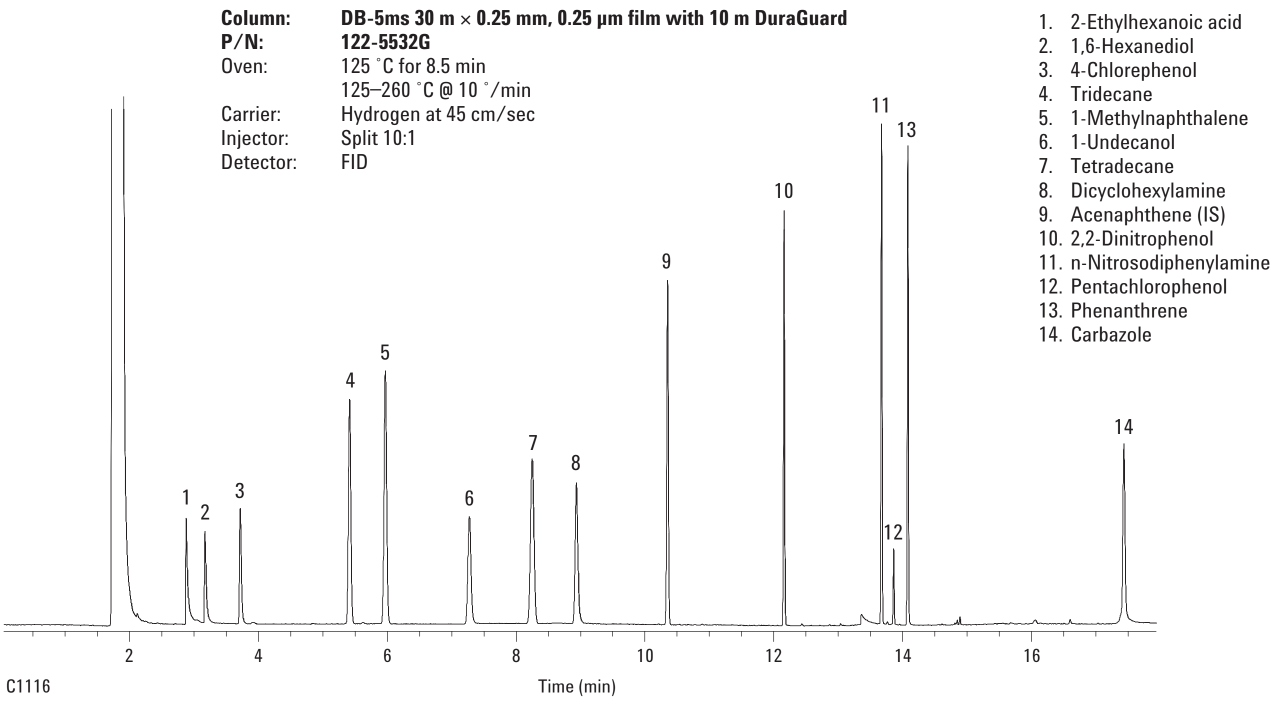
MSD Transfer Line

DuraGuard columns help minimize source contamination without the potential for leaks. The vacuum system of the MSD makes it especially difficult to maintain a leak free system - particularly the closer the connection is to the MSD. The use of unions with Mass Spec Detectors has always been tricky and prone to leakage. By using a single piece of fused silica, there are no additional connections to cause leaks.

Using a piece of deactivated fused silica as the transfer line to an MSD can reduce the frequency of source cleaning. Often the MSD transfer line temperature is at or above the columns upper temperature limit and thermal degradation of the stationary phase occurs. Volatile polymer breakdown products are carried into the MSD and can deposit in the MSD ion source. Using deactivated fused silica tubing as the MSD transfer line eliminates the presence of polymer in the heated zone and decreases the amount of material that can contaminate the MSD source thus decreasing the frequency of required source cleanings.

Results

Figure 1 is an FID chromatogram of a complex test mixture separated using a combination DuraGuard column. Note the peak shape quality for notoriously difficult to analyze compounds.



Column:	**DB-5ms 30 m × 0.25 mm, 0.25 µm film with 10 m DuraGuard**
P/N:	**122-5532G**
Oven:	125 °C for 8.5 min 125–260 °C @ 10 °/min
Carrier:	Hydrogen at 45 cm/sec
Injector:	Split 10:1
Detector:	FID

1. 2-Ethylhexanoic acid
2. 1,6-Hexanediol
3. 4-Chlorephenol
4. Tridecane
5. 1-Methylnaphthalene
6. 1-Undecanol
7. Tetradecane
8. Dicyclohexylamine
9. Acenaphthene (IS)
10. 2,2-Dinitrophenol
11. n-Nitrosodiphenylamine
12. Pentachlorophenol
13. Phenanthrene
14. Carbazole

Figure 1. Chromatogram of test mixture using combination guard and analytical columns.

Want a Guard Column or Retention Gap of a Different Internal Diameter?

If you would prefer a guard column with a different diameter than your analytical column, save yourself the hassle of assembling union connections and let us do it for you! Agilent Technologies offers the dependable Leak-free connection service to meet your analytical needs: short guard columns, long guard columns, different diameters, or dual columns. Whatever you need, Agilent Technologies can provide through our Custom Column shop.

Our Leak-free connection service results in a dependable, long lasting leak-free connection. We use high quality glass press fit unions with polyimide sealing resin to ensure the connection will last. See Figure 2. At Agilent Technologies our technicians have years of experience in creating leak-free connections and in using special techniques to keep the polyimide sealing resin out of the flow path. Once the connection is carefully made, the resin is cured and the product is tested for leaks.

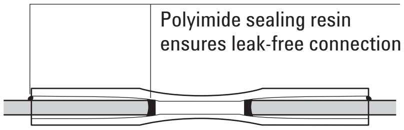


Figure 2. Detail of glass press fit union with polyimide sealing resin.

DuraGuard Column Order Guide

Part number	Phase	Inner diameter (mm)	Length (m)	Film thickness (µm)	DRGD Length (m)
122-1032G	DB-1	0.25	30	0.25	10
122-5532G	DB-5ms	0.25	30	0.25	10
122-5536G	DB-5ms	0.25	30	0.5	10
122-5533G	DB-5ms	0.25	30	1	10
122-5562G	DB-5ms	0.25	60	0.25	10
125-5537G	DB-5ms	0.53	30	0.5	10
122-1232G	DB-XLB	0.25	30	0.25	10
125-0732G	DB-1701	0.53	30	1	10
125-1334G5	DB-624	0.53	30	3	5

DuraGuard columns of different phases and dimensions are available through Agilent Technologies custom column shop. Any DB polysiloxane or low bleed phase can be made as a DuraGuard column with 0.18 mm id or larger fused silica tubing. Ask for a custom column quote (part number 100-2000 and specify the phase, id, length, and film thickness of analytical column, and desired length of DuraGuard).

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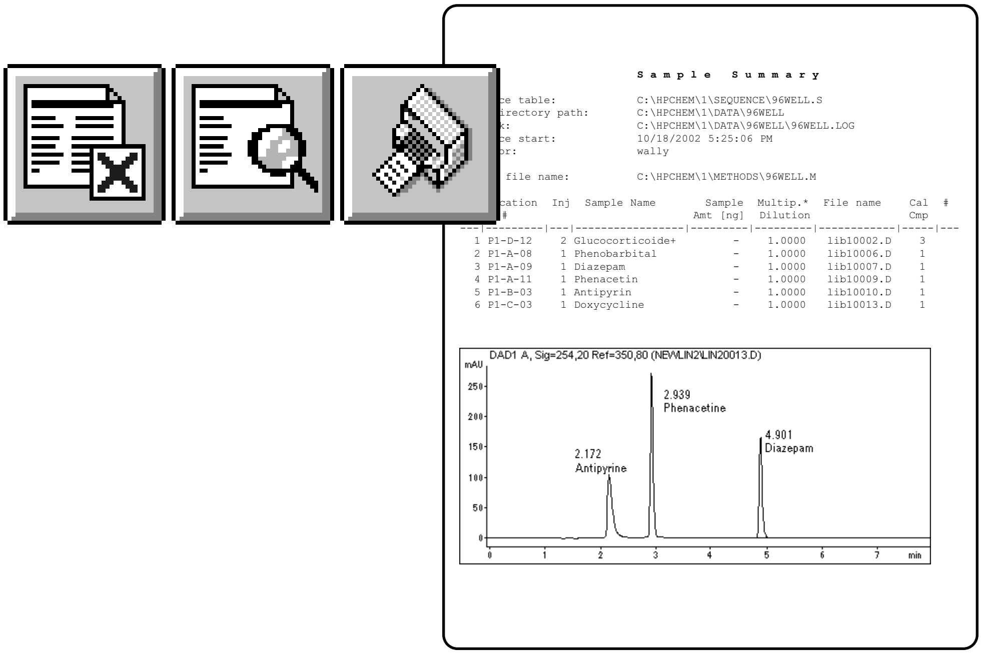
Agilent Technologies

Using Agilent ChemStation to generate summary reports for a single analysis or a sequence of analyses

Application

Angelika Gratzfeld-Huesgen



```
                         S a m p l e   S u m m a r y

  ce table:              C:\HPCHEM\1\SEQUENCE\96WELL.S
  irectory path:         C:\HPCHEM\1\DATA\96WELL
  k:                     C:\HPCHEM\1\DATA\96WELL\96WELL.LOG
  ce start:              10/18/2002 5:25:06 PM
  or:                    wally

   file name:            C:\HPCHEM\1\METHODS\96WELL.M

  cation  Inj  Sample Name        Sample  Multip.*  File name    Cal  #
  #                              Amt [ng]  Dilution              Cmp
---|---------|---|-----------------|---------|---------|------------|-----|---
  1 P1-D-12    2 Glucocorticoide+        -    1.0000   lib10002.D    3
  2 P1-A-08    1 Phenobarbital           -    1.0000   lib10006.D    1
  3 P1-A-09    1 Diazepam                -    1.0000   lib10007.D    1
  4 P1-A-11    1 Phenacetin              -    1.0000   lib10009.D    1
  5 P1-B-03    1 Antipyrin               -    1.0000   lib10010.D    1
  6 P1-C-03    1 Doxycycline             -    1.0000   lib10013.D    1
```

Introduction

The Agilent ChemStation base software includes a wide range of built-in report styles and types. For example, it provides standard reports such as area percent (AREA%), external standard (ESTD), internal standard (ISTD), and normalized (NORM) reports as well as system suitability reports and sequence summary reports with statistical evaluation of retention times, areas, heights and more.

For each type of report the user can determine the amount of information that is included in the report. The ChemStation base software also provides a report editor for customizing reports — a topic that is beyond the scope of this note.

This Application Note describes how to set up the different report types, explaining the software screens and giving example reports. The main objective is to give guidelines and to provide strategies on how to use the different built-in reports in the ChemStation base software.

Equipment

The data for the report examples was generated using an Agilent 1100 Series HPLC system comprising the following modules.

- high pressure gradient pump
- micro-vacuum degasser
- well plate sampler
- thermostatted column compartment
- diode array detector

The Agilent ChemStation base software including the 3D data evaluation module, revision A.08.04, was used for instrument control, data acquisition, data handling, sample tracking, and reporting.

Report setup on ChemStation

The standard reporting function in the ChemStation base software provides for single run reports or sample-set reports for a full sequence of runs, whereby these so-called sequence summary reports can only be generated after completion of the sequence. The content of the sequence summary reports is defined by the acquisition sequence.

Further, the ChemStation base software includes a wide range of built-in standard reports that allow users to define the content and amount of printed information. Whereas this functionality meets the requirements of most standard applications to a large extent, it does not have the flexibility to create additional table elements for non-chromatographic information, charts or custom calculations. If such extended reporting capabilities are required, it is recommended to use the ChemStation Plus data system including the ChemStore data organization module.

The ChemStation base software offers four types of report.

- Individual run reports, which can be generated automatically after each run or sequence, provide quick and easy printouts of results.

- Sequence summary reports provide comprehensive infomation for a full set of samples, including full GLP/GMP details. They are generated automatically at the end of a sequence and may include individual reports as well as statistical summary reports.

- Batch reports provide direct printouts of first-pass review modifications and results. They are generated during reprocessing of data from a complete sequence or of a subset of one sequence using ChemStation batch review.

- Advanced custom reports for requirements that go beyond the scope of the previous types. These include customized reports for individual runs or complete sequences and can also be obtained automatically after each run or sequence.

The following sections focus on the individual-run and sequence-summary report types, which are built-in as standard in the ChemStation base software, and explain in detail how to use and set up these report types.

Qualitative reports for individual runs

Qualitative reports are used mainly during the development of a separation or when a quick decision is needed as to whether a compound is present or not. Here the separation of peaks is of primary interest and a short AREA% report is sufficient. Particularly during method development it does not make sense to obtain reports with quantitative results.

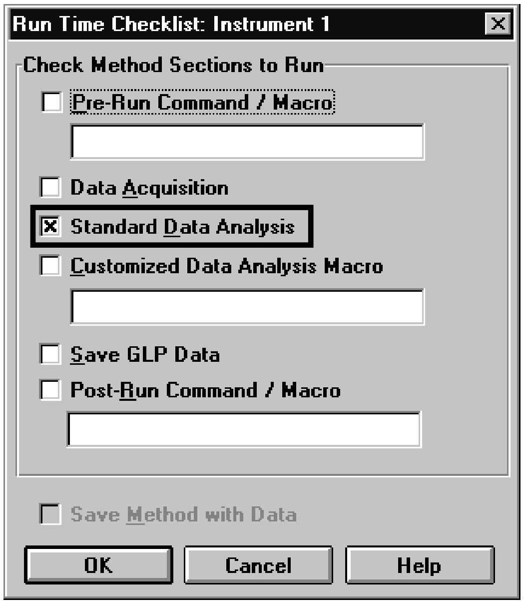
Setup

To obtain an automated printout of an individual report such as a short AREA% report, the item *Standard Data Analysis* must be selected in the *Run Time Checklist*, which is part of the overall method for acquisition, data analysis and reporting, see figure 1. This screen is part of the *Edit Entire Method* dialog or can be accessed directly from the *Method* menu of the *Method and Run Control* view.

The item shown in figure 1 must be selected when the calculation of results is required, such as for printing reports, including sequence summary reports, with or without individual run reports.

Configuration

To obtain qualitative reports the item *Calculate* in the group *Quantitative Results* must be set to *Percent* as shown in figure 2.


Run Time Checklist: Instrument 1

Check Method Sections to Run

☐ Pre-Run Command / Macro

☐ Data Acquisition

☒ Standard Data Analysis

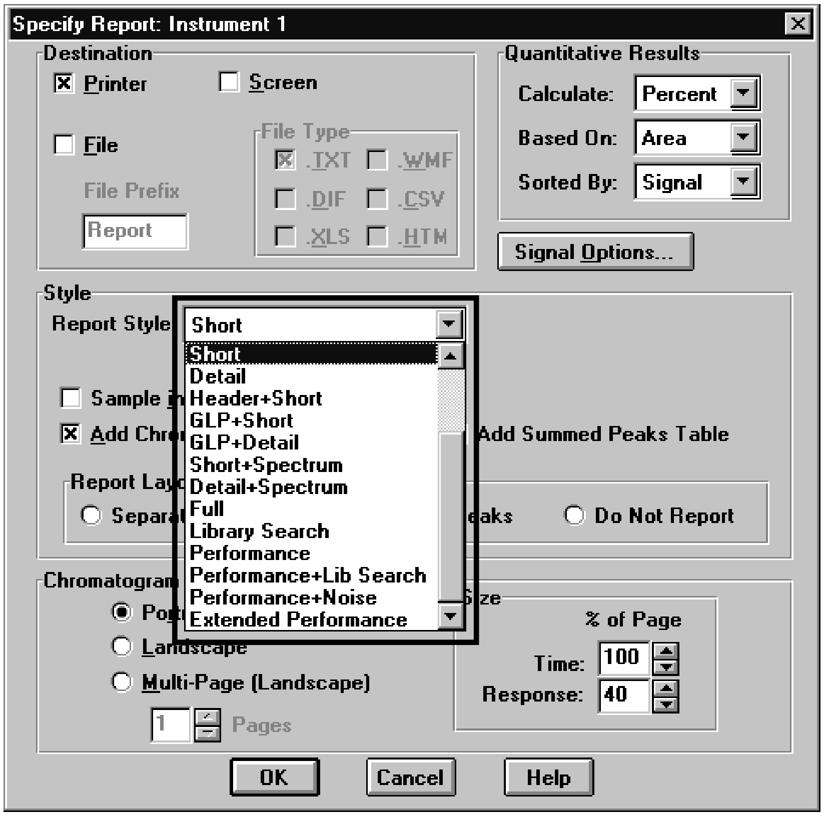
☐ Customized Data Analysis Macro

☐ Save GLP Data

☐ Post-Run Command / Macro

☐ Save Method with Data

Figure 1
Activating *Standard Data Analysis*, including integration and quantification as part of the ChemStation method, is mandatory to obtain automated printouts of all report types available in the ChemStation base software


Specify Report: Instrument 1

Destination

☒ Printer ☐ Screen

☐ File

File Prefix: Report

File Type: ☒ .TXT ☐ .WMF ☐ .DIF ☐ .CSV ☐ .XLS ☐ .HTM

Quantitative Results

Calculate: Percent

Based On: Area

Sorted By: Signal

Style

Report Style: Short

☐ Sample i

☒ Add Chr

Add Summed Peaks Table

Report Lay

○ Separ

aks

○ Do Not Report

Chromatogram

● Po

○ Landscape

○ Multi-Page (Landscape)

1 Pages

ize

% of Page

Time: 100

Response: 40

Figure 2
Specifying individual run reports

There are three ways to set up reports for individual runs.

1. Using the report smart icon in the *Method and Run Control* view.
2. Using part of the *Edit Entire Method* wizard
3. Using the *Data Analysis* view by selecting *Report* and then *Specify Report*.

Figure 2 shows the setup screen for run reports. Several report styles are available, covering a broad spectrum of report types. The report output can be sent to a printer, displayed on the screen or saved to a file. Multiple report destinations can be selected at a time. Other report parameters allow to include chromatograms, in landscape or portrait format or even distributed over several pages, and to define the way unknown compounds are reported.

An example of an AREA% report is given on page 12, containing information about the used method, data filename, time of injection, chromatogram and report.

The report styles that are available depend on the installed software modules. For example, the report styles Short+Spectrum, Detail+Spectrum and Library Serach are only available when the 3D data evaluation module is installed.

During method development the combination of *Percent* and *Performance* in reporting can be a valid tool to find out about k', resolution, selectivity, peak width and, for isocratic runs, the number of plates. An example is given on page 19.

Calculation procedures such as **Percent** (for others such as ESTD and ISTD, see section "Quantitative reports for individual runs") can be combined with any of the available standard reports shown in figure 2.

Qualitative reports can not use calculations based on standards such as ESTD and ISTD.

Quantitative reports for individual runs

Quantitative reports offer compound identification and compound quantification. They are mainly used with known samples or reference results in method optimization and quality control areas.

Setup

Before a quantitative report can be generated, standard samples with known compound concentrations have to be run and a calibration table has to be set up.

Peak integration should always be optimized before a peak is used as a reference in the calibration table and before the calibration tasks are done. To optimize integration, load a sample file with known sample concentration and then use the *Integration* tool set in the *Data Analysis* screen. When integration is optimized and saved, the calibration table can be created.

The calibration table is set up in *Data Analysis* from the *Calibration* menu, see figure 3.

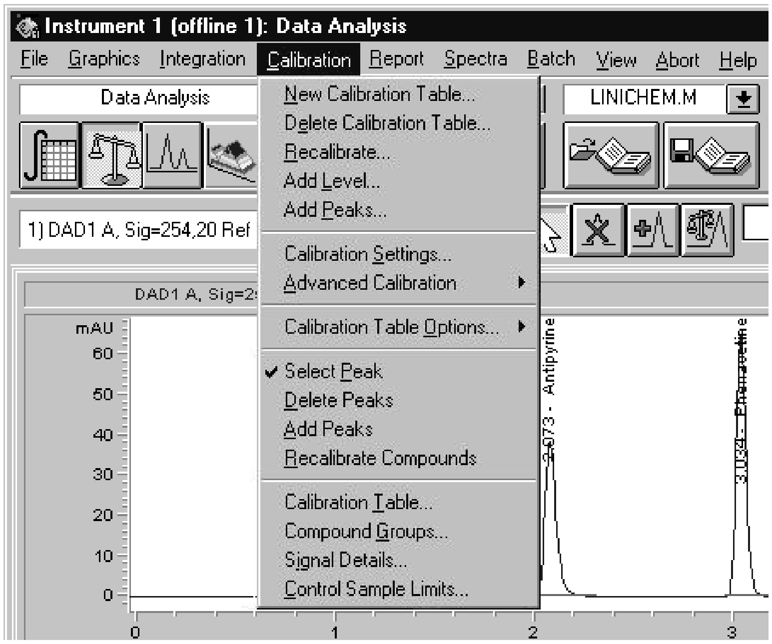


Figure 3
Calibration setup menu

In the following example we set up a multilevel calibration with four calibration levels. Multilevel calibrations use multiple files to complete the calibration. One file defines one level—completion of a four-level calibration thus requires four files. The steps involved are as follows.

1. Load the first file and click on *New Calibration Table.*
2. Calibrate each peak by selecting the peak (left mouse click), and filling in compound name and compound amount.
3. Repeat step 2 for all peaks.
4. When all peaks in the file are calibrated, load the next file with the next concentration. Use the *Add Level* tool to fill in the amounts for the next concentration level (level two).
5. Repeat step 4 for level three and four.

The calibration is stored as part of the ChemStation method. It is saved by simply saving the method. Every calibration update is easily accessible by loading the method, modifying (for example, updating) the calibration files and saving the new method revision.

Setup

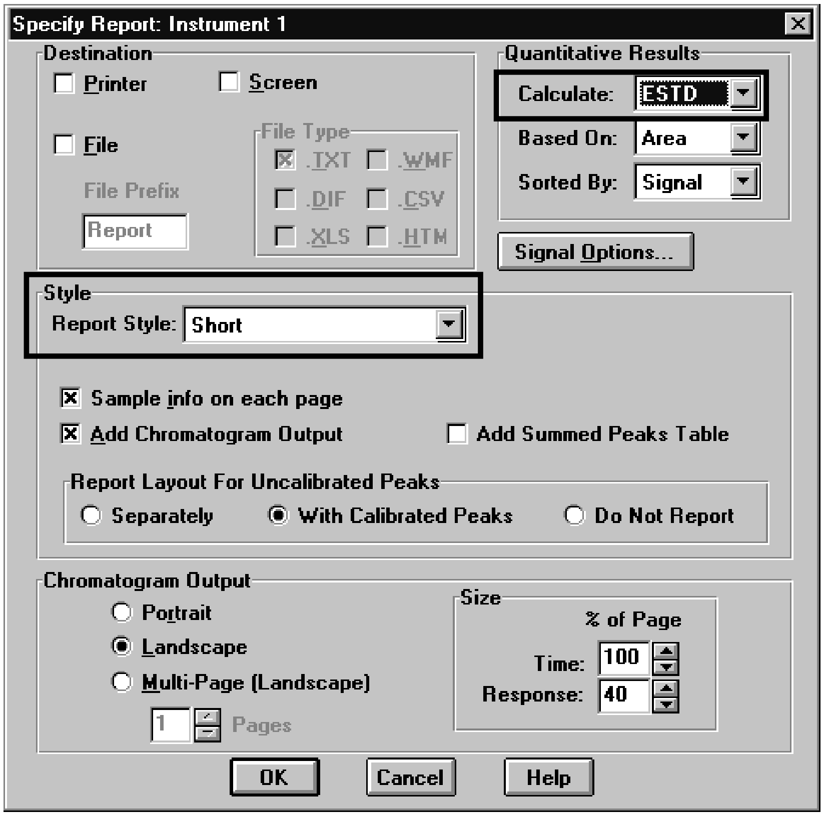
When the calibration is complete all prerequisites for generating a quantitative report are met. The first step in generating a report is to specify the report style as described in the section “Qualitative reports for individual runs.” The calibration of the method now offers access to all predefined report styles such as standards reports or normalized reports or, when running a sequence, to sequence summary reports (see separate section later.)

The calculation of results can be a normalized (NORM) area determination or based on an external standard (ESTD) or internal standard (ISTD). Result calculations can be based on area or height. Figure 4 shows selection of *External Standard Method* as calculation procedure and *Short* as *Report Style*. An example is given on page 13.

Configuration

Additional report features can be specified such as output format for the chromatogram (including multipage outputs), picture size and the documentation of uncalibrated (which means unknown) peaks in the *Specify Report* screen as shown in figure 4. Any report style (see figure 2) can also be combined with any calculation procedure. Examples are given on pages 13 through 21.

- ESTD combined with report style *Short* (p 13)
- ESTD combined with report style *Library Search* (p 14)
- ESTD combined with report style *GLP+Short* (p 16)
- ESTD combined with report style *Performance* (p 19)
- ESTD combined with report style *Detail* (p 20)


Specify Report: Instrument 1

Destination: ☐ Printer ☐ Screen ☐ File
File Prefix: Report
File Type: ☒ .TXT ☐ .WMF ☐ .DIF ☐ .CSV ☐ .XLS ☐ .HTM

Quantitative Results
Calculate: ESTD
Based On: Area
Sorted By: Signal

Style
Report Style: Short
☒ Sample info on each page
☒ Add Chromatogram Output
☐ Add Summed Peaks Table

Report Layout For Uncalibrated Peaks: ○ Separately ● With Calibrated Peaks ○ Do Not Report

Chromatogram Output: ○ Portrait ● Landscape ○ Multi-Page (Landscape)
1 Pages

Size (% of Page)
Time: 100
Response: 40

Figure 4
Selection of external standard report and short report style

Similar to the calibration, the report configuration is saved with the ChemStation method. Thus all data analysis steps for integration, calibration, result calculation and reporting are saved under one "umbrella" tool. Once setup, reuse of all steps is automated by simply reapplying the method to any sample under investigation.

The method that has been set up for data acquisition, integration, calibration and reporting has to be saved under a unique name to ensure that samples are analyzed and evaluated using the correct conditions.

Final report output

Final report outputs are quick and easy to obtain with ChemStation. Both qualitative and quantitative reports offer the same options and use identical tools to generate the final report.

Reports can be
- sent to a printer
- displayed on the screen for a quick review or preview when setting up report options
- saved to a file in HTML, CSV, XML, TXT, WMF, or DIF format

It is possible to combine all output types, for example, to get a printed copy on paper, an online report display on the screen and a file copy on the local hard disk.

The user can choose either
- automated report output at the end of each sample analysis (or reanalysis), or
- interactive report output at user request

Automated report output
An automated report is output whenever the ChemStation method is executed and at least one report destination is selected in the *Specify Report* screen, see figure 4. If no report output is desired, simply leave all report destination check boxes blank.

Method execution typically is used to analyze a sample or to reapply changes in calculations or calibration during data analysis. To execute a method, simply press *F5* or select *Run method* from the ChemStation *Run control* menu as shown in figure 5.

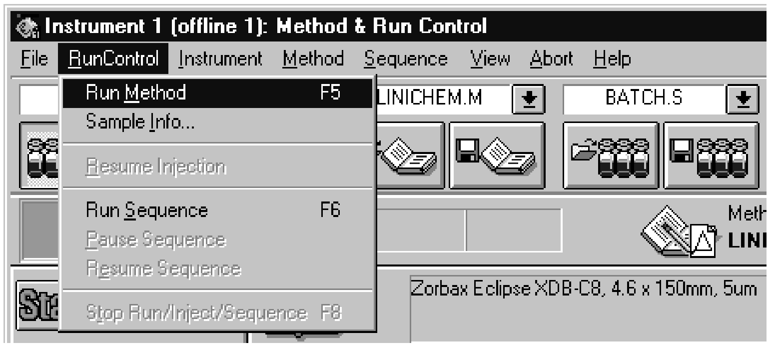


Figure 5
Run method for automated method execution and result output

If the user wants to re-analyze data without data acquisition, *Data Acquisition* must be disabled in the *Run Time Checklist*, see figure 1.

Interactive report printout
Manual report output is available from the ChemStation *Data Analysis* view. It is designed to preview report outputs on the screen during report configuration or to get an individual sample report during interactive result analysis or result review.

The *Data Analysis* view is designed to set up advanced reports such as library searches, detailed spectrum reports and others. It has a separate report menu and additional smart icons for report setup, preview and output to a printer as shown in figure 6.

When the user wants a report during their data review session, they simply press the preview or print button and immediately get the report on the screen or on paper.

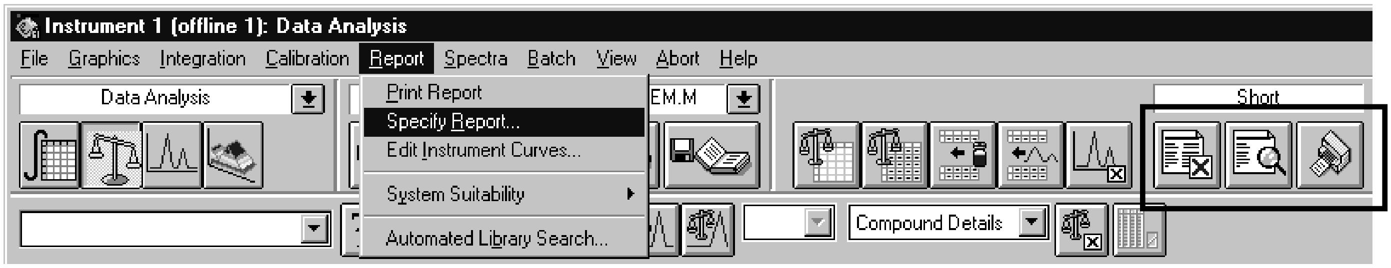


Figure 6
Report menu and smart icons (far right) in ChemStation Data Analysis view

Sequence summary reports

In contrast to individual run reports, sequence summary reports can only be generated for a complete set of samples that have been analyzed in one continuos sequence. The sequence summary report (also referred to as a system suitability report) is designed to meet the specific needs of GLP and GMP regulations in the pharmaceutical industry as well as comparable ISO and DIN regulations in other industries.

In addition to result calculation and result documentation, all regulations require additional documentation on how the results have been obtained and how "well" the analytical system behaved during analysis. The sequence summary report is a single all-inclusive report style, combining the analytical result with full documentation of how the result was obtained and the system suitability information, thereby providing a comprehensive report that addresses all regulatory requirements.

Sequence summary reports are frequently used in quality control work. These reports include the analytical results along with documented evidence of the system's suitability for the analytical purpose. System suitability is defined in the various Pharmacopoeia guidelines and it typically includes system performance information based on parameters such as peak width, theoretical plate number, resolution and others.

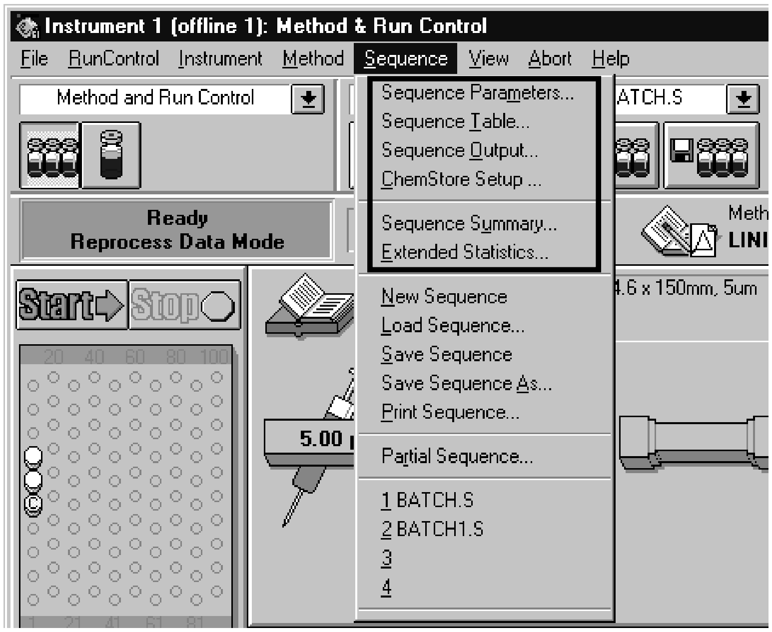


Figure 7
Entries need to be made in these sections to obtain automatically a sequence summary report at the end of a sequence

All these parameters are available in the report style, but the user must configure the report to suit their own specific needs. The following section describes setup and configuration of a sequence summary report in ChemStation.

Setup and configuration

After each sequence of runs a sequence summary report can be printed. Typically this is done to obtain statistical results and determine system suitability. In addition to the entries in the sequence table and before the report can be calculated and printed, several data inputs for sequence parameter and sequence output are required, see figure 7.

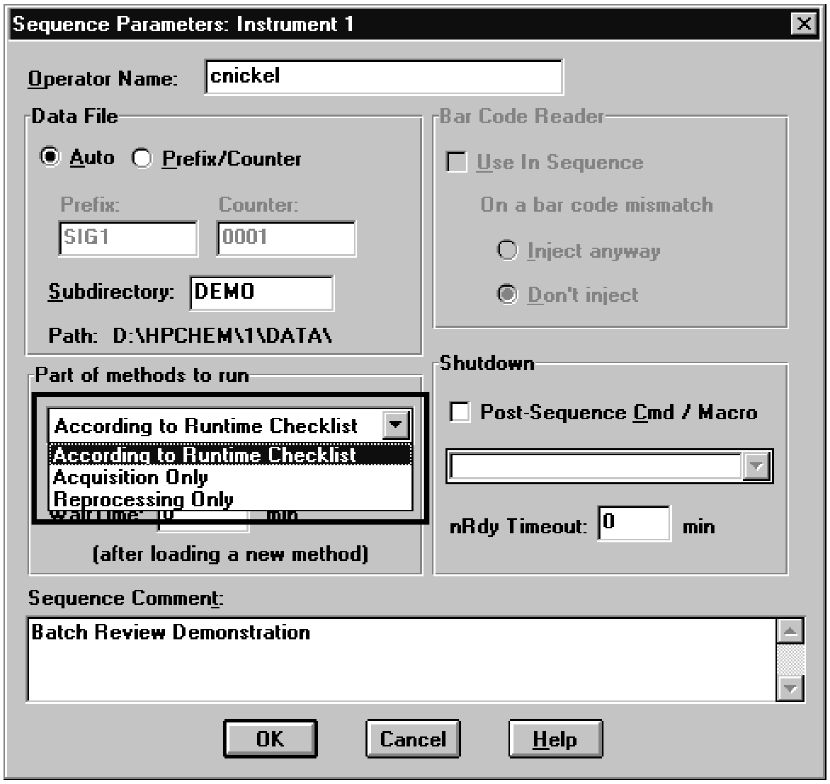
In the *Sequence Parameters* screen (figure 8) the item *Parts of Method to Run* must be set to *According to Runtime Checklist*. This entry determines which part of a method is executed during a sequence and *According to Runtime Checklist* refers to the run-time checklist configuration that was previously edited as part of the method in order to obtain integration and quantitative results.

If data acquisition is completed and the user wants to reanalyze a sequence of samples without data acquisition, the option *Reprocessing Only* allows to recalculate the sequence summary report easily.

In the *Sequence Output* screen the report destination and the content of a sequence summary report are defined by selecting the appropriate check boxes, see figure 9.

The content of the sequence summary report is defined by the items on the right side of the scrreen shown in figure 9. Selecting *Setup* in the *Sequence Output* dialog box accesses this configuration screen. The sequence summary report allows a variety of informations to be printed in one continuously enumerated report.

In addition to a wide selection of statistical results from sample and/or calibration runs, other items can be selected such as sample summary reports that list all acquired samples, com-


Sequence Parameters: Instrument 1

Operator Name: cnickel

Data File

● Auto ○ Prefix/Counter

Prefix: SIG1
Counter: 0001
Subdirectory: DEMO
Path: D:\HPCHEM\1\DATA\

Bar Code Reader

☐ Use In Sequence

On a bar code mismatch

○ Inject anyway

● Don't inject

Part of methods to run

According to Runtime Checklist

According to Runtime Checklist
Acquisition Only
Reprocessing Only

Wait Time: 0 min
(after loading a new method)

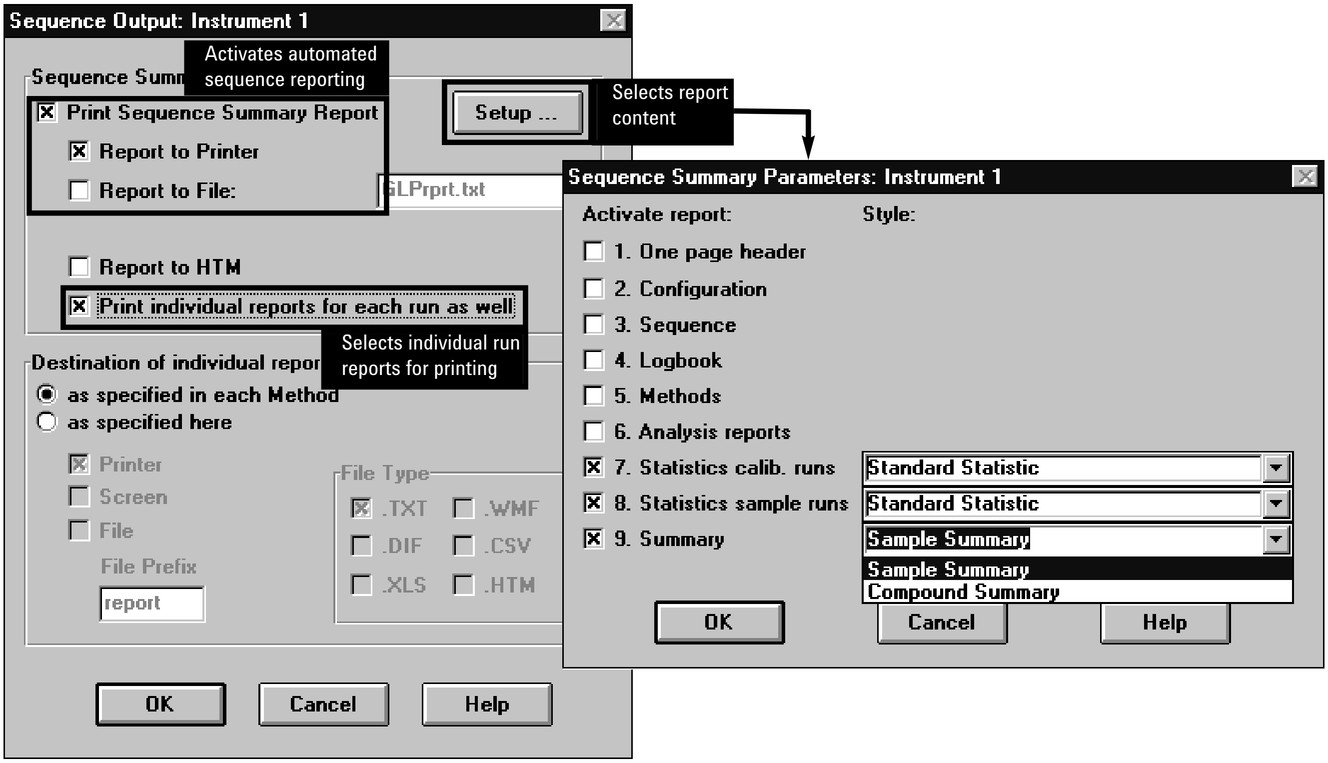
Shutdown

☐ Post-Sequence Cmd / Macro

nRdy Timeout: 0 min

Sequence Comment:
Batch Review Demonstration

Figure 8
Sequence parameters screen


Sequence Output: Instrument 1

Activates automated sequence reporting

Sequence Summary

☒ Print Sequence Summary Report

☒ Report to Printer

☐ Report to File: GLPrprt.txt

☐ Report to HTM

☒ Print individual reports for each run as well

Selects individual run reports for printing

Destination of individual reports

● as specified in each Method

○ as specified here

☒ Printer
☐ Screen
☐ File

File Prefix: report

File Type

☒ .TXT ☐ .WMF
☐ .DIF ☐ .CSV
☐ .XLS ☐ .HTM

Selects report content

Sequence Summary Parameters: Instrument 1

Activate report: / Style:

☐ 1. One page header
☐ 2. Configuration
☐ 3. Sequence
☐ 4. Logbook
☐ 5. Methods
☐ 6. Analysis reports
☒ 7. Statistics calib. runs — Standard Statistic
☒ 8. Statistics sample runs — Standard Statistic
☒ 9. Summary — Sample Summary

Sample Summary
Compound Summary

Figure 9
Selection of report destination and content of a sequence summary report

plete printouts of all parameters in the methods that were used, printouts of sequence logbooks and so on.

It is also possible to include the individual result reports for each run as part of the summary report instead of individual printouts after the end of each run.

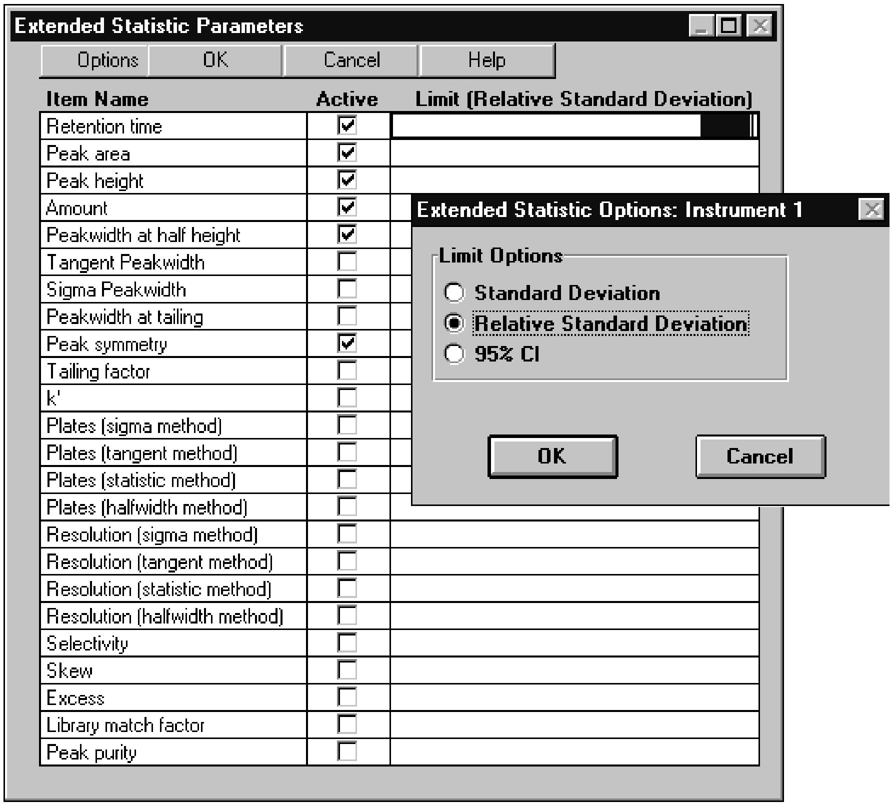
The statistical evaluation of sequence runs is defined in the *Extended Statistic Parameter* screen, see figure 10. Statistical results can be obtained for all parameter shown in this dialog box. Either standard deviation or relative standard deviation or 95% confidence interval can be applied and upper/lower limits for each parameter can be specified.

A calibrated method is necessary to be able obtain statistical results.

Figure 11 shows the *Sequence Table* screen, in which it is important to ensure that the sample type is correctly set to *Sample*, *Calibration* or *Control Sample*, because statistical calculations can be selected based on sample type.

Figure 12 shows an example of a sequence summary report. It contains information about the analyzed samples such as location, sample name, filename, and so on. The header includes information such as operator name, the used chromatographic method, and date of acquisition.

Further report examples can be found on pages 11 through 35.

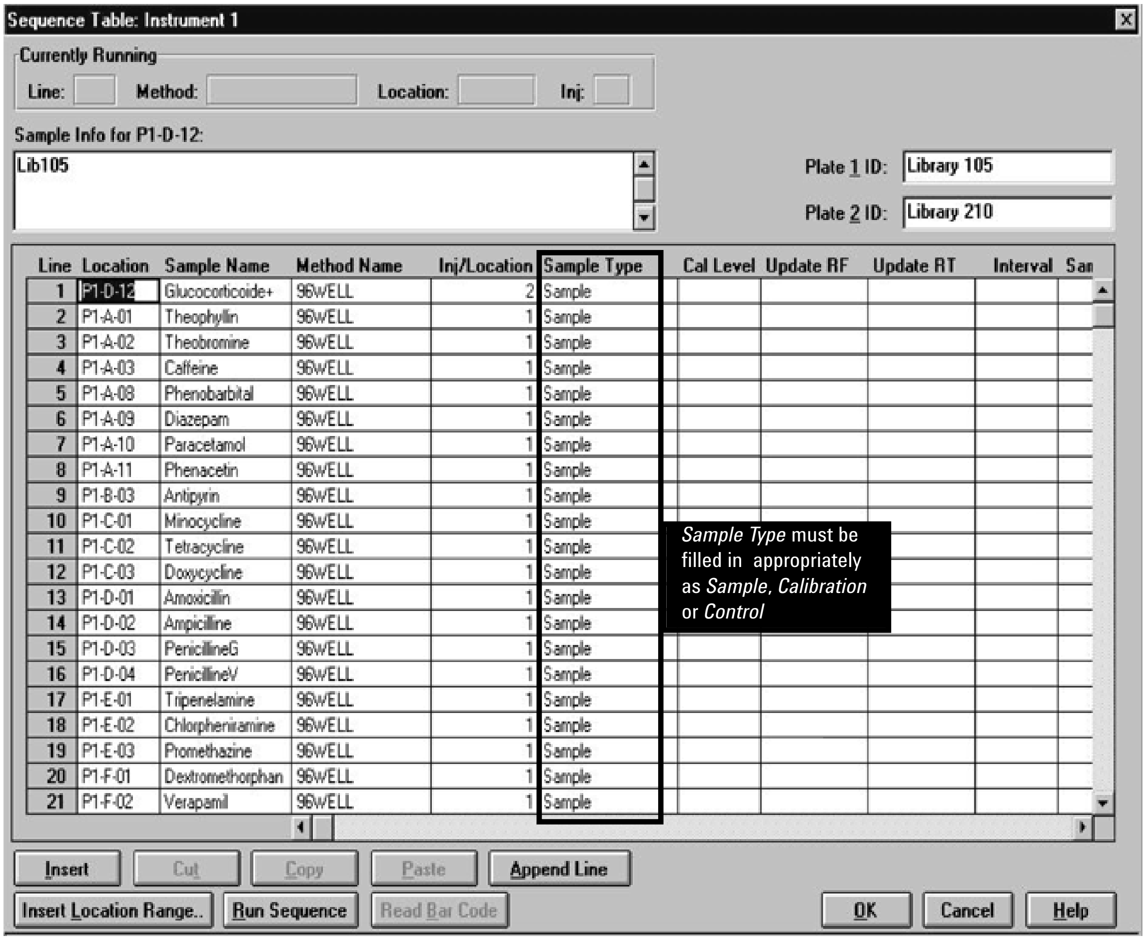


Item Name	Active	Limit (Relative Standard Deviation)
Retention time	☑	
Peak area	☑	
Peak height	☑	
Amount	☑	
Peakwidth at half height	☑	
Tangent Peakwidth	☐	
Sigma Peakwidth	☐	
Peakwidth at tailing	☐	
Peak symmetry	☑	
Tailing factor	☐	
k'	☐	
Plates (sigma method)	☐	
Plates (tangent method)	☐	
Plates (statistic method)	☐	
Plates (halfwidth method)	☐	
Resolution (sigma method)	☐	
Resolution (tangent method)	☐	
Resolution (statistic method)	☐	
Resolution (halfwidth method)	☐	
Selectivity	☐	
Skew	☐	
Excess	☐	
Library match factor	☐	
Peak purity	☐	

Extended Statistic Options: Instrument 1

Limit Options
○ Standard Deviation
● Relative Standard Deviation
○ 95% CI

Figure 10
Setup of statistical calculations for sequence runs



Line:

Method:

Location:

Inj:

Sample Info for P1-D-12:

Lib105

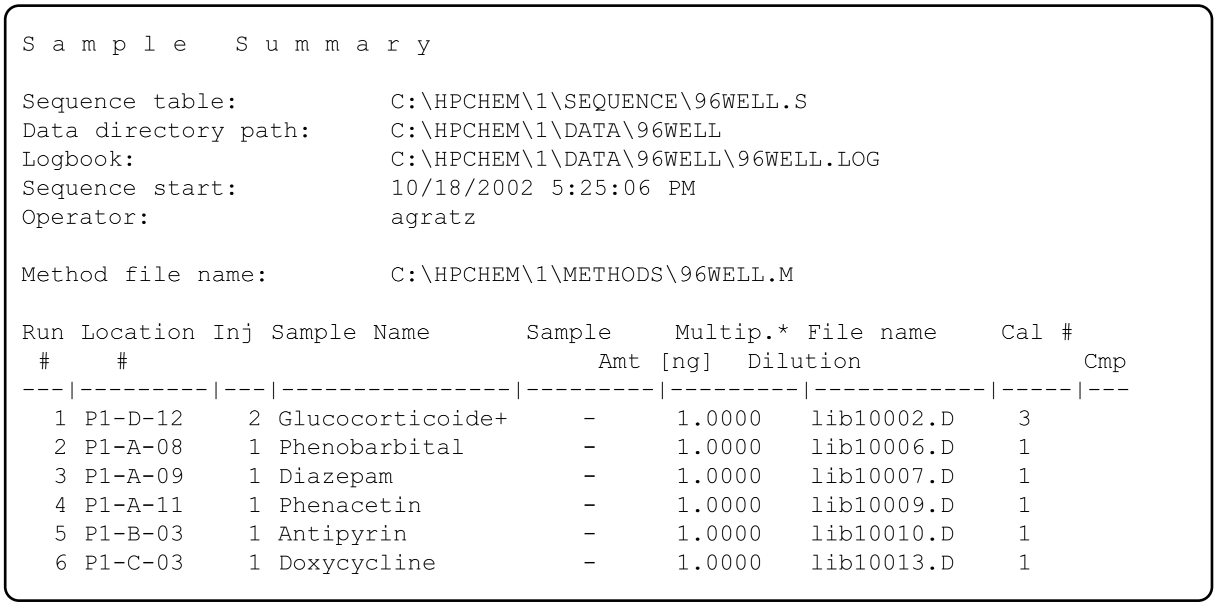
Plate 1 ID: Library 105

Plate 2 ID: Library 210

Line	Location	Sample Name	Method Name	Inj/Location	Sample Type	Cal Level	Update RF	Update RT	Interval	San
1	P1-D-12	Glucocorticoide+	96WELL	2	Sample					
2	P1-A-01	Theophyllin	96WELL	1	Sample					
3	P1-A-02	Theobromine	96WELL	1	Sample					
4	P1-A-03	Caffeine	96WELL	1	Sample					
5	P1-A-08	Phenobarbital	96WELL	1	Sample					
6	P1-A-09	Diazepam	96WELL	1	Sample					
7	P1-A-10	Paracetamol	96WELL	1	Sample					
8	P1-A-11	Phenacetin	96WELL	1	Sample					
9	P1-B-03	Antipyrin	96WELL	1	Sample					
10	P1-C-01	Minocycline	96WELL	1	Sample					
11	P1-C-02	Tetracycline	96WELL	1	Sample					
12	P1-C-03	Doxycycline	96WELL	1	Sample					
13	P1-D-01	Amoxicillin	96WELL	1	Sample					
14	P1-D-02	Ampicilline	96WELL	1	Sample					
15	P1-D-03	PenicillineG	96WELL	1	Sample					
16	P1-D-04	PenicillineV	96WELL	1	Sample					
17	P1-E-01	Tripenelamine	96WELL	1	Sample					
18	P1-E-02	Chlorpheniramine	96WELL	1	Sample					
19	P1-E-03	Promethazine	96WELL	1	Sample					
20	P1-F-01	Dextromethorphan	96WELL	1	Sample					
21	P1-F-02	Verapamil	96WELL	1	Sample					

Sample Type must be filled in appropriately as *Sample*, *Calibration* or *Control*

Figure 11
The Sequence Table screen



```
S a m p l e   S u m m a r y

Sequence table:          C:\HPCHEM\1\SEQUENCE\96WELL.S
Data directory path:     C:\HPCHEM\1\DATA\96WELL
Logbook:                 C:\HPCHEM\1\DATA\96WELL\96WELL.LOG
Sequence start:          10/18/2002 5:25:06 PM
Operator:                agratz

Method file name:        C:\HPCHEM\1\METHODS\96WELL.M

Run Location Inj Sample Name       Sample    Multip.* File name     Cal #
 #     #                            Amt [ng]  Dilution                    Cmp
---|---------|---|----------------|---------|---------|------------|-----|---
  1 P1-D-12    2 Glucocorticoide+     -      1.0000   lib10002.D    3
  2 P1-A-08    1 Phenobarbital        -      1.0000   lib10006.D    1
  3 P1-A-09    1 Diazepam             -      1.0000   lib10007.D    1
  4 P1-A-11    1 Phenacetin           -      1.0000   lib10009.D    1
  5 P1-B-03    1 Antipyrin            -      1.0000   lib10010.D    1
  6 P1-C-03    1 Doxycycline          -      1.0000   lib10013.D    1
```

Figure 12
Example of a sequence sample summary report

Conclusion

The built-in single-run and sequences summary reports that are available in the ChemStation base software offer a wide range of reporting capabilities. The various reports give access to all important sample-related information quickly and easily. For all report types the user can select the amount of information to be included, from a simple qualitative report on one page through detailed quantitative reports to comprehensive and powerful sequence summary reports. Knowledge of a report editor is not required to be able to set up the ChemStation reports.

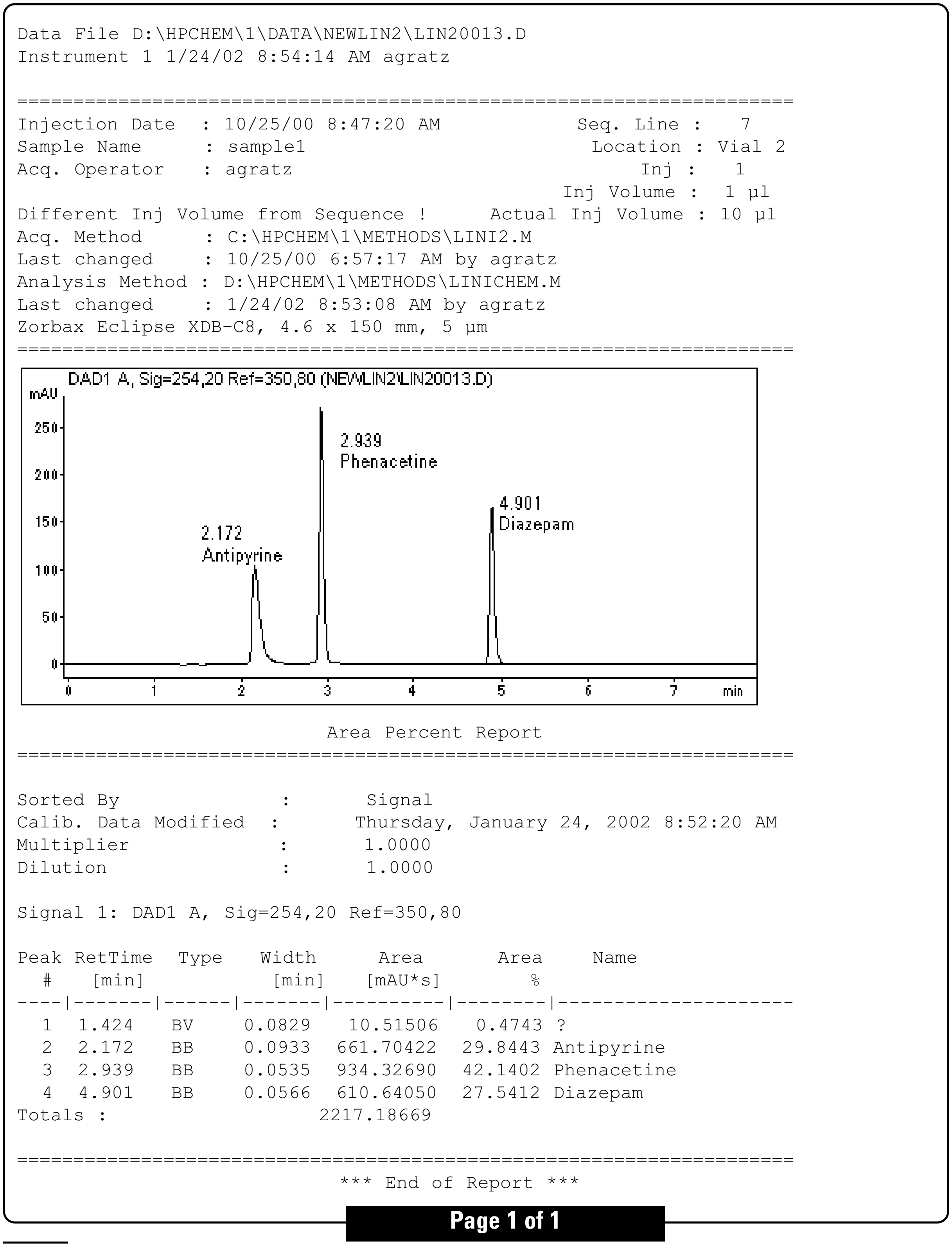
Reports can be obtained after each run or at the end of a sequence. With the ChemStation Method concept users starting from scratch can have a printed result copy of any type in less than 10 minutes – once set up the report is available within seconds after run completion. ChemStation reports are easy to configure, fast to obtain and quickly stored and managed.

Appendix

The following pages show examples of summary reports that can be generated with the ChemStation base software. The examples were generated using the print-to-file function and may have different pagination than a report printed directly from the ChemStation. Reports shown include:

- Short Area Percent Report
- Short ESTD Report
- Spectral Library Search Report
- Short GLP Report
- Performance Report
- Detail Report
- Extended Performance Report
- Sequence Summary Report – Compound Summary
- Sequence Summary Report – Standard Statistics for Sample Runs

Short Area Percent Report

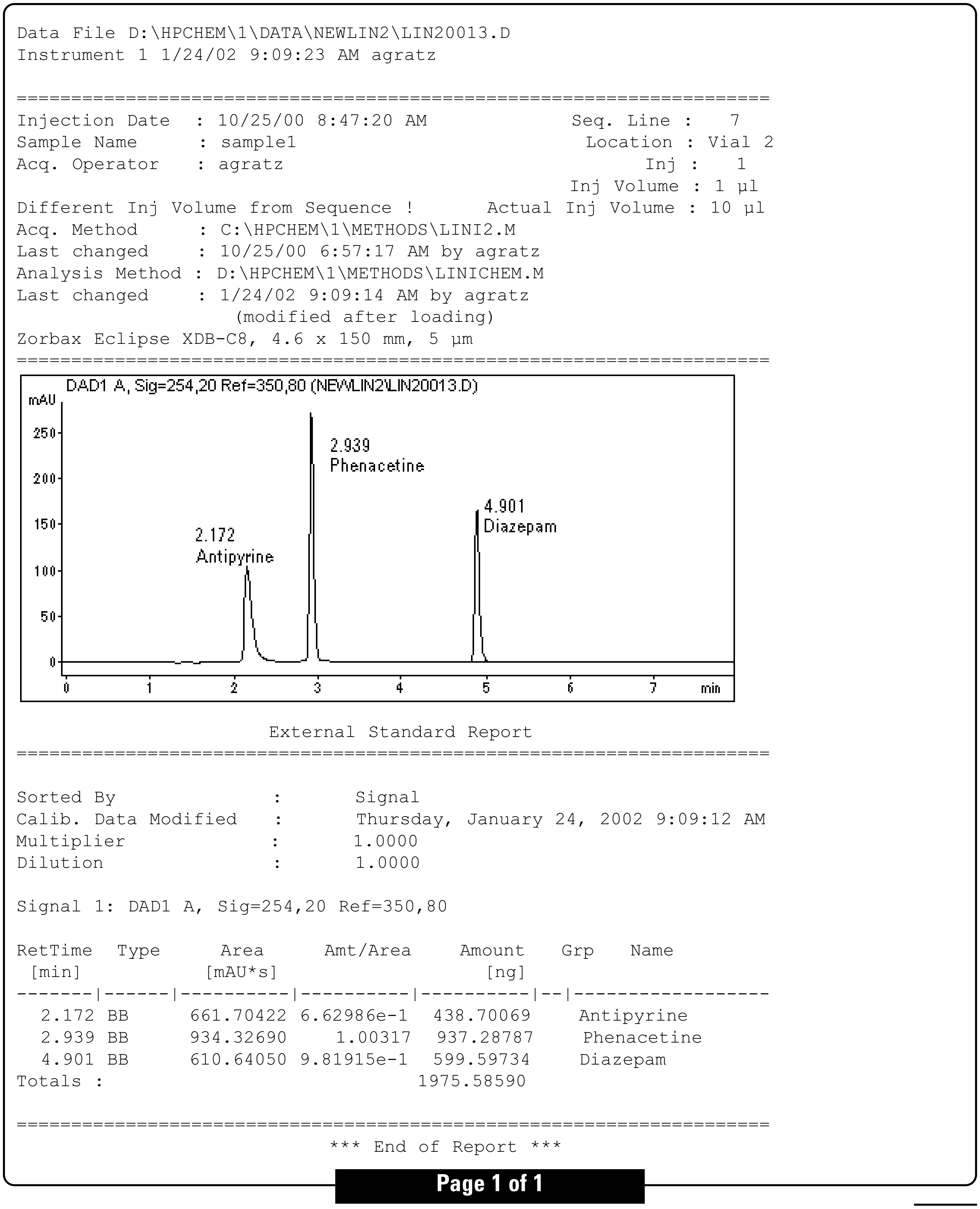


```
Data File D:\HPCHEM\1\DATA\NEWLIN2\LIN20013.D
Instrument 1 1/24/02 8:54:14 AM agratz

====================================================================
Injection Date   : 10/25/00 8:47:20 AM           Seq. Line :    7
Sample Name      : sample1                        Location : Vial 2
Acq. Operator    : agratz                              Inj :    1
                                                Inj Volume :  1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 10 µl
Acq. Method      : C:\HPCHEM\1\METHODS\LINI2.M
Last changed     : 10/25/00 6:57:17 AM by agratz
Analysis Method : D:\HPCHEM\1\METHODS\LINICHEM.M
Last changed     : 1/24/02 8:53:08 AM by agratz
Zorbax Eclipse XDB-C8, 4.6 x 150 mm, 5 µm
====================================================================
```

```
                           Area Percent Report
====================================================================

Sorted By              :       Signal
Calib. Data Modified  :       Thursday, January 24, 2002 8:52:20 AM
Multiplier             :       1.0000
Dilution               :       1.0000

Signal 1: DAD1 A, Sig=254,20 Ref=350,80

Peak RetTime  Type   Width     Area       Area     Name
  #   [min]          [min]    [mAU*s]       %
----|-------|------|-------|----------|--------|---------------------
  1  1.424    BV    0.0829   10.51506   0.4743 ?
  2  2.172    BB    0.0933  661.70422  29.8443 Antipyrine
  3  2.939    BB    0.0535  934.32690  42.1402 Phenacetine
  4  4.901    BB    0.0566  610.64050  27.5412 Diazepam
Totals :                   2217.18669

====================================================================
                          *** End of Report ***
```

Page 1 of 1

Short ESTD Report

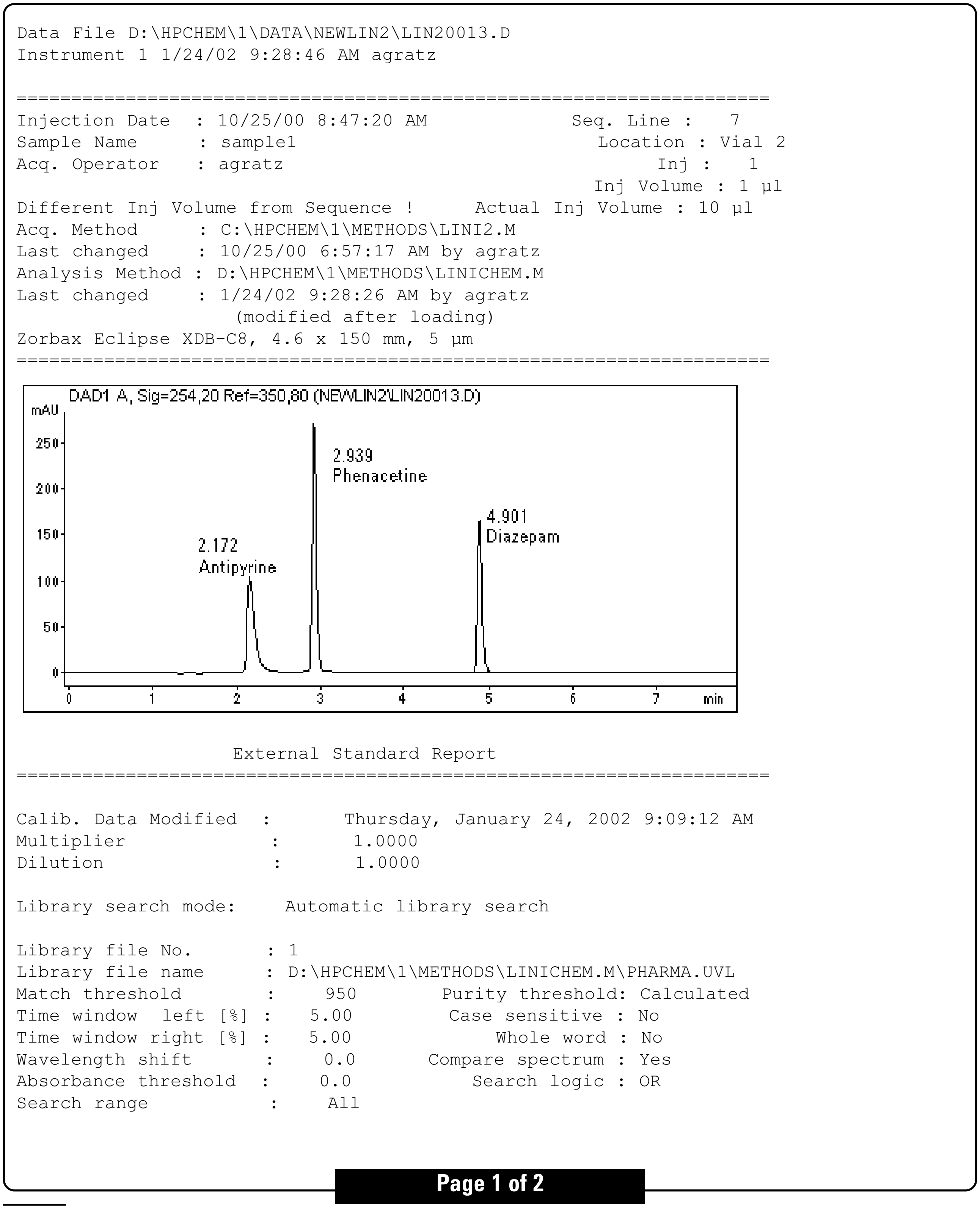


```
Data File D:\HPCHEM\1\DATA\NEWLIN2\LIN20013.D
Instrument 1 1/24/02 9:09:23 AM agratz

=====================================================================
Injection Date  : 10/25/00 8:47:20 AM           Seq. Line :    7
Sample Name     : sample1                        Location : Vial 2
Acq. Operator   : agratz                              Inj :    1
                                               Inj Volume : 1 µl
Different Inj Volume from Sequence !      Actual Inj Volume : 10 µl
Acq. Method     : C:\HPCHEM\1\METHODS\LINI2.M
Last changed    : 10/25/00 6:57:17 AM by agratz
Analysis Method : D:\HPCHEM\1\METHODS\LINICHEM.M
Last changed    : 1/24/02 9:09:14 AM by agratz
                    (modified after loading)
Zorbax Eclipse XDB-C8, 4.6 x 150 mm, 5 µm
=====================================================================
```

```
                       External Standard Report
=====================================================================

Sorted By               :       Signal
Calib. Data Modified    :       Thursday, January 24, 2002 9:09:12 AM
Multiplier              :       1.0000
Dilution                :       1.0000

Signal 1: DAD1 A, Sig=254,20 Ref=350,80

RetTime  Type     Area      Amt/Area    Amount    Grp   Name
 [min]          [mAU*s]                  [ng]
-------|------|----------|----------|----------|--|------------------
  2.172 BB     661.70422 6.62986e-1  438.70069    Antipyrine
  2.939 BB     934.32690    1.00317  937.28787    Phenacetine
  4.901 BB     610.64050 9.81915e-1  599.59734    Diazepam
Totals :                            1975.58590

=====================================================================
                          *** End of Report ***
```

Page 1 of 1

Spectral Library Search Report

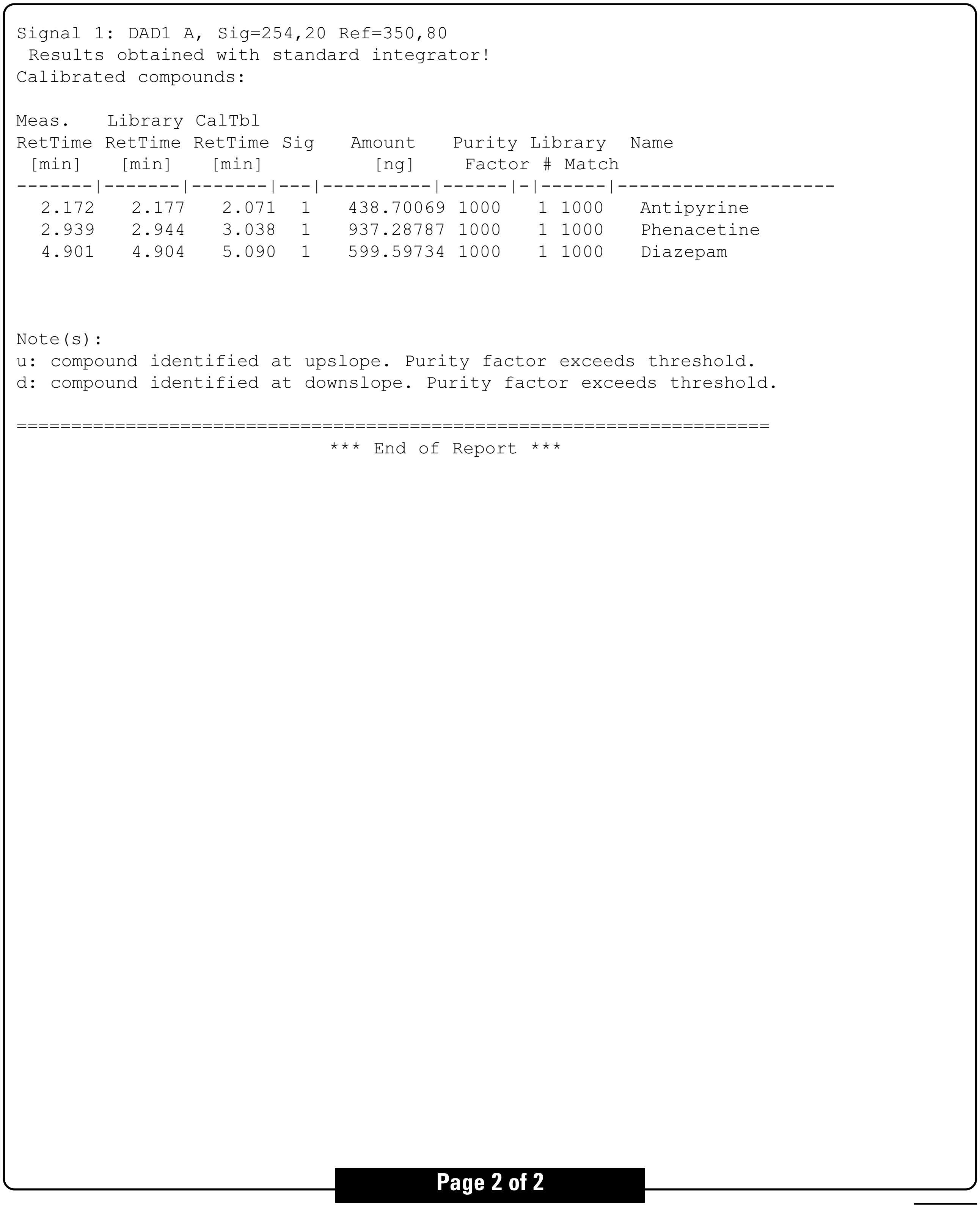


```
Data File D:\HPCHEM\1\DATA\NEWLIN2\LIN20013.D
Instrument 1 1/24/02 9:28:46 AM agratz

=====================================================================
Injection Date  : 10/25/00 8:47:20 AM            Seq. Line :    7
Sample Name     : sample1                          Location : Vial 2
Acq. Operator   : agratz                                Inj :    1
                                                  Inj Volume : 1 µl
Different Inj Volume from Sequence !      Actual Inj Volume : 10 µl
Acq. Method     : C:\HPCHEM\1\METHODS\LINI2.M
Last changed    : 10/25/00 6:57:17 AM by agratz
Analysis Method : D:\HPCHEM\1\METHODS\LINICHEM.M
Last changed    : 1/24/02 9:28:26 AM by agratz
                    (modified after loading)
Zorbax Eclipse XDB-C8, 4.6 x 150 mm, 5 µm
=====================================================================
```

```
                    External Standard Report
=====================================================================

Calib. Data Modified  :       Thursday, January 24, 2002 9:09:12 AM
Multiplier             :       1.0000
Dilution               :       1.0000

Library search mode:     Automatic library search

Library file No.       : 1
Library file name      : D:\HPCHEM\1\METHODS\LINICHEM.M\PHARMA.UVL
Match threshold        :     950        Purity threshold: Calculated
Time window  left [%] :    5.00         Case sensitive : No
Time window right [%] :    5.00             Whole word : No
Wavelength shift       :     0.0      Compare spectrum : Yes
Absorbance threshold  :     0.0           Search logic : OR
Search range           :     All
```

Page 1 of 2

Spectral Library Search Report (continued)



```
Signal 1: DAD1 A, Sig=254,20 Ref=350,80
 Results obtained with standard integrator!
Calibrated compounds:

Meas.   Library CalTbl
RetTime RetTime RetTime Sig   Amount   Purity Library  Name
 [min]   [min]   [min]          [ng]    Factor # Match
-------|-------|-------|---|----------|------|-|------|--------------------
  2.172   2.177   2.071  1   438.70069 1000   1 1000   Antipyrine
  2.939   2.944   3.038  1   937.28787 1000   1 1000   Phenacetine
  4.901   4.904   5.090  1   599.59734 1000   1 1000   Diazepam



Note(s):
u: compound identified at upslope. Purity factor exceeds threshold.
d: compound identified at downslope. Purity factor exceeds threshold.

===================================================================
                            *** End of Report ***
```

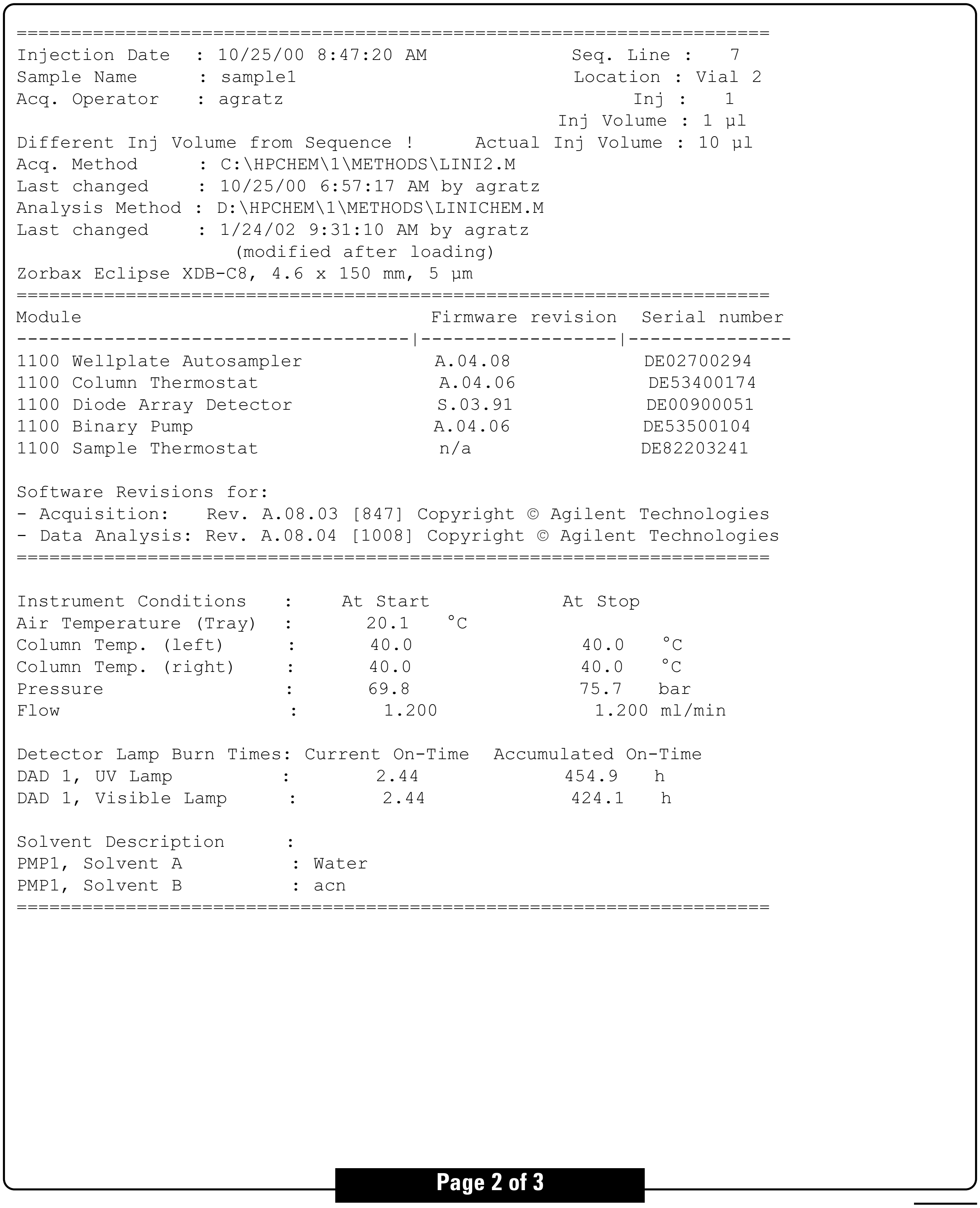
Page 2 of 2

Short GLP Report

```
Data File D:\HPCHEM\1\DATA\NEWLIN2\LIN20013.D
Instrument 1 1/24/02 9:31:21 AM agratz

This is a special file, named RPTHEAD.TXT, in the directory of a method
which allows you to customize the report header page.
It can be used to identify the laboratory which uses the method.

This file is printed on the first page with the report styles:

   Header+Short, GLP+Short, GLP+Detail, Short+Spec, Detail+Spec, Full


                   XXXX   XXX
                  XX  XX   XX
                 XX        XX       XXXXX   XXX XX
                 XX        XX XXX  XX     X XX X XX
                 XX    X   XXX XX  XXXXXXX  XX X XX
                  XX  XX   XX  XX  XX       XX   XX
                   XXXX   XXX  XXX  XXXXX   XXX  XXX



      XXXXXX     X                  X         XX
     XX    X    XX                 XX
     XX        XXXXX    XXXXX     XXXXX     XXX      XXXX    XX XXX
      XXXXX     XX           X     XX        XX      XX  XX   XXX XX
          XX    XX      XXXXXX     XX        XX      XX  XX   XX  XX
     X    XX    XX XX  X    XX     XX XX     XX      XX  XX   XX  XX
     XXXXXX      XXX   XXXXX X      XXX     XXXX     XXXX    XX  XX



                                                              X
           XX XXX    XXXXX   XX XXX      XXXX   XX XXX    XXXXXX
            XXX XX  XX    X   XX  XX    XX  XX   XXX XX    XX
            XX      XXXXXXX   XX  XX    XX  XX   XX        XX
            XX      XX         XXXXX    XX  XX   XX         XX XX
           XXXX      XXXXX    XX         XXXX   XXXX        XXX
                              XXXX



           XXX                             XXX
            XX                              XX
            XX       XXXXX    XXXXX        XX    XXXXX   XX XXX
            XX XXX  XX    X        X    XXXXX   XX     X   XXX XX
            XXX XX  XXXXXXX  XXXXXX   XX  XX     XXXXXXX   XX
            XX  XX  XX       X    XX   XX  XX   XX         XX
           XXX  XXX  XXXXX   XXXXX X   XXXX X    XXXXX   XXXX
```

Page 1 of 3

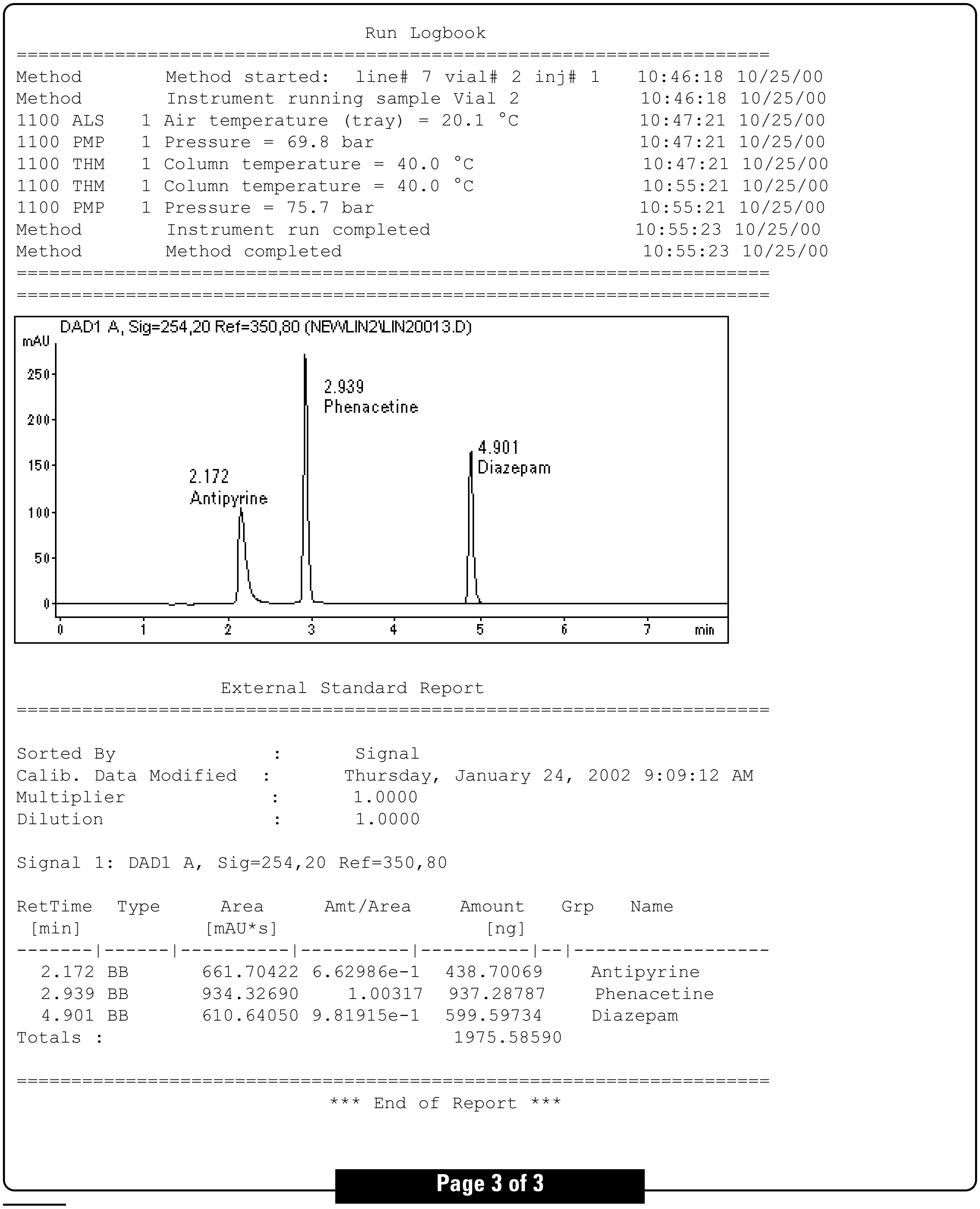
Short GLP Report (continued)



```
====================================================================
Injection Date  : 10/25/00 8:47:20 AM            Seq. Line :    7
Sample Name     : sample1                         Location : Vial 2
Acq. Operator   : agratz                               Inj :    1
                                                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 10 µl
Acq. Method     : C:\HPCHEM\1\METHODS\LINI2.M
Last changed    : 10/25/00 6:57:17 AM by agratz
Analysis Method : D:\HPCHEM\1\METHODS\LINICHEM.M
Last changed    : 1/24/02 9:31:10 AM by agratz
                   (modified after loading)
Zorbax Eclipse XDB-C8, 4.6 x 150 mm, 5 µm
====================================================================
Module                               Firmware revision  Serial number
------------------------------------|------------------|---------------
1100 Wellplate Autosampler           A.04.08            DE02700294
1100 Column Thermostat               A.04.06            DE53400174
1100 Diode Array Detector            S.03.91            DE00900051
1100 Binary Pump                     A.04.06            DE53500104
1100 Sample Thermostat               n/a                DE82203241

Software Revisions for:
- Acquisition:   Rev. A.08.03 [847] Copyright © Agilent Technologies
- Data Analysis: Rev. A.08.04 [1008] Copyright © Agilent Technologies
====================================================================

Instrument Conditions    :    At Start            At Stop
Air Temperature (Tray)   :      20.1   °C
Column Temp. (left)      :      40.0               40.0   °C
Column Temp. (right)     :      40.0               40.0   °C
Pressure                 :      69.8               75.7   bar
Flow                     :       1.200              1.200 ml/min

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       2.44             454.9   h
DAD 1, Visible Lamp     :       2.44             424.1   h

Solvent Description      :
PMP1, Solvent A          : Water
PMP1, Solvent B          : acn
====================================================================
```

Page 2 of 3

Short GLP Report (continued)

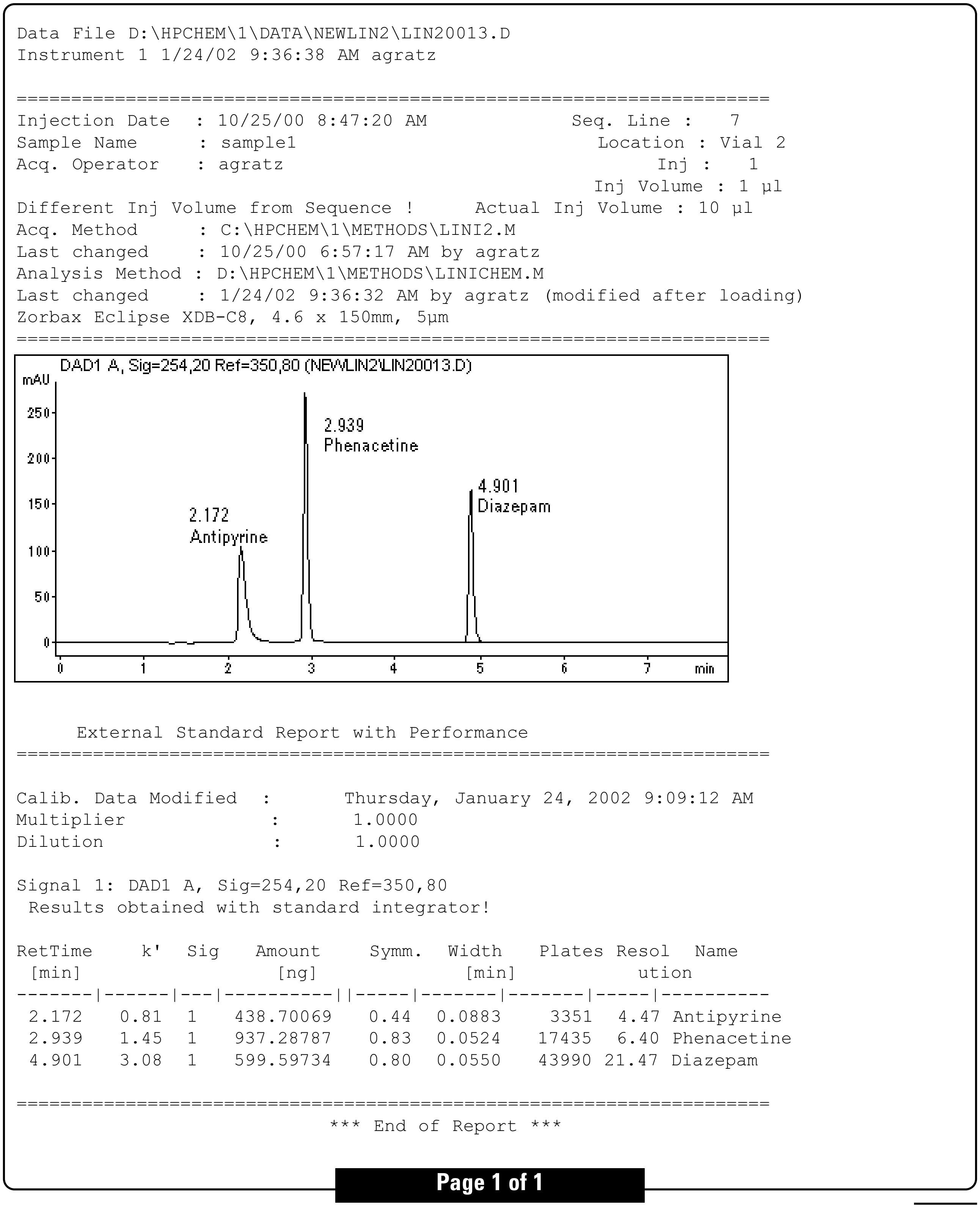


```
                                Run Logbook
====================================================================
Method        Method started:  line# 7 vial# 2 inj# 1   10:46:18 10/25/00
Method        Instrument running sample Vial 2          10:46:18 10/25/00
1100 ALS    1 Air temperature (tray) = 20.1 °C          10:47:21 10/25/00
1100 PMP    1 Pressure = 69.8 bar                       10:47:21 10/25/00
1100 THM    1 Column temperature = 40.0 °C              10:47:21 10/25/00
1100 THM    1 Column temperature = 40.0 °C              10:55:21 10/25/00
1100 PMP    1 Pressure = 75.7 bar                       10:55:21 10/25/00
Method        Instrument run completed                  10:55:23 10/25/00
Method        Method completed                          10:55:23 10/25/00
====================================================================
====================================================================
```

```
                  External Standard Report
====================================================================

Sorted By              :      Signal
Calib. Data Modified   :     Thursday, January 24, 2002 9:09:12 AM
Multiplier             :      1.0000
Dilution               :      1.0000

Signal 1: DAD1 A, Sig=254,20 Ref=350,80

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                 [ng]
-------|------|----------|----------|----------|--|------------------
  2.172 BB     661.70422 6.62986e-1  438.70069    Antipyrine
  2.939 BB     934.32690    1.00317  937.28787    Phenacetine
  4.901 BB     610.64050 9.81915e-1  599.59734    Diazepam
Totals :                             1975.58590

====================================================================
                        *** End of Report ***
```

Page 3 of 3

Performance report

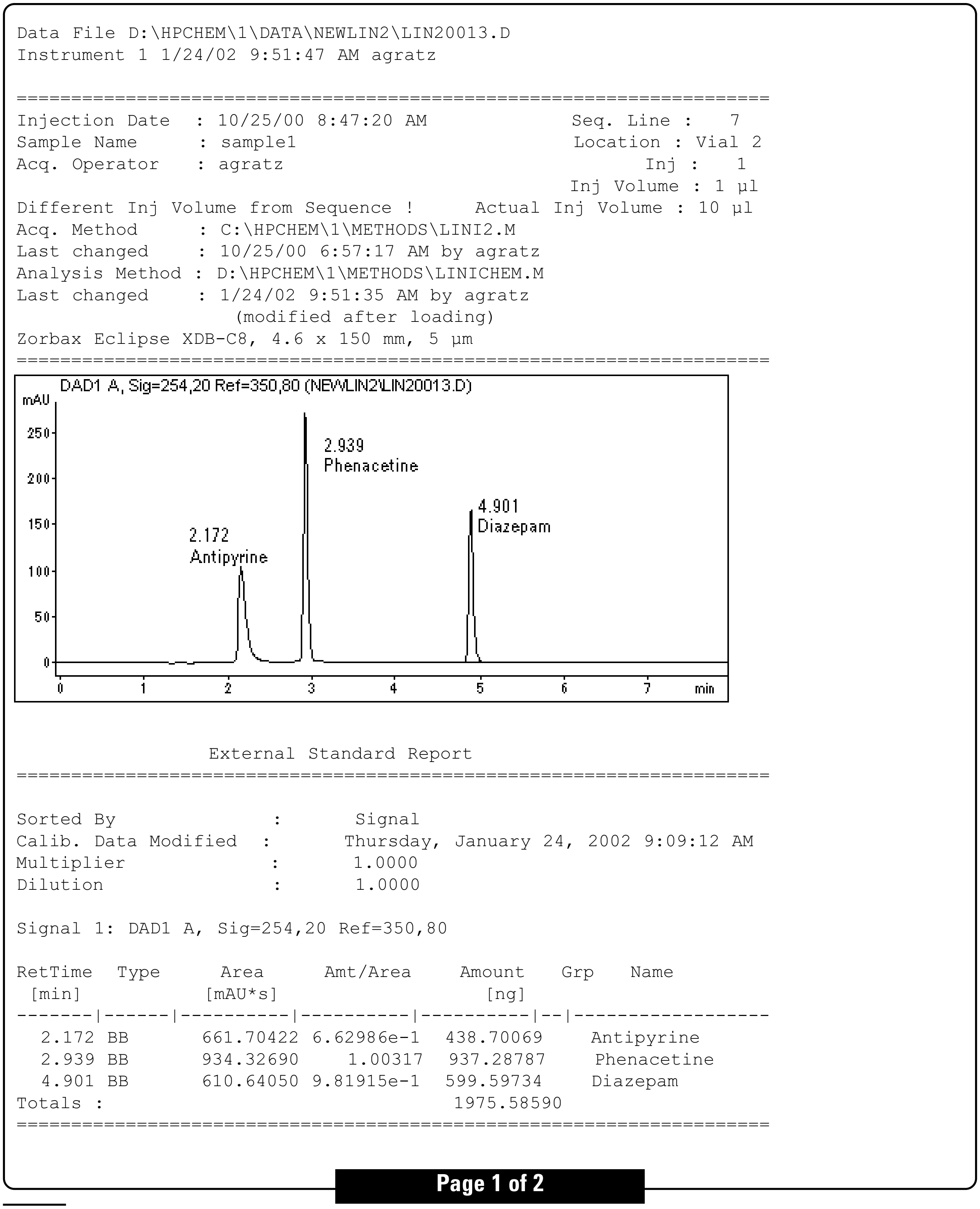


```
Data File D:\HPCHEM\1\DATA\NEWLIN2\LIN20013.D
Instrument 1 1/24/02 9:36:38 AM agratz

=====================================================================
Injection Date  : 10/25/00 8:47:20 AM            Seq. Line :    7
Sample Name     : sample1                          Location : Vial 2
Acq. Operator   : agratz                                Inj :    1
                                                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 10 µl
Acq. Method     : C:\HPCHEM\1\METHODS\LINI2.M
Last changed    : 10/25/00 6:57:17 AM by agratz
Analysis Method : D:\HPCHEM\1\METHODS\LINICHEM.M
Last changed    : 1/24/02 9:36:32 AM by agratz (modified after loading)
Zorbax Eclipse XDB-C8, 4.6 x 150mm, 5µm
=====================================================================
```

```
     External Standard Report with Performance
=====================================================================

Calib. Data Modified  :      Thursday, January 24, 2002 9:09:12 AM
Multiplier             :      1.0000
Dilution               :      1.0000

Signal 1: DAD1 A, Sig=254,20 Ref=350,80
 Results obtained with standard integrator!

RetTime    k'  Sig   Amount    Symm.  Width    Plates Resol  Name
 [min]               [ng]             [min]           ution
-------|------|---|----------||-----|-------|-------|-----|----------
 2.172   0.81  1   438.70069   0.44  0.0883     3351  4.47 Antipyrine
 2.939   1.45  1   937.28787   0.83  0.0524    17435  6.40 Phenacetine
 4.901   3.08  1   599.59734   0.80  0.0550    43990 21.47 Diazepam

=====================================================================
                            *** End of Report ***
```

Page 1 of 1

Detail report

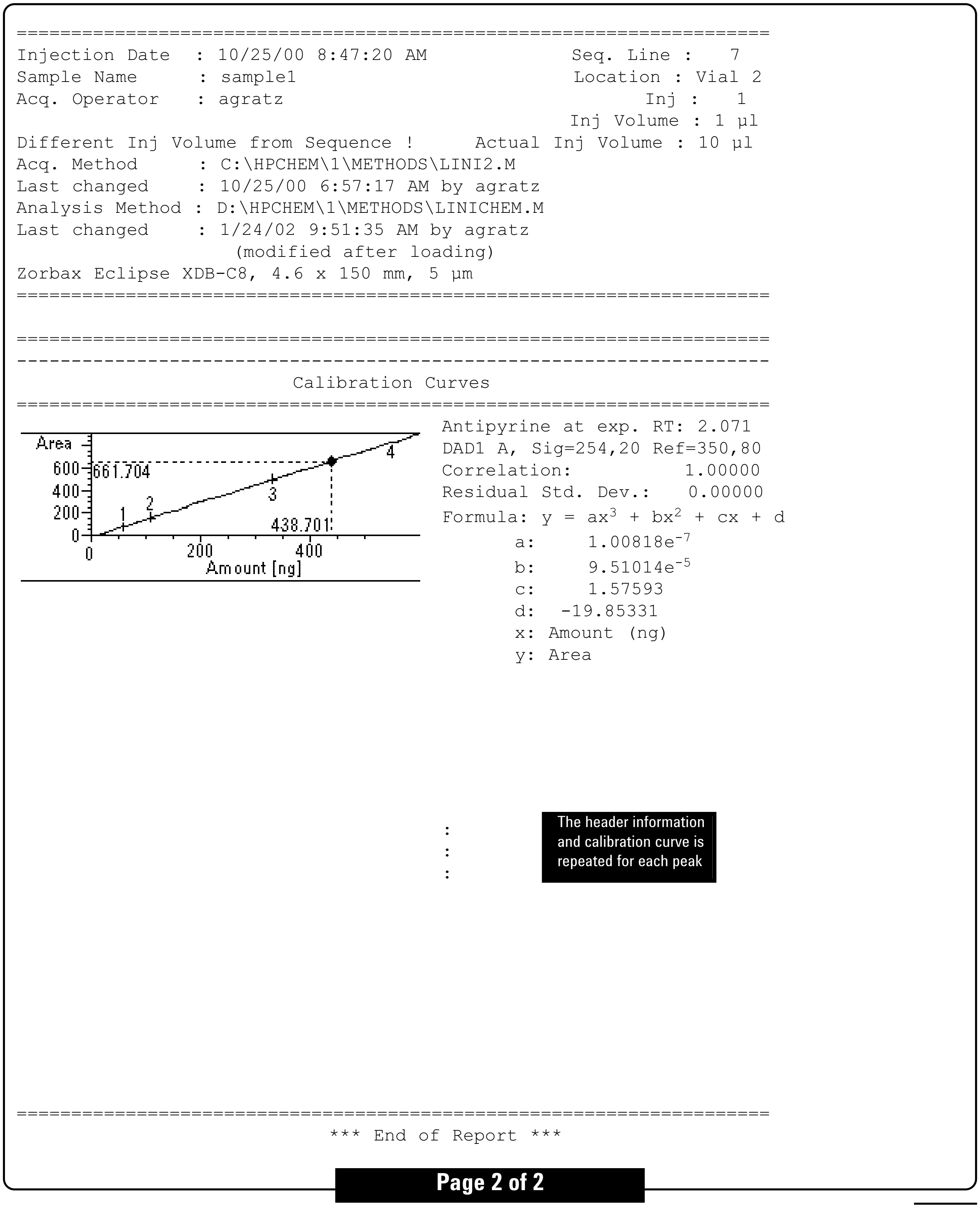


```
Data File D:\HPCHEM\1\DATA\NEWLIN2\LIN20013.D
Instrument 1 1/24/02 9:51:47 AM agratz

=====================================================================
Injection Date  : 10/25/00 8:47:20 AM             Seq. Line :    7
Sample Name     : sample1                         Location : Vial 2
Acq. Operator   : agratz                                 Inj :    1
                                                 Inj Volume : 1 µl
Different Inj Volume from Sequence !      Actual Inj Volume : 10 µl
Acq. Method     : C:\HPCHEM\1\METHODS\LINI2.M
Last changed    : 10/25/00 6:57:17 AM by agratz
Analysis Method : D:\HPCHEM\1\METHODS\LINICHEM.M
Last changed    : 1/24/02 9:51:35 AM by agratz
                    (modified after loading)
Zorbax Eclipse XDB-C8, 4.6 x 150 mm, 5 µm
=====================================================================
```

```
                 External Standard Report
=====================================================================

Sorted By              :      Signal
Calib. Data Modified   :     Thursday, January 24, 2002 9:09:12 AM
Multiplier             :      1.0000
Dilution               :      1.0000

Signal 1: DAD1 A, Sig=254,20 Ref=350,80

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                 [ng]
-------|------|----------|----------|----------|--|------------------
  2.172 BB      661.70422 6.62986e-1  438.70069    Antipyrine
  2.939 BB      934.32690    1.00317  937.28787    Phenacetine
  4.901 BB      610.64050 9.81915e-1  599.59734    Diazepam
Totals :                             1975.58590
=====================================================================
```

Page 1 of 2

Detail report (continued)



```
====================================================================
Injection Date  : 10/25/00 8:47:20 AM            Seq. Line :    7
Sample Name     : sample1                        Location : Vial 2
Acq. Operator   : agratz                                Inj :    1
                                                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 10 µl
Acq. Method     : C:\HPCHEM\1\METHODS\LINI2.M
Last changed    : 10/25/00 6:57:17 AM by agratz
Analysis Method : D:\HPCHEM\1\METHODS\LINICHEM.M
Last changed    : 1/24/02 9:51:35 AM by agratz
                    (modified after loading)
Zorbax Eclipse XDB-C8, 4.6 x 150 mm, 5 µm
====================================================================

====================================================================
--------------------------------------------------------------------
                         Calibration Curves
====================================================================
```

```
Antipyrine at exp. RT: 2.071
DAD1 A, Sig=254,20 Ref=350,80
Correlation:           1.00000
Residual Std. Dev.:    0.00000
Formula: y = ax^3 + bx^2 + cx + d
      a:     1.00818e^-7
      b:     9.51014e^-5
      c:     1.57593
      d:   -19.85331
      x: Amount (ng)
      y: Area
```

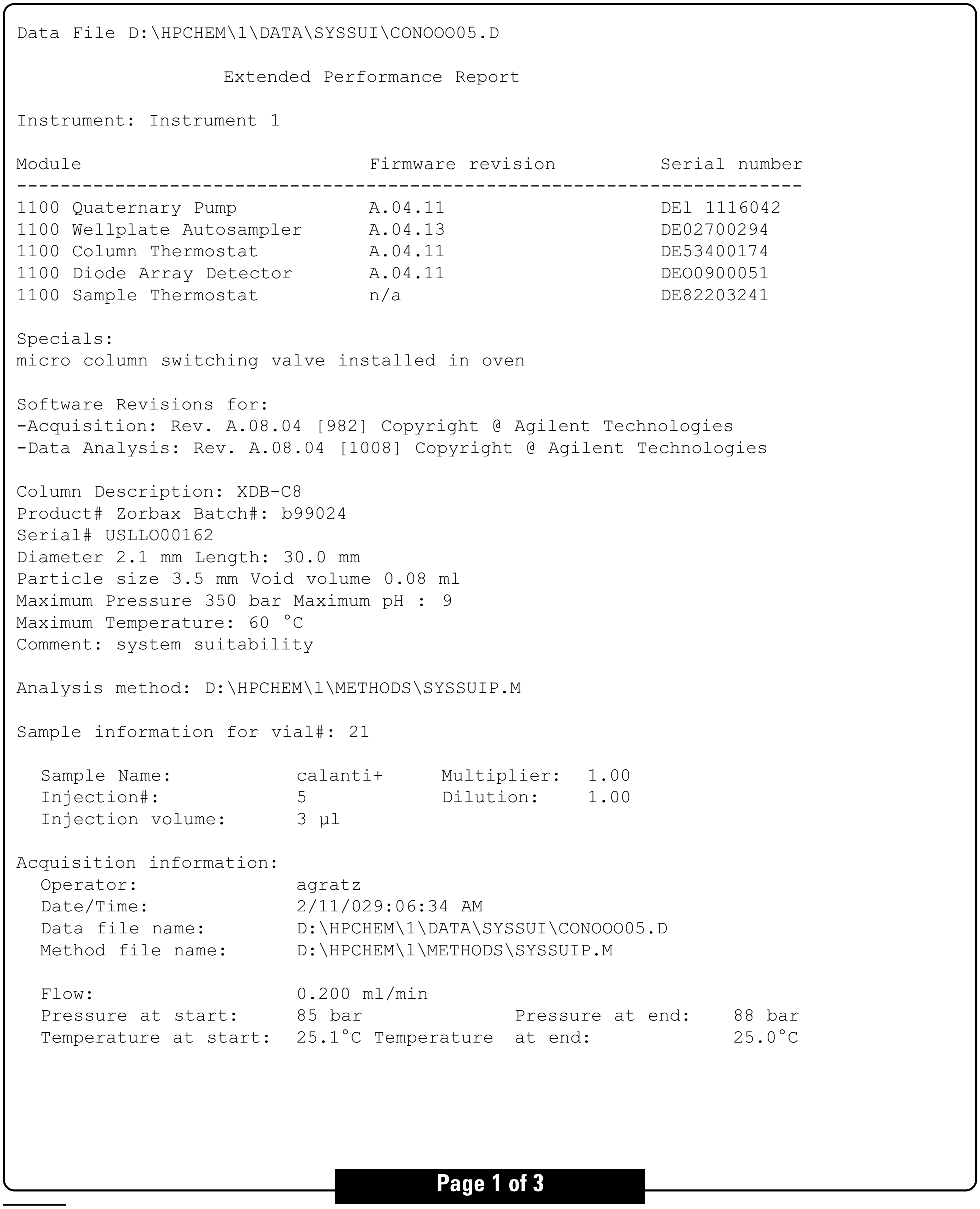
:
:
:

The header information and calibration curve is repeated for each peak

```
====================================================================
                         *** End of Report ***
```

Page 2 of 2

Extended Performance Report

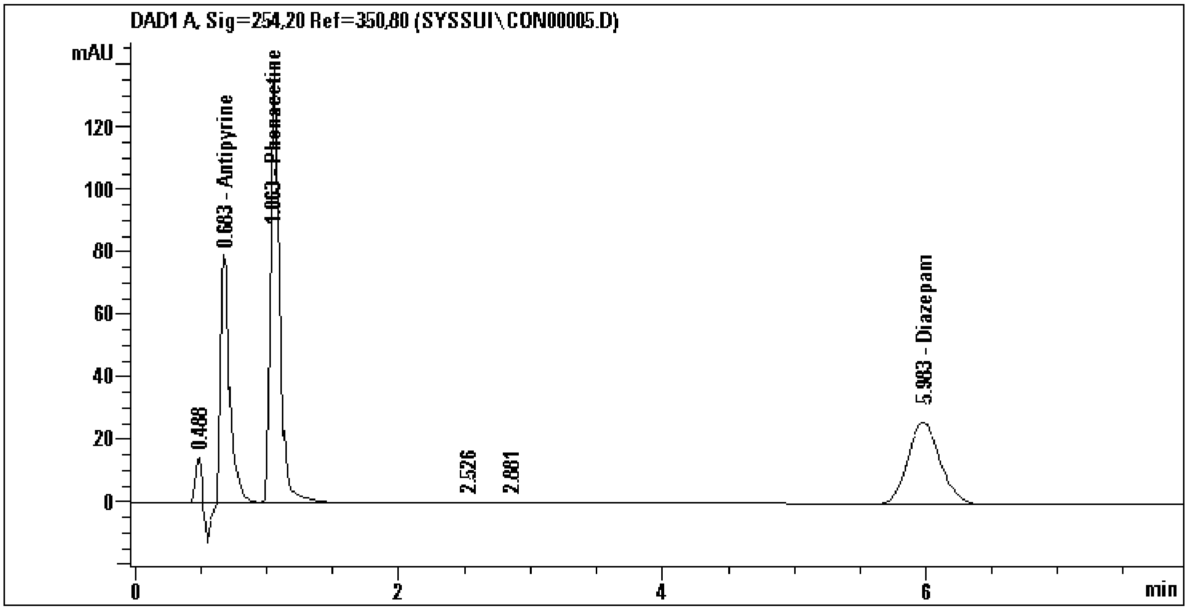


```
Data File D:\HPCHEM\1\DATA\SYSSUI\CONOOO05.D

                   Extended Performance Report

Instrument: Instrument 1

Module                          Firmware revision          Serial number
-----------------------------------------------------------------------
1100 Quaternary Pump            A.04.11                    DEl 1116042
1100 Wellplate Autosampler      A.04.13                    DE02700294
1100 Column Thermostat          A.04.11                    DE53400174
1100 Diode Array Detector       A.04.11                    DEO0900051
1100 Sample Thermostat          n/a                        DE82203241

Specials:
micro column switching valve installed in oven

Software Revisions for:
-Acquisition: Rev. A.08.04 [982] Copyright @ Agilent Technologies
-Data Analysis: Rev. A.08.04 [1008] Copyright @ Agilent Technologies

Column Description: XDB-C8
Product# Zorbax Batch#: b99024
Serial# USLLO00162
Diameter 2.1 mm Length: 30.0 mm
Particle size 3.5 mm Void volume 0.08 ml
Maximum Pressure 350 bar Maximum pH :  9
Maximum Temperature: 60 °C
Comment: system suitability

Analysis method: D:\HPCHEM\l\METHODS\SYSSUIP.M

Sample information for vial#: 21

  Sample Name:            calanti+     Multiplier:  1.00
  Injection#:             5            Dilution:    1.00
  Injection volume:       3 µl

Acquisition information:
  Operator:               agratz
  Date/Time:              2/11/029:06:34 AM
  Data file name:         D:\HPCHEM\1\DATA\SYSSUI\CONOOO05.D
  Method file name:       D:\HPCHEM\l\METHODS\SYSSUIP.M

  Flow:                   0.200 ml/min
  Pressure at start:      85 bar              Pressure at end:    88 bar
  Temperature at start:   25.1°C Temperature  at end:             25.0°C
```

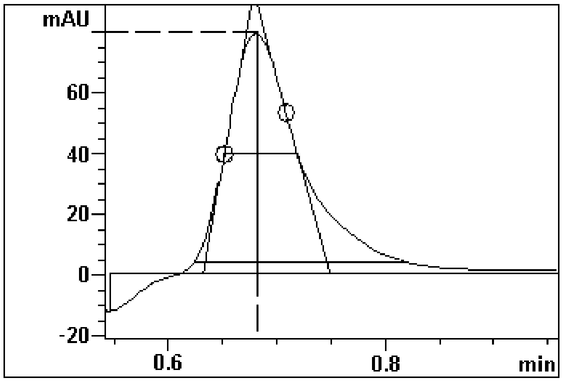
Page 1 of 3

Extended Performance Report (continued)

```
Solvents:              PMP1, Solvent A     water
                       PMP1, Solvent B     ACN
                       PMP1, Solvent C
                       PMP1, Solvent D

Signal description: DAD1 A, Sig=254,20 Ref=350,80
```



```
Compound# 2   :  Antipyrine
Amount [ng]:        51.1385

Peak description [min]:
      Signal: DAD1 A, Sig=254,20 Ref=350,80
      RetTime: 0.583      K':    0.706
      Height:  79.78  Area:      371.2
      Start:      0.546   End:   0.956
      Skew:    0.898    Excess:  1.643
      Width at half height:      0.067
             5 sigma:            0.196
             tangent:            0.117
             tailing:            0.190
      Symmetry:                  0.483
      USP Tailing:               1.657
      Integration type:            HV
      Time increment [macc]:     400.0
      Data points:                  66
```



Page 2 of 3

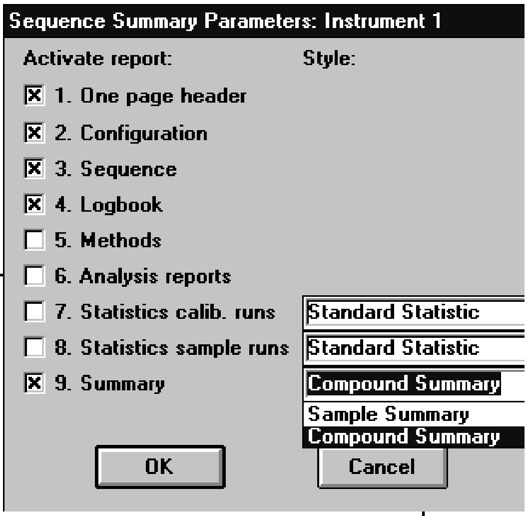
Extended Performance Report (continued)

```
Statistical moments (BB peak detection):    Efficiency:  Plates per ...
     M0:  514.1                                    column       meter
     M1:  0.699               Tangent method         541        18020
     M2:  0.00341             Halfwidth method       581        19360
     M3:  0.000179            5 sigma method         385        10153
     M4: 0.000054             Statistical            143        4782

Relationship to preceeding peak:             Selectivity: 3.217
Resolution Tangent method: 2.015             5 sigma method 1.700
Halfwidth method 2.034                       Statistical method 1.067



                                      :
                                      :
                                      :



====================================================================
                            *** End of Report ***
```

The peak description and statistical moments are repeated for each compound

Page 3 of 3

Sequence Summary Report – Compound Summary



Sequence Summary Parameters: Instrument 1

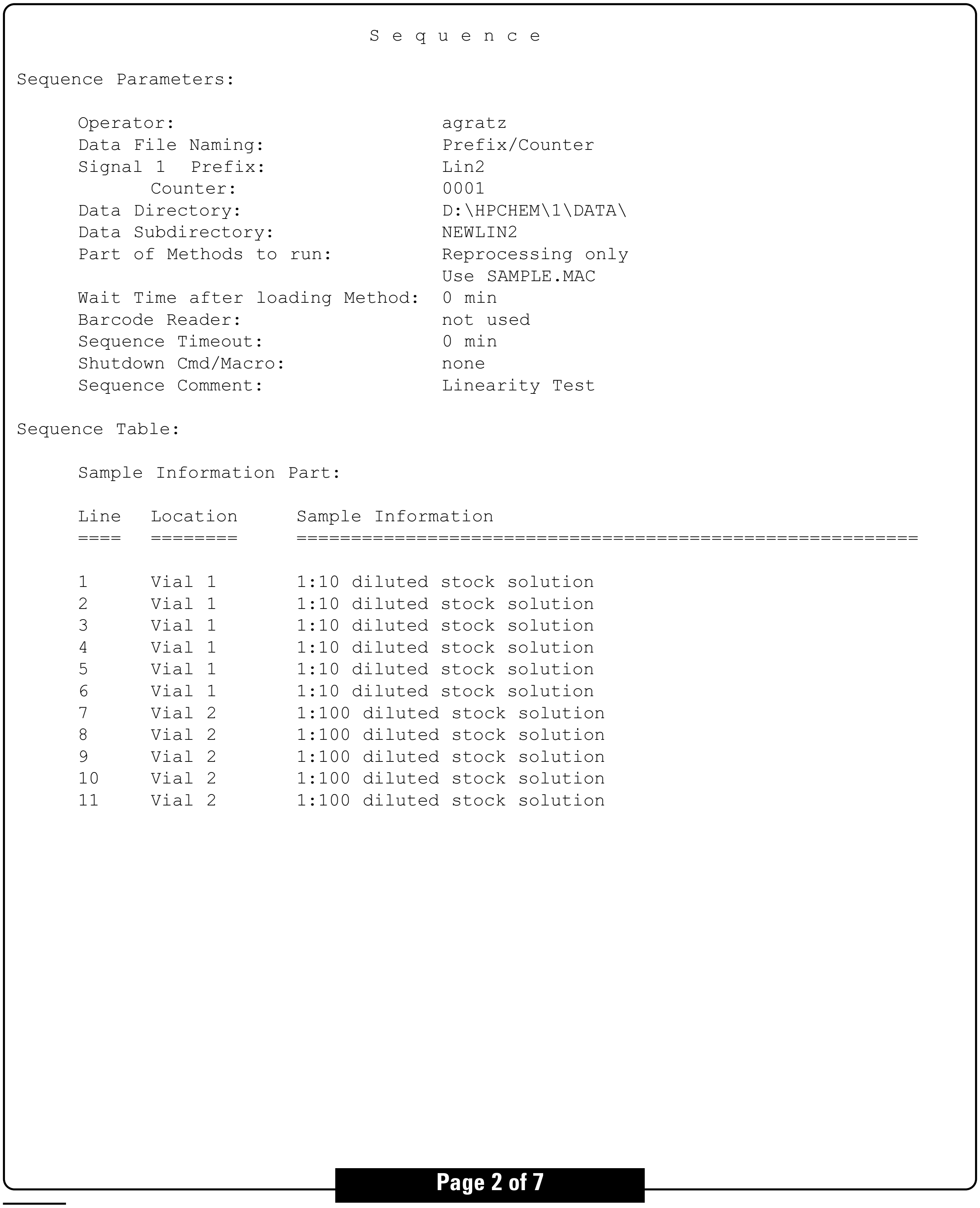
Activate report: Style:

- ☒ 1. One page header
- ☒ 2. Configuration
- ☒ 3. Sequence
- ☒ 4. Logbook
- ☐ 5. Methods
- ☐ 6. Analysis reports
- ☐ 7. Statistics calib. runs — Standard Statistic
- ☐ 8. Statistics sample runs — Standard Statistic
- ☒ 9. Summary — Compound Summary

```
                            XXXXXX     XX        XXXXXX
                           XX     XX    XX         XX    XX
                           XX            XX        XX    XX
                           XX            XX        XXXXXX
                           XX    XX     XX         XX
                           XX     XX    XX         XX
                           XX     XX    XX         XX
                            XXXXXX     XXXXXX    XX


                                S E Q U E N C E

                                 S U M M A R Y

                                  R E P O R T








                                   A.G Huesgen

                                   ..................................
                                   Date/Signature


              I n s t r u m e n t   C o n f i g u r a t i o n

Instrument: Instrument 1

Module                                Firmware revision   Serial number
------------------------------------|--------------------|---------------
1100 Wellplate Autosampler            A.04.08             DE02700294
1100 Column Thermostat                A.04.06             DE53400174
1100 Diode Array Detector             S.03.91             DE00900051
1100 Binary Pump                      A.04.06             DE53500104
1100 Sample Thermostat                n/a                 DE82203241

Software Revisions for:
- Acquisition: Rev. A.08.03 [847] Copyright © Agilent Technologies
- Data Analysis: Rev. A.08.04 [1008] Copyright © Agilent Technologies
```

Page 1 of 7

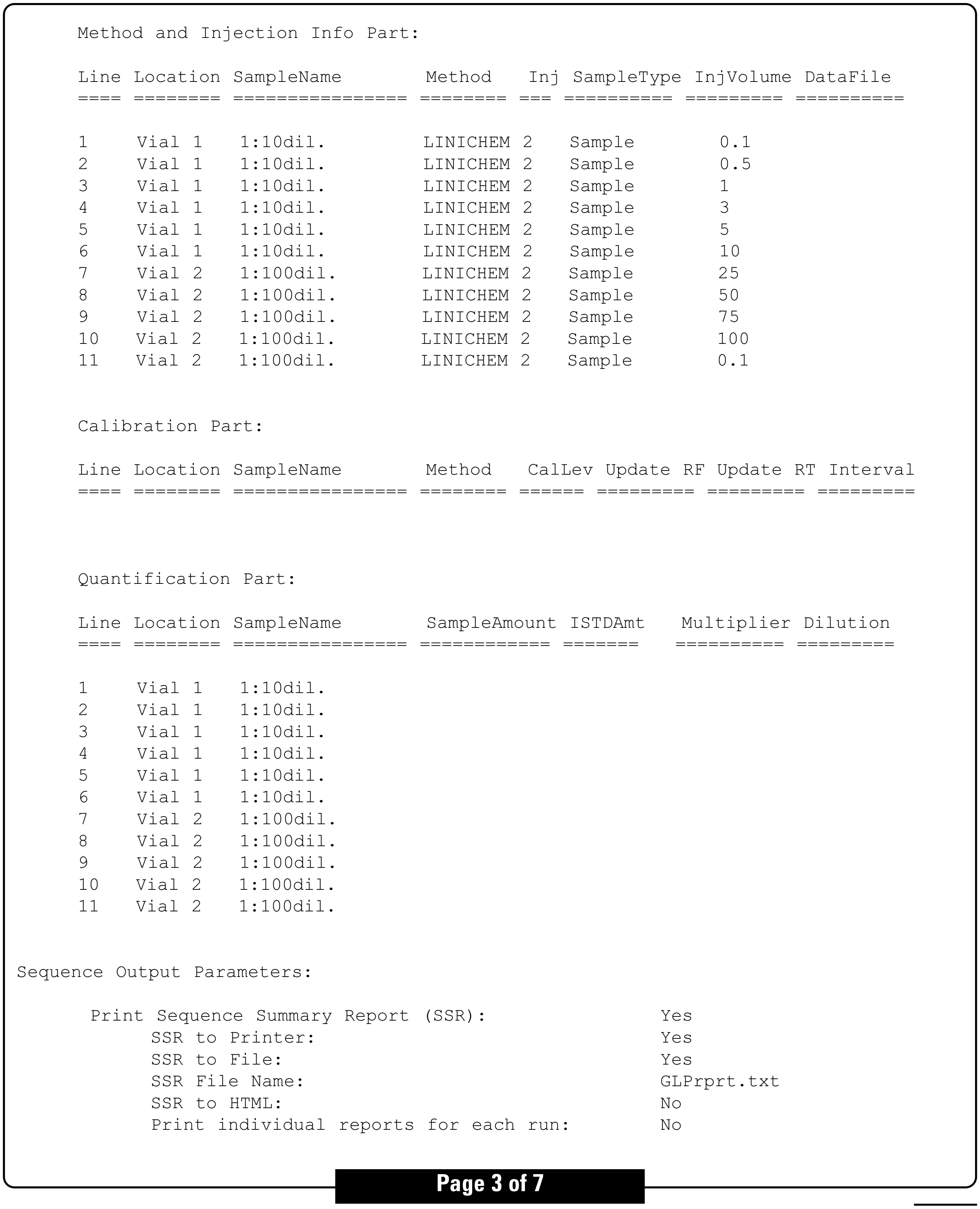
Sequence Summary Report – Compound Summary (continued)



```
                                S e q u e n c e

Sequence Parameters:

      Operator:                        agratz
      Data File Naming:                Prefix/Counter
      Signal 1  Prefix:                Lin2
            Counter:                   0001
      Data Directory:                  D:\HPCHEM\1\DATA\
      Data Subdirectory:               NEWLIN2
      Part of Methods to run:          Reprocessing only
                                       Use SAMPLE.MAC
      Wait Time after loading Method:  0 min
      Barcode Reader:                  not used
      Sequence Timeout:                0 min
      Shutdown Cmd/Macro:              none
      Sequence Comment:                Linearity Test

Sequence Table:

      Sample Information Part:

      Line  Location     Sample Information
      ====  ========     =========================================================

      1     Vial 1       1:10 diluted stock solution
      2     Vial 1       1:10 diluted stock solution
      3     Vial 1       1:10 diluted stock solution
      4     Vial 1       1:10 diluted stock solution
      5     Vial 1       1:10 diluted stock solution
      6     Vial 1       1:10 diluted stock solution
      7     Vial 2       1:100 diluted stock solution
      8     Vial 2       1:100 diluted stock solution
      9     Vial 2       1:100 diluted stock solution
      10    Vial 2       1:100 diluted stock solution
      11    Vial 2       1:100 diluted stock solution
```

Page 2 of 7

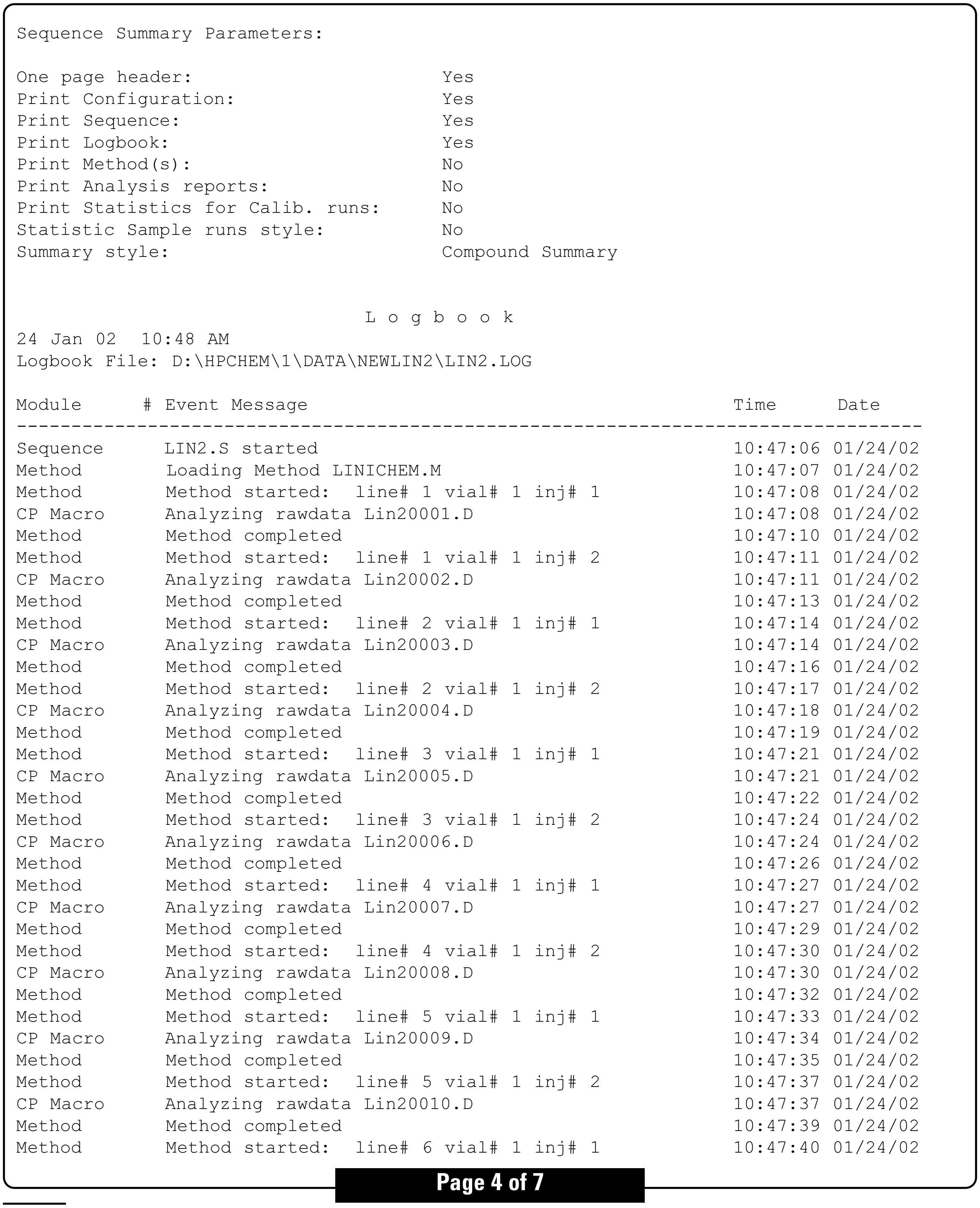
Sequence Summary Report – Compound Summary (continued)



```
     Method and Injection Info Part:

     Line Location SampleName       Method   Inj SampleType InjVolume DataFile
     ==== ======== ================ ======== === ========== ========= ==========

     1    Vial 1   1:10dil.         LINICHEM 2   Sample       0.1
     2    Vial 1   1:10dil.         LINICHEM 2   Sample       0.5
     3    Vial 1   1:10dil.         LINICHEM 2   Sample       1
     4    Vial 1   1:10dil.         LINICHEM 2   Sample       3
     5    Vial 1   1:10dil.         LINICHEM 2   Sample       5
     6    Vial 1   1:10dil.         LINICHEM 2   Sample       10
     7    Vial 2   1:100dil.        LINICHEM 2   Sample       25
     8    Vial 2   1:100dil.        LINICHEM 2   Sample       50
     9    Vial 2   1:100dil.        LINICHEM 2   Sample       75
     10   Vial 2   1:100dil.        LINICHEM 2   Sample       100
     11   Vial 2   1:100dil.        LINICHEM 2   Sample       0.1


     Calibration Part:

     Line Location SampleName       Method   CalLev Update RF Update RT Interval
     ==== ======== ================ ======== ====== ========= ========= =========



     Quantification Part:

     Line Location SampleName       SampleAmount ISTDAmt   Multiplier Dilution
     ==== ======== ================ ============ =======   ========== =========

     1    Vial 1   1:10dil.
     2    Vial 1   1:10dil.
     3    Vial 1   1:10dil.
     4    Vial 1   1:10dil.
     5    Vial 1   1:10dil.
     6    Vial 1   1:10dil.
     7    Vial 2   1:100dil.
     8    Vial 2   1:100dil.
     9    Vial 2   1:100dil.
     10   Vial 2   1:100dil.
     11   Vial 2   1:100dil.


Sequence Output Parameters:

      Print Sequence Summary Report (SSR):                Yes
           SSR to Printer:                                Yes
           SSR to File:                                   Yes
           SSR File Name:                                 GLPrprt.txt
           SSR to HTML:                                   No
           Print individual reports for each run:         No
```

Page 3 of 7

Sequence Summary Report – Compound Summary (continued)



```
Sequence Summary Parameters:

One page header:                       Yes
Print Configuration:                   Yes
Print Sequence:                        Yes
Print Logbook:                         Yes
Print Method(s):                       No
Print Analysis reports:                No
Print Statistics for Calib. runs:      No
Statistic Sample runs style:           No
Summary style:                         Compound Summary


                                L o g b o o k
24 Jan 02  10:48 AM
Logbook File: D:\HPCHEM\1\DATA\NEWLIN2\LIN2.LOG

Module      # Event Message                                       Time     Date
-----------------------------------------------------------------------------------
Sequence      LIN2.S started                                      10:47:06 01/24/02
Method        Loading Method LINICHEM.M                           10:47:07 01/24/02
Method        Method started:  line# 1 vial# 1 inj# 1             10:47:08 01/24/02
CP Macro      Analyzing rawdata Lin20001.D                        10:47:08 01/24/02
Method        Method completed                                    10:47:10 01/24/02
Method        Method started:  line# 1 vial# 1 inj# 2             10:47:11 01/24/02
CP Macro      Analyzing rawdata Lin20002.D                        10:47:11 01/24/02
Method        Method completed                                    10:47:13 01/24/02
Method        Method started:  line# 2 vial# 1 inj# 1             10:47:14 01/24/02
CP Macro      Analyzing rawdata Lin20003.D                        10:47:14 01/24/02
Method        Method completed                                    10:47:16 01/24/02
Method        Method started:  line# 2 vial# 1 inj# 2             10:47:17 01/24/02
CP Macro      Analyzing rawdata Lin20004.D                        10:47:18 01/24/02
Method        Method completed                                    10:47:19 01/24/02
Method        Method started:  line# 3 vial# 1 inj# 1             10:47:21 01/24/02
CP Macro      Analyzing rawdata Lin20005.D                        10:47:21 01/24/02
Method        Method completed                                    10:47:22 01/24/02
Method        Method started:  line# 3 vial# 1 inj# 2             10:47:24 01/24/02
CP Macro      Analyzing rawdata Lin20006.D                        10:47:24 01/24/02
Method        Method completed                                    10:47:26 01/24/02
Method        Method started:  line# 4 vial# 1 inj# 1             10:47:27 01/24/02
CP Macro      Analyzing rawdata Lin20007.D                        10:47:27 01/24/02
Method        Method completed                                    10:47:29 01/24/02
Method        Method started:  line# 4 vial# 1 inj# 2             10:47:30 01/24/02
CP Macro      Analyzing rawdata Lin20008.D                        10:47:30 01/24/02
Method        Method completed                                    10:47:32 01/24/02
Method        Method started:  line# 5 vial# 1 inj# 1             10:47:33 01/24/02
CP Macro      Analyzing rawdata Lin20009.D                        10:47:34 01/24/02
Method        Method completed                                    10:47:35 01/24/02
Method        Method started:  line# 5 vial# 1 inj# 2             10:47:37 01/24/02
CP Macro      Analyzing rawdata Lin20010.D                        10:47:37 01/24/02
Method        Method completed                                    10:47:39 01/24/02
Method        Method started:  line# 6 vial# 1 inj# 1             10:47:40 01/24/02
```

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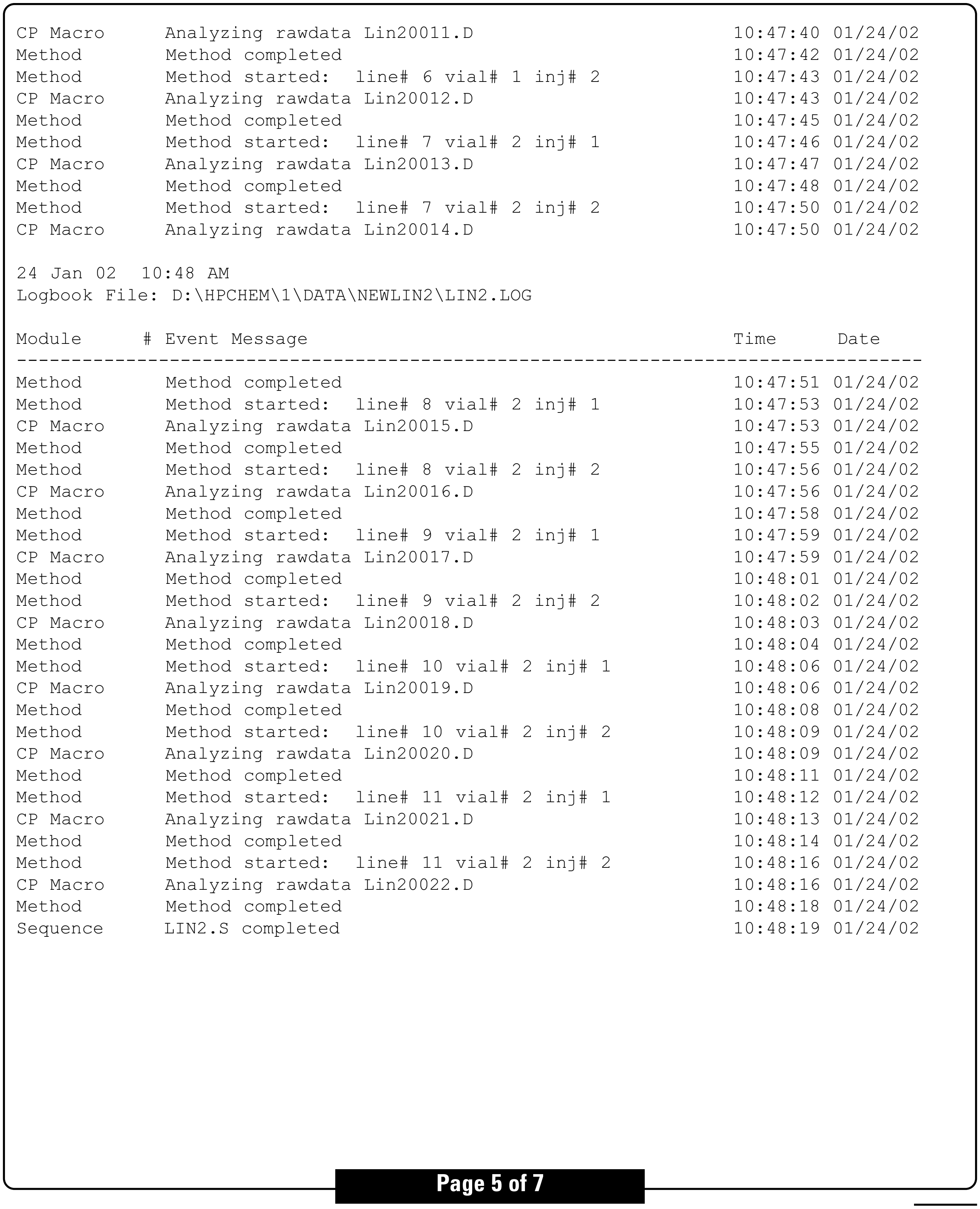
Sequence Summary Report – Compound Summary (continued)



```
CP Macro     Analyzing rawdata Lin20011.D                        10:47:40 01/24/02
Method       Method completed                                    10:47:42 01/24/02
Method       Method started:  line# 6 vial# 1 inj# 2             10:47:43 01/24/02
CP Macro     Analyzing rawdata Lin20012.D                        10:47:43 01/24/02
Method       Method completed                                    10:47:45 01/24/02
Method       Method started:  line# 7 vial# 2 inj# 1             10:47:46 01/24/02
CP Macro     Analyzing rawdata Lin20013.D                        10:47:47 01/24/02
Method       Method completed                                    10:47:48 01/24/02
Method       Method started:  line# 7 vial# 2 inj# 2             10:47:50 01/24/02
CP Macro     Analyzing rawdata Lin20014.D                        10:47:50 01/24/02

24 Jan 02  10:48 AM
Logbook File: D:\HPCHEM\1\DATA\NEWLIN2\LIN2.LOG

Module     # Event Message                                       Time     Date
----------------------------------------------------------------------------------
Method       Method completed                                    10:47:51 01/24/02
Method       Method started:  line# 8 vial# 2 inj# 1             10:47:53 01/24/02
CP Macro     Analyzing rawdata Lin20015.D                        10:47:53 01/24/02
Method       Method completed                                    10:47:55 01/24/02
Method       Method started:  line# 8 vial# 2 inj# 2             10:47:56 01/24/02
CP Macro     Analyzing rawdata Lin20016.D                        10:47:56 01/24/02
Method       Method completed                                    10:47:58 01/24/02
Method       Method started:  line# 9 vial# 2 inj# 1             10:47:59 01/24/02
CP Macro     Analyzing rawdata Lin20017.D                        10:47:59 01/24/02
Method       Method completed                                    10:48:01 01/24/02
Method       Method started:  line# 9 vial# 2 inj# 2             10:48:02 01/24/02
CP Macro     Analyzing rawdata Lin20018.D                        10:48:03 01/24/02
Method       Method completed                                    10:48:04 01/24/02
Method       Method started:  line# 10 vial# 2 inj# 1            10:48:06 01/24/02
CP Macro     Analyzing rawdata Lin20019.D                        10:48:06 01/24/02
Method       Method completed                                    10:48:08 01/24/02
Method       Method started:  line# 10 vial# 2 inj# 2            10:48:09 01/24/02
CP Macro     Analyzing rawdata Lin20020.D                        10:48:09 01/24/02
Method       Method completed                                    10:48:11 01/24/02
Method       Method started:  line# 11 vial# 2 inj# 1            10:48:12 01/24/02
CP Macro     Analyzing rawdata Lin20021.D                        10:48:13 01/24/02
Method       Method completed                                    10:48:14 01/24/02
Method       Method started:  line# 11 vial# 2 inj# 2            10:48:16 01/24/02
CP Macro     Analyzing rawdata Lin20022.D                        10:48:16 01/24/02
Method       Method completed                                    10:48:18 01/24/02
Sequence     LIN2.S completed                                    10:48:19 01/24/02
```

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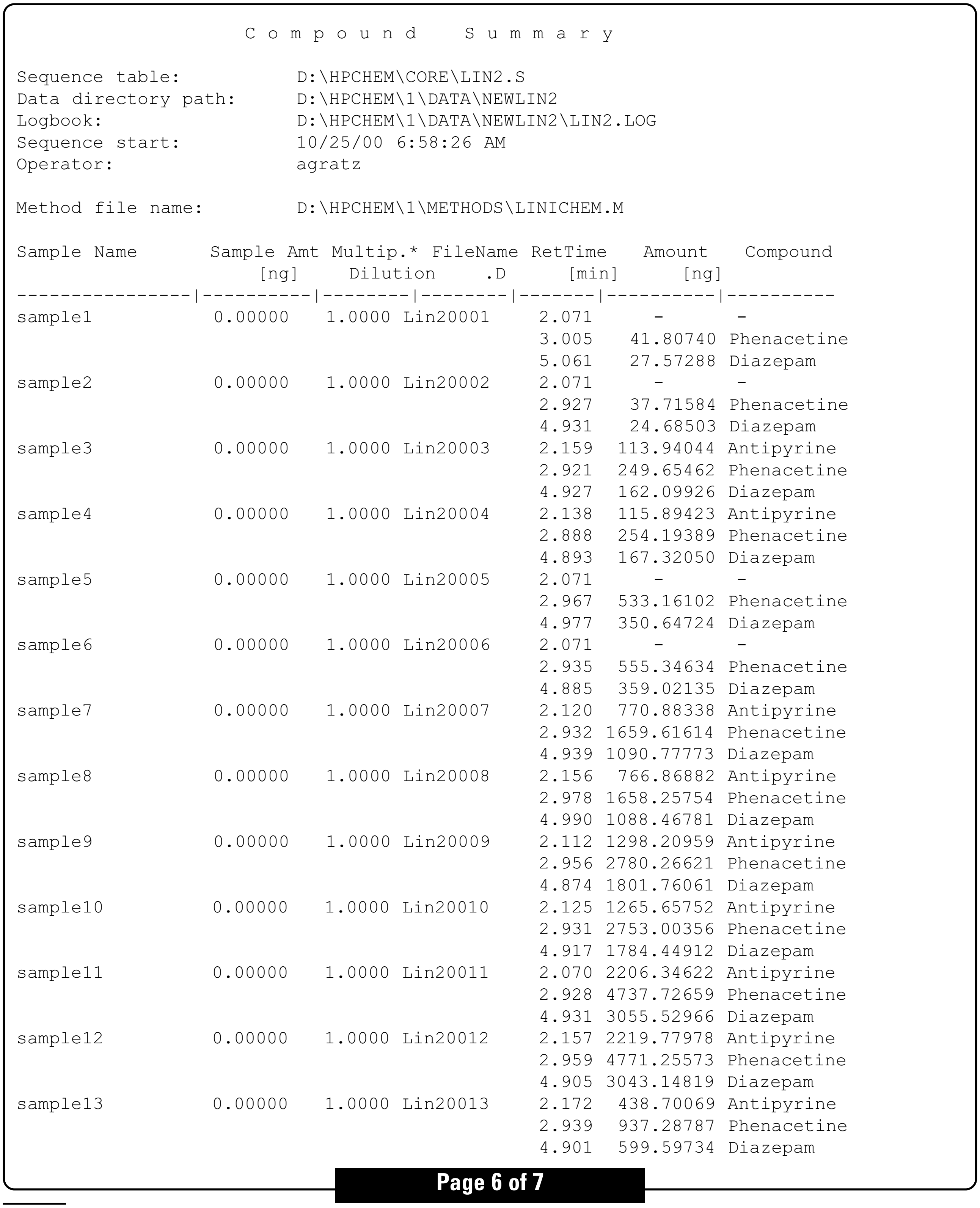
Sequence Summary Report – Compound Summary (continued)



```
                     C o m p o u n d    S u m m a r y

Sequence table:          D:\HPCHEM\CORE\LIN2.S
Data directory path:     D:\HPCHEM\1\DATA\NEWLIN2
Logbook:                 D:\HPCHEM\1\DATA\NEWLIN2\LIN2.LOG
Sequence start:          10/25/00 6:58:26 AM
Operator:                agratz

Method file name:        D:\HPCHEM\1\METHODS\LINICHEM.M

Sample Name       Sample Amt Multip.* FileName RetTime   Amount   Compound
                      [ng]    Dilution     .D     [min]     [ng]
----------------|----------|--------|--------|-------|----------|----------
sample1          0.00000   1.0000 Lin20001    2.071      -        -
                                              3.005   41.80740 Phenacetine
                                              5.061   27.57288 Diazepam
sample2          0.00000   1.0000 Lin20002    2.071      -        -
                                              2.927   37.71584 Phenacetine
                                              4.931   24.68503 Diazepam
sample3          0.00000   1.0000 Lin20003    2.159  113.94044 Antipyrine
                                              2.921  249.65462 Phenacetine
                                              4.927  162.09926 Diazepam
sample4          0.00000   1.0000 Lin20004    2.138  115.89423 Antipyrine
                                              2.888  254.19389 Phenacetine
                                              4.893  167.32050 Diazepam
sample5          0.00000   1.0000 Lin20005    2.071      -        -
                                              2.967  533.16102 Phenacetine
                                              4.977  350.64724 Diazepam
sample6          0.00000   1.0000 Lin20006    2.071      -        -
                                              2.935  555.34634 Phenacetine
                                              4.885  359.02135 Diazepam
sample7          0.00000   1.0000 Lin20007    2.120  770.88338 Antipyrine
                                              2.932 1659.61614 Phenacetine
                                              4.939 1090.77773 Diazepam
sample8          0.00000   1.0000 Lin20008    2.156  766.86882 Antipyrine
                                              2.978 1658.25754 Phenacetine
                                              4.990 1088.46781 Diazepam
sample9          0.00000   1.0000 Lin20009    2.112 1298.20959 Antipyrine
                                              2.956 2780.26621 Phenacetine
                                              4.874 1801.76061 Diazepam
sample10         0.00000   1.0000 Lin20010    2.125 1265.65752 Antipyrine
                                              2.931 2753.00356 Phenacetine
                                              4.917 1784.44912 Diazepam
sample11         0.00000   1.0000 Lin20011    2.070 2206.34622 Antipyrine
                                              2.928 4737.72659 Phenacetine
                                              4.931 3055.52966 Diazepam
sample12         0.00000   1.0000 Lin20012    2.157 2219.77978 Antipyrine
                                              2.959 4771.25573 Phenacetine
                                              4.905 3043.14819 Diazepam
sample13         0.00000   1.0000 Lin20013    2.172  438.70069 Antipyrine
                                              2.939  937.28787 Phenacetine
                                              4.901  599.59734 Diazepam
```

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Sequence Summary Report – Compound Summary (continued)

```
sample14          0.00000   1.0000 Lin20014     2.137  431.19756 Antipyrine
                                                2.920  922.41613 Phenacetine
                                                4.914  598.82718 Diazepam
sample15          0.00000   1.0000 Lin20015     2.130 1050.21043 Antipyrine
                                                2.956 2257.23577 Phenacetine
                                                4.946 1454.09021 Diazepam
sample16          0.00000   1.0000 Lin20016     2.071      -       -
                                                3.062 2266.63554 Phenacetine
                                                4.914 1450.54300 Diazepam
sample17          0.00000   1.0000 Lin20017     2.112 1860.82017 Antipyrine
                                                2.958 4083.57167 Phenacetine
                                                4.943 2601.71134 Diazepam
sample18          0.00000   1.0000 Lin20018     2.114 1846.79895 Antipyrine
                                                2.970 4045.19575 Phenacetine
                                                4.970 2576.86650 Diazepam
sample19          0.00000   1.0000 Lin20019     2.152 2485.47770 Antipyrine
                                                3.019 5268.86688 Phenacetine
                                                4.973 3410.01754 Diazepam
sample20          0.00000   1.0000 Lin20020     2.135 2489.66113 Antipyrine
                                                2.975 5298.02094 Phenacetine
                                                4.943 3415.39103 Diazepam
sample21          0.00000   1.0000 Lin20021     2.155 2961.16799 Antipyrine
                                                3.010 6013.24563 Phenacetine
                                                5.003 4037.60722 Diazepam
sample22          0.00000   1.0000 Lin20022     2.156 2983.41614 Antipyrine
                                                3.042 6012.35737 Phenacetine
                                                4.988 4010.73532 Diazepam


===================================================================
                            *** End of Report ***
```

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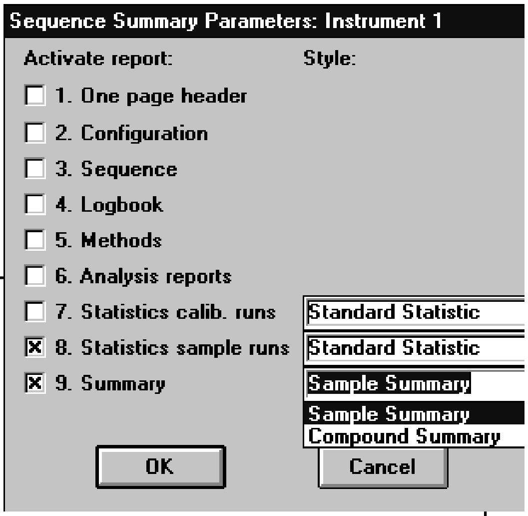
Sequence Summary Report – Standard Statistics for Sample Runs



Sequence Summary Parameters: Instrument 1

Activate report: Style:

☐ 1. One page header

☐ 2. Configuration

☐ 3. Sequence

☐ 4. Logbook

☐ 5. Methods

☐ 6. Analysis reports

☐ 7. Statistics calib. runs — Standard Statistic

☒ 8. Statistics sample runs — Standard Statistic

☒ 9. Summary — Sample Summary

```
                  S t a t i s t i c   R e p o r t

Sequence table:         D:\HPCHEM\1\SEQUENCE\NEWLIN.S
Data directory path:    D:\HPCHEM\1\DATA\NEWLIN
Operator:               agratz

Method file name:       D:\HPCHEM\1\METHODS\LINI2.M

Run Location Inj      Inj. Date/Time       File Name   Sample Name
 #             #
---|--------|---|-----------------------|----------|----------------
  1 Vial 2   1    8/24/00 12:42:04 AM    new00061.D  sample1
  2 Vial 2   2    8/24/00 12:51:09 AM    new00062.D  sample2
  3 Vial 2   3    8/24/00 1:00:14 AM     new00063.D  sample3
  4 Vial 2   4    8/24/00 1:09:18 AM     new00064.D  sample4
  5 Vial 2   5    8/24/00 1:18:21 AM     new00065.D  sample5
  6 Vial 2   6    8/24/00 1:27:25 AM     new00066.D  sample6
  7 Vial 2   7    8/24/00 1:36:30 AM     new00067.D  sample7
  8 Vial 2   8    8/24/00 1:45:34 AM     new00068.D  sample8
  9 Vial 2   9    8/24/00 1:54:38 AM     new00069.D  sample9
 10 Vial 2  10    8/24/00 2:03:42 AM     new00070.D  sample10


Compound: Antipyrine (Signal: DAD1 A, Sig=254,20 Ref=350,80)

Run Type RetTime   Amount      Area       Height    Width  Symm.
 #        [min]     [ng]     [mAU*s]     [mAU]     [min]
---|----|-------|----------|----------|----------|-------|------
  1 BV    2.071   26.23064  834.52417  215.75279  0.0594  0.74
  2 BV    2.071   26.28149  836.14185  216.26503  0.0594  0.74
  3 BV    2.070   26.22879  834.46539  215.85945  0.0594  0.74
  4 BV    2.070   26.27553  835.95233  216.52124  0.0594  0.74
  5 BV    2.070   26.21720  834.09644  215.51944  0.0594  0.74
  6 BV    2.070   26.19317  833.33203  216.02470  0.0593  0.74
  7 BV    2.070   26.27779  836.02423  216.93185  0.0592  0.74
  8 BV    2.072   26.29524  836.57941  216.89178  0.0593  0.74
  9 BV    2.072   26.22549  834.36017  216.09763  0.0593  0.74
 10 BV    2.071   26.21184  833.92590  216.06882  0.0593  0.74
--------|-------|----------|----------|----------|-------|-----
Mean:     2.071   26.24372  834.94019  216.19327  0.0594  0.74
S.D.:    6.81e-4 3.53636e-2   1.12509  4.66512e-1 6.63e-5  1e-3
RSD :      0.033 1.34751e-1 1.34751e-1 2.15784e-1  0.1117  0.20
95% CI:  4.87e-4 2.52976e-2 8.04838e-1 3.33722e-1 4.74e-5  1e-3
```

Page 1 of 3

Sequence Summary Report – Standard Statistics for Sample Runs

```
Compound: Phenacetine (Signal: DAD1 A, Sig=254,20 Ref=350,80)

Run Type RetTime   Amount      Area       Height    Width  Symm.
 #        [min]     [ng]      [mAU*s]      [mAU]    [min]
---|----|-------|----------|----------|----------|-------|-----
  1 BB    3.035   12.05932 1203.01074  357.49438  0.0528  0.88
  2 BB    3.035   12.07862 1204.93591  357.76285  0.0527  0.87
  3 BB    3.035   12.05487 1202.56653  357.16501  0.0527  0.88
  4 BB    3.035   12.07567 1204.64221  357.80615  0.0527  0.88
  5 BB    3.036   12.05951 1203.02979  356.62448  0.0528  0.87
  6 BB    3.036   12.02965 1200.05090  356.52957  0.0528  0.88
  7 BB    3.037   12.08083 1205.15625  357.92139  0.0527  0.88
  8 BB    3.037   12.06433 1203.51099  357.60211  0.0527  0.88
  9 BB    3.039   12.05340 1202.42065  356.89868  0.0527  0.87
 10 BB    3.038   12.04430 1201.51282  356.41678  0.0528  0.88
--------|-------|----------|----------|----------|-------|-----
Mean:     3.036   12.06005 1203.08368  357.22214  0.0527  0.88
S.D.:    1.35e-3 1.59266e-2    1.58880 5.70986e-1 3.70e-5  6e-3
RSD :      0.045 1.32061e-1 1.32061e-1 1.59840e-1  0.0702  0.68
95% CI:  9.69e-4 1.13932e-2    1.13656 4.08458e-1 2.65e-5  4e-3


Compound: Diazepam (Signal: DAD1 A, Sig=254,20 Ref=350,80)

Run Type RetTime   Amount      Area       Height    Width  Symm.
 #        [min]     [ng]      [mAU*s]      [mAU]    [min]
---|----|-------|----------|----------|----------|-------|-----
  1 BB    5.085   17.51478  820.56067  228.97469  0.0556  0.84
  2 BB    5.086   17.54309  821.88702  229.58243  0.0557  0.84
  3 BB    5.085   17.51162  820.41229  229.04759  0.0557  0.84
  4 BB    5.084   17.54478  821.96600  229.60602  0.0557  0.84
  5 BB    5.086   17.51105  820.38562  229.37668  0.0556  0.84
  6 BB    5.087   17.47411  818.65503  228.69946  0.0556  0.85
  7 BB    5.088   17.54951  822.18774  229.63567  0.0556  0.84
  8 BB    5.088   17.51423  820.53491  229.10289  0.0556  0.84
  9 BB    5.090   17.51381  820.51508  229.17131  0.0557  0.84
 10 BB    5.090   17.50570  820.13525  228.79688  0.0556  0.84
--------|-------|----------|----------|----------|-------|-----
Mean:     5.087   17.51827  820.72396  229.19936  0.0556  0.84
S.D.:    2.12e-3 2.24801e-2    1.05318 3.38200e-1 3.77e-5  2e-3
RSD :      0.042 1.28324e-1 1.28324e-1 1.47557e-1  0.0678  0.29
95% CI:  1.52e-3 1.60813e-2 7.53401e-1 2.41934e-1 2.70e-5  2e-3
```

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Sequence Summary Report – Standard Statistics for Sample Runs

```
                   S a m p l e    S u m m a r y


Sequence table:                       D:\HPCHEM\1\SEQUENCE\NEWLIN.S
Data directory path:                  D:\HPCHEM\1\DATA\NEWLIN
Logbook:                              D:\HPCHEM\1\DATA\NEWLIN\NEWLIN.LOG
Sequence start:                       8/24/00 12:42:04 AM
Statistic report on calibration runs: 1
Operator:                             agratz

Method file name:                     D:\HPCHEM\1\METHODS\LINI2.M

Run Location Inj Sample Name Sample Amt Multip.* File name Cal # Page
 #             #                    [ng]    Dilution              Cmp  #
---|--------|---|----------------|----------|--------|----------|-|---|---
  1 Vial 2     1  sample1                -   1.0000  new00061.D *    3  -
  2 Vial 2     2  sample2                -   1.0000  new00062.D *    3  -
  3 Vial 2     3  sample3                -   1.0000  new00063.D *    3  -
  4 Vial 2     4  sample4                -   1.0000  new00064.D *    3  -
  5 Vial 2     5  sample5                -   1.0000  new00065.D *    3  -
  6 Vial 2     6  sample6                -   1.0000  new00066.D *    3  -
  7 Vial 2     7  sample7                -   1.0000  new00067.D *    3  -
  8 Vial 2     8  sample8                -   1.0000  new00068.D *    3  -
  9 Vial 2     9  sample9                -   1.0000  new00069.D *    3  -
 10 Vial 2    10  sample10               -   1.0000  new00070.D *    3  -


=========================================================================
                            *** End of Report ***
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www.agilent.com/chem/nds

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Agilent Technologies

Achieving fastest analyses with the Agilent 1200 Series Rapid Resolution LC system and 2.1-mm id columns

Application Note

Michael Frank

Abstract

The need to increase the daily throughputs of LC systems is a constant desire. Now, with the Agilent 1200 Series Rapid Resolution LC system highest throughputs are possible, and in combination with the Agilent ZORBAX RRHT columns and the increased pressure and temperature range of the LC system, excellent chromatographic resolution can be achieved even at run times below one minute.

This Application Note describes the correct set-up of the instrument which is the key for optimal results with narrow bore columns, such as a 2.1 mm x 50 mm column packed with sub two micron particles. Peak capacities in the range of fifty in analysis times as short as 24 seconds and peak widths as narrow as 200 milliseconds are shown. The well-balanced use of all possible module options to achieve shortest cycle times with throughputs far beyond 1500 samples per day is described.

Agilent 1260 Infinity LC Verified

Introduction

Particularly analytical service laboratories in the pharmaceutical industry, responsible for analyzing chemical libraries[1] or performing MS based quantifications of certain ADME-properties and drug metabolism studies of drug candidates[2] are faced with the challenge to increase their throughput, but also to maintain a high chromatographic resolution. In 2003 Agilent Technologies introduced sub two micron particles in their RRHT column series. Because of the small particle size, the chromatographic resolution obtainable with these columns is superior to standard particle sizes such as 3.5 µm or even 5 µm. Due to a unique silica manufacturing process, Agilent ZORBAX RRHT columns show a significantly reduced backpressure, if compared to similar column dimensions of other manufacturers. Excellent chromatographic results are achieved in a very short analysis time with the Agilent 1200 Series Rapid Resolution LC system, which facilitates an increased pressure range and flow rates from 0.05 up to 5 mL/min using column diameters ranging from 2.1-mm id up to 4.6-mm id. This Application Note will focus on 2.1-mm id columns only.

Not only are the run times of the analyses important for high throughput, but also the overhead time. The Agilent 1200 Series Rapid Resolution LC system can be optimized to achieve highest throughputs with exceptionally good overall system performance.

Experimental

An important issue when dealing with narrow bore columns, especially in gradient mode where smallest peak widths can be achieved, is to have small extra column volumes. This also includes any volumes in front of the sampling device, because any volume after the solvent mixing point will increase the time for the gradient composition to reach the column. This results in an increased run time. The Agilent 1200 Series Rapid Resolution LC system can be reconfigured within a few minutes to provide appropriate system volumes for different column ids. Here, the pumps are set-up in the low delay volume configuration with an internal volume of approximately 120 µL. All other modules are optimized for lowest delay volumes by using the low delay volume capillary kit (G1316-68744). Consequently, only capillaries of 0.12 mm id are used beyond the injection valve. In the Agilent 1200 Series thermostatted column compartment SL the newly introduced low dispersion heat exchangers with 1.6 µL internal volume were used. In some experiments, the Agilent 1200 Series Rapid Resolution LC is set up for alternating column regeneration to achieve highest throughput using the ACR-capillary kit (G1316-68721) and 2.1-mm id columns[3]. The high pressure rated 2-position/10-port valve in the thermostatted column compartment was only placed into the flow path if alternating column regeneration was used indeed.

The instrument set-up is as follows (figure 1):

- Agilent 1200 Series binary pump SL with the new Agilent 1200 Series micro vacuum degasser
- Agilent 1200 Series high performance autosampler SL
- Agilent 1200 Series thermostatted column compartment SL, equipped with a high pressure, 2-position/10-port valve, facilitating alternating column regeneration
- Agilent 1200 Series diode-array detector SL with a 2-µL/3-mm cell
- ZORBAX SB C18, 2.1 mm id x 50 mm, 1.8 µm

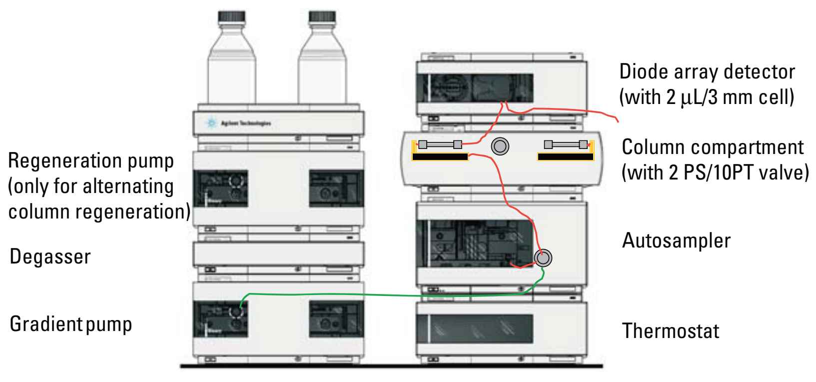

Figure 1
System setup with low delay volume for high speed applications using 2.1-mm id columns with lengths from 20 to 50 mm.

The Agilent 1200 Series binary pump SL is designed to fulfill the demands for high throughput, highest performance, optimum resolution and lowest pump ripple. The pump hardware is significantly different from the standard binary pump. In the Agilent 1200 Series binary pump SL the pressure transducer is separate from the damper which has been modified to have a lower delay volume (pressure dependent ranging from 80-280 µL). In this study the pumps were used in the low delay volume configuration without the mixer and damper in the flow path. In contrast to the standard binary pump the pump heads of the binary pump SL have an additional damping coil (500 µL volume each) to allow damping in the low delay volume configuration. This does not add to the gradient delay volume because it is before the mixing point. Anyhow, pressure ripples are also strongly suppressed by the Electronic Damping Control (EDC). The pressure range of the pump and all other modules is increased to 600 bar.

Only one sample, the so-called “phenone-mix”, was used in the course of this study to keep variations low. The sample consists of nine compounds: acetanilid, acetophenone, propiophenone, butyrophenone, benzophenone, valerophenone, hexanophenone, heptanophenone and octanophenone. Unless otherwise stated, the concentration was 0.1 µg/µL for each compound except butyrophenone which was 0.2 µg/µL. The solvent was water-acetonitril 2:1.

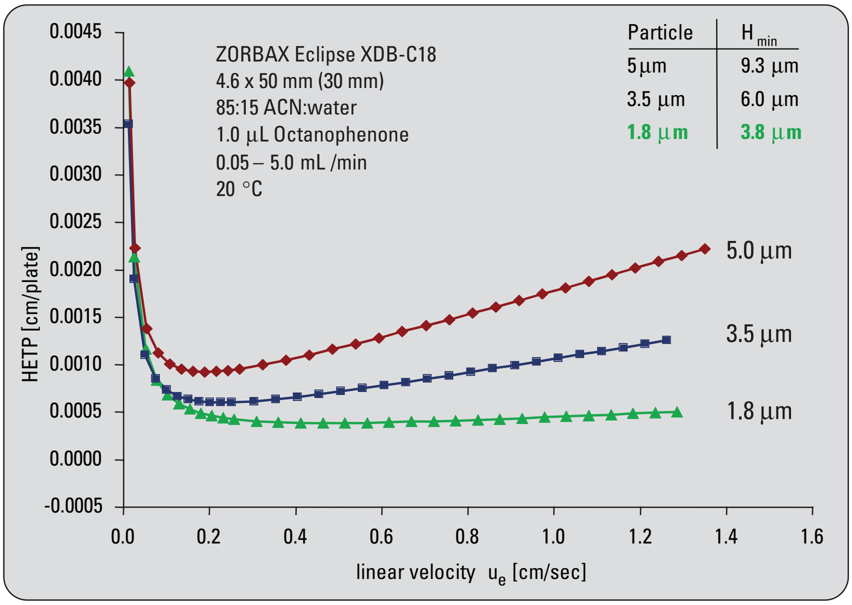

Figure 2
Van Deemter curves of columns packed with 1.8 µm, 3.5 µm and 5.0 µm particles.

Results and discussion

The most frequently sold particle size in chromatographic columns today is 5 µm. Of course, fast and ultra fast LC is also possible with columns packed with particles of these larger diameters – the reduced back pressure is even beneficial to allow higher flow rates. However, resolution will be sacrificed because conditions are usually far on the right side of the van-Deemter-optimum. Here, the big advantage of the RRHT columns with particles of less than 2 µm diameter is proven. The van Deemter optimum is shifted further to the right and the curve is much flatter at the onset because the “resistance of mass transfer” term is diminished (figure 2). In figure 3 the analysis on a 2.1-mm id column with 1.8-µm particles is compared to the linear scaled analysis on the same stationary phase but on 5 µm particles packed in a 4.6-mm id-column. The gain in resolution is obvious – from Rs = 2.1 up to Rs = 3.5 for the critical pair which matches the theoretically expected value of a 1.66 fold increase in resolution. Also note that there is a saving in solvent consumption of 8.6 mL in the “standard” HPLC analysis and only 1.8 mL in the ultra fast HPLC analysis.

For gradient separation the dependencies of the capacity factor can be expressed as:

$$k^* = 0.87 \cdot tg \cdot \frac{F}{Vm \cdot \Delta\%B \cdot S}$$

(tg = gradient time, F = flow rate, Vm = column void volume, △% B = gradient steepness, S = solvent and solute dependent factor)

If the product of the gradient time and flow rate, the so-called gradient volume, is kept constant together with all other parameters, the gradient time might be decreased while the flow rate is increased. Thus, the capacity factors of two compounds will stay constant and if no large alteration of the plate height occurs, the resolution will not change significantly, either. The final point is the big advantage of the sub two micron particles – the van-Deemter curve is nearly flat on the right side of the minimum (figure 2) and flow rates can be increased with only little increase in plate heights. However, the equation is an empirical one and deviations may occur especially under extreme conditions.

With a two-step approach, highest gradient speeds with virtually no loss or only little loss in resolution can be achieved. In the first step, start from a medium temperature and begin to increase the flow rate up to the pressure maximum. Subsequently the temperature should be increased to lower the viscosity of the solvent and then the flow rate is increased again. It may be worthwhile to check the resolution with two identical gradients but with different temperatures to see the influence of the temperature change on the resolution which may be very compound dependent. In figure 4 the result of this approach is shown. A nearly 7-fold increase in separation speed could be achieved with still baseline separation of the critical pair before meeting the pressure and temperature limit (the maximum temperature is a function of flow, temperature, number of controlled Peltier elements and of the heat capacity of the solvent used).

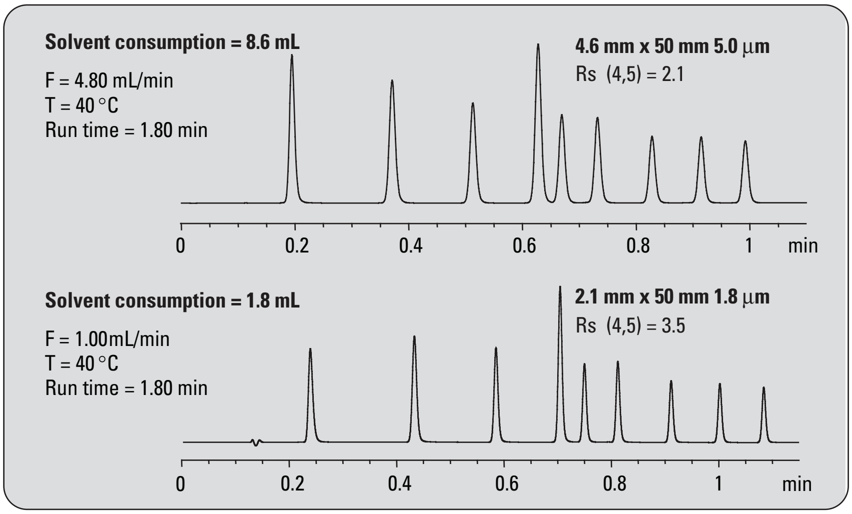

Figure 3
Analysis with 1.8-µm particle column vs. 5.0 µm particle column.

Conditions:	4.6-mm id column used on standard Agilent 1200 system	
Solvent:	A = Water, B = ACN	
Temperature:	40 °C	
Column:	**2.1 mm x 50 mm, 1.8 µm**	**4.6 mm x 50 mm, 5.0 µm**
Flow:	1.0 mL/min	4.8 mL/min (scaled from 2.1 mm col.)
Gradient:	0.00 min 35 %B	0.00 min 35 %B
	0.90 min 95 %B	0.90 min 95 %B
	1.10 min 95 %B	1.10 min 95 %B
	1.11 min 35 % B	1.11 min 35 % B
Stoptime:	1.15 min	1.15 min
Posttime:	0.70 min	0.70 min
Wavelength:	245 nm (8), ref. 450 nm (100)	245 nm (8), ref. 450 nm (80)
Peakwidth:	>0.0025 min (0.05 s res.time), 80 Hz	>0.01 min (>0.2 s), 20 Hz
Injection volume:	1 µL	5 µL (not scaled)

Conditions:	
Solvent:	A = water, B = ACN
Temp.:	40 °C, 80 °C, 95 °C
Flow:	0.35, 0.70, 1.20, 2.00, 2.40 mL/min
Gradient:	0.00 min 35 %B
	2.60 min 95 %B
	3.20 min 95 %B
	3.21 min 35 %B
	Time values for F = 0.35 mL/min. For all other flow rates times are scaled so that (t_g x F) = 0.90 mL
Stop time:	3.20 min
Post time:	2.00 min
Wavelength:	245 nm (8), Ref. 450 nm (100)
Peak width:	>0.0025 min (0.05 s response time), 80 Hz

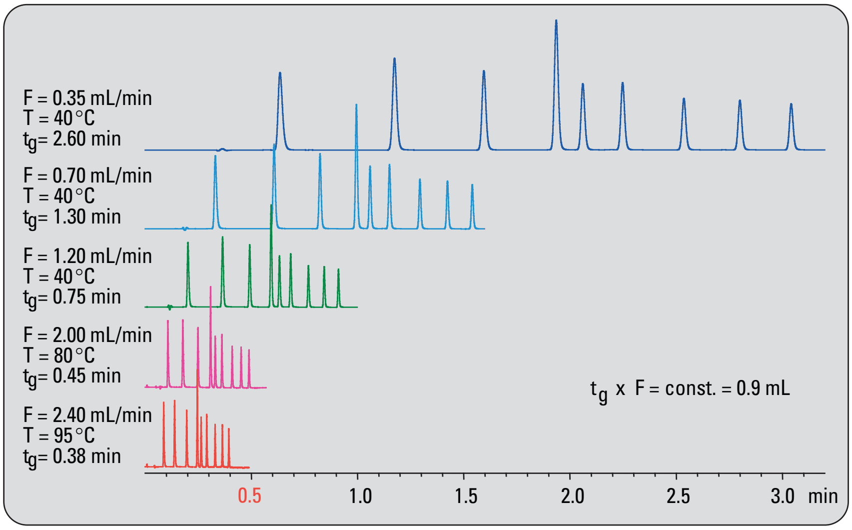

Figure 4
Increasing separation speed by increasing temperature and flow rate while decreasing gradient time.

The last chromatogram is enlarged in figure 5 and reveals the details of this separation. The first peak is eluted after only five seconds and peaks with a width at half height of less than 200 ms are achievable. Within twenty-four seconds nine compounds are separated with a peak capacity in the range of fifty.

Retention time precision at highest analysis speed

High analysis speed is meaningless without precision. One basic performance criteria for HPLC pumps is the precision of gradient formation measured by the precision of retention times of repeated gradients. However, the stability of the column temperature must also be taken into consideration, because temperature fluctuations will also influence the retention times of a given sample. In table 1 and figure 6 the results from the 10-fold repeated analysis of a standard sample are listed and since the deviation between individual runs is so small, the octanophenone peak is enlarged in a separate window. This sample contains compounds that are both not retained and refer to isocraticly eluted compounds found at the starting conditions of the gradient, as well as highly unpolar and strongly retained compounds. The analyses

---

Conditions:

Solvent: A = Water, B = ACN
Temp.: 40 °C, 80 °C
Flow: 0.35 mL/min, 1.20 mL/min, 2.0 mL/min
Gradient: 0.00 min 35%B
2.60 min 95%B
3.20 min 95%B
3.21 min 35%B
Time values for F = 0.35 mL/min.
For all other flow rates times are scaled so that (time x flow) = 0.90 mL
Stop time: 3.20 min
Post time: 2.00 min
Injection vol.:1.0 µL

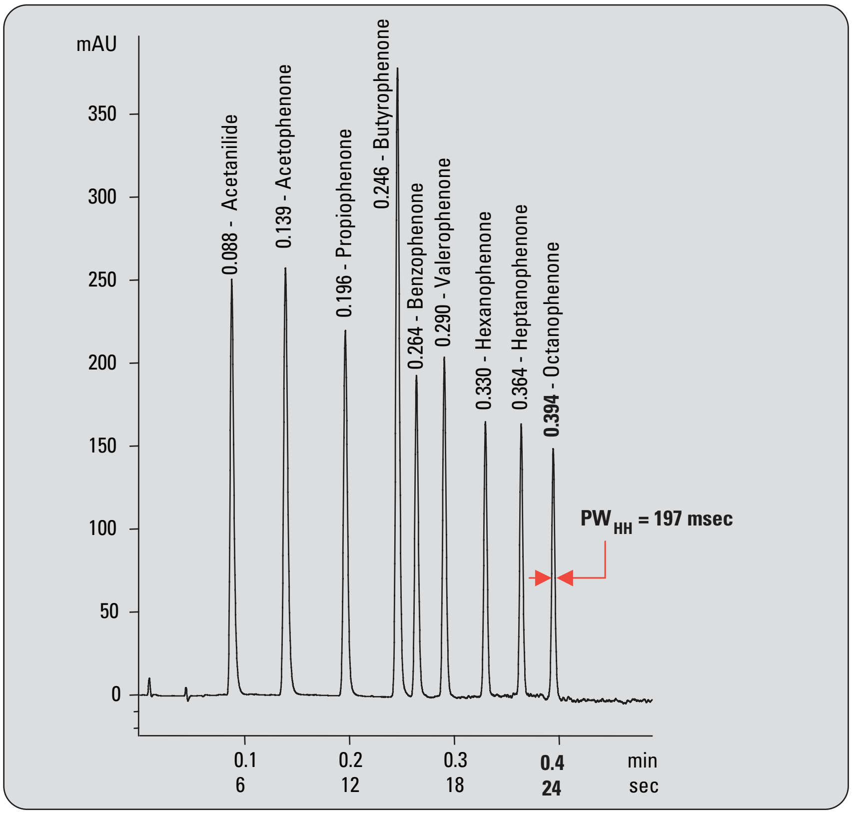

Figure 5
Separation of a nine compound mixture under ultra fast conditions.

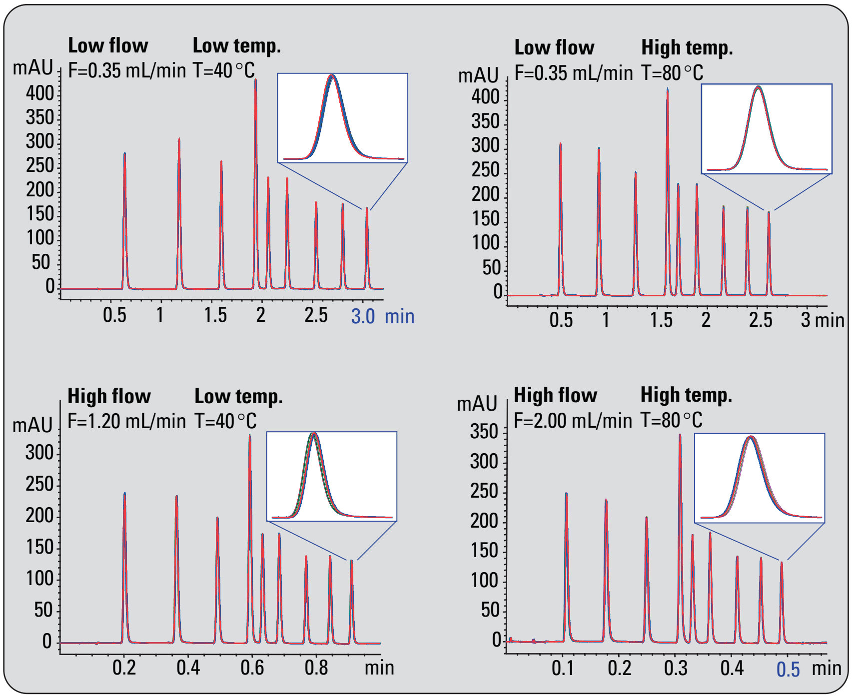

Figure 6
Overlaid chromatograms of the repeated analysis of a 9 compound mixture under various conditions.

were done at high and low flow rates as well as with high and low temperatures as in the examples shown earlier. In all cases the mean retention time precision is below 0.3 % RSD, which was the specification of the Agilent 1100 Series LC system. Of course, the results are also in line with the specifications for the new Agilent 1200 Series Rapid Resolution LC system which is < 0.07 % RSD or < 0.02 min SD, whichever is met first. At these high gradient speeds, the SD criteria are always met. The RSD criteria are also met for both fast-LC gradients of 2.6 min duration (0.35 mL/min flow rate). Even at ultra-fast gradient speeds, the retention time precisions are still below or only slightly higher than 0.1% RSD (table 1).

Improving the cycle-time

Not only is the gradient speed important when dealing with high-throughput analysis but furthermore the over all cycle time of the entire system, which is the time between two consecutive analyses. A good method to measure the cycle time is by using the time stamp the data file is assigned by the operating system of the computer. Clearly, optimizing the cycle time has some drawbacks. For example, extensive needle cleaning procedures are in contradiction with a high sampling speed. Table 2 gives an overview of important parameters influencing the cycle time. Using 1.8-µm particle size columns together with an optimized HPLC system very short run times can be achieved without sacrificing chromatographic resolution. Combining short run times together with low overhead times will result in a high daily throughput. In figure 7 the cycle time and daily throughput is shown for two

	0.35 mL/min, 40°C		0.35 mL/min, 80°C		1.20 mL/min, 40°C		2.00 mL/min, 80°C	
	SD	% RSD	SD	% RSD	SD	% RSD	SD	% RSD
Average	0.00107	0.067	0.00084	0.070	0.00048	0.098	0.00031	0.134

Table 1
Standard deviations (mAU) and %RSD (n=10) of the retention times under different chromatographic conditions in temperature and flow.

Module	Parameter	Effect on cycle time	Other effects
Pump	Low delay volume setting	Reduced retention times, run time can be shortened, reduced cycle time	Increased pressure ripple, slightly increased mixing noise if modifiers such as TFA are used.
Autosampler	Automatic Delay Volume Reduction (ADVR) – activated	Reduced delay volume, reduced retention times, run time can be shortened, reduced cycle time	Increased carry-over
	ADVR activated and Overlapped Injection (OI)	Enables parallel sampling, thus reduces the cycle time independently of the below listed settings (as long as the overall sampling speed does not exceed the gradient and post time)	Increased carry-over
	no OI – Needle Wash	Increased sampling time with increasing wash time	Reduced carry-over with longer needle wash time
	no OI – Equilibration time	Increased sampling time with increased equilibration time	Better injection precision with longer equilibration time
	no OI – Draw/Eject speed	Low speed causes increased sampling time	Low speed results in better injection precision
Column compartment	Alternating column regeneration	Saves column wash-out and equilibration time, reduces cycle time enormously	Additional hardware required, slightly increased extra column volume, slightly different retention times between columns possible
Detector	Pre-run and/or post-run balance	Increased cycle time	Baseline drifts possible if not applied
	Spectral data acquisition with high data rate, small band width and broad wavelength range large data files	Depending on computer power and additional processes running might increase cycle time because of writing speed	Reduced information content if no spectral data acquired or with lower resolution
Software	Data analysis with acquisition	Increased cycle time, depending on computer power and number of peaks	Data analysis has to be done offline is no set
	Save method with data	Slightly increased cycle time	Information is missing if method is not saved
	Execution of pre-run or post-run macros	Increased cycle time, depending on macro	Depending on macro
System	LC controlled over local network between computer and LC (and MS) only	Faster data and method transfer between computer and LC because of reduced net work traffic reduced cycle time	Additional hardware might be necessary (use independent acquisition computer)
	Number of detectors	More detectors produce a higher data amount and lower the data transfer speed, resulting in higher cycle times	More detectors higher information content

Table 2
Influence of various parameters on the overall cycle time.

different methods – both giving virtually the same resolution. The first method (0.45 min gradient) utilizes alternating column regeneration and high temperatures to allow high flow rates and speed optimized settings. A cycle time of 49 s could be achieved, resulting in a theoretical daily throughput of more than 1700 samples per day. The second method (0.90 min gradient) does not use high temperatures or alternating column regeneration and the time saving of some simple and often forgotten method options are shown. By optimizing these parameters the real cycle time gets as close to 8 s to the run time (stop time plus post time) and allows a daily throughput of more than 700 samples per day. By sub-optimal method set up this can easily drop to below 500 samples per day if options like automatic delay volume reduction, overlapped injection or offline data-analysis are not used.

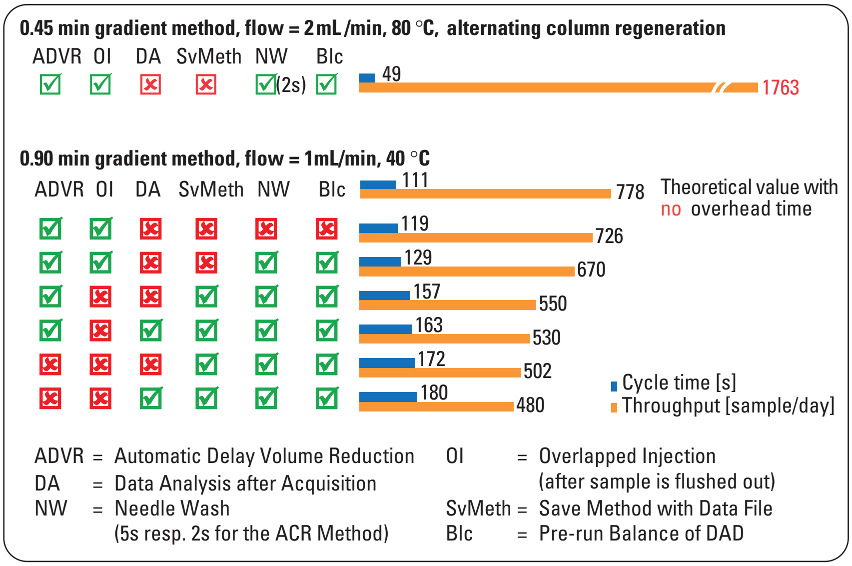

Figure 7
Cycle time and daily throughput optimization.

Chromatographic conditions:

Alternating Column Regeneration Method

Solvent:	A = Water, B = ACN	
Temp.:	80 °C	
Flow:	2.0 mL/min	
ADVR:	Yes	
Gradient:	**Gradient-Pump**	**Regeneration-Pump**
	0.00 min 35 %B	0.00 min 35 %B
	0.45 min 95 %B	0.01 min 95 %B
	0.46 min 35 %B	0.11 min 95 %B
	0.57 min 35 %B	0.12 min 35 %B
Stoptime:	0.57 min	no limit
Posttime:	off	off
Wavelength:	245 nm (8), ref. 450 nm (100)	
Peak width:	> 0.0025 min (0.05 s response time), 80 Hz	
Spectra:	none	
Injection volume:	1.0 µL	
Injector:	Overlapped injection, 2 s needle wash, sample flush-out factor = 10, draw/eject speed = 100 µL/min	
Valve:	next position	

No Alternating Column Regeneration Method

Solvent:	A = Water, B = ACN	
Temp.:	40 °C	
Flow:	1.0 mL/min	
ADVR:	Yes	No
Gradient:	0.00 min 35 %B	0.00 min 35 %B
	0.90 min 95 %B	0.90 min 95 %B
	1.10 min 95 %B	1.10 min 95 %B
	1.11 min 35 %B	1.11 min 35 %B
Stoptime:	1.15 min	*1.40 min (add. 300 µL extra column volume, increased retention times)*
Posttime:	0.70 min	0.70 min
Wavelength:	245 nm (8), ref. 450 nm (100)	
Peak width:	> 0.0025 min (0.05 s response time), 80 Hz	
Spectra:	all, 190-500 nm, BW = 1 nm	
Injection volume:	1.0 µL	
Injector:	See figure 7, 2 s equilibration time	

Conclusion

The Agilent 1200 Series Rapid Resolution LC system is a powerful tool to achieve highest chromatographic resolutions and also highest throughputs. The extended pressure range allows the usage of columns packed with stationary phases with particles sizes below 2 µm, for example, Agilent RRHT columns with particle sizes of 1.8 µm. These columns not only allow an increase in linear flow rates with virtually no loss in resolution but also have an inherently higher resolution compared to 3.5 µm or even 5.0 µm particle sizes. The possibility to switch the pump into its low delay volume configuration allows the use of the entire bandwidth of today's widely used column ids – from 4.6 mm down to 2.1 mm and even 1.0 mm. As illustrated above, the system has uncompromised performance characteristics even at highest gradient speeds.

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Improving the Effectiveness of Method Translation for Fast and High Resolution Separations

Application

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Abstract

The increased availability of sub-2-micron (STM) columns and increased demand for methods friendly to mass spectrometers has led to strong trend toward conversion of existing HPLC methods to smaller diameter and smaller particle size columns. While the conversion is a simple mathematical exercise requiring the scaling flow rates, gradient times and injection volumes, many users observe less than perfect results. Here we look closely at the problem and propose calculations that improve the speed and/or resolution in a more predictable and beneficial way.

Introduction

Methods developed on older columns packed with large 5- or 10-µm particles are often good candidates for modernization by replacing these columns with smaller dimension columns packed with smaller particle sizes. The potential benefits include reduced analysis time and solvent consumption, improved sensitivity and greater compatibility with mass spectrometer ionization sources.

Simplistically, a column of 250-mm length and containing 5-µm particles can be replaced by a 150-mm length column packed with 3-µm particles. If the ratio of length to particle size is equal, the two columns are considered to have equal resolving power. Solvent consumption is reduced by L1/L2, here about 1.6-fold reduction in solvent usage per analysis. If an equal mass of analyte can then be successfully injected, the sensitivity should also increase by 1.6-fold due to reduced dilution of the peak as it travels through a smaller column of equal efficiency.

LC/MS (Liquid Chromatography/Mass Spectrometry) ionization sources, especially the electrospray ionization mode, have demonstrated greater sensitivity at lower flow rates than typically used in normal LC/UV (UltraViolet UV/VIS optical detection) methods, so it may also be advantageous to reduce the internal diameter of a column to allow timely analysis at lower flow rates. The relationship of flow rate between different column diameters is shown in Equation 1.

$$\mathrm{Flow}_{\mathrm{col.\,1}} \times \left[\frac{\mathrm{Diam.}_{\mathrm{column2}}}{\mathrm{Diam.}_{\mathrm{column1}}}\right]^2 = \mathrm{Flow}_{\mathrm{col.\,2}} \qquad \text{(eq. 1)}$$

The combined effect of reduced length and diameter contributes to a reduction in solvent consumption and, again assuming the same analyte mass can be injected on the smaller column, a proportional increase in peak response. We normally scale the injection mass to the size of the column,

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though, and a proportional injection volume would be calculated from the ratio of the void volumes of the two columns, multiplied by the injection volume on the original column.

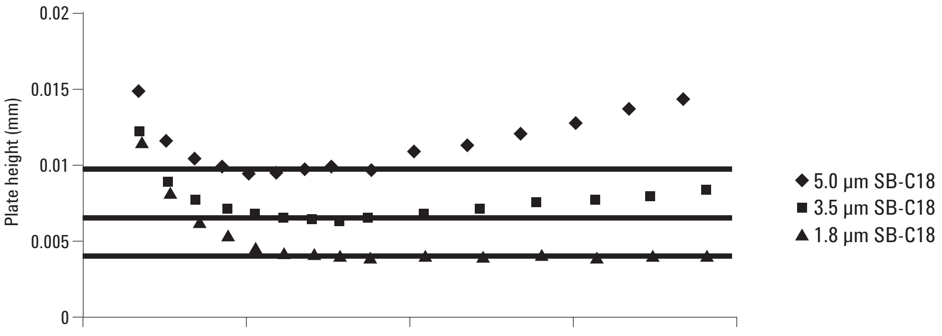
$$\text{Inj. vol.}_{\text{col. 1}} \times \left[\frac{\text{Volume}_{\text{column2}}}{\text{Volume}_{\text{column1}}}\right] = \text{Inj. vol.}_{\text{col. 2}} \quad \text{(eq. 2)}$$

For isocratic separations, the above conditions will normally result in a successful conversion of the method with little or no change in overall resolution. If one wishes to improve the outcome of the method conversion, though, there are several other parameters that should be considered. The first of these parameters is the column efficiency relative to flow rate, or more correctly efficiency to linear velocity, as commonly defined by van Deemter [1] and others, and the second is the often overlooked effect of extracolumn dispersion on the observed or empirical efficiency of the column.

Van Deemter observed and mathematically expressed the relationship of column efficiency to a variety of parameters, but we are most interested here in his observations that there is an optimum linear velocity for any given particle size, in a well-packed HPLC column, and that the optimum linear velocity increases as the particle size decreases. Graphically, this is often represented in van Deemter plots as shown in Figure 1, a modified version of the original plot [2].

In Figure 1 we observe that the linear velocity at which 5-µm materials are most efficient, under the conditions used by the authors, is about 1 mm/sec. For 3.5-µm materials the optimum linear velocity is about 1.7 mm/sec and has a less distinct optimum value, suggesting that 3.5-µm materials would give a more consistent column efficiency over a wider flow range. For the 1.8-µm materials, the minimum plate height, or maximum efficiency, is a broad range beginning at about 2 mm/sec and continuing past the range of the presented data. The practical application of this information is that a reduction in particle size, as discussed earlier, can often be further optimized by increasing the linear velocity which results in a further reduction in analysis time. This increase in elution speed will decrease absolute peak width and may require the user to increase data acquisition rates and reduce signal filtering parameters to ensure that the chromatographic separation is accurately recorded in the acquisition data file.

The second important consideration is the often overlooked effect of extracolumn dispersion on the observed or empirical efficiency of the column. As column volume is reduced, peak elution volumes are proportionately reduced. If smaller particle sizes are also employed there is a further reduction in the expected peak volume. The liquid chromatograph, and particularly the areas where the analytes will traverse, is a collection of various connecting capillaries and fittings which will cause a measurable amount of bandspreading. From the injector to the detector flow cell, the cumulative dispersion that occurs degrades the column performance and results in observed efficiencies that can be far below the values that would be estimated by purely theoretical means. It is fairly typical to see a measured dispersion of 20 to 100 µL in an HPLC system. This has a disproportionate effect on the smallest columns and smallest particle sizes, both of which are expected to yield the smallest



Lin. vel.	mm/sec	1	2	3	4	5
4.6 mm	mL/min	0.7	1.4	2.1	2.8	3.5
3 mm	mL/min	0.3	0.6	0.9	1.2	1.5
2.1 mm	mL/min	0.14	0.29	0.44	0.58	0.73
1 mm	mL/min	0.033	0.066	0.1	0.133	0.166

Figure 1. **van Deemter plot with various flow rates and particle sizes.**

possible peak volumes. Care must be taken by the user to minimize the extracolumn volume and to reduce, where practical, the number of connecting fittings and the volume of injection valves and detector flow cells.

For gradient elution separations, where the mobile phase composition increases through the initial part of the analysis until the analytes of interest have been eluted from the column, successful method conversion to smaller columns requires that the gradient slope be preserved. While many publications have referred to gradient slope in terms of % change per minute, it is more useful to express it as % change per column volume. In this way, the change in column volume during method conversion can be used to accurately render the new gradient condition. If we think of each line of a gradient table as a segment, we can express the gradient by the following equation:

$$\%\text{ Gradient slope} = \left[\frac{(\text{End\%} - \text{Start\%})}{\#\text{Column volumes}}\right] \quad \text{(eq. 3)}$$

Note that the use of % change per column volume rather than % change per minute frees the user to control gradient slope by altering gradient time and/or gradient flow rate. A large value for gradient slope yields very fast gradients with minimal resolution, while lower gradient slopes produce higher resolution at the expense of increased solvent consumption and somewhat reduced sensitivity. Longer analysis time may also result unless the gradient slope is reduced by increasing the flow rate, within acceptable operating pressure ranges, rather than by increasing the gradient time.

Resolution increases with shallow gradients because the effective capacity factor, k*, is increased. Much like in isocratic separations, where the capacity term is called k', a higher value directly increases resolution. The effect is quite dramatic up to a k value of about 5 to 10, after which little improvement is observed. In the subsequent examples, we will see the results associated with the calculations discussed above.

Experimental Conditions

System

Agilent 1200 Series Rapid Resolution LC consisting of:
G1379B micro degasser
G1312B binary pump SL
G1367C autosampler SL, with thermostatic temperature control
G1316B Thermostatted column compartment SL
G1315C UV/VIS diode array detector SL, flow cell as indicated in individual chromatograms
ChemStation 32-bit version B.02.01

Columns

Agilent ZORBAX SB-C18, 4.6 mm × 250 mm, 5 µm
Agilent ZORBAX SB-C18, 3.0 mm × 150 mm, 3.5 µm

Mobile phase conditions

Organic solvent:	Acetonitrile
Aqueous solvent:	25 mm phosphoric acid in Milli-Q water

Gradient Conditions

Gradient slope:	7.8% or 2.3% per column volume, as indicated. See individual chromatograms for flow rate and time

Sample

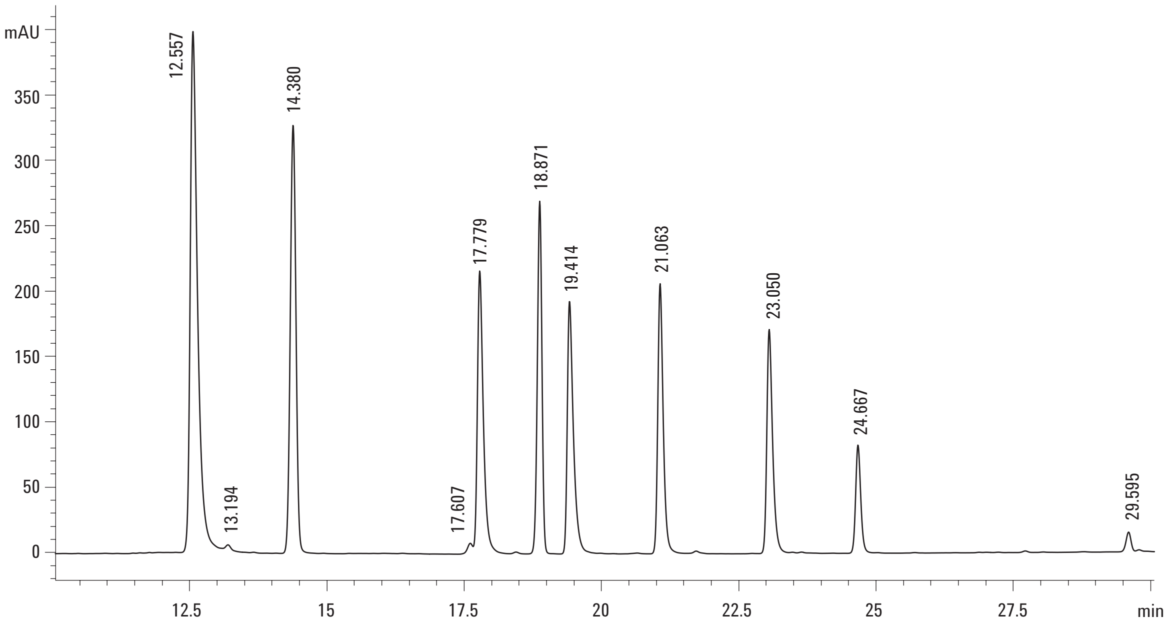
Standard mixture of chlorinated phenoxy acid herbicides, 100 µg/mL in methanol

Results

The separation was initially performed on a standard 4.6 × 250 mm, 5-µm ZORBAX SB-C18 column thermostatted to 25 °C (Figure 2) using conditions referenced in US EPA Method 555. The method was then scaled in flow and time for exact translation to a 3.0 × 150 mm, 3.5-µm column (Figure 3). Solvent consumption is reduced from 60 mL to 15.5 mL per analysis.

The separation was then re-optimized for faster separation with the identical slope, 7.8%, by increasing the flow rate from 0.43 to 1.42 mL/min, and proportionately reducing the gradient time (Figure 4). Finally, increased resolution is demonstrated by keeping the original times used in Figure 3 with the increased flow rate (Figure 5). This yields a gradient with identical time but a reduced slope of 2.3%. The increased resolution of peaks 4 and 5 is readily apparent.

The conditions in Figure 4, 7.8% slope at increased linear velocity on 3.0 × 150 mm, 3.5-µm material, yield a separation with comparable resolution to the original 4.6 × 250 mm method, but with only a 12-minute total analysis time. This is excellent for



Conditions

EPA Method 555 with ZORBAX SB-C18 columns and fast DAD detector

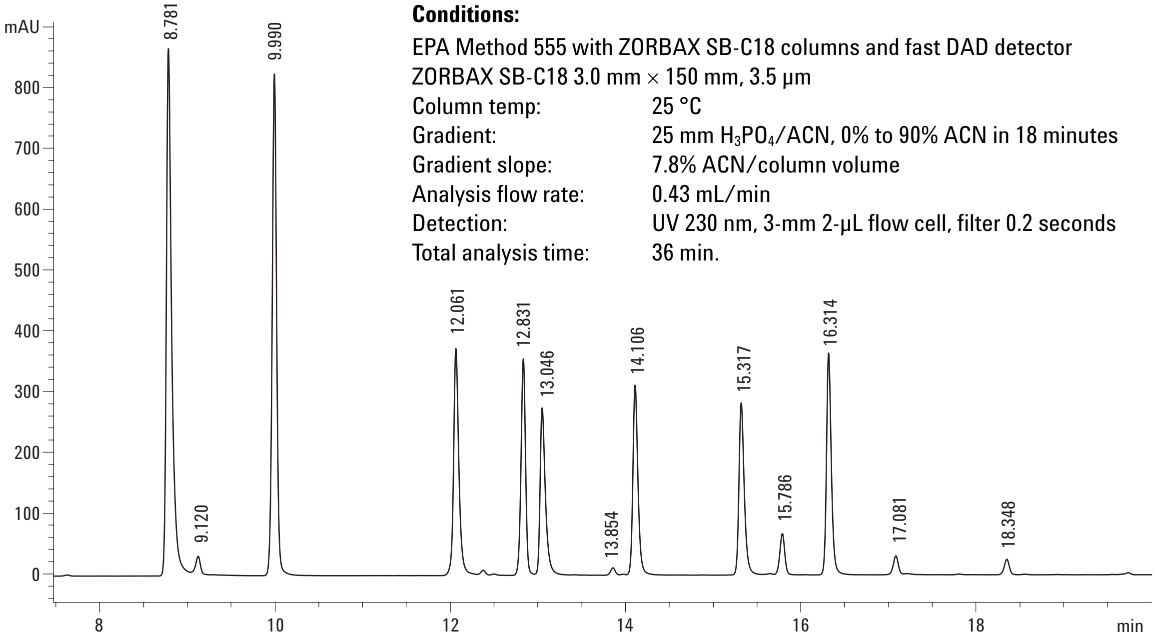
ZORBAX SB-C18 4.6 mm × 250 mm, 5 µm

Column temp:	25 °C
Gradient:	10% to 90% ACN vs. 25 mM H_3PO_4
Gradient slope:	7.8% ACN/column volume
Analysis flow rate:	1 mL/min

Group A Compounds

Total analysis time:	60 min
Detection:	UV 230 nm, 10-mm 13-µL flow cell, filter 2 seconds (default)

Figure 2. Gradient separation of herbicides on 4.6 × 250 mm 5-µm ZORBAX SB-C18.



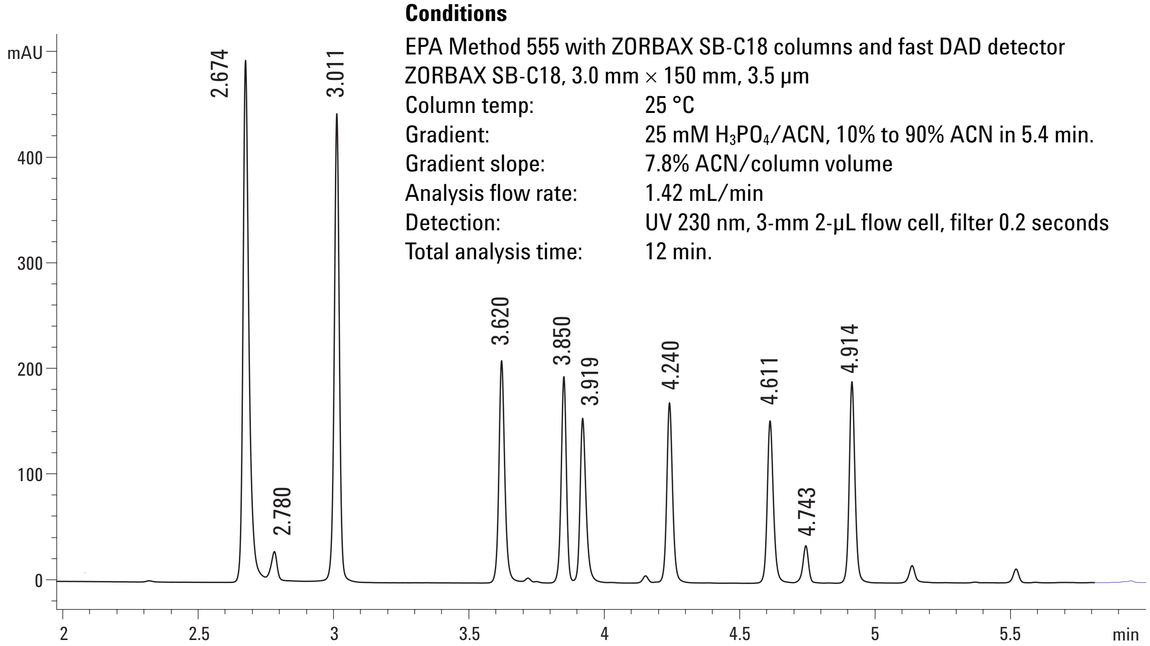
Conditions:

EPA Method 555 with ZORBAX SB-C18 columns and fast DAD detector

ZORBAX SB-C18 3.0 mm × 150 mm, 3.5 µm

Column temp:	25 °C
Gradient:	25 mm H_3PO_4/ACN, 0% to 90% ACN in 18 minutes
Gradient slope:	7.8% ACN/column volume
Analysis flow rate:	0.43 mL/min
Detection:	UV 230 nm, 3-mm 2-µL flow cell, filter 0.2 seconds
Total analysis time:	36 min.

Figure 3. Gradient separation of herbicides on 3.0 × 150 mm, 3.5-µm ZORBAX SB-C18.

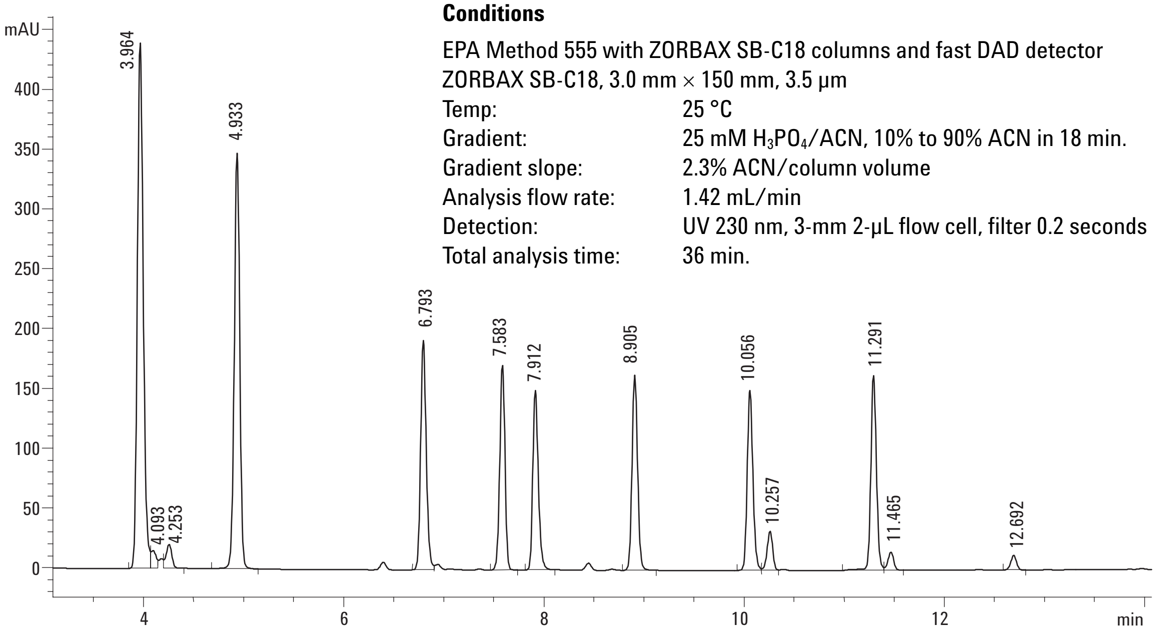


Conditions

EPA Method 555 with ZORBAX SB-C18 columns and fast DAD detector
ZORBAX SB-C18, 3.0 mm × 150 mm, 3.5 µm

Column temp:	25 °C
Gradient:	25 mM H_3PO_4/ACN, 10% to 90% ACN in 5.4 min.
Gradient slope:	7.8% ACN/column volume
Analysis flow rate:	1.42 mL/min
Detection:	UV 230 nm, 3-mm 2-µL flow cell, filter 0.2 seconds
Total analysis time:	12 min.

Figure 4. **High speed gradient separation of herbicides on 3.0 × 150 mm, 3.5-µm ZORBAX SB-C18.**



Conditions

EPA Method 555 with ZORBAX SB-C18 columns and fast DAD detector
ZORBAX SB-C18, 3.0 mm × 150 mm, 3.5 µm

Temp:	25 °C
Gradient:	25 mM H_3PO_4/ACN, 10% to 90% ACN in 18 min.
Gradient slope:	2.3% ACN/column volume
Analysis flow rate:	1.42 mL/min
Detection:	UV 230 nm, 3-mm 2-µL flow cell, filter 0.2 seconds
Total analysis time:	36 min.

Figure 5. **Reduced slope gradient separation of herbicides on 3.0 × 150 mm, 3.5-µm ZORBAX SB-C18.**

high throughput screening and quantitation of a large number of samples. Figure 5, with the gradient slope reduced to 2.3%, results in a high-resolution separation with a calculated R value of 3.3 vs. the standard 3.0 × 150 mm separation value of 1.9, for the critical pair seen in Figure 5 at 7.5 to 8 minutes.

In Table 1 the column has been replaced with a low dead volume connecting union in a system fitted with 0.12-mm id capillary tubing at all points of sample contact. A 1-µL injection of dilute actone is made to determine the bandspreading contribution of the system, with various flow cells. Multiple flow cells were tested, and the average result reported, where possible. The elution volume summarizes the total volume of all tubing in the system. While the absolute volume from the 2-µL to the 13-µL flow cells is 11 µL, we observe an increase of 15 to 16 µL because of the larger diameter inlet tubing integral to the larger volume flow cells.

Table 1. Volumetric Measurements of Various Flow Cells

Flow cell	Elution volume (µL)	Half height width (µL)	5 Sigma width (µL)
New SL 2 µL 3 mm	11	5	12
Micro 6 mm 1.7 µL (n = 2)	14	6	18
Semi-micro 6 mm 5 µL (n = 2)	13	6.5	18.5
Standard 10 mm 13 µL	26	11	26
New SL 10 mm 13 µL	27	11	25

Conclusion

Careful analysis of the existing gradient conditions, coupled with an awareness of the need to accurately calculate new flow and gradient conditions can lead to an easy and reliable conversion of existing methods to new faster or higher resolution conditions. In addition, awareness of extracolumn dispersion, especially with small and high resolution columns, will ensure good column efficiency which is critical to a successful translation of the method.

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Improving Productivity and Extending Column Life with Backflush

Application Brief

Chin-Kai Meng

All Industries

A previous application note [1] has shown that multiple GC signals and MS signals can be acquired from a single sample injection. When a 3-way splitter is connected to the end of a column, column effluent can be directed proportionally to two GC detectors as well as the MSD. This multi-signal configuration provides full-scan data for library searching, SIM data for quantitation, and element selective detector data for excellent selectivity and sensitivity from complex matrices.

The system used in this study consists of a 7683ALS, a 7890A GC with split/splitless inlet, 3-way splitter, µECD, dual flame photometric detector (DFPD), and a 5975C MSD. Figure 1 shows four chromatograms from a single injection of a milk extract. The synchronous SIM/scan feature of the 5975C MSD provides data useful for both screening (full scan data) and quantitation (SIM data). DFPD provides both P and S signals without the need to switch light filters.

Noticeably in the full scan TIC in Figure 1, a significant number of matrix peaks were observed after 32 minutes. It is not uncommon to add a "bake-out" oven ramp to clean the column after analyzing complex samples. The bake-out period is used to quickly push the late eluters out of the column to be ready for the next injection. Therefore, it is common to use a higher oven temperature than required for the analysis and an extended bake-out period at the end of a normal

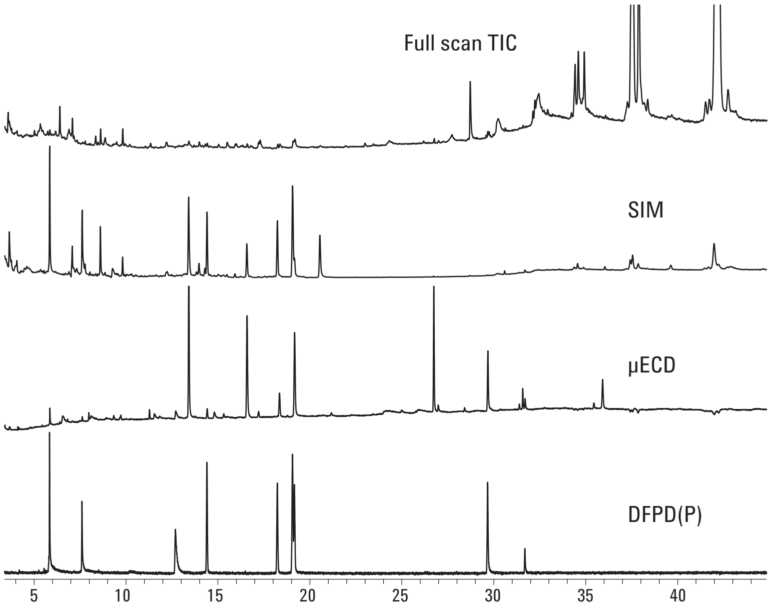

Figure 1. Four chromatograms collected simultaneously from a single injection of a milk extract.

Highlights

- Backflush – a simple technique to remove high boilers from the column faster and at a lower column temperature to cut down analysis time and increase column lifetime.
- The milk extract example shows that a 7-minute 280 °C backflush cleaned the column as well as a 33-minute 320 °C bake-out. The cycle time was reduced by more than 30%.
- Using backflush, excess column bleed and heavy residues will not be introduced into the MSD, thus reducing ion source contamination.

over program to clean out the column, which adds to the cycle time and shortens the column lifetime. Adding the bake-out period to the milk extract analysis, additional matrix peaks were observed even up to 72 minutes, while target compounds already eluted before 42 minutes. This means that 30 minutes were lost in productivity for each injection.

Backflush [2] is a simple technique to drastically decrease the cycle time by reversing the column flow to push the late eluters out of the inlet end of the column. Late eluters stay near the front of the column until the oven temperature is high enough to move them through the column. When the column flow is reversed before the late eluters start to move down the column, these late eluters will take less time and at a lower oven temperature to exit the inlet end of the column.

There are many benefits in using backflush:

- Cycle time is reduced (no bake-out period, cooling down from a lower oven temperature)
- Column bleed is reduced (no high-temperature bake-out needed), resulting longer column life
- Ghost peaks are eliminated (no high boilers carryover into subsequent runs)
- Contamination that goes into the detector is minimized, which is especially valuable for the MSD (less ion source cleaning)

Figure 2 shows three total ion chromatograms from the Agilent 7890A GC/5975C MSD. The top chromatogram is a milk extract analysis with all the target compounds eluted before 42 minutes (over program goes to 280 °C). However, an additional 33-minute bake-out period at 320 °C was needed to move the high boilers out of the column. This bake-out period was almost as long as the required time to elute all target compounds. The middle chromatogram is the same milk extract analysis stopped at 42 minutes with a 7-minute backflush post-run at 280 °C added to the analysis. The bottom chromatogram is a blank run after the backflushing was completed. The blank run shows that the column was very clean after backflushing. The example shows that a 7-minute backflush cleaned the column as well as a 33-minute bake-out.

The milk extract example in Figure 2 illustrates the backflush technique in reducing cycle time and column bleed. The cycle time was reduced by more than 30% and the column was kept at 280 °C, without going to the bake-out temperature of 320 °C. A column effluent splitter or QuickSwap is required to do the backflush.

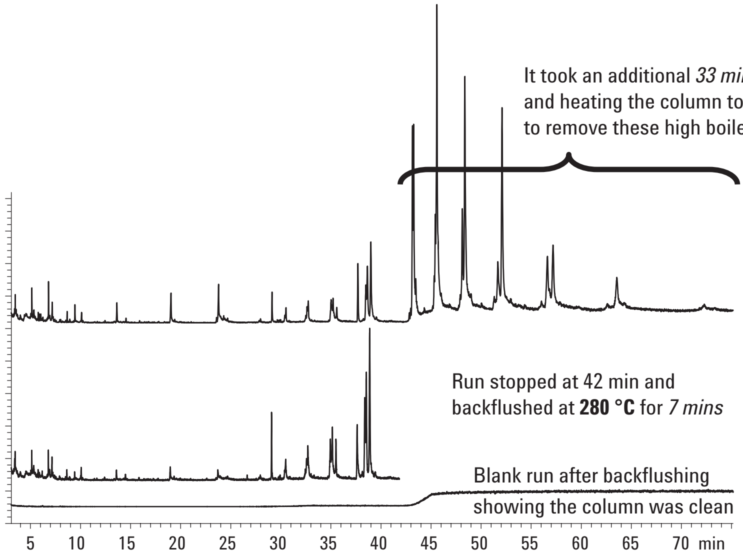

Figure 2. **Three total ion chromatograms comparing the results with and without backflush.**

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1. Chin-Kai Meng and Bruce Quimby, "Identifying Pesticides with Full Scan, SIM, µECD, and FPD from a Single Injection," Agilent Application Note, 5989-3299EN, July 2005.
2. Matthew Klee, "Simplified Backflush Using Agilent 6890 GC Post Run Command," Agilent Application Note, 5989-5111EN, June 2006.

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High-Pressure Liquid Injection Device for the Agilent 7890A and 6890 Series Gas Chromatographs

Application

Hydrocarbon Processing

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Abstract

In gas chromatography, sampling and representative analysis of highly volatile liquefied hydrocarbons with high precision and accuracy can be challenging. In the solution described here, a unique sample injection device based on a needle interface and liquid rotary valve has been designed for sampling light petroleum matrices with broad boiling point distributions. The 7890A GC-based system consists of a 4-port liquid valve, a deactivated removable needle, and auxiliary flow. The needle is directly installed on one port of the valve. This compact device is installed directly over the top of a split/splitless inlet. The unit is operated automatically just like a typical liquid autosampler; however, the needle is not withdrawn. Various pressurized liquid samples have been run on this device, such as liquefied natural gas (calibration standard), ethylene, propylene, and butadiene. Excellent repeatability is obtained with RSDs typically below 1% in quantitative analyses.

Introduction

There are several known techniques for injecting volatile liquefied hydrocarbons in gas chromatographs. The simplest tools are high-pressure syringes. However, the pressure limit is not high enough to analyze light hydrocarbons such as liquefied natural gas and ethylene. The traditional methods [1, 2] include the use of vaporizing regulators and rotary sampling valves. During sampling, discrimination of the analytes will take place for samples with wide boiling points due to condensing of heavy components and selective vaporization of light components in transfer lines. Recently, piston sampling valves were introduced and are commercially available [3]. These can suffer from discrimination and short service lifetimes at high vaporization temperatures or high sample pressures.

Combining the advantages of simple syringes and high-pressure rotary valves, a unique sample injection device has been designed. The system consists of a 4-port liquid sampling valve, a Siltek deactivated needle, and a split/splitless inlet. This compact device is installed directly over the GC inlet. This unit is operated just like a typical liquid autosampler; however, the needle is not withdrawn. The maximum limit of sample pressure is 5,000 psig. Various pressurized gas samples have been evaluated on this device such as liquefied natural gas (calibration standard), ethylene, propylene, and butadiene. Excellent repeatability is obtained with 0.47% to 1.09% RSD in quantitative analyses. Wide boiling point hydrocarbon samples (C5 to C40) have also been analyzed using this injector, with excellent quantitative results.

Experimental

Injection Device

The high-pressure liquid injection (HPLI) device consists of components as shown in Figure 1.

- **Valve:** Internal sample valve from Valco Instruments Co. Inc. 4-port equipped with a sample volume of 0.06 µL. Other rotor sizes are available from Valco Instruments Co. The valve works under 75 °C and 5,000 psi.
- **EPC:** An auxiliary flow from a 7890A Aux module is connected to port P. In sample analysis, the flow can be set at 50 mL/min to 200 mL/min. The higher auxiliary flow gives better peak shape.

The following components are recommended. These are not supplied in the option or accessory kit.

- **Filter:** To remove particles from samples, it is necessary to install a filter between the sample line and port S.
- **Restrictor:** To maintain sample pressure, a metering valve (Agilent PN 101-0355) is connected to the end of the sample exit line tubing. Restrictor is not included in option or accessory kit.

Guideline for choosing Aux flow source

7890AGC

G3471A Pneumatic Control Module (PCM) or

G3470A Aux EPC module

6890GC

G1570A Aux EPC or

G2317A PCM module

The PCM is the preferred source for both GCs.

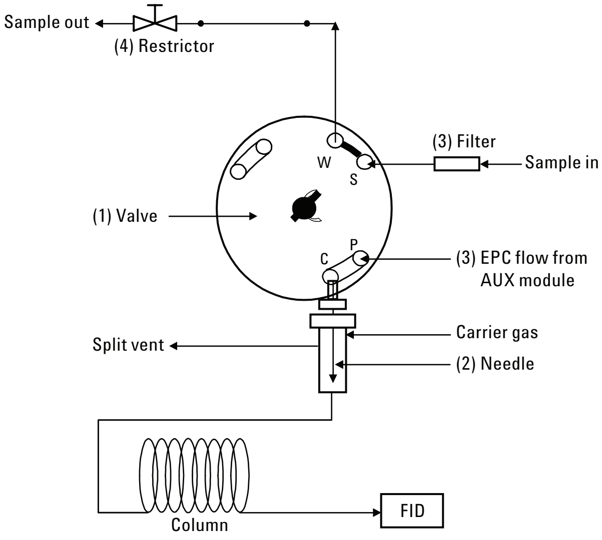


Figure 1. Flow diagram of the HPLI device.

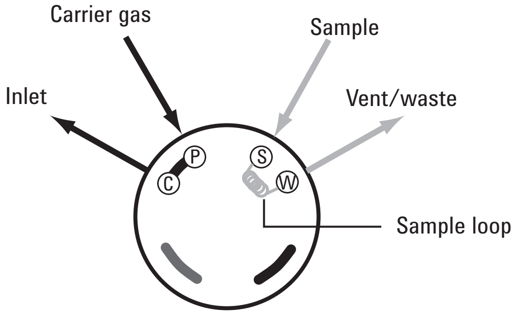
Samples for System Evaluation

- Liquefied natural gas: Calibration standard, 1,200 psi, with nC7-nC9 (0.102%–0.0503%)
- Liquefied ethylene: Purity 99.5, 1,200 psi
- Pressurized propylene: Grade C. P., purity 99.0%, 200 psi
- Pressurized propane + n-butane: 50.0%:50.0%, 200 psi
- Pressurized 1, 3-butadiene: Purity 99.5%, 180 psi
- n-Hexane + 1.0 % 2# BP standard (Agilent PN 5080-8768, nC5–nC18)
- nC5–nC40 D2887 1# BP standard (Agilent PN 5080-8716, diluted by CS_2)
- Glycols, including monoethylene glycol, diethylene glycol, and triethylene glycol
- C8 to C16 hydrocarbons at 100 ppm each

Operating Process

The valve is operated with an Agilent pneumatic air actuator. To load the sample, the valve is set at the OFF position (Figure 1). The sample is loaded from port S and vented to port W. The pneumatic and sample paths in load and inject positions are shown in Figure 2. To maintain the sample in the liquid phase and to avoid “bubbles” in the sample line, it is important to adjust resistance of the metering valve and check for possible leaks at the connections. To inject, the valve is switched to the

Load



Inject

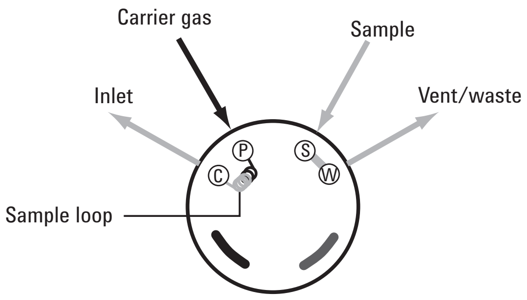


Figure 2. Pneumatic and sample paths in load and inject positions.

ON position. A 2- to 3-second injection time should be used.

The system should always be carefully checked for leaks before introduction of high-pressure hydrocarbons. Instrumental conditions and application-specific columns are shown in Table 1 and Table 2, respectively.

When the valve is actuated, a stream of carrier gas from the Aux EPC or PCM will enter the inlet and combine with the inlet carrier flow; the combined flow will vent through the split vent. Therefore, the actual split ratio will be higher than the value set from ChemStation. The actual split ratio can be calculated by measuring the split vent flow.

Figure 3. Agilent pneumatic air actuator/valve assembly installed on the 7890A.

Table 1. Instrumental Conditions

Gas chromatograph	Agilent 7890A
Injection source	HPLI device at near ambient temperature
Injection port	Split/splitless, 250 °C (350 °C for C5–C40)
Sample size	0.5-µL (0.2 µL for C5–C40) device supplied with 0.06-µL rotor
Carrier gas	Helium
Aux or PCM	150 mL/min (Helium)
FID	250 °C (350 °C for C5–C40) H_2, 35 mL/min Air, 400 mL/min

Table 2. Columns and Parameters

Samples	Columns	Column flow mL/min	Split ratio	Temperature program	Sample pressure psig
Natural gas	30 m × 0.53 mm × 0.5 µm DB-1 #125-1037	8	40:1	35 °C, 1 min 20 °C/min to 180 °C, 1 min	1200
Ethylene	50 m × 0.53 mm × 15 µm AL2O3 PLOT/KCL + 30 m × 0.53 mm × 5 µm DB-1, #19095P-K25 and #125-1035	8	20:1	35 °C, 2 min 4 °C/min to 160 °C, 3.8 min	1100
Propylene	50 m × 0.53 mm HP AL2O3 PLOT + 30 m × 0.53 mm × 5 µm DB-1	7	25:1	35 °C, 2 min 4 °C/min to 160 °C, 1.8 min	180
Propane + n-butane	30 m × 0.53 mm × 1.0 µm DB-1, #125-103J	5	50:1	35 °C	150
1,3-Butadiene	50 m × 0.53 mm AL2O3 PLOT/KCL	10	15:1	35 °C, 2 min 10 °C/min to 195 °C, 15 min	180
n-Hexane	30 m × 0.53 mm × 1.0 µm DB-1	5	50:1	45 °C	N/A
nC5-nC40	10 m × 0.53 mm × 0.88 µm HP-1, #19095Z-021	10	15:1	35 °C, 1 min 15 °C/min to 350 °C, 5 min	N/A
Glycols	30 m × 0.25 mm × 1.0 µm HP-1 ms	1.8	15:1	50 °C, 3 min 15 °C/min to 250 °C, 2 min	

Results and Discussion

Check for Carryover

A set of normal hydrocarbons was used to perform a basic check of the system, looking for good peak shape and lack of carryover.

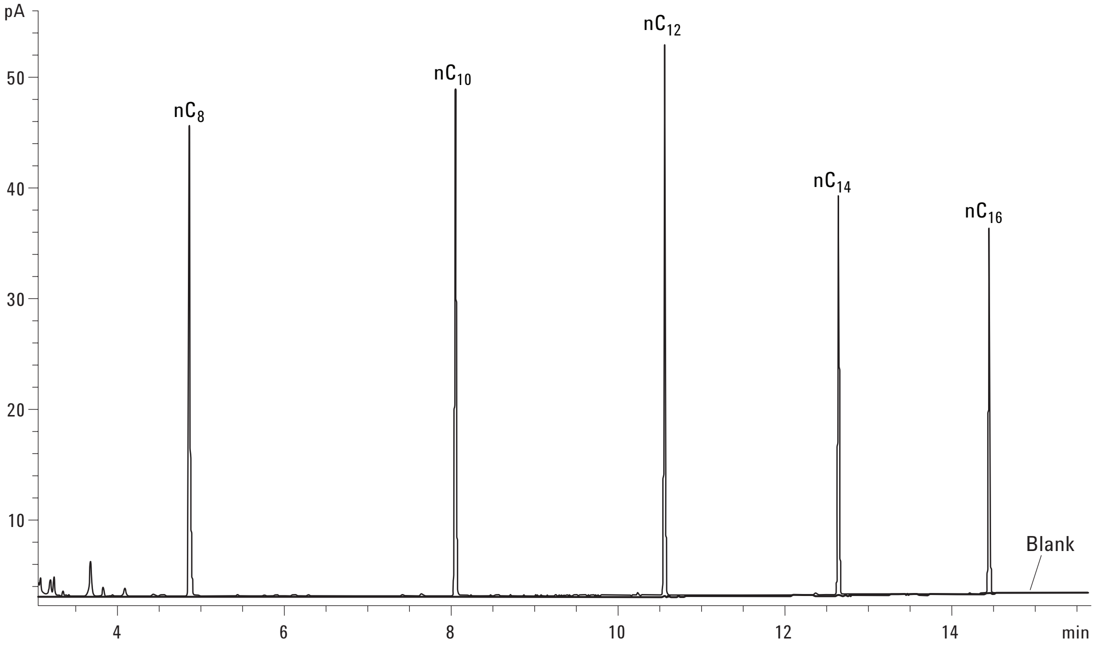


Figure 4. Overlay of standard versus blank (100 ppm each in cyclohexane).

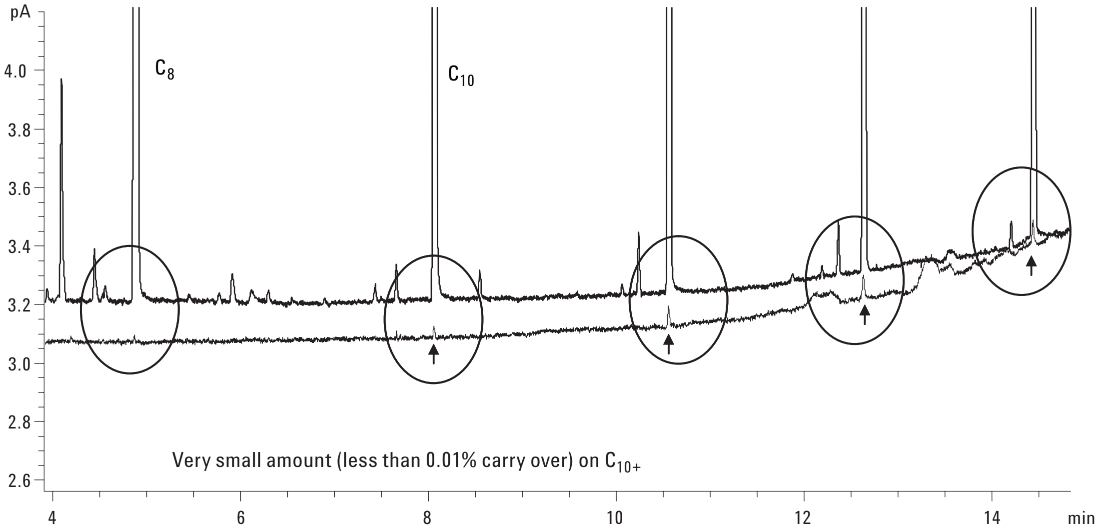


Figure 5. Carryover less than 0.01% on C_{10+}.

Sample Analysis

A series of glycols was used to model performance of the device for highly polar analytes. Minimal peak tailing is seen, due in part to the inertness of the needle interface. Also, carryover is very low.

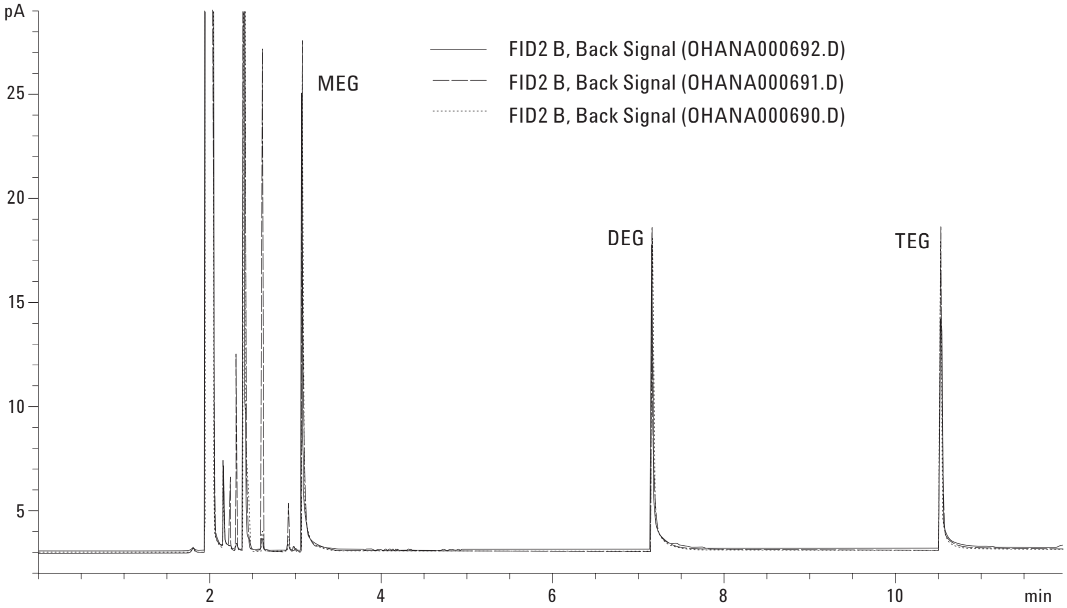


Figure 6. Triplicate run of 100 ppm each of MEG, DEG, and TEG in IPA.

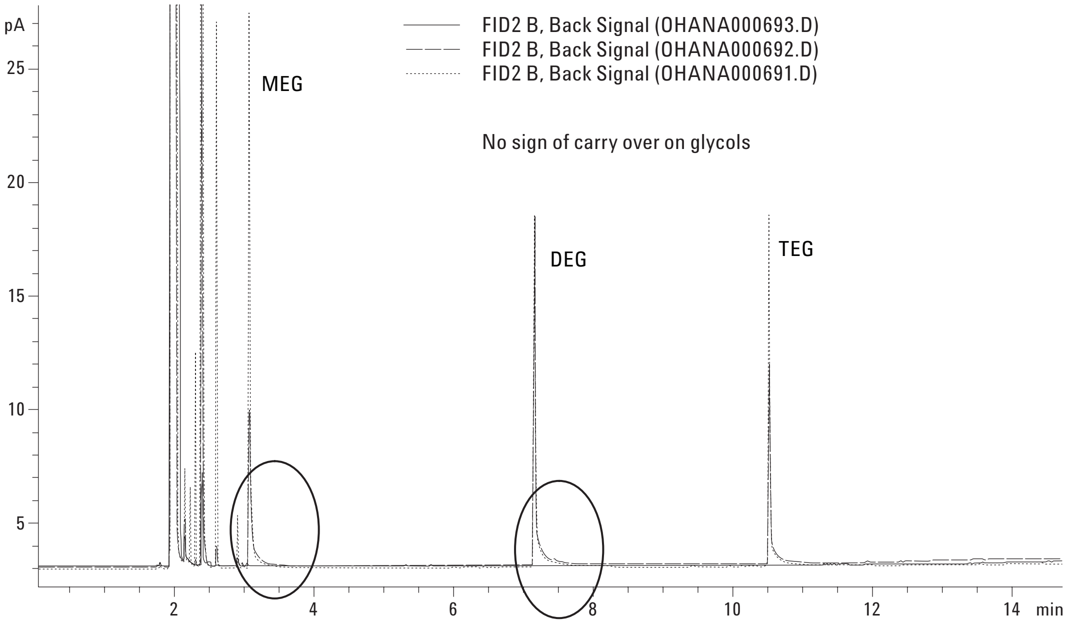


Figure 7. Glycols versus blank. Two standard duplicates, blank run immediately after injection of standard.

A. Liquefied Natural Gas

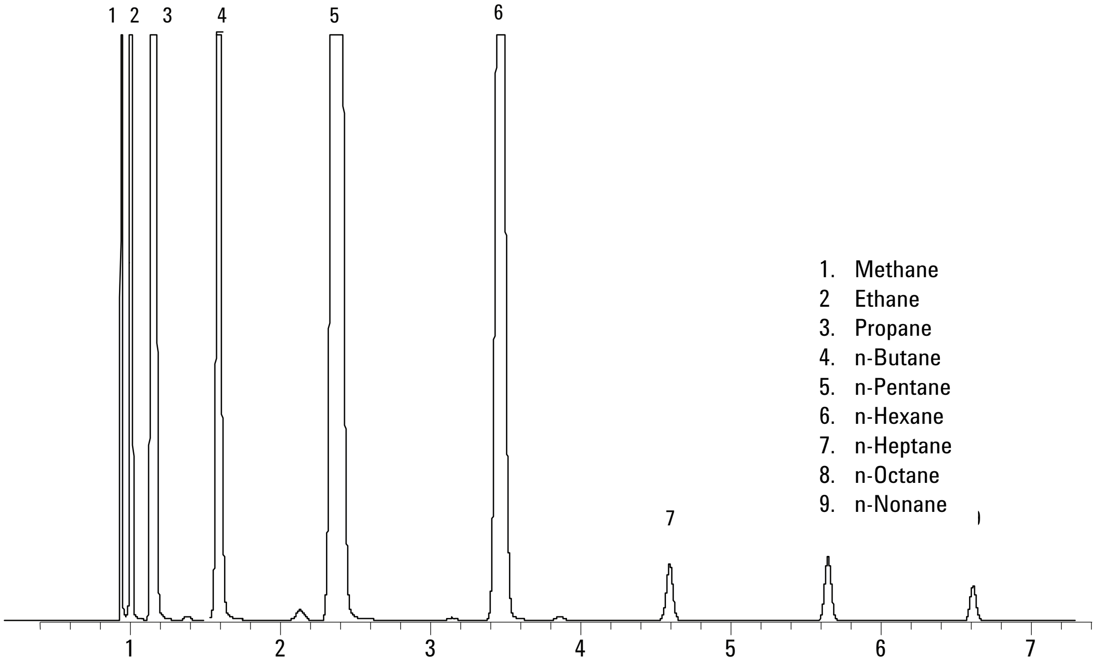


Figure 8. Chromatogram of liquefied natual gas (calibration standard).

Low discrimination is seen in Figure 8 for liquefied natural gas (LNG). Excellent repeatability is obtained with RSDs of less than 1%.

B. Liquefied Ethylene

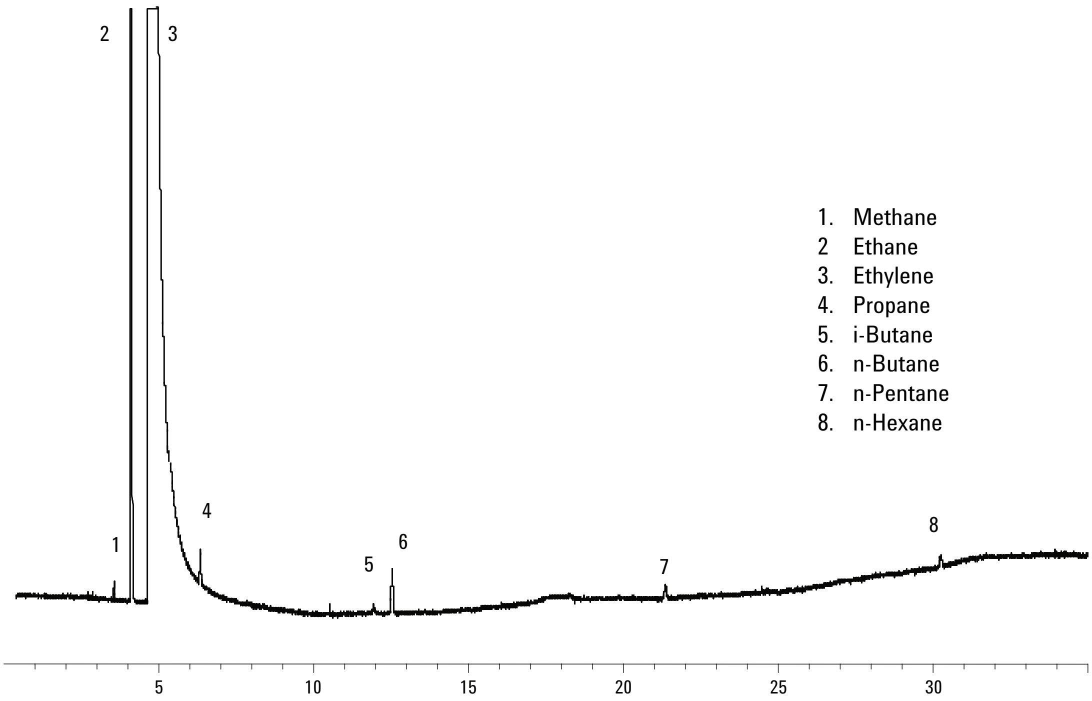


Figure 9. Chromatogram of liquefied ethylene.

The sample in Figure 9 is analyzed by ASTM D6159, "Standard Test Method for Impurities in Ethylene by Gas Chromatography." The method detection limits (MDLs) for the two methods are listed in Table 3.

The MDL using the HPLI device is 10 times lower than reported in the ASTM method due largely to the lack of peak tailing.

Table 3. MDLs (ppm V) by ASTM D6159 and HPLI

Components	ASTM D6159	HPLI
Methane	5.57–62.3	0.27
Ethane	35.1–338	0.78
Propane	8.07–59.7	0.88
i-Butane	7.74–48.4	0.38
Butane	4.97–56.1	1.61
n-Pentane		0.61
n-Hexane		0.74

C. Pressurized Propylene

This sample is analyzed by the same conditions as in ASTM D6159 (above method for ethylene analysis). The chromatogram is shown in Figure 10.

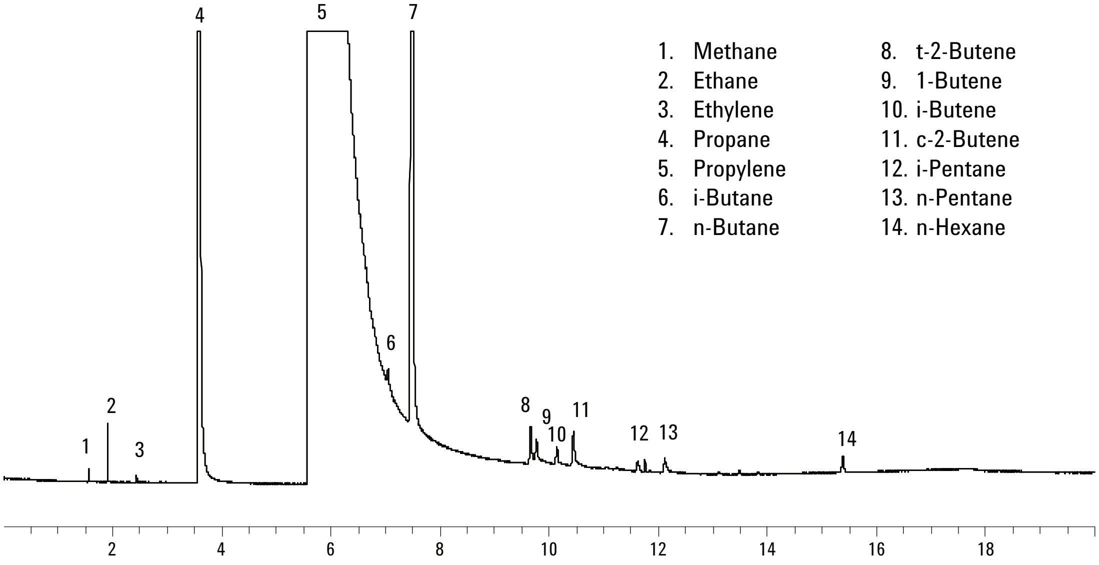


Figure 10. Chromatogram of pressurized propylene.

D. Pressurized 1,3-Butadiene

As an example of C4 hydrocarbons analysis, Figure 11 shows a typical result for 1,3-Butadiene.

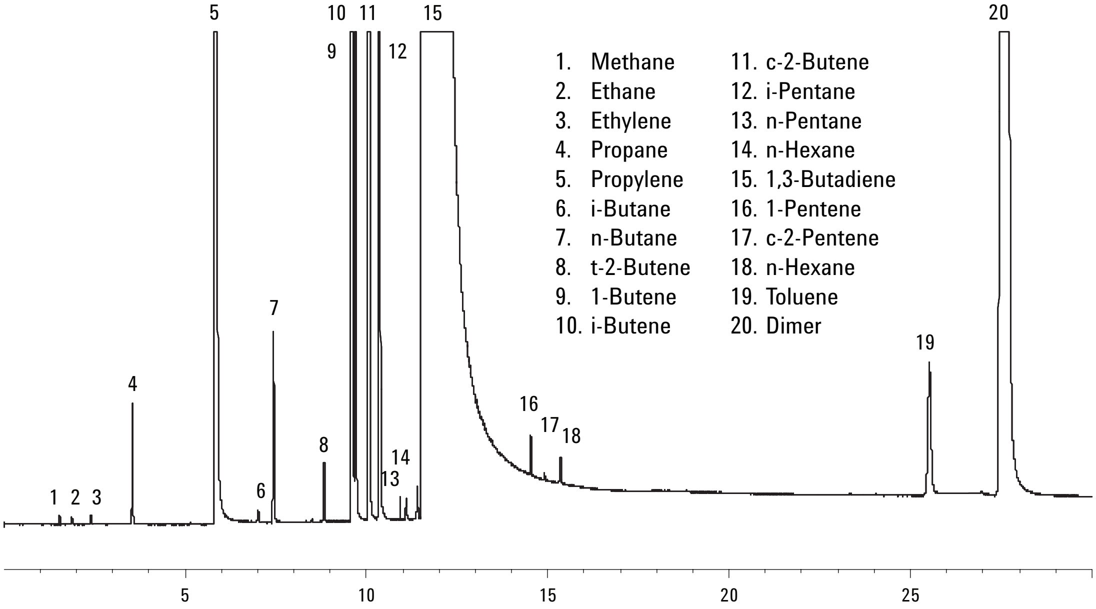


Figure 11. Chromatogram of pressurized 1,3-butadiene.

E. Pressurized Propane + n-Butane

This is a quantitative calibration sample:
Propane:n-Butane = 50%:50%.
The chromatogram is shown in Figure 12 with the results of a quantitative analysis shown in Table 4.

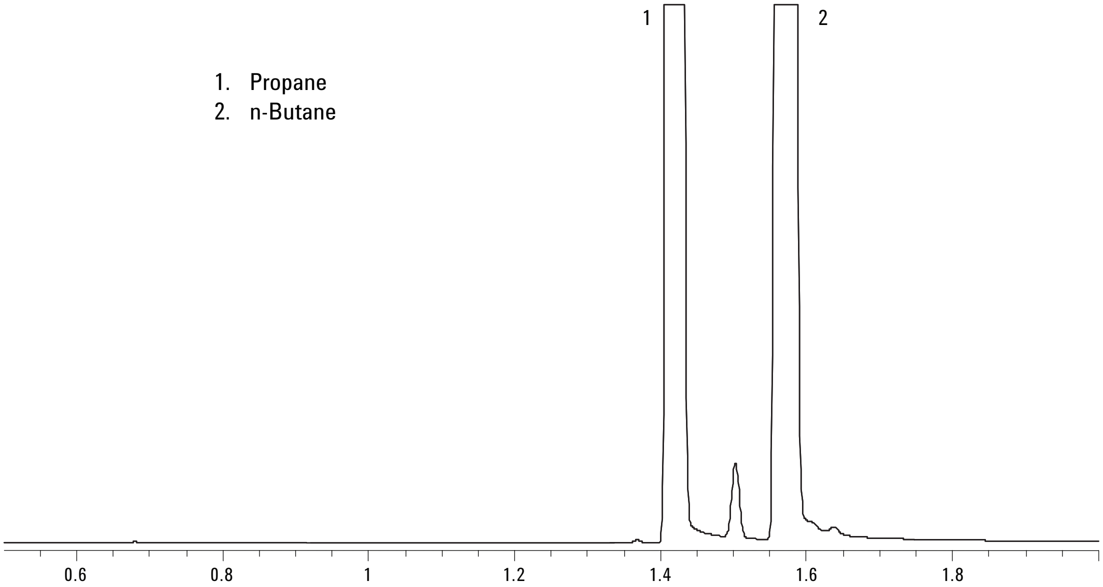


Figure 12. Chromatogram of pressurized propane + n-butane.

Table 4. Quantitative Analysis of Pressurized Propane 50.0% + n-Butane 50.0%. One Percent Difference Between the Blend (actual) and the Analysis Result

	Propane	**n-Butane**
Response factor	1.03	1.01
Density	0.5139	0.5788
Blend by V%	50.0	50.0
By wt%	47.031	52.969
Analysis		
By area%	45.441	54.559
By wt%	45.927	54.073

F. n-Hexane + 1.0% BP Standard (C5-C18)

To check the quantitative results, a small amount (1.0% BP standard) of C5 to C18 hydrocarbons was added to n-hexane (Figure 13). Table 5 shows the analytical results obtained by adding the C5 to C18 hydrocarbons with both the HPLI device and the automatic liquid sampler (ALS). In Figure 14, chromatograms by HPLI (top) and by ALS (bottom) are shown.

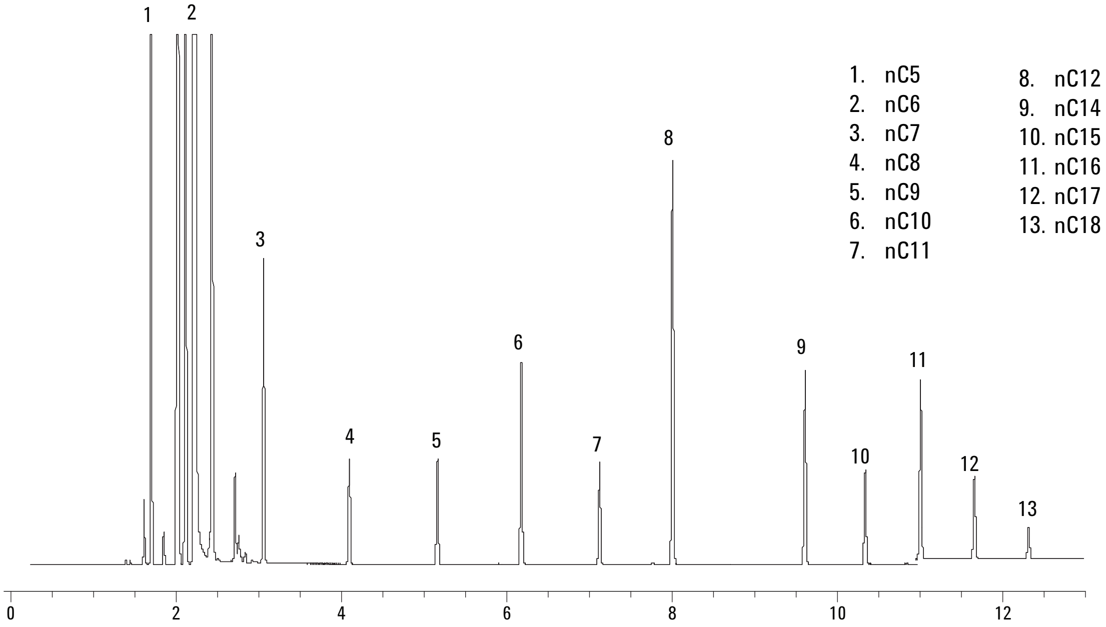


Figure 13. Chromatogram of n-hexane + 1.0% BP standard.

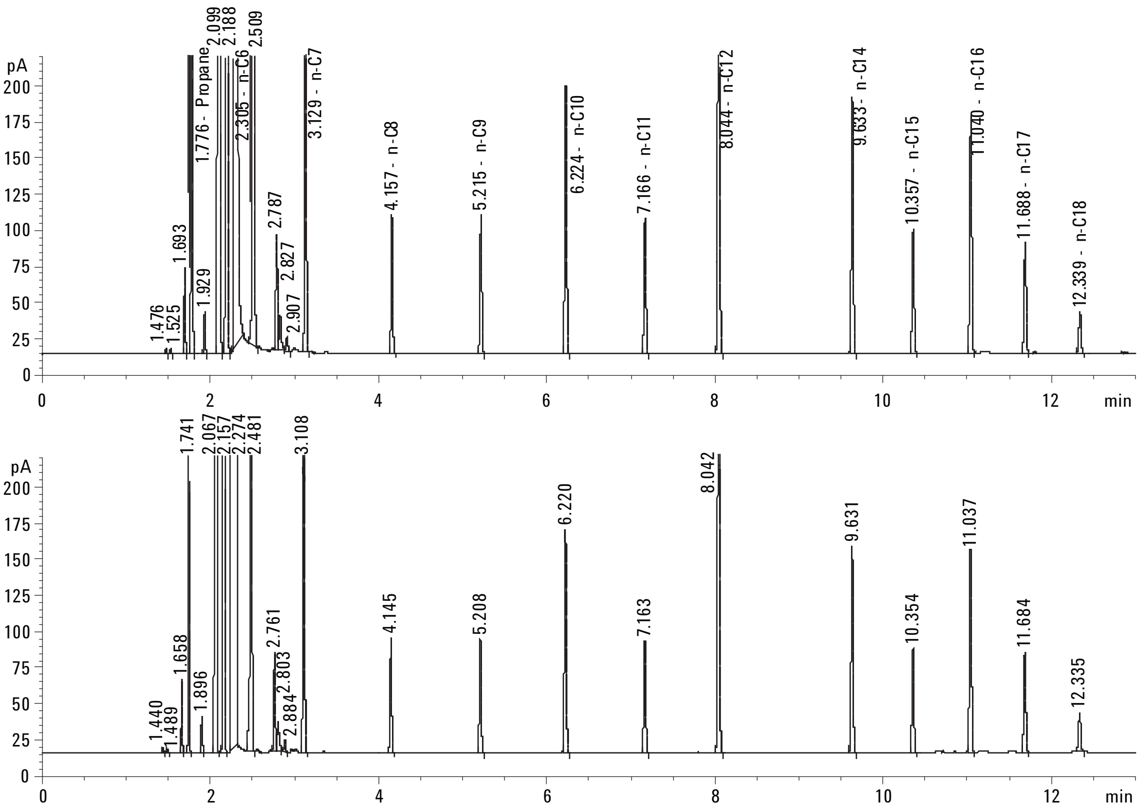


Figure 14. Chromatograms of n-hexane + 1.0% BP standard. Top: HPLI. Bottom: ALS (syringe).

Table 5. Analytical Results for C5-C18 by HPLI and ALS

	HPLI		AUTO INJECTOR	
COMPONENTS	**Area %**	**Width (min)**	**Area %**	**Width (min)**
nC5	0.282		0.279	
nC6	96.950	0.0209	96.922	0.0195
nC7	0.146		0.148	
nC8	0.0524		0.0532	
nC9	0.0537		0.0548	
nC10	0.109		0.111	
nC11	0.0550		0.0559	
nC12	0.219		0.221	
nC14	0.109		0.110	
nC15	0.0532		0.0547	
nC16	0.102		0.109	
nC17	0.0484		0.0546	
nC18	0.0203		0.0239	

The peak width of hexane at top: 0.0209 min
The peak width of hexane at bottom: 0.0195 min

There are no significant differences in quantitative results up to nC14. Compared with the results from an ALS injection, the HPLI device yields results about 10% lower in response above approximately nC16.

G. nC5-nC40 (D2887 BP Standard Diluted by CS_2)

A sample with hydrocarbons (nC5-nC40 D2887 1# BP standard diluted by CS_2) is also run on HPLI. The chromatogram is shown in Figure 15.

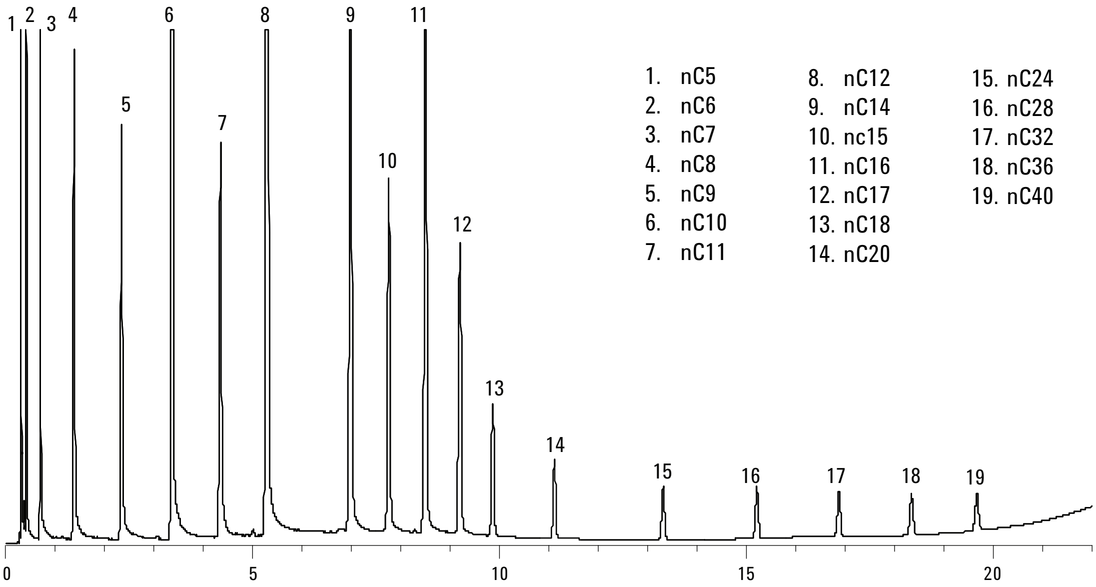


Figure 15. Chromatogram of nC5-nC40 (D2887 BP standard diluted by CS_2).

A lack of discrimination is seen with the HPLI device. In the future, it would be interesting to run some unstable condensates for evaluating the device.

From the above GC evaluation, excellent analytical results could be obtained using the HPLI device. These are summarized below.

1. Excellent repeatability
2. Capable of quantitative results
3. No significant peak width broadening
4. The wide boil point hydrocarbon samples could be analyzed by this device with minimal discrimination.

Conclusions

A unique sample injection device for the Agilent 7890A GC based on a unique deactivated interface and liquid rotary valve has been designed for sampling light petroleum matrices with broad boiling point distributions from methane to as high as C40. It is installed directly over a split/splitless GC inlet. The maximum sample pressure is 3,000 psig, although typical samples will have pressures under 1,500 psig. Various pressurized liquid samples have been tested on this device with high accuracy and precision. The sampler is quick to install and easy to operate. As with all high-pressure sampling systems, appropriate safety precautions must be followed.

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Acknowledgement

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Agilent Technologies

A Column-Flow Independent Configuration for QuickSwap

Application

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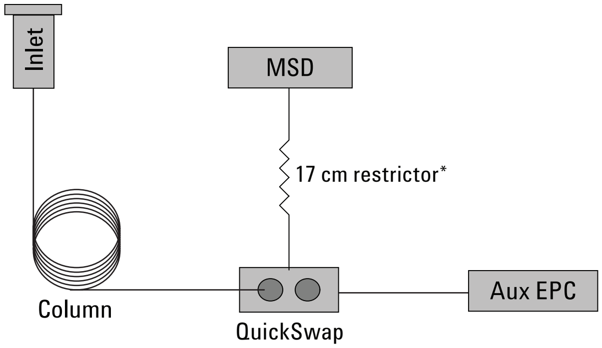
Abstract

A flexible configuration of QuickSwap is presented that allows use of larger id columns, pressure pulse injections, and variable column flow rates without having to change the restrictor or QuickSwap pressure. The split configuration can be set up such that the MSD is run at optimal flow rate. Examples are presented for several different columns and experimental conditions.

Introduction

QuickSwap is a recently introduced Capillary Flow Technology device designed to improve the usability of GC/MSD systems. It allows you to change columns and do inlet maintenance without venting the mass spectrometer. It also facilitates use of the backflush technique. The basic concepts, benefits, and use of QuickSwap are described in several Agilent Technologies publications [1-4] and are illustrated in Figures 1 and 2.

As can be seen from Figure 1, if the column is disconnected from QuickSwap, a flow of inert gas from the Aux EPC will prevent air from entering the MSD.



*QuickSwap restrictor, P, and T are selected for desired flow to MSD, usually the maximum flow that the current application requires.

Figure 1. General concept of QuickSwap.

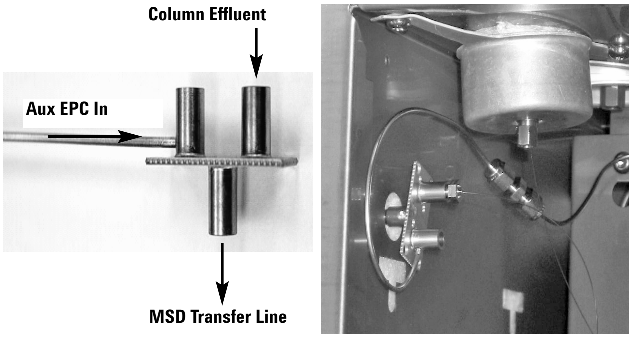


Figure 2. QuickSwap is pictured on the left showing permanent (Aux EPC In) and temporary connections. A picture of a normal QuickSwap installation is shown on the right.

In the standard configuration of QuickSwap, you must determine before installation what the maximum expected flow will be from the analytical capillary column being used. This value is in turn used to select the proper restrictor size (the four available sizes are 92 µm, 100 µm, 110 µm, and 120 µm id), the transfer line temperature, and QuickSwap pressure.

If the flow from the analytical column exceeds that originally planned for, then the pressure at QuickSwap will exceed its setpoint and the GC will go "not ready." This can happen if you do any of the following:

- Do pressure pulse injections, wherein the flow during injection is typically two to three times that during the run
- Increase column flow rate, as you might do when doing a method speed-up with method translation
- Do a retention time locking calibration, where inlet pressure is increased 20% over the nominal pressure
- Change to larger-dimension columns

In these examples, you would need to increase QuickSwap pressure and/or lower restrictor temperature or cool the system and install a new restrictor in order to accommodate the higher flows.

On the other hand, if you were to use a restrictor that allowed excess flow to the MSD, method performance (for example, detection limit and linear dynamic range) might be worse. So, it is important to plan carefully when using the normal QuickSwap configuration to get the right balance in performance and usability.

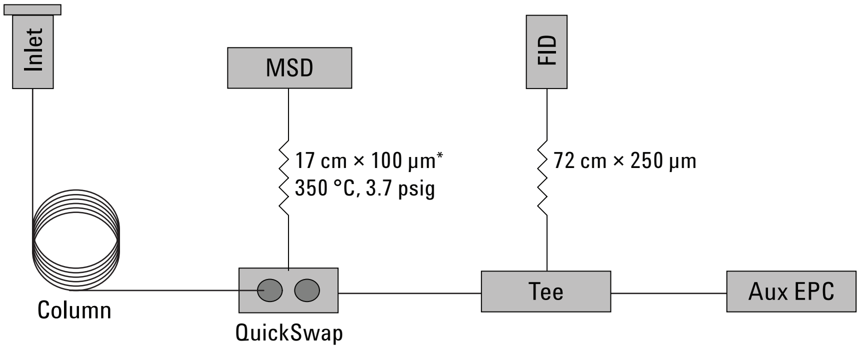
In general, when flow to the MSD changes,

- Tune parameters can change
- Response can change
- S/N and limit of detection can change

An alternate configuration was conceived of that allows the MSD to be run at optimal flow rate and improves flexibility and usability of QuickSwap [QS] in a wider range of potentially useful situations. This configuration incorporates a split between the Aux EPC module and QS and is illustrated in Figure 3.

This configuration has several advantages over the standard configuration. It:

- Simplifies initial setup (restrictor choices)
- Simplifies changes to existing methods



*In this example, the restrictor, transfer line temperature, and QuickSwap pressure were chosen to allow approximately 1 mL/min flow to the MSD—corresponding to its optimal performance regime.

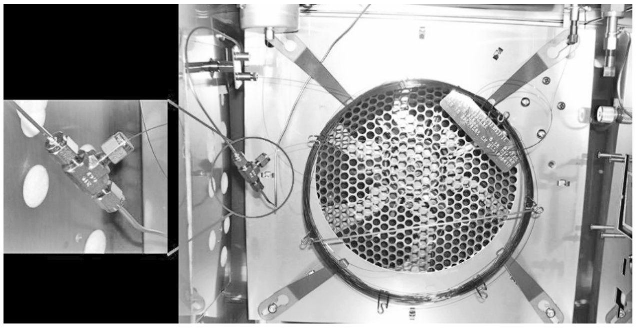
Figure 3. Flexible configuration includes addition of a split vent path on the Aux EPC line leading to QuickSwap.

- Simplifies retention time locking applications with QS
- Allows pressure pulse injections without having to change QS restrictor
- Allows more aggressive backflush conditions than if larger restrictors were used
- Allows method translation and speed up without having to change QS restrictor
- Allows use of medium- and large-bore columns with MSD

In some applications, there are some valid reasons why you might consider larger-bore capillary columns. These include:

- Higher sample capacity (solvent peaks don't tail as much, polar solutes don't front as much)
- Better robustness (better able to handle dirty samples)
- More amenable to large-volume injections—especially the solvent vapor exit version
- Less problematic cool on-column injections (more rugged larger id needles can be used)

However, the problem of higher flow rates associated with larger id columns has limited applications in GC/MS. MSD users are probably aware that there is an optimum flow above which MSD performance degrades. For most MSDs with electron impact sources and standard drawout lenses, optimal performance coincides with a flow rate range of 1 to 1.5 mL/min. Above that, signal and S/N fall approximately linearly with respect to flow rate increases.



Experimental

An 80-ppm mixture of semivolatiles and surrogates was selected based on a validated "fast" USEPA 8270 method [5]. A reference chromatogram is shown in Figure 4.

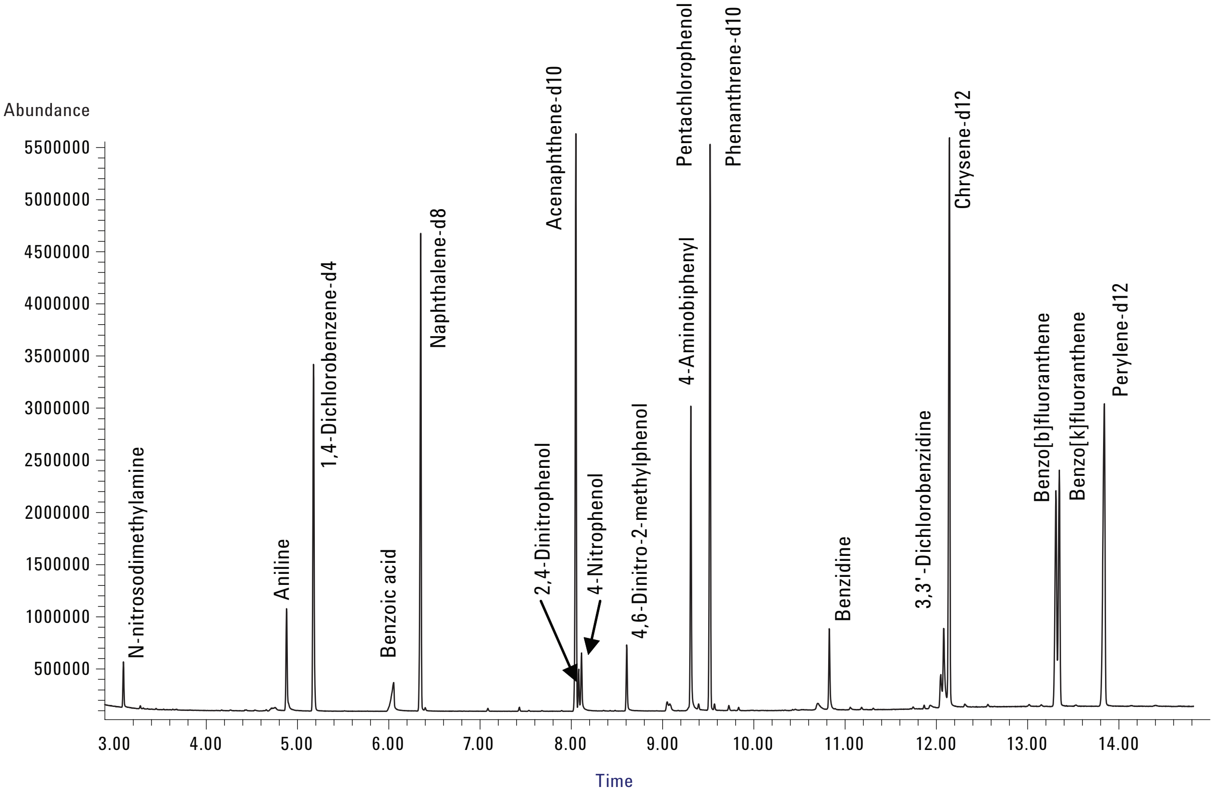


Figure 4. Reference chromatogram for Fast 8270 method.

Restrictor and setpoints were chosen for the flexible split configuration such that approximately 1 mL/min would go to the MSD. Several different combinations of QuickSwap restrictor and setpoints could be used to yield a flow rate in the optimal range for MSD with EI source. These are listed in Table 1.

Table 1. Restrictor and Setpoint Combinations Corresonding to the Optimal Flow Rate Range of the MSD

QuickSwap restrictor id (µm)	QuickSwap pressure (psig)	Transfer line temperature (°C)	Flow to MSD (mL/min)
92 (G3185-60361)	4.0	250	1.0
92	4.0	195	1.2
100 (G3185-60362)	3.7	350	1.0
100	2.7	250	1.2
110 (G3185-60363)	0.5	350	1.0
110	1.4	325	1.2

Referring back to Figure 3, now let's examine the flexible QuickSwap configuration in more detail. In this study, the 1/16-inch Swagelok union connecting the line from QuickSwap to that coming from the Aux EPC was replaced with a stainless steel tee (refer to the parts list). To the third leg of the tee, a restrictor was added leading to a flame ionization detector (FID) to allow monitoring of vented material. In an alternate configuration, one can put the tee outside the oven by cutting the Aux EPC tubing on the top of the GC, and then plumb the restrictor to a separate split vent trap (such as that used to trap vented sample on the split/splitless inlet; refer to the parts list). This configuration is recommended to capture potentially noxious sample components that are vented if an FID is not being used to combust them. The split vent trap cartridge is also easily replaced with a fresh one if and when it is necessary.

The dimensions of the vent restrictor is not as critical as the one used for QuickSwap. The vent flow rate needs to be more than that reasonably expected for the analytical column used and experiments to be conducted. However, there is little downside to using a restrictor with "moderately excessive flow," except that one is wasting clean purge gas from the Aux EPC. In this example, the restrictor was chosen to yield approximately 10 mL/min at the initial oven temp (50 °C) and QuickSwap pressure (3.7 psig).

For experiments where the column flow is less than the 1 mL/min nominal flow to the MSD, makeup gas would be supplied by the Aux EPC to make up the difference and pure purge gas would vent through the FID. In those cases where the column flow exceeds 1 mL/min, the excess would back up the Aux EPC line to the tee, where it will mix with the purge gas and be vented to the FID and detected. In effect, any flow > 1 mL/min is vented while the flow to the MSD remains constant at its optimum.

To test the flexibility of this configuration, several different sizes of columns and several different flow rates were examined using the same semivolatiles sample used earlier. The columns and conditions are listed in Table 2. Again, constant pressure mode conditions were chosen to yield approximately the same void times for the three different columns so that solute retention times would be similar. Later, other flows were tried as were constant flow modes.

Table 2. Conditions for Constant Pressure Mode Experiments (Void times nominally matched at 1.239 min. Conditions: Oven program: 50 °C (1 min) → 350 °C (3 min) @ 20 °C/min; QuickSwap restrictor = 17 cm x 100 µm id at 3.7 psig and 350 °C, yielding 1.0 mL/min flow to MSD; 0.5 µL splitless injection with a 2-min purge delay, inlet at 275 °C)

Dimensions	Head pressure	Initial flow (@ 50 °C)	Ending flow (350 °C)	Relative capacity
20 m x 180 µm	20.5 psig	0.70 mL/min	0.23 mL/min	1 X
30 m x 250 µm	23.4 psig	2.18 mL/min	0.72 mL/min	2.2 X
30 m x 530 µm	7.93 psig	6.85 mL/min	2.26 mL/min	18 X

The results of the comparison are shown in Figure 5. Several points are worth stating.

1. Columns were quickly switched without venting the MSD (a key benefit of QuickSwap).
2. No pump down, retuning, or equilibration time were required prior to applying new pressure setpoints and acquiring data for the different columns.
3. The retention times are approximately the same on each column—a result of determining the setpoints that would yield the same void time.
4. Peak widths, shapes and heights reflect a composite of chromatographic phenomena such as relative stationary phase capacities, column efficiencies, deviation of actual flow from optimal flow, and the amount of post-column split to vent. For example, one might think that the 180-µm id column should have the narrowest peaks (highest efficiency); however, one can see from Table 2 that the flow rate decreases from the optimal flow rate of 0.7 mL/min at the start of the run to well below that at the end. This will cause peaks to be wider than they would be at optimal flow. In contrast, the flow rate of the 250-µm id column starts higher than the 1 mL/min optimal flow but remains at an optimal or faster-than-optimal rate for most of the run. This will cause the peak widths for the 250-µm id column to be narrower than that of the 180-µm id column.
5. The benzoic acid peak (#4) is less distorted on the 530-µm id column as a consequence of the larger column capacity. This is one of the benefits of using larger id columns.
6. The relative elution order is the same for the three columns. This is a consequence of matching void times and using constant pressure mode. This would not be the case when using constant flow mode (see Figure 7).

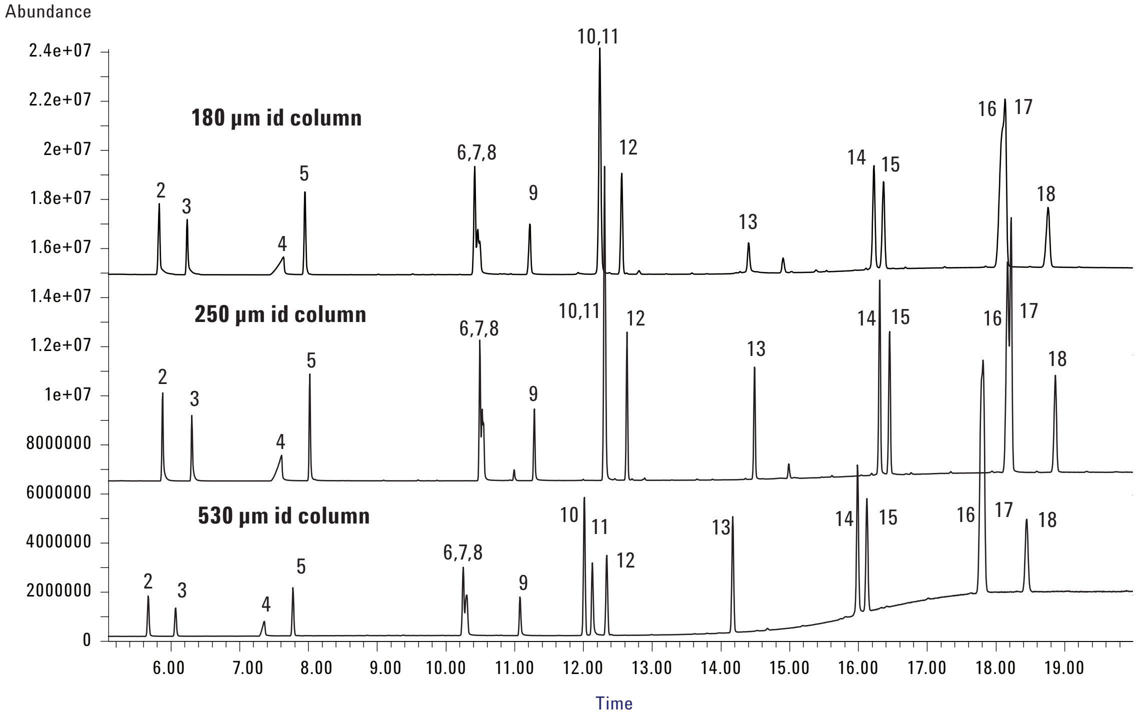


Figure 5. **Constant pressure mode analysis with three different column dimensions; 0.5-µL splitless injections of 80-ppm semivolatiles test sample, with flow conditions from Table 2.**

As can be seen in Figure 6, the FID signal indicates what was split to the FID when column flow exceeded the 1 mL/min flow to the MSD. At no time does the 180-µm id column flow exceed 1 mL/min, so there is nothing vented and no FID signal. For the 250-µm id column, the flow at initial conditions is > 1 mL/min, and the excess flow is split to the FID, as indicated by a solvent peak. Yet as flow decreases during the run (a normal consequence of constant pressure mode conditions), column effluent all goes to the MSD and FID signal remains flat. For the 530-µm id column, flow is always > 1 mL/min, so some flow is always being vented through the FID. This is easily seen in the inset of Figure 6, where the scale is expanded and peaks can be seen throughout the FID chromatogram.

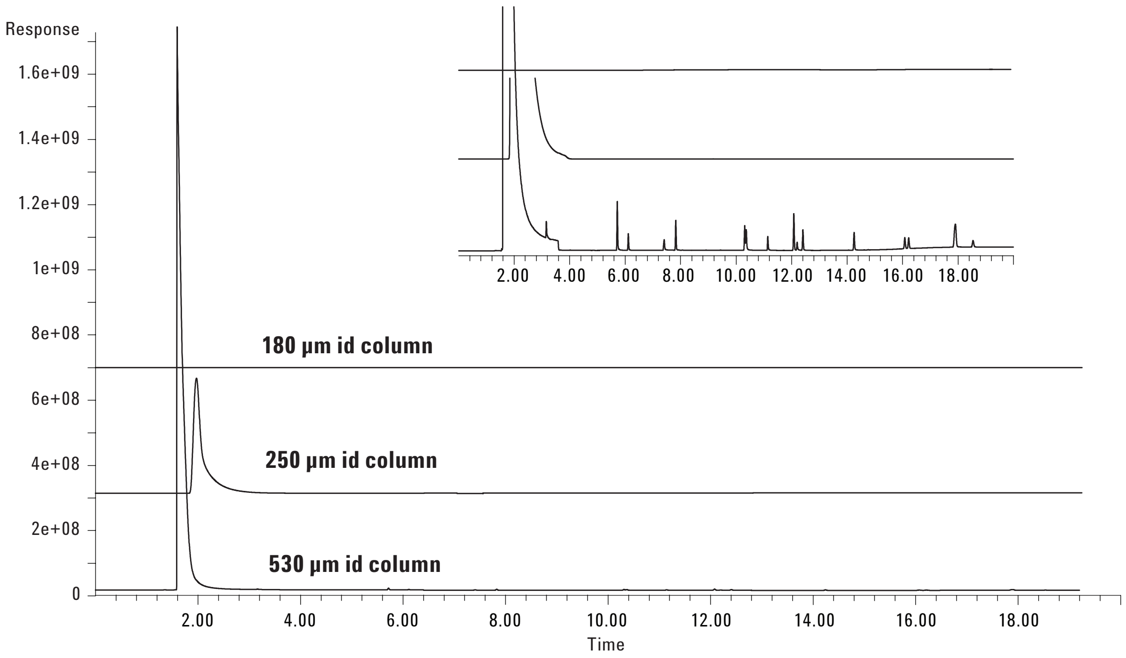


Figure 6. **FID signal of vent stream shows what is vented when column flow exceeds flow to MSD.**

Table 3. **Constant Flow Mode Conditions (Lower flow for each column is its optimal flow, the higher is 2X optimum. Other instrumental paramters were the same as those used for constant pressure mode experiments.)**

Dimensions	Outlet flow
20 m X 180 µm	0.72 mL/min
20 m X 180 µm	1.44 mL/min
30 m X 250 µm	2.5 mL/min
30 m X 250 µm	1.0 mL/min
30 m X 530 µm	2.1 mL/min
30 m X 530 µm	7.0 mL/min

Constant flow mode was also evaluated. Conditions for constant flow modes are given in Table 3. Two flow rates were chosen for each column: optimal flow rates (the lower of the two) and 2X optimum.

The MSD TIC for each column at optimal flow rates is shown in Figure 7, with the corresponding FID vent signal in Figure 8. It can clearly be seen that for the 250-µm and 180-mm id columns, no column effluent is split to the FID. Since the flow rate of the 530-µm id column is approximately 2X the flow the MSD, half of the column effluent is split to the FID.

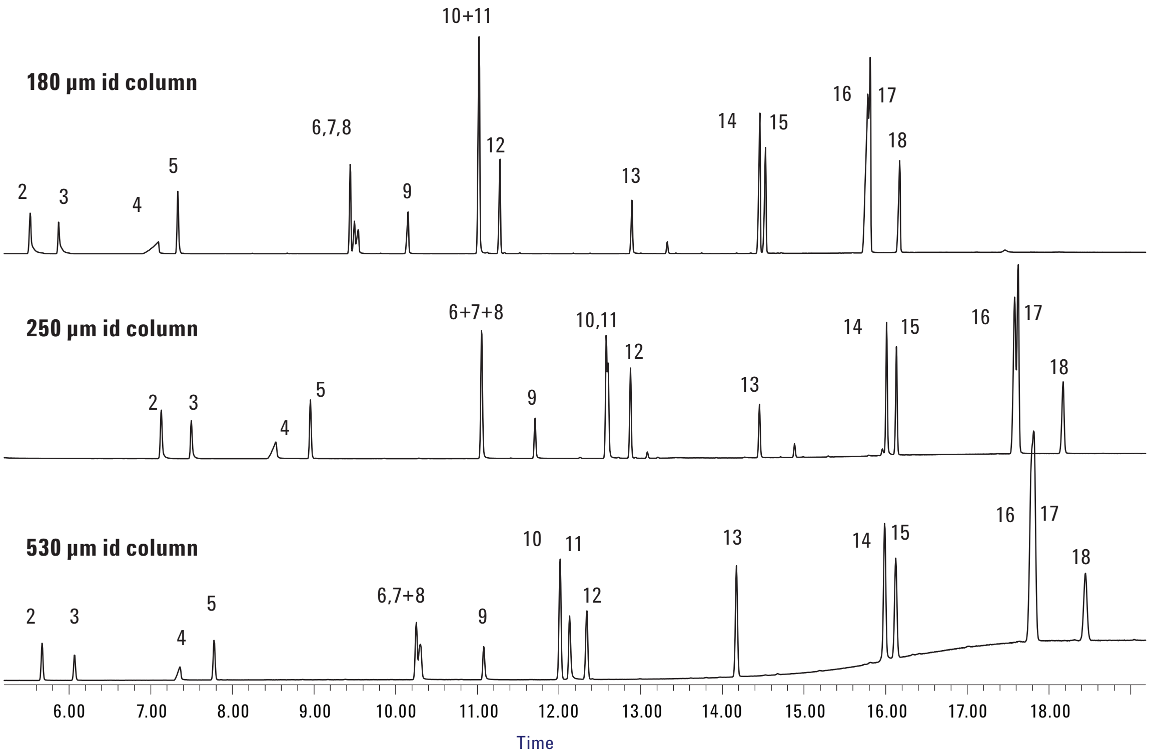


Figure 7. **TIC chromatograms for the three columns under optimal constant flow mode conditions.**

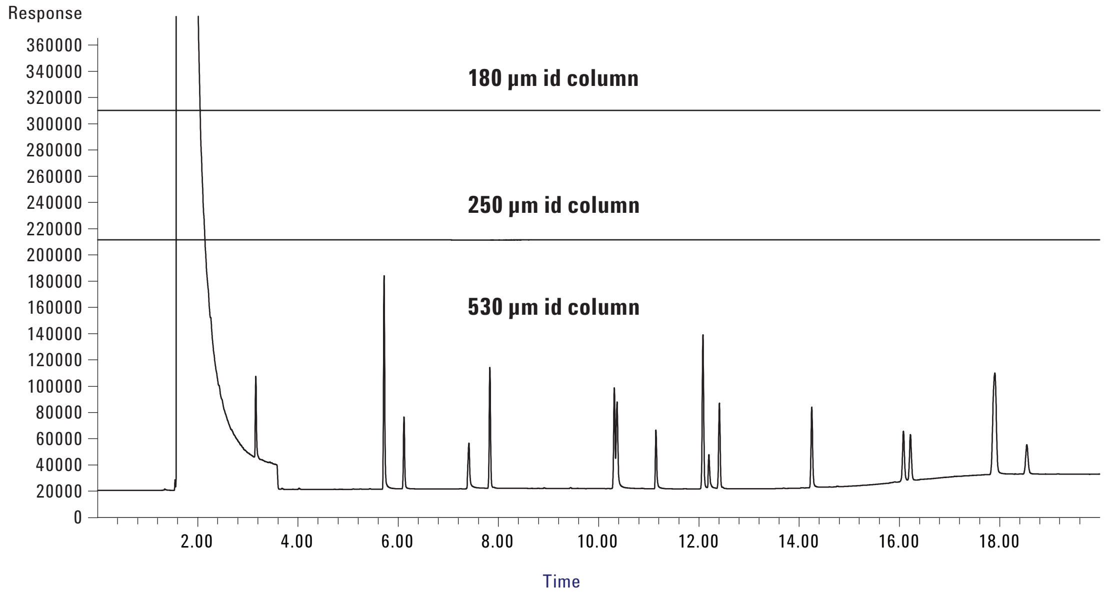


Figure 8. **FID vent signal for three columns under optimal flow conditions. Only the 530-µm id column has a flow that exceeds the 1 mL/min flow to the MSD.**

Results for the 2X optimal flow conditions are shown in Figures 9 and 10. The flexibility of the QuickSwap split configuration is highlighted here in that no adjustments were made to QuickSwap restrictor size, transfer line temperature, or Aux EPC pressure in order to accommodate all of the flow changes. Only the columns and their individual flow conditions were changed. The QuickSwap split passively accommodated all excess flow.

Notice in Figure 9 that the higher the excess column flow, the less of the sample goes to the MSD (more is split to vent, as seen in Figure 10). The fact that less sample is getting to the MSD might be considered a serious disadvantage for some analyses, but this is tempered by the fact that the larger column has higher sample capacity, so larger sample volumes could be injected without suffering overload (peak distortion). In addition, the larger diameter columns usually generate wider peaks, so a larger value can be selected for MSD sampling (for example, samples = 2^3 or 2^4 instead of 2^2). This will result in higher S/N. So, if one seeks the benefits of larger id columns for MS analysis, one can easily accommodate them with this QuickSwap configuration with only a small compromise.

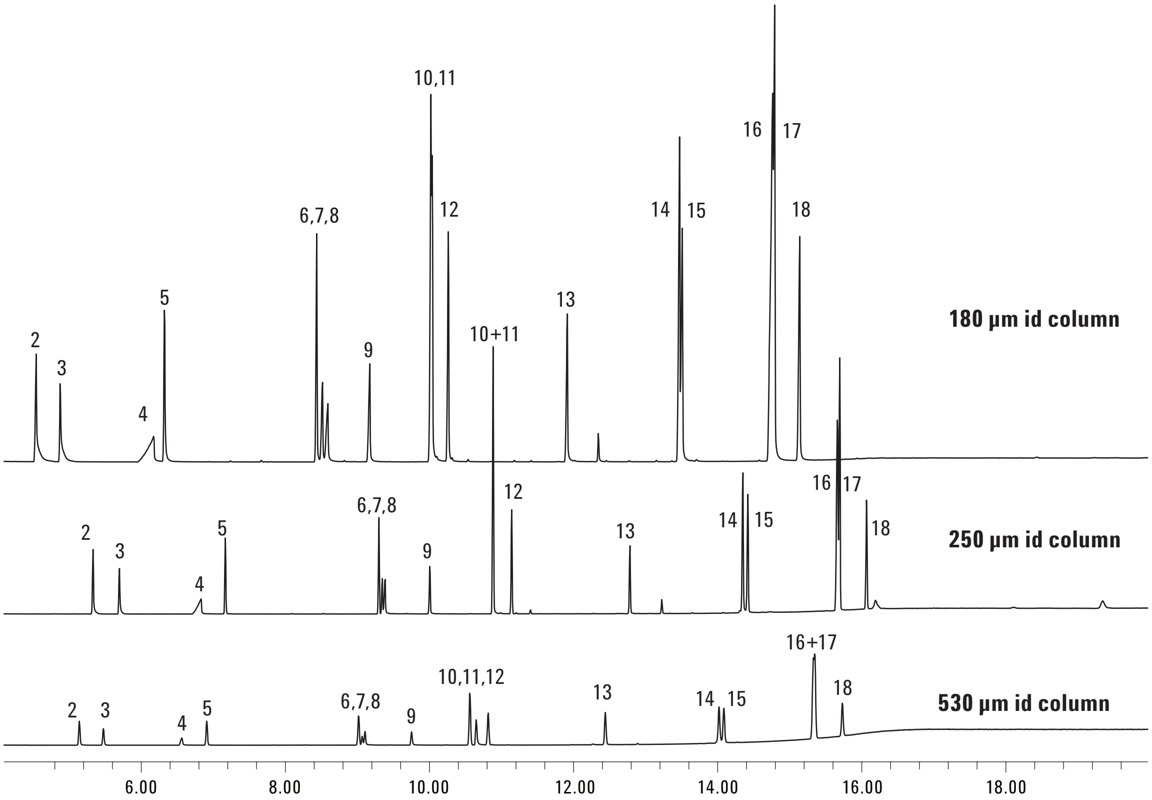


Figure 9. **Comparison of MSD TIC chromatograms for three columns run at 2X optimal constant flow mode. Scale is constant for the three, showing the absolute amount of sample reaching the MSD.**

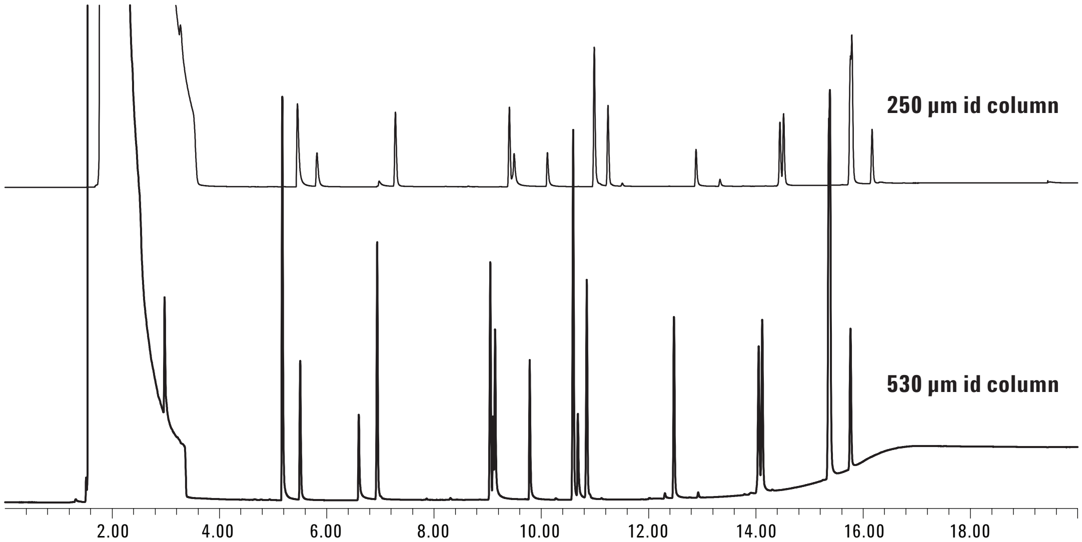


Figure 10. FID vent signals for the two largest columns operated at 2X optimal constant flow rate conditions.

Pressure-pulse injection is often used to minimize the time labile samples stay in the inlet and to avoid inlet overload when large volume sample injections. With this technique, pressures are typically two to three times the starting pressure of the standard analysis. As such, the flow through the column is increased significantly. In the standard QuickSwap configuration, this higher flow can exceed the ability of the chosen QuickSwap restrictor to handle at the selected QuickSwap (Aux EPC) pressure. When this happens, pressure exceeds the setpoint, the GC goes “not ready,” and automated injection does not proceed. With the flexible split configuration for QuickSwap described herein, the extra flow during pressure pulse injection is vented, so there is no issue with maintaining setpoint.

A pressure pulse injection was done with the 250-µm id column to verify that the split configuration would accommodate the extra flow. The pulse pressure was 50 psi (approximately two times the standard pressure) for 1 min, after which the pressure returned to 23.41 psig for the remainder of the run. For the standard run, the pressure was 23.41 psig for the whole time. No other changes were made to experimental conditions.

Figure 11 compares MSD TIC chromatograms for the standard and pulsed-pressure experiments. One can see a slightly earlier retention time for the first couple of peaks in the pressure pulse experiment (this is typical due to the higher initial column flows). Other than that, the chromatograms are indistinguishable.

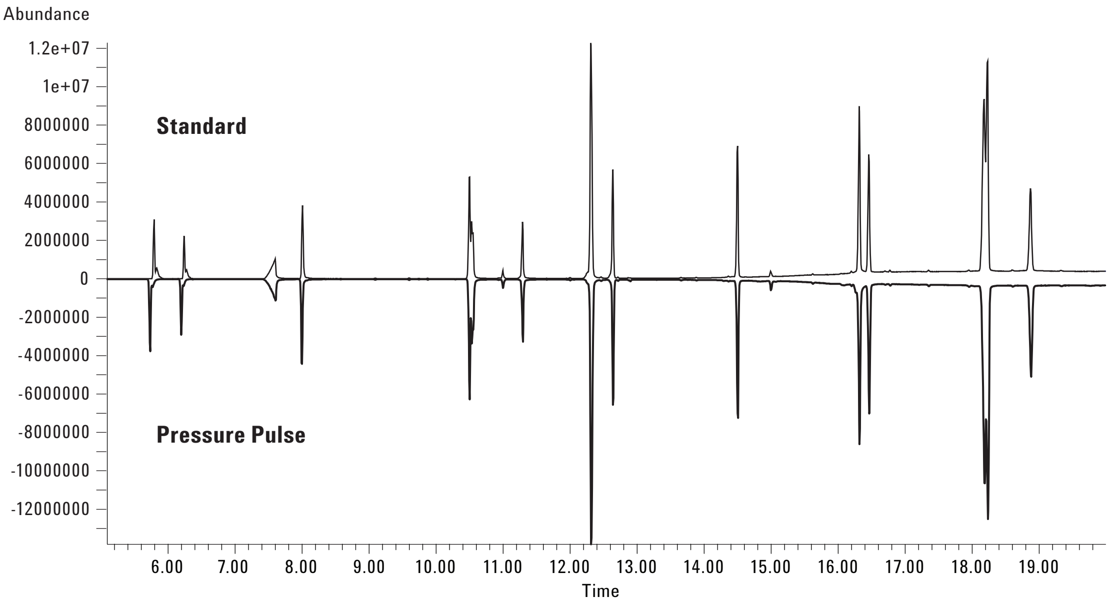


Figure 11. Comparison of standard and pressure-pulse injection modes. No adjustment of QuickSwap pressure was required for the pressure-pulse mode—a benefit of using QuickSwap split configuration.

As can be seen from the FID vent signal, (Figure 12), more solvent is vented in the pressure-pulse injection than in the standard because of the higher initial flow. Yet for the analytical portion of the run after completion of the pressure pulse period (1 min), the column flows are the same in the two cases and decrease to near or below 1 mL/min. As a result, there is no excess column flow to split to the FID and the FID baseline is flat.

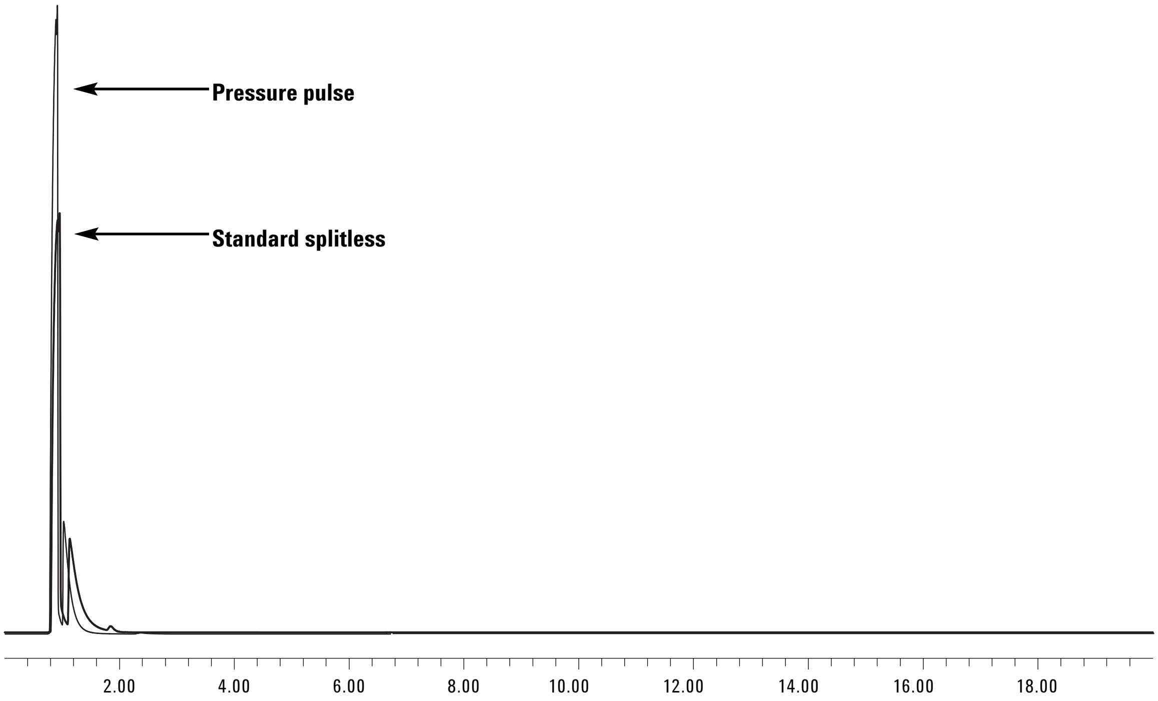


Figure 12. FID vent signal for pressure-pulse injection versus standard splitless injection.

Conclusions

The QuickSwap split configuration provides a flexible and simple alternative to the standard configuration. The split configuration can benefit MSD users who change columns frequently, seek the benefits of using larger id columns, and/or use pressure pulse injection. The configuration allows the MSD to run at optimal flow conditions while accommodating a wide range of column flows.

References

1. “How QuickSwap Works,” f03002.pdf.
2. “Agilent G3185B QuickSwap Accessory Installation and Setup,” Agilent publication number G3185-90100.
3. “Agilent G3185B QuickSwap Accessory Reference Manual,” Agilent publication number G3185-90101.
4. “Simplified Backflush Using Agilent 6890 GC,” Agilent publication number 5989-5111EN.
5. “Fast USEPA 8270 Semivolatiles Analysis Using the 6890N/5975 Inert GC/MSD,” Agilent publication number 5989-2981EN.

Parts List

Part	Description	Part number
QuickSwap	Kit	G3185B
QuickSwap restrictors	92 µm	G3185-60361
	100 µm	G3185-60362
	110 µm	G3185-60363
1/16" tee	Regular	0100-0782
	ZDV	0100-0969
SilTite 1/16" ferrules	For connecting 1/16" SS lines	G2855-2055
Deactivated FS	250-µm id FID vent restrictor	160-2255-5
Split vent trap	Kit—vent alternative to FID	G1544-0124
1/16" straight union		0100-0124
SilTite ferrules for capillary	250 µm	5188-5361
column connections	320 µm	5188-5362
	530 µm	5188-5363
20 m X 180 mm X 0.36 mm	DB-5.625	121-5622
30 m X 250 mm X 0.5 mm	DB-5MS	122-5536
30 m X 530 mm X 1 mm	DB-5	125-503J

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Agilent Technologies

Parallel GC for Complete Refinery Gas Analysis

Application

Hydrocarbon Processing

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Abstract

An Agilent 7890A gas chromatograph configured with three parallel channels with simultaneous operation provides a complete, high-resolution analysis for refinery gas in six minutes. The system uses an optimized combination of several packed columns and PLOT alumina columns to allow fast separation of light hydrocarbons and permanent gases with the same oven temperature program. A third channel with TCD with nitrogen (or argon) carrier gas improves the hydrogen sensitivity and linearity. This application also shows the excellent performance for natural gas analysis.

Introduction

Refinery gas is a mixture of various gas streams produced in refinery processes. It can be used as a fuel gas, a final product, or a feedstock for further processing. An exact and fast analysis of the components is essential for optimizing refinery processes and controlling product quality. Refinery gas stream composition is very complex, typically containing hydrocarbons, permanent gases, sulfur compounds, and so on. Successful separation of such a complex gas mixture is often difficult using a single-channel GC system. Three parallel channel analyses allow a separation problem to be divided into three sections. Each channel can optimize a particular part of the separation. TCD with helium carrier gas can be used for permanent gases analysis like O_2, N_2, CO, CO_2, H_2S, and COS. However, hydrogen has only a small difference in thermal conductivity compared to helium, making analysis by TCD using helium carrier gas difficult. To achieve full-range capability for hydrogen, an additional TCD with nitrogen or argon as a carrier is required. Light hydrocarbons are separated on an alumina PLOT column and detected on a FID.

The Agilent 7890A GC now supports an optional third detector (TCD), allowing simultaneous detection across three channels; this provides a complete analysis of permanent gases, including nitrogen, hydrogen, helium, oxygen, carbon monoxide, carbon dioxide, and hydrocarbons to nC_5, C_6+ fraction within six minutes.

Experimental

A single Agilent 7890A GC is configured with three channels, including one FID, and two TCDs. Light hydrocarbons are determined on the FID channel. One TCD with nitrogen or argon carrier is used for the determination of hydrogen and helium. The other TCD with helium carrier is used for the detection of all other required permanent gases. Figure 1 shows the valve drawing. The system conforms to published methods such as ASTM D1945 [1], D1946 [2], and UOP 539 [3].

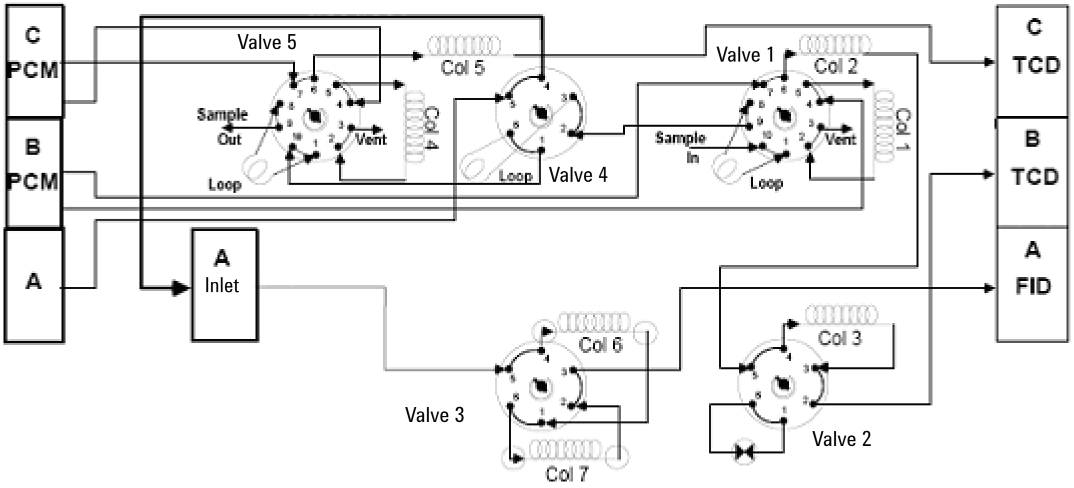
The FID channel is for light hydrocarbon analysis. The sample from valve 4 is injected via the capillary injector into valve 3 to permit an early backflush of the grouped heavier hydrocarbons (normally C_6+). Valve 3 is a sequence reversal with a short DB1 (column 6) for separating the hexane plus fraction (C_6+) from the lighter components. C_1 through C_5 hydrocarbons are separated on a PLOT alumina column. As soon as the light components C_1 through C_5 pass through the DB1column, valve 3 is switched to reverse the sequence of the DB1 and PLOT aluminum column so that components heavier than nC_6, including nC_6, are backflushed early. As a result, group C_6+ is followed by the individual hydrocarbons from the PLOT alumina column.

A new tube connector based on capillary flow technology is used to connect the valve to the capillary column to enhance the hydrocarbons analysis by improving the peak shape.

The second TCD channel (B TCD) employs three packed columns and two valves for the separation of permanent gases including O_2, N_2, CO, and CO_2 using helium as a carrier gas. Valve 1 is a 10-port valve used for gas sampling and backflushing heavier components; normally components heavier than ethylene are backflushed to vent when H_2S is not required to be analyzed. A six-port isolation valve (valve 2) with adjustable restrictor is used to switch the molecular sieve 5A column in and out of the carrier stream. Initially, the isolated valve is in the OFF position so that unresolved components air, CO, and CH_4 pass quickly through the HayeSep Q (column 2) onto the molecular sieve (column 3). The valve is then switched to the ON position to trap them in column 3 and allow the CO_2 to bypass this column. When the CO_2 has eluted, valve 2 is switched back into the flow path to allow O_2, N_2, CH_4, and CO to elute from the molecular sieve column.

The third TCD channel (C TCD) is for the analysis of H_2. Sample from the 10-port valve (valve 5) is injected into a precolumn (column 4, HayeSep Q) when H_2 with its coeluted compounds O_2, N_2, and CO pass through the short precolumn HayeSep Q onto the molecular sieve 5A column (column 5). Valve 5 is switched so that CO_2 and other compounds will be backflushed to vent, while H_2 is separated on the molecular sieve 5A.

Typical GC conditions for fast refinery gas analysis are listed in Table 1. The refinery gas standard mixture that was used for the method develoment is listed in Table 2.



Column 1 HayeSep Q 80/100 mesh
Column 2 HayeSep Q 80/100 mesh
Column 3 Molsieve 5A 60/80 mesh
Column 4 HayeSep Q 80/100 mesh

Column 5 Molsieve 5A 60/80 mesh
Column 6 DB-1
Column 7 HP-PLOT Al_2O_3
PCM: Electronic pneumatics control (EPC) module

Figure 1. RGA valve system.

Table 1. Typical GC Conditions for Fast Refinery Gas Analysis

Valve temperature	120 °C
Oven temperature program	60 °C hold 1 min, to 80 °C at 20°C/min, to 190 °C at 30 °C/min
FID channel	
Front inlet	150°C, split ratio: 30:1 (uses higher or lower split ratio according to the concentrations of hydrocarbons)
Column	6: DB-1 7: HP-PLOT Al2O3 S
Column flow (He)	3.3 mL/min (12.7 psi at 60 °C), constant flow mode
FID	
Temperature	200 °C
H_2 flow	40 mL/min
Air flow	400 mL/min
Make up (N_2)	40 mL/min
Second TCD channel	
Column	1: HayeSep Q 80/100 mesh 2: HayeSep Q, 80/100 mesh 3: Molecular sieve 5A, 60/80 mesh
Column flow (He)	25 mL/min (36 psi at 60 °C), constant flow mode
Procolumn flow (He)	22 mL/min at 60 °C (7 psi), constant pressure mode
TCD	
Temperature	200 °C
Reference flow	45 mL/min
Make up	2 mL/min
Third TCD channel	
Column	4: HayeSep Q 80/100, mesh 5: Molecular sieve 5A, 60/80, mesh
Column flow (N_2)	24 mL/min, (26 psi at 60 °C), constant flow mode
Procolumn flow (N_2)	7 psi, (24 mL/min at 60 °C), constant pressure mode
TCD	
Temperature	200 °C
Reference flow	30 mL/min
Make up	2 mL/min

Table 2. RGA Calibration Gas Standards

	Compound	% (V/V)		Compound	% (V/V)
1	Methane	5.98	15	i-Pentane	0.101
2	Ethane	5.07	16	n-pentane	0.146
3	Ethylene	2.99	17	1,3-Butadiene	1.46
4	Propane	8.04	18	Propyne	0.476
5	Cyclopropane	0.50	19	t-2-Pentene	0.195
6	Propylene	3.04	20	2-Methyl-2-butene	0.149
7	i-Butane	2.71	21	1-Pentene	0.094
8	n-Butane	2.11	22	c-2-Pentene	0.146
9	Propadiene	0.94	23	n-Hexane	0.099
10	Acetylene	1.72	24	H_2	15.00
11	t-2-Butene	1.55	25	O_2	2.00
12	1-Butene	1.00	26	CO	1.50
13	i-Butene	0.808	27	CO_2	3.00
14	c-2-Butene	1.230	28	N_2	BL

Results and Discussion

Enhance Gas Analysis with Union Connector

The system uses the new union connector based on capillary flow technology for connecting the capillary column to the valve, enhancing the peak shapes in gas analysis and making the connections easier. Figure 2 shows the comparison of peak shapes obtained from a traditional polyamide connector and the new union connecter. With the new union connecter the improvement in peak shape is readily apparent.

Fast Refinery Gas Analysis (RGA)

Use of an optimized combination of several packed columns and a PLOT alumina column allows fast separation of light hydrocarbons and permanent gases with the same oven temperature program without the need of an additional oven.

The separation results from each channel are illustrated in Figure 3.

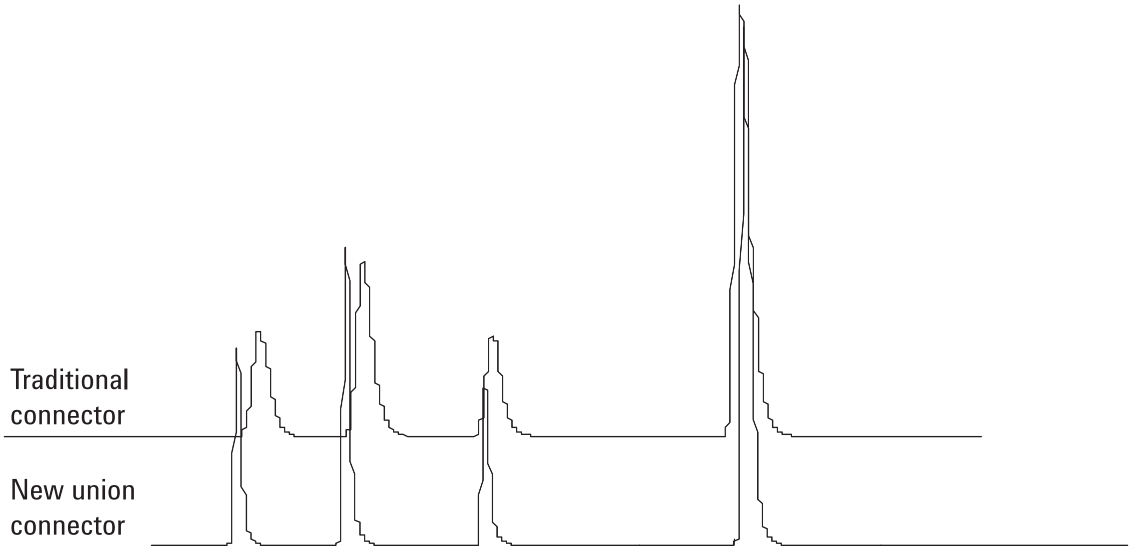


Figure 2. **Hydrocarbon peaks obtained from traditional tube connector and new union connector.**

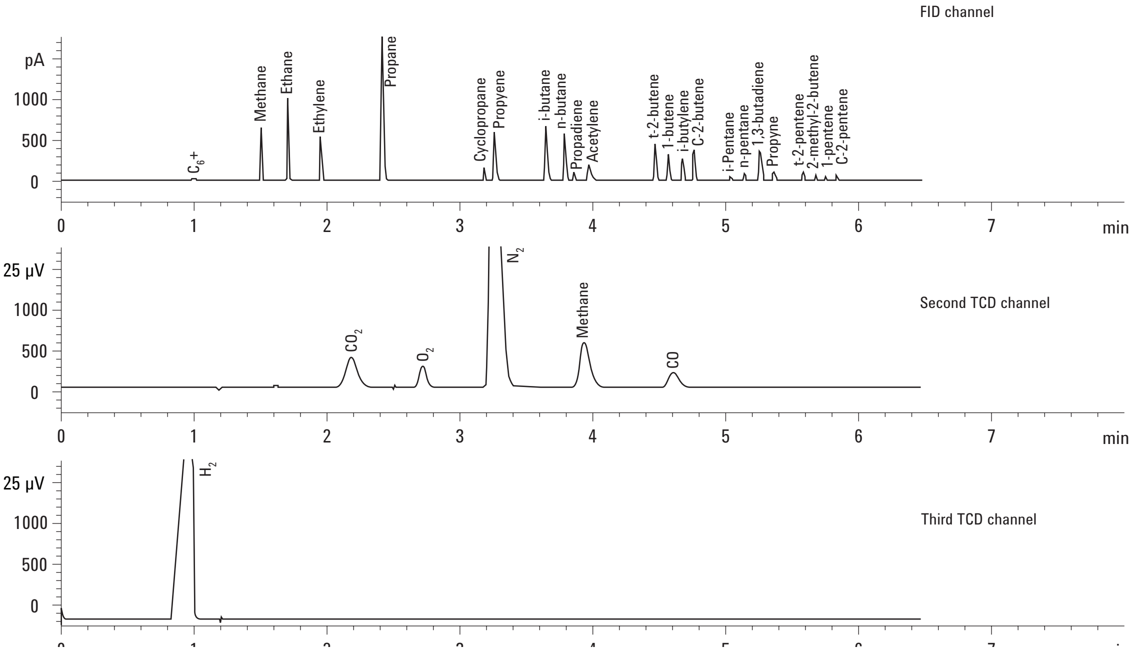


Figure 3. **Refinery gas calibration standards analysis. The concentrations for each compound are shown in Table 2.**

The top chromatogram (FID channel) is the hydrocarbon analysis. The PLOT alumina column provides excellent separation of hydrocarbons from C_1 to nC_5, including 22 isomers. Components heavier than nC_6 are backflushed early as a group (C_6+) through the precolumn. The middle chromatogram (second TCD channel) is the separation of permanent gases using helium as a carrier gas. The bottom chromatogram (third TCD channel) is the separation of hydrogen, since hydrogen has only a little difference in thermal conductivity compared to helium. Use of an additional TCD with nitrogen (or argon) as a carrier gas improves the hydrogen detectability and linearity.

Table 3 shows very good repeatability for both retention time and area for analysis of the refinery gas standard.

Table3. Repeatability-Refinery Gas Analysis (6 runs) with 1 Run Excluded

	Retention time			**Area**		
Compounds	**Average**	**Std. dev.**	**RSD%**	**Average**	**Std. dev.**	**RSD%**
C_6+	0.99648	0.00031	0.03	59.01	1.10	1.86
Methane	1.50780	0.00046	0.03	490.02	1.45	0.30
Ethane	1.70788	0.00052	0.03	807.40	2.35	0.29
Ethylene	1.95732	0.00071	0.04	472.31	1.31	0.28
Propane	2.41706	0.00075	0.03	1950.35	5.96	0.31
Cyclopropane	3.18506	0.00075	0.02	145.62	0.45	0.31
Propyene	3.26195	0.00072	0.02	732.90	2.01	0.27
i-butane	3.64883	0.00055	0.02	885.04	3.15	0.36
n-butane	3.79161	0.00070	0.02	682.13	2.59	0.38
Propadiene	3.86098	0.00095	0.02	109.08	0.65	0.60
Acetylene	3.96990	0.00120	0.03	348.17	2.39	0.69
t-2-butene	4.47301	0.00106	0.02	507.88	2.59	0.51
1-butene	4.57118	0.00110	0.02	332.39	2.03	0.61
i-butylene	4.67529	0.00121	0.03	260.95	1.95	0.75
c-2-butene	4.76367	0.00112	0.02	403.80	3.47	0.86
i-pentane	5.03923	0.00090	0.02	45.03	0.05	0.11
n-pentane	5.14583	0.00099	0.02	69.23	0.40	0.58
1,3-butadiene	5.25906	0.00122	0.02	485.49	3.66	0.75
Propyne	5.36385	0.00155	0.03	101.08	0.41	0.40
t-2-pentene	5.58664	0.00121	0.02	82.85	0.66	0.79
2-methyl-2-butene	5.68220	0.00117	0.02	62.54	0.61	0.98
1-pentene	5.75553	0.00126	0.02	39.57	0.38	0.96
c-2-pentene	5.83970	0.00131	0.02	59.08	0.50	0.85
CO_2	2.18561	0.00221	0.10	2040.33	2.37	0.12
O_2	2.72634	0.00060	0.02	930.68	6.53	0.70
N^2	3.25170	0.00044	0.01	22500.18	68.87	0.31
CO	4.61692	0.00083	0.02	903.09	2.77	0.31
H_2	0.9869	0.00099	0.10	16097.38	106.53	0.66

Typical natural gas also can be characterized with the system using the same conditions for the fast RGA. The chromatograms of natural gas on the three channels are shown in Figure 4; hydrogen (3% Mol) and helium (1% Mol) are separated on the third TCD channel.

Flexibility for Hydrocarbon Analysis

The system is very flexible for hydrocarbon analysis. By setting up different valve (valve 3) switch times, the early backflush group can be C_6+ followed by individual C_1 to C_5 hydrocarbons as mentioned in fast RGA, or C_7+ followed by individual C_1 to C_6 hydrocarbons, or no backflush to separate C_1 to C_9 individual hydrocarbons. The top chromatogram in Figure 5 is the result with backflush group of C_6+, the middle one is that of C_7+, and the bottom one is that of no backflush. With such flexibility, a wide range of refinery gas and natural gas compositions can be measured reliably without hardware or column changes.

H_2S and COS Analysis

H_2S and COS (methyl-mercaptan) can be analyzed on the rear TCD channel by adding an additional delay to the backflush time (valve 1) to allow H_2S and COS to elute onto column 2 (HayeSep Q). The analysis time is extended an additional 3 to 4 minutes, and requires a sample containing no water. Figure 6 shows the chromatogram of H_2S at approximately 500 ppm and COS 300 ppm with 1 mL sample size. The Nickel tubing packed columns and Hastelloy-C valves can be chosen for high concentration of H_2S analysis to minimize corrosion.

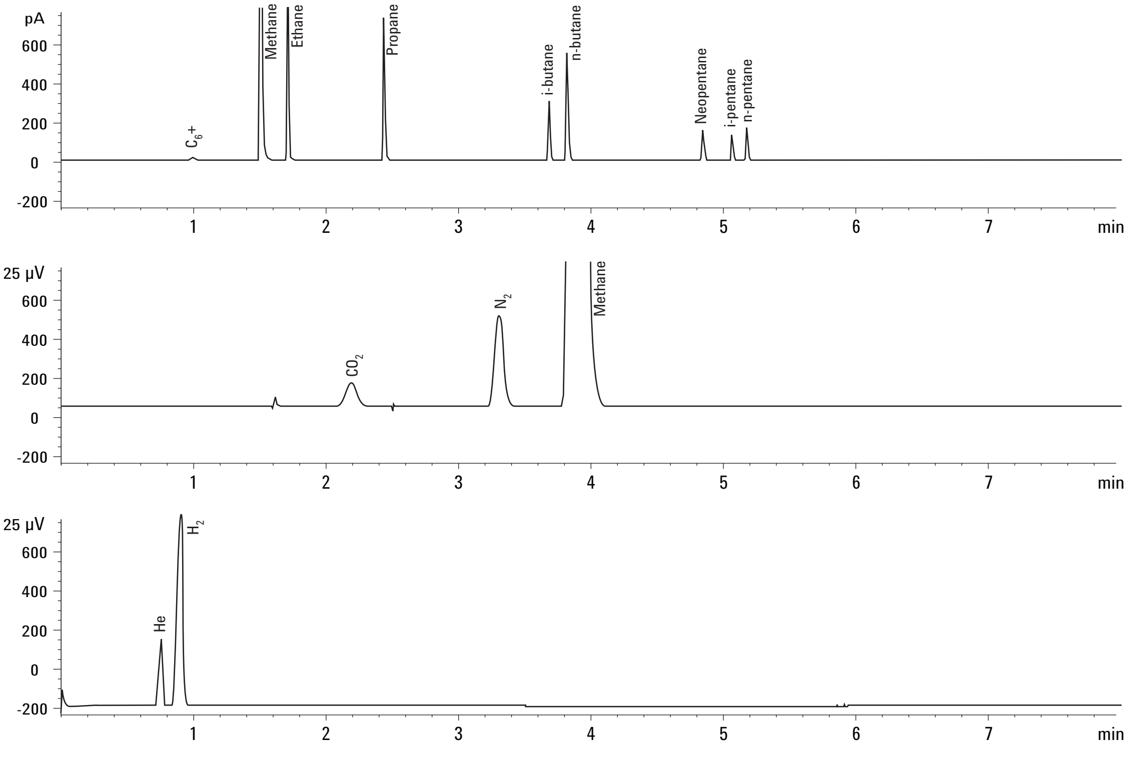


Figure 4. Natural gas analysis of a calibration gas.

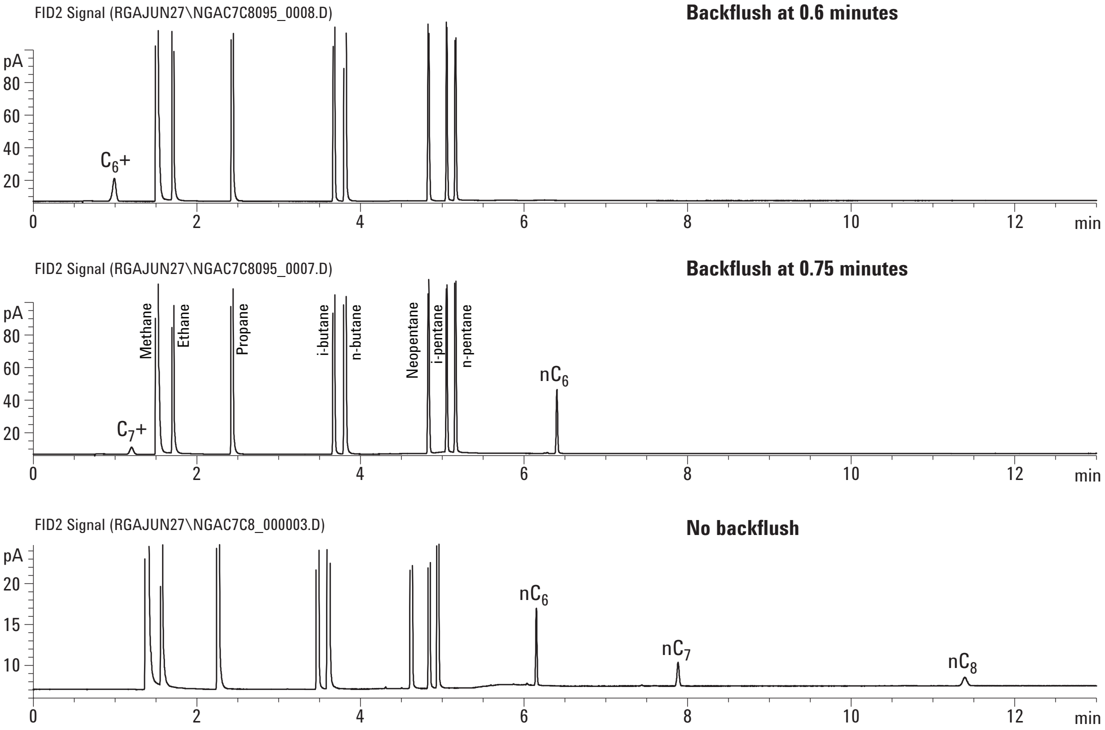


Figure 5. Chromatograms of light hydrocarbons on FID channel with different backflush times .

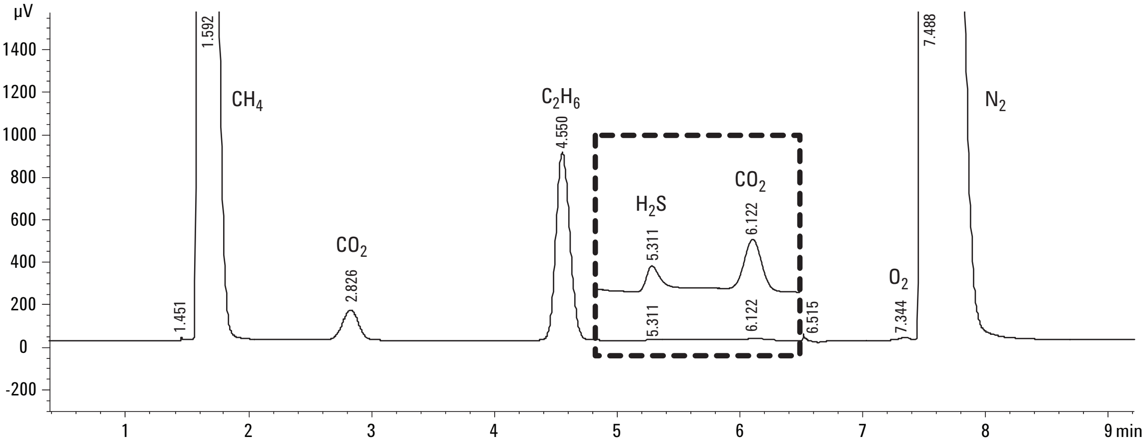


Figure 6. H_2S at approximately 500 ppm and COS 300 ppm on second TCD channel.

Oven program: 50 hold 2 minutes, to 150 °C at 30 °C/min, hold 3 minutes, to 190 °C at 30 °C/min, hold 1 minute
Sample loop: 1 mL

Reporting

A macro program provides automated gas properties calculation. It gives a report in mole %, weight %, volume %, or any combination of the three. If required, heat values for the gas analyzed and other standard calculations are also available. Reports can be calculated using formulas given in the ASTM/GPA or ISO standards.

Conclusions

An exact and fast analysis of the components in refinery gas is essential for optimizing refinery processes and controlling product quality.

One 7890A GC configured with three parallel channels with simultaneous operation provides complete analysis of permanent gases, including nitrogen, hydrogen, helium, oxygen, carbon monoxide, carbon dioxide, and all hydrocarbons to C_5 and C_6+ as a group within six minutes. A second TCD with nitrogen or argon as a carrier gas improves the hydrogen sensitivity and linearity.

The configuration is very flexible for hydrocarbon analysis, different backflush times may be set to obtain the early backflush group for C_6+ or C_7+, or no backflush to separate C_1 to C_{10} individual hydrocarbons. In these cases, the analysis time is increased by 6 minutes. H_2S and COS can be analyzed on the same GC configuration; it requires 3 to 4 minutes of additional time.

A macro program provides automated gas properties calculation. Reports can be calculated using formulas given in the ASTM/GPA or ISO standards. It gives a report in mole %, weight %, volume %, or any combination of the three.

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2. ASTM D1946-90 (2006), "Standard Practice for Analysis of Reformed Gas by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
3. UOP Method 539, "Refinery Gas Analysis by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428, USA.

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Parallel GC for Complete RGA Analysis

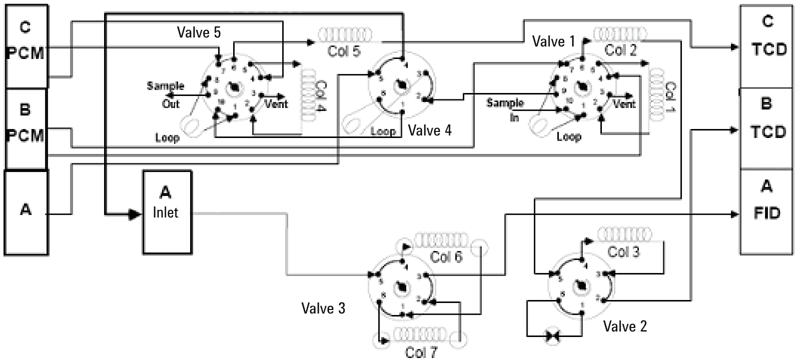
Application Brief

Chunxiao Wang

A previous application brief [1] has shown that a 7890A GC configured with three parallel channels provides a complete refinery gas analysis (RGA) within six minutes. The configuration for fast RGA in the brief has been updated by adding a fifth valve, which can now be supported by the 7890A GC. The updated configuration is almost the same as the previous one except for the third channel (TCD) for H_2 analysis using N_2 or Ar as carrier gas to improve H_2 detectability and linearity. The updated configuration uses a 10-port valve with a pre-column for backflushing late-eluting components while H_2 is separating on the molsieve column instead of a three-way splitter plus split/splitless inlet.

Refinery gases are mixtures of various gas streams produced in refinery processes. They can be used as a fuel gas, a final product, or a feedstock for further processing. The composition of refinery gas streams is very complex, typically containing hydrocarbons, permanent gases, sulfur compounds, etc. An exact and fast analysis of the components is essential for optimizing refinery processes and controlling product quality.

The Agilent 7890A GC now supports an optional detector (TCD), allowing simultaneous detection across three channels. This provides a complete analysis of permanent gases, including nitrogen, hydrogen, oxygen, carbon monoxide,



Column 1 HayeSep Q 80/100 mesh
Column 2 HayeSep Q 80/100 mesh
Column 3 Molsieve 5A 60/80 mesh
Column 4 HayeSep Q 80/100 mesh
Column 5 Molsieve 5A 60/80 mesh
Column 6 DB-1
Column 7 HP-PLOT Al_2O_3
PCM: Electronic pneumatics control (EPC) module

Figure1. RGA valve system.

Highlights

- One 7890A GC configured with three parallel channels with simultaneous detection provides a comprehensive, fast, and high-resolution analysis of refinery gas in 6 minutes.
- Use of optimized columns allows faster analysis of hydrocarbons and permanent gases using a single oven temperature program without the need for an additional column oven.
- A third TCD channel can be used for improving hydrogen detection and linearity by using nitrogen (or argon) as carrier gas.
- A new, easy-to-use union tubing connector based on capillary flow technology is used to connect valves and capillary columns to improve the chromatographic performance, including peak shape.
- Excellent results are achieved. The lowest detection limit is 50 ppm for all compounds, 500 ppm for hydrogen sulfide.
- ChemStation macro program is supplied for RGA reporting.
- The system can be obtained by ordering option SP1 7890-0322 for the standard fast RGA and 7890-0338 for the fast RGA with Hastelloy valves and nickel tubing for H_2S containing samples on the 7890A.

carbon dioxide, and hydrocarbons to nC6. The total run time is less than 6 minutes. The configuration is suitable for most refinery gas streams such as atmospheric overhead, FCC overhead, fuel gas, and recycle gases.

In this analysis, a single Agilent 7890A GC is configured with three channels, including an FID channel and 2 TCD channels. Light hydrocarbons are determined on the FID channel using an alumina column. One TCD is used with nitrogen or argon carrier gas for improved determination of hydrogen and helium; the other TCD is used with helium carrier for the detection of all other required permanent gases. The configuration is shown in Figure 1. An Agilent union tube connector, based on capillary flow technology, is used to quickly and easily connect the valve and capillary column for improved performance. The system conforms to published methods such as ASTM D1945 [2], D1946 [3], and UOP 539 [4].

Separation resulting from each channel is illustrated in Figure 2. The top chromatogram shows the hydrocarbon analysis. A PLOT AL2O3 column provides excellent separation of hydrocarbons from C1 to nC5 containing 22 isomers. Components heavier than nC6 are backflushed early in the run as a group (C6+) through a short DB-1 pre-column.The middle chromatogram shows the separation of permanent gases using helium as the carrier gas on the second TCD channel (B TCD). H_2S and COS can be analyzed on the second TCD channel as well, requiring 3 to 4 additional minutes. The bottom chromatogram shows the separation of hydrogen. Because hydrogen has only a small difference in thermal conductivity compared to helium, it requires an additional TCD with nitrogen or argon as the carrier gas to improve the hydrogen detectability and linearity. All channels operate simultaneously to provide a comprehensive, fast analysis with high resolution of components. A macro program automatically provides the calculation of gas properties. Reports can be generated using formulas specified in the ASTM/GPA and/or ISO standards. Reports in mole%, weight%, volume%, or any combination of the three are available.

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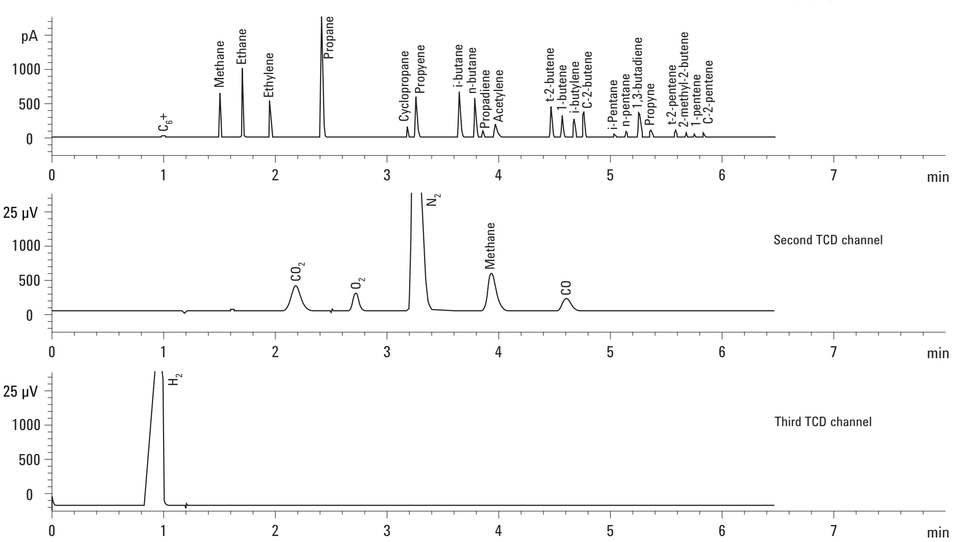

Figure 2. **Refinery gas calibration standards analysis.**

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GC/MS Analysis of PCBs in Waste Oil Using the Backflush Capability of the Agilent QuickSwap Accessory

Application

Environmental

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Abstract

Polychlorinated biphenyls (PCBs) in waste oil are typically analyzed by GC-ECD or GC/MS after solid phase extraction (SPE) cleanup. However, not all problematic matrix components are completely removed during cleanup and are injected into the analytical system, thereby contaminating the column and the detector.

In this application, a practical example of backflushing is presented using the Agilent QuickSwap accessory installed on a 7890 GC/5975 MSD system. Benefits of using QuickSwap instead of the traditional high-temperature bakeout procedure are demonstrated. Column and detector contamination were significantly reduced and sample throughput increased.

Introduction

The determination of polychlorinated biphenyls (PCBs) in mineral oils, including transformer oil, waste oil, or solid waste in general, is a routine application in environmental laboratories. After dilution/dissolution of the oil sample, a solid-phase extraction sample cleanup is used to remove most of the matrix components. Several SPE methods are commonly applied, and some custom cartridges are available specifically for this purpose. According to EN 12766, for instance, a combination of silica and acidified silica/anion exchange ($SiOH-H_2SO_4/SA$) adsorbents is prescribed. The oil samples are diluted and applied to the cartridge in hexane solution and the PCB fraction is then immediately eluted with hexane rinse. The polar matrix compounds remain on the SPE cartridges [1].

In the PCB fraction, however, apolar matrix compounds elute from the cartridge with the PCBs. In one regard, this is not an immediate analytical problem, because when this sample fraction is analyzed by selective detectors like GC-ECD or GC/MS in selected ion monitoring (SIM) mode, the co-extracted solutes are not directly detected. However, their presence contaminates the inlet, column, and detector, causing continuously decreasing system performance. Symptoms such as drifting and increasingly noisy baseline, integration difficulties, decreasing chromatographic resolution, changing column selectivity, and decreasing detector S/N force more frequent inlet system, column, and MS source maintenance and potentially require re-running some samples.

Backflush is a technique that has recently become easier to implement with capillary GC separations due to the availability of Capillary Flow Technology devices [2-9]. One such device is the Agilent QuickSwap, whose primary function is to simplify changing columns and doing maintenance on GC/MS systems. QuickSwap provides a flow of clean carrier gas that excludes air from the mass spectrometer when columns are disconnected.

An auxiliary electronic pressure control (aux EPC) module or pressure control module (PCM) is typically used to supply the purge gas to QuickSwap and thereby offers the ability to program the pressure during the run. To backflush a capillary column, one need only raise the pressure of QuickSwap (the outlet of the column) higher than that of the inlet (the head of the column). The column flow reverses, eliminating remaining sample components from the head of the column and passing them out of the split vent of the inlet and onto the split vent trap.

Backflushing a column after elution of the compounds of interest is a very effective way of eliminating column contamination. Low-volatility contaminants from the most recently injected sample tend to remain at the head of the column until high oven temperatures are reached. So, by reversing the flow through the column, these contaminants need only flow a short distance to be removed from the column. In the traditional bake-out, they would need to travel through the full length of the column to be removed. In addtion to more effective removal of contaminants, cycle time is significantly reduced, columns are spared from exposure to the high temperatures typical of bake-outs, and detector contamination is reduced.

Sample Preparation

A typical procedure was used to prepare a BCR reference sample (BCR-449, waste mineral oil, high PCB level). A 10% dilution of the oil was made in hexane (1 g in 10 mL). From this solution, 250 µL was applied to a series-combination of two cartridges: a 3 mL cartridge filled with 500 mg of silica treated with H_2SO_4 + 500 mg strong anion exchange resin and a 3-mL cartridge filled with 500 mg silica. The cartridges were preconditioned with hexane. The PCBs were eluted with 4 mL hexane. An aliquot of this solution was used for GC/MS analyses.

GC Conditions

All analyses were performed on an Agilent 7890A GC/5975 MSD system with QuickSwap option number 113 (with Aux EPC module). Injection was done using a 7683 ALS. The GC/MS conditions can be summarized in Table 1:

Table 1. GC/MS System Conditions

Column	30 m x 0.25 mm id × 0.25 µm df	HP-5MS (Agilent P/N 19091-433)
Inlet	S/SI in splitless mode	280 °C, 0.75 min purge delay Purge flow rate: 50 mL/min
Carrier gas	Helium	
Run pressure	150 kPa constant pressure	2 mL/min initial flow rate
Backflush pressure	28 kPa	
QuickSwap	GC option number 113 or	Accessory kit G3185B
Restrictor	17 cm × 110 µm id restrictor	Part number G3185-60363
Column outlet (QuickSwap)	Helium	
Run pressure	28 kPa He using AUX EPC	Through elution of PCBs
Backflush pressure	150 kPa	Held for 5 min after PCBs
Oven temperature program A (no backflush)	50 °C (1 min), 25 °C/min to 200 °C, 10°C/min to 330°C (10 min)	Total run time 30 min
Oven temperature program B (with backflush)	50 °C (1 min), 25 °C/min to 200 °C, 10 °C/min to 300 °C (5 min)	Total run time 22 min
MSD Setpoints	1.5 min solvent delay	260 °C MSD transfer line
SIM/scan settings (AutoTuned)	SIM ions 256, 258, 290, 292, 324, 326, 360, 362, 394, 396 (25 ms dwell time each)	Scan range 40–350 amu

Table 2. Sample Sequence

Run 1	Analysis of waste oil extract by GC/MS in scan/SIM mode – no backflush (oven program A)
Run 2	Blank run – no sample injection, no backflush (oven program A), same as run 1
Runs 3–5	Additional blank runs – same conditions as above (data not shown)
Run 6	Analysis of waste oil extract by GC/MS in scan/SIM mode – with backflush (oven program B)
Run 7	Blank run – no sample injection – same program as in runs 1–5

Results

Total ion chromatograms (TICs) obtained from GC/MS SIM mode are shown in Figure 1 (traditional bakeout with no backflush, A; with backflush, B). The PCBs of interest elute in the 9- to 16-min time range. The profiles obtained by both methods are very similar in PCB resolution and intensity. When these results are carefully scrutinized, little or no difference is noted. However, a clear baseline drop is observed in chromatogram B at 16.5 min, corresponding to the initiation of backflush. In usual backflush methods, the oven temperature ramp and MS data acquisition are stopped when backflush is initiated. In Figure 1B, oven temperature was held at 300 °C, but acquisition was left on to show the drop in baseline when column flow reversed. In contrast to the backflush chromatogram (B), a "hump" is observed extending to 22 min in chromatogram A. This shows the presence of high-boiling matrix interferences in the sample extract and demonstrates the need for removal of these, either through a bakeout or backflush. By the end of the bakeout in 1B, the baseline appears to return to the initial level, indicating that the interferences had been removed.

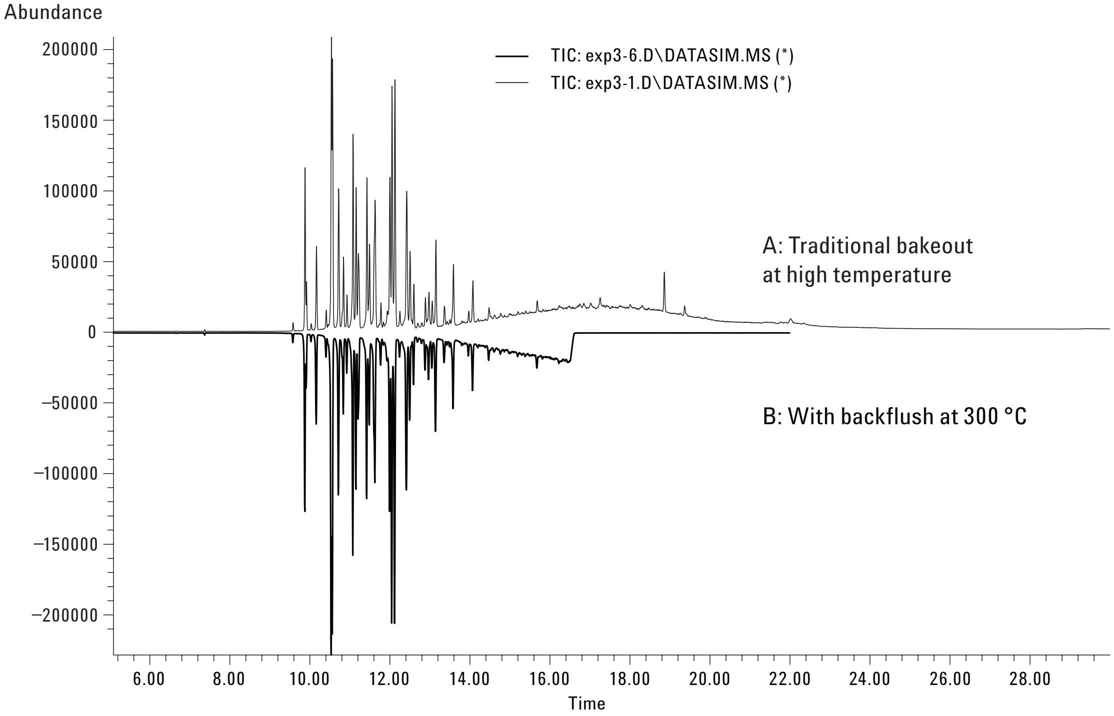

Figure 1. GC/MS total ion chromatograms (TICs) obtained for the analysis of PCBs in waste mineral oil without backflush (A) and with backflush (B)

A helpful recent enhancement of Agilent MSDs is the ability to acquire both SIM and scan data in the same run, termed "simultaneous SIM/Scan." The advantage of simultaneous SIM/Scan is that the benefits of improved detection limits for target compounds with SIM acquisition can be coupled with the benefit of having full-scan data with which to identify unknowns using a library search or spectral interpretation. For the same analytical runs shown in Figure 1 (based on SIM data), total ion chromatograms from full scan data are shown in Figure 2A (no backflush) and Figure 2B (with backflush). The sample matrix interferents can be even more easily seen in these chromatograms. Since all ions in the 40 to 350 amu range are being monitored, the considerable amounts of material eluting after the PCBs of interest dominates the chromatogram. In fact, in the TICs shown in Figure 2, the low-level PCBs are not discernable due to the dominance of the hydrocarbon background. It appears that all the interferents were effectively removed by the bakeout, because the signal returns to baseline even though this was not the case.

To better demonstrate the inferiority of traditional bakeout to backflushing for removing residual components, a blank run (no injection) was made after each of the analytical runs previously shown. The TIC scan-mode chromatogram after sample analysis with bakeout is shown in Figure 3A. To contrast the efficacy of backflush in removing contamination, the blank run done directly after sample analysis with backflush is shown in Figure 3B. In this chromatograph, only signal from normal column bleed was observed. In Figure 3A, the higher level of contamination was seen even after doing the 10 min bakeout at 330 °C and observing the apparent return of signal back to baseline. From this comparison, it is a clear that by relying on a typical bakeout, low-volatility material would continue to build up in the analytical system from run to run, ever increasing the level of background and interfering with subsequent analyses, requiring the column to be prematurely replaced. By backflushing, the low-volatility material was efficiently removed at lower temperatures in less time, while simultaneously lowering source contamination. Column lifetime would improve dramatically. In addition, the backflush method required less cooldown time after the run (from 300 °C instead of 330 °C). Total cycle time was thereby reduced by more than 25% by using backflush.

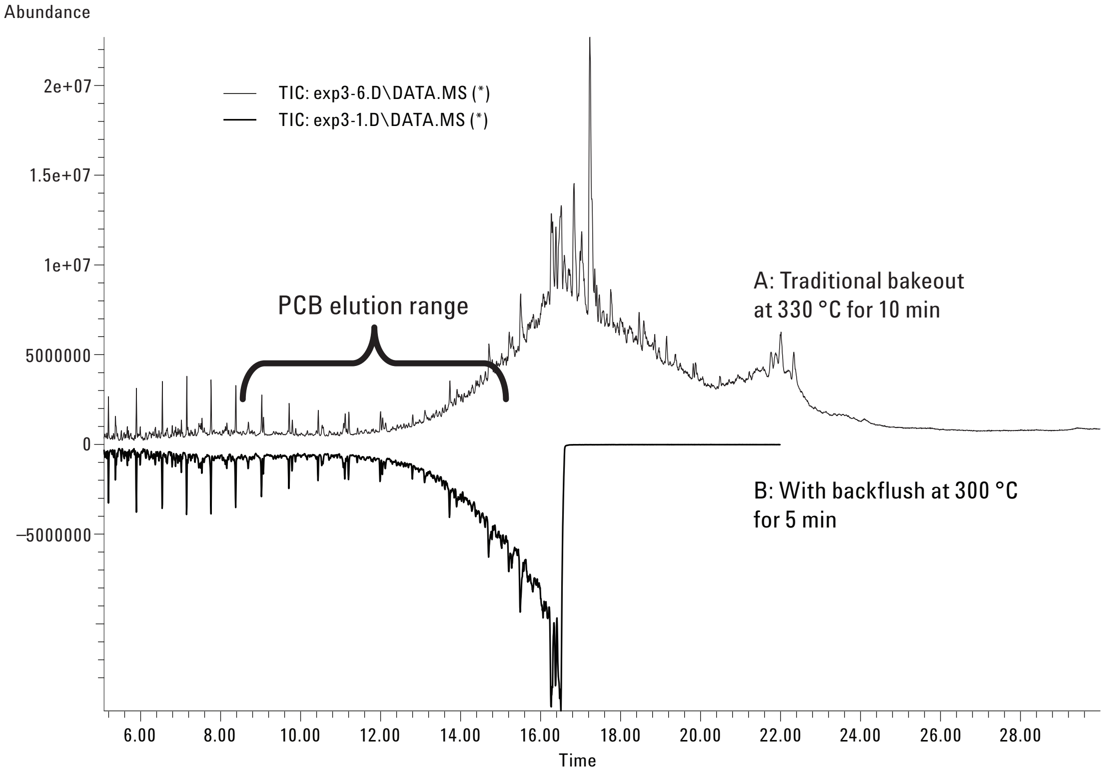

Figure 2. **GC/MS TIC scan chromatograms obtained for the analysis of PCBs in waste mineral oil without backflush (A) and with backflush (B).**

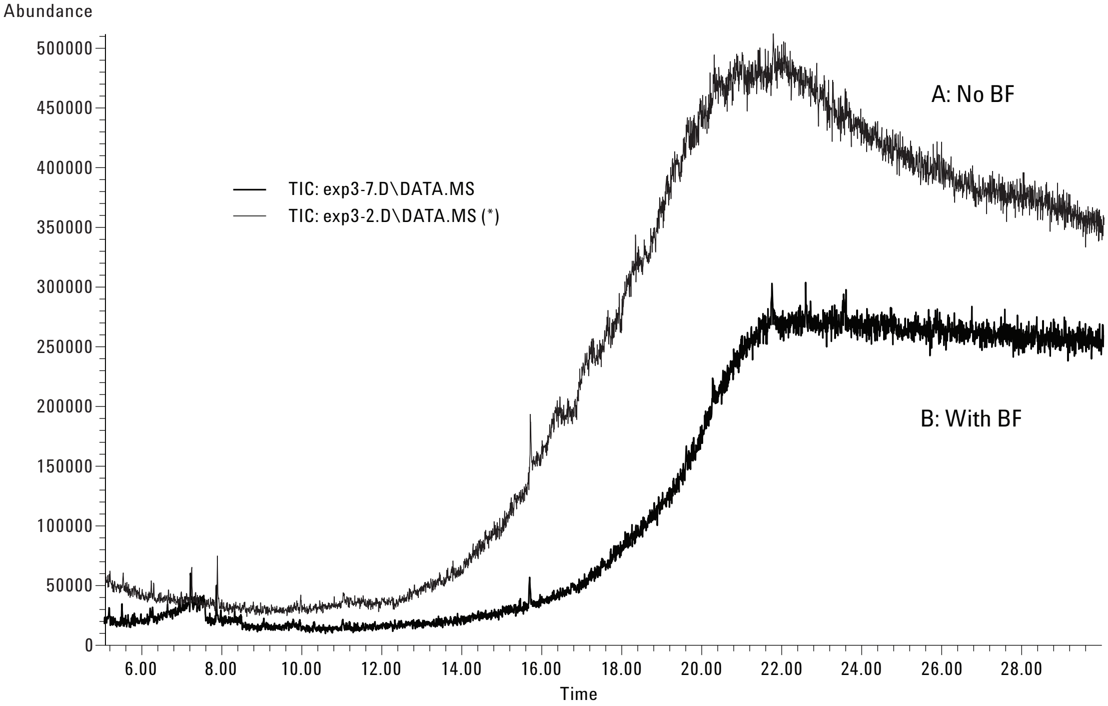

Figure 3. **GC/MS TIC chromatograms obtained from scan data for a blank run after the analysis of a sampling with traditional bakeout (no backflush) (A) and with the use of backflush (B).**

Conclusion

The benefits from using the backflush capability of QuickSwap on the 7890 GC/MSD were illustrated using an analysis of PCBs in waste mineral oil. The analytical portion of the analysis method was unchanged. There were no negative consequences from adding a backflush to the method. Several advantages were illustrated: improved cycle time, reduced column contamination, improved projected column lifetime, and reduced contamination of the MSD source. Adding backflush to current methods should be seriously considered to increase both laboratory productivity and quality of results.

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Agilent Technologies

Fast Analysis of Aromatic Solvent with 0.18 mm ID GC column

Application

Gas Chromatography

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Abstract

Fast GC is one possible way to improve productivity. By reducing the internal diameter of the capillary column, a higher efficiency per unit of column length is obtained in capillary GC. Combined with shorter column length, the application of high-efficiency 0.18-mm-id GC column results in faster analyses compared to conventional 0.25-mm- or 0.32-mm-id columns without losing measurement performance. A single, rapid GC method for aromatic solvent purity analysis is described.

Introduction

Determination of the purity of aromatic hydrocarbons is critical for many QA and QC laboratories in the chemical and petrochemical industry. In an effort to standardize analysis procedures, the American Society of Testing and Materials (ASTM) has developed and published a number of GC methods specifically for an aromatic compound or a class of aromatic compounds such as styrene, o-xylene, p-xylene, and ethylbenzene. Table 1 lists 10 ASTM methods along with the recommended columns and specifications [1].

Many QA/QC labs need to run these different ASTM methods to ensure the quality of all products. These analyses can be difficult and expensive to perform. Because many of these ASTM methods are remarkably alike, it is highly desirable to develop a single method that is the chromatographic equivalent of the individual methods. Detailed discussions on an unified aromatic solvent method are available in the literature [2, 3].

Due to demands for increased productivity, many QC/QA laboratories need to analyze large numbers of samples every day. Faster analysis is highly desirable for increased sample throughput and therefore lower cost per sample.

Table 1. Ten ASTM Methods for the GC Analysis of Aromatic Solvents

ASTM Method	Title	Liquid phase	Column type	Report specifications
D2306	Std test for C8 aromatic hydrocarbons	0.25 µm Carbowax	Capillary 50 m × 0.25 mm	wt% of individual C8 HC
D2360	Std test for trace impurities in monocyclic hydrocarbons	0.32 µm Carbowax	Capillary 60 m × 0.32 mm	wt% of individual aromatic impurities, total impurities, purity
D3760	Std test for cumene	0.25 µm Carbowax	Capillary 50 m × 0.32 mm	wt% of individual impurities, cumene purity (wt%)
D3797	Std test for o-xylene	0.5 µm Carbowax	Capillary 60 m × 0.32 mm	wt% of individual impurities, o-xylene purity (wt%)
D3798	Std test for p-xylene	0.25 µm Carbowax	Capillary 50 m × 0.32 mm	wt% of individual impurities, total impurities, p-xylene purity (wt %)
D4492	Std test for benzene	0.25 µm Carbowax	Capillary 50 m × 0.32 mm	wt% of individual impurities, benzene purity (wt%)
D4534	Std test for benzene in cyclic products	10% TCEPE on Chromasorb P	Packed 3.7 m × 3.175 mm	wt% of benzene
D5060	Std test for impurities in ethylbenzene	0.5 µm Carbowax	Capillary 60 m × 0.32 mm	wt% of individual impurities, ethylbenzene purity
D5135	Std test for styrene	0.5 µm Carbowax	Capillary 60 m × 0.32 mm	wt% of individual impurities, styrene purity
D5917	Std test for trace impurities in monocyclic hydrocarbons (ESTD Cal)	0.25 µm Carbowax	Capillary 60 m × 0.32 mm	wt% individual impurities, wt% total nonaromatics, wt% total C9 aromatics, purity of main component

Experimental

High-Efficiency Capillary GC Columns

Efficiency is often related to the number of theoretical plates, which increases linearly with decreasing column internal diameter (id). For instance, 0.18 mm id columns typically produce 5,800 to 6,600 theoretical plates per meter, whereas columns with 0.25 to 0.32 mm id typically produce 3,600 to 4,600 plates per meter. The efficiency improvement for the 0.18 mm id columns allows for better signal-to-noise ratios. Since decreasing the internal diameter results in an increase of the column efficiency per meter, the column length can be reduced while keeping the resolution constant. Therefore, the use of 0.18 mm id columns, also known as the high-efficiency GC columns, can help gas chromatographers substantially reduce their sample analysis time.

While it is true that an even smaller id column, such as 0.1 mm id, could lead to higher efficiency per meter, routine analysis with such a column imposes high demands on instrumentation. It requires higher inlet pressures, better split control, and faster oven temperature heating rates. On the contrary, 0.18 mm id columns are conveniently compatible with existing standard GC equipment without the need for system modifications. Smaller id, shorter length columns require less carrier flow to achieve separations, thus reduce carrier gas usage. Therefore, high-efficiency 0.18 mm id columns can provide an easy and inexpensive way to speed up GC analysis without compromising resolution.

One note of caution when going to smaller id columns is lower sample capacity. With some special samples, it is important to find a balance among speed, sensitivity, and resolution to meet the laboratory goals. For most applications in the chemical, petrochemical, food, or flavor/fragrance industries, however, the use of HE GC columns can offer an important reduction in analysis time and, consequently, a higher sample throughput.

The purpose of this application is to demonstrate in depth the use of high-efficiency 0.18 mm id columns for faster analysis of aromatic solvents with the unified aromatic solvent analysis method.

Results and Discussion

One Agilent 6890N Series gas chromatograph and two Agilent 7890 gas chromatographs were used for this work. Each GC was equipped with a split/splitless capillary inlet, a flame ionization detector (FID), and an Agilent 7683 Automatic Liquid Sampler (ALS). The split/splitless inlets were fitted with a long-lifetime septa (Agilent part no. 5183-4761) and split-optimized liners (Agilent part no. 5183-4647). Injections were made using 10-µL syringes (Agilent part no. 5181-3354). Agilent ChemStation was used for all instrument control, data acquisition, and data analysis.

A 50-mL n-Hexane solution was prepared containing 0.1 wt% of 27 compounds; that is, all the aromatic solvents and impurities specified for analysis by the 10 ASTM methods.

Table 2 lists the experimental conditions for Method 1 where the unified aromatic solvent analysis was performed using a conventional 60 m × 0.32 mm × 0.5 µm HP-INNOWax column (Agilent part no. 19091N-213). The GC chromatogram is shown in Figure 1.

Table 2. Conditions for Unified Aromatic Solvents Method Using a Conventional Column (Method 1)

Column	HP-INNOWax, 60 m × 0.32 mm × 0.50 µm
Carrier gas	Helium at 20.00 psi constant pressure mode
Inlet	Split/splitless at 250 °C 100:1 split ratio
Oven temp	75 °C (10 min); 3 °C/min to 100 °C (0 min) 10 °C/min to 145 °C (0 min)
Detector	FID at 250 °C
Data acquisition rate	At 20 Hz
Injection size	1 µL

The experiment was then repeated with a high-efficiency 20 m × 0.18 mm × 0.18 µm HP-INNOWax column (Agilent part no. 19091N-577) (Method 2). Agilent GC Method Translation Software (http://www.chem.agilent.com/cag/servsup/usersoft/files/GCTS.htm) was used to translate Method 1 to Method 2. Three translation modes, namely the "translate only," "best efficiency," and "fast analysis," were attempted with the new column dimensions. However, co-elution of dodecane and o-xylene was observed for all three translated methods. According to ASTM methods, some modifications of the temperature programs were therefore necessary to achieve a similar resolution to Method 1. The resulting experimental conditions are provided in Table 3 along with the chromatogram in Figure 2.

Table 3. Conditions for Aromatic Solvents Separations on a High-Efficiency Column (Method 2)

Column	HP-Innowax, 20 m × 0.18 mm × 0.18 µm
Carrier gas	Helium at 25.00 psi constant pressure mode
Inlet	Split/splitless at 250 °C 100:1 split ratio
Oven temp	50 °C (2 min); 15 °C/min to 90 °C (0 min); 20 °C/min to 145 °C (1min)
Detector	FID at 250 °C
Data acquisition rate	At 50 Hz
Injection size	0.2 µL

In order to achieve even faster separation while balancing speed and resolution, Agilent GC Method Translation Software was used to translate Method 1 to Method 3 while selecting "fast analysis" mode and using the same high-efficiency GC column. But dodecane and o-xylene could not achieve baseline separation with the obtained method as stated previously. According to ASTM methods, the obtained method conditions were used with minor adjustments of the initial temperature from 75 °C to 70 °C and the initial hold of 2 minutes to 3 minutes. Then baseline separation was obtained for dodecane and o-xylene (Rs = 2.78). Detailed experimental conditions are provided in Table 4 with the GC chromatogram in Figure 3.

Table 4. Conditions for Fast Aromatic Solvents Analysis (Method 3)

Column	HP-INNOWax, 20 m × 0.18 mm × 0.18 µm
Carrier gas	Helium at 33.00 psi constant pressure mode
Inlet	Split/splitless at 250 °C 100:1 to 600:1 split ratio
Oven temp	70 °C (3 min); 45 °C/min to 145 °C (1 min)
Detector	FID at 250 °C
Data acquisition rate	At 50 Hz
Injection size	0.2 to 1.0 µL

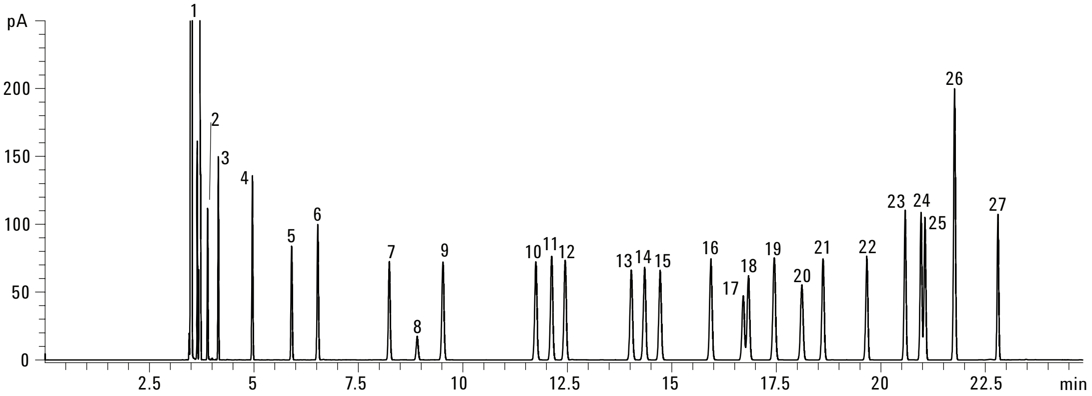


Figure 1. Unified aromatic solvent method with a 60 m × 0.32 mm × 0.5 µm HP-INNOWax column.

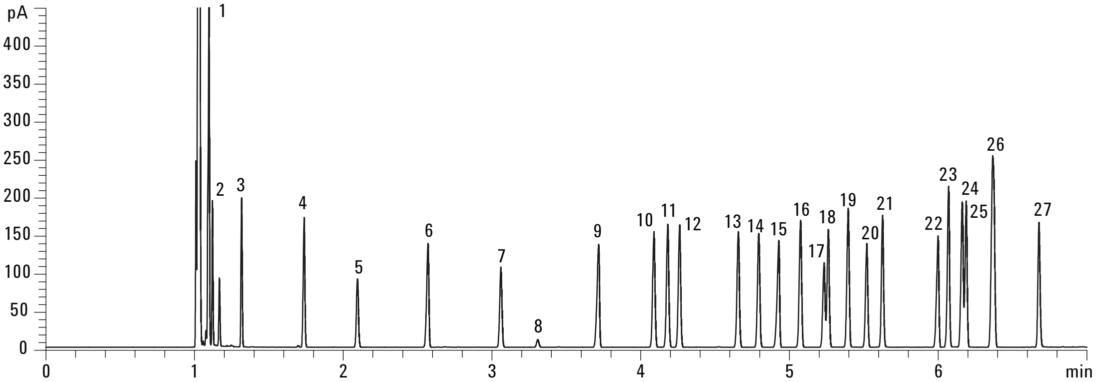


Figure 2. Separation of the same aromatic solvent with a 20 m × 0.18 mm × 0.18 µm HP-INNOWax column.

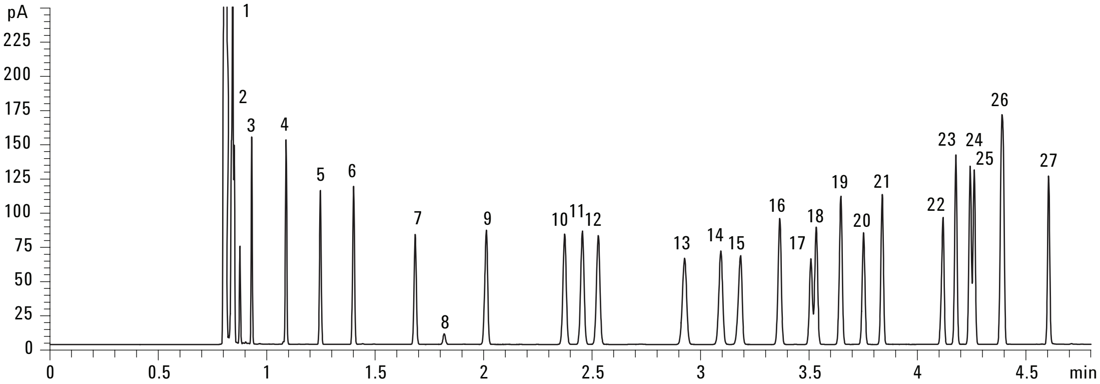


Figure 3. Optimized unified aromatic solvent method with a 20 m × 0.18 mm × 0.18 µm HP-INNOWax column.

1 Heptane
2 Cyclohexane
3 Octane
4 Nonane
5 Benzene
6 Decane
7 Toluene
8 1,4-Dioxan
9 Undecane
10 Ethylbenzene
11 p-Xylene
12 m-Xylene
13 Cumene
14 Dodecane
15 o-Xylene
16 Propylbenzene
17 p-Ethyltoluene
18 m-Ethyltoluene
19 t-Butylbenzene
20 s-Butylbenzene
21 Styrene
22 Tridecan
23 1,3-Diethylbenzene
24 1,2-Diethylbenzene
25 n-Butylbenzene
26 a-Methylstyrene
27 Phenylacetylene

Figures 1, 2, and 3 show the chromatograms of the hexane solution containing an aggregate of aromatic solvents and impurities for Method 1, Method 2, and Method 3, respectively. As indicated in the three chromatograms, baseline resolution was achieved for most of the compounds of interest except for two compound pairs, which were only partially resolved. The first pair, p-ethyltoluene and m-ethyltoluene, was also not resolved in the original ASTM method (D-5060, impurities in ethylbenzene) and, along with o-ethyltoluene, was reported as total ethyltoluene. A second pair, diethylbenzene and n-butylbenzene, was also partially resolved. However, this should not present a problem since they are not typically found together within the same material. Diethylbenzene is sometimes found as a contaminant in ethyl benzene (ASTM Method D-5060) while n-butyl benzene is used as the internal standard for cumene analysis (ASTM Method D-3760).

The sample run time for Method 1 was 23 minutes (Figure 1), whereas it was 7 minutes for Method 2 (Figure 2). The 3x speedup was achieved by using a shorter and narrower bore high-efficiency column. The optimized Method 3 allowed for even faster analysis time at 5 minutes (Figure 3), resulting in 4.6x speedup as compared to Method 1. As shown in Table 5, similar resolution was obtained in spite of significant acceleration, indicating that fast sample throughput can be achieved with the high-efficiency columns without compromise on resolution.

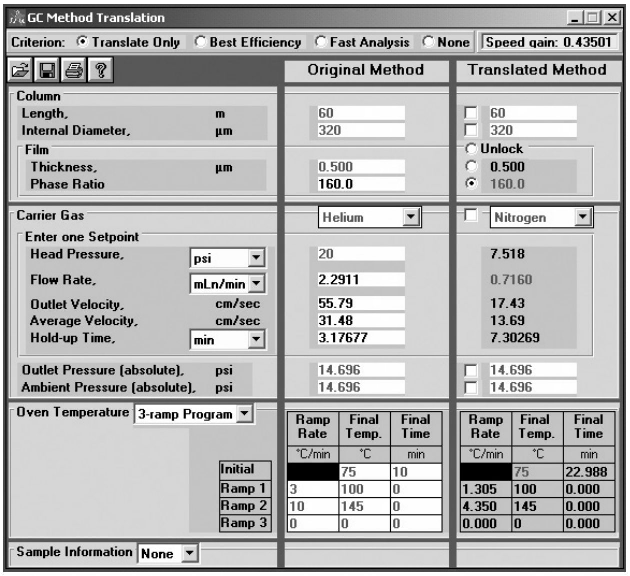
Influence of Carrier Gas on Analysis Time

The type of carrier gas and its velocity highly impact resolution and retention time. Too high or too low of a carrier gas velocity results in loss of resolution. It is therefore important to set a correct gas velocity to achieve a right balance of resolution and analysis time.

Hydrogen, helium, and nitrogen are the most common carrier gases used. The use of hydrogen as a carrier gas provides a faster analysis with almost equivalent resolution because the optimum linear carrier gas velocity is higher due to the higher diffusivity of hydrogen. At the optimal flow rates of 12, 20, and 35 cm/s for nitrogen, helium, and hydrogen, respectively, the analysis times would be 35/12 to 35/20 to 1 for nitrogen, helium, and hydrogen, respectively.

Nitrogen vs. Helium Carrier Gas

To investigate the effect of carrier gas on sample analysis time, Agilent GC method translation software was used where "translate only" mode was chosen so that all experimental conditions were held constant except for the carrier gas. Method 1 was translated to Method 4 where a nitrogen carrier was used (see Figure 4 and Table 6). As shown in Figure 5, the run time for a nitrogen carrier was about 60 minutes compared to 23 minutes with a helium carrier when using a 60 m × 0.32 mm × 0.5 µm HP-INNOWax column.


GC Method Translation

Criterion: ● Translate Only ○ Best Efficiency ○ Fast Analysis ○ None

Speed gain: 0.43501

		Original Method	Translated Method
Column			
Length,	m	60	☐ 60
Internal Diameter,	µm	320	☐ 320
Film			○ Unlock
Thickness,	µm	0.500	○ 0.500
Phase Ratio		160.0	● 160.0
Carrier Gas		Helium	☐ Nitrogen
Enter one Setpoint			
Head Pressure,	psi	20	7.518
Flow Rate,	mLn/min	2.2911	0.7160
Outlet Velocity,	cm/sec	55.79	17.43
Average Velocity,	cm/sec	31.48	13.69
Hold-up Time,	min	3.17677	7.30269
Outlet Pressure (absolute),	psi	14.696	☐ 14.696
Ambient Pressure (absolute),	psi	14.696	☐ 14.696

Oven Temperature: 3-ramp Program

	Original Ramp Rate °C/min	Original Final Temp. °C	Original Final Time min	Translated Ramp Rate °C/min	Translated Final Temp. °C	Translated Final Time min
Initial		75	10		75	22.988
Ramp 1	3	100	0	1.305	100	0.000
Ramp 2	10	145	0	4.350	145	0.000
Ramp 3	0	0	0	0.000	0	0.000

Sample Information: None

Figure 4. **Method translation software input screen for a nitrogen carrier.**

Table 6. Experimental Conditions for Unified Aromatic Solvents Method Using Nitrogen Carrier Gas (Method 4)

Column	HP-INNOWax, 60 m × 0.32 mm × 0.50 µm
Carrier gas	Nitrogen at 7.60 psi constant pressure mode
Inlet	Split/splitless at 250 °C 100:1 split ratio
Oven temp	75 °C (23 min); 1.3 °C/min to 100 °C (0 min) 4.4 °C/min to 145 °C (0 min)
Detector	FID at 250 °C
Data acquisition rate	At 20 Hz
Injection size	0.2 µL

Table 5. Comparison of Resolution of Difficult-to-Separate Compound Pairs Under Different Experimental Conditions

Compound	Ethylbenzene/p-xylene	p-Xylene/m-xylene	p-Ethyltoluene/m-ethyltoluene	Diethylbenzene/n-butylbenzene
Method 1	3.25	3.10	1.10	1.11
Method 2	3.14	2.72	1.00	0.97
Method 3	2.84	2.47	0.94	0.88

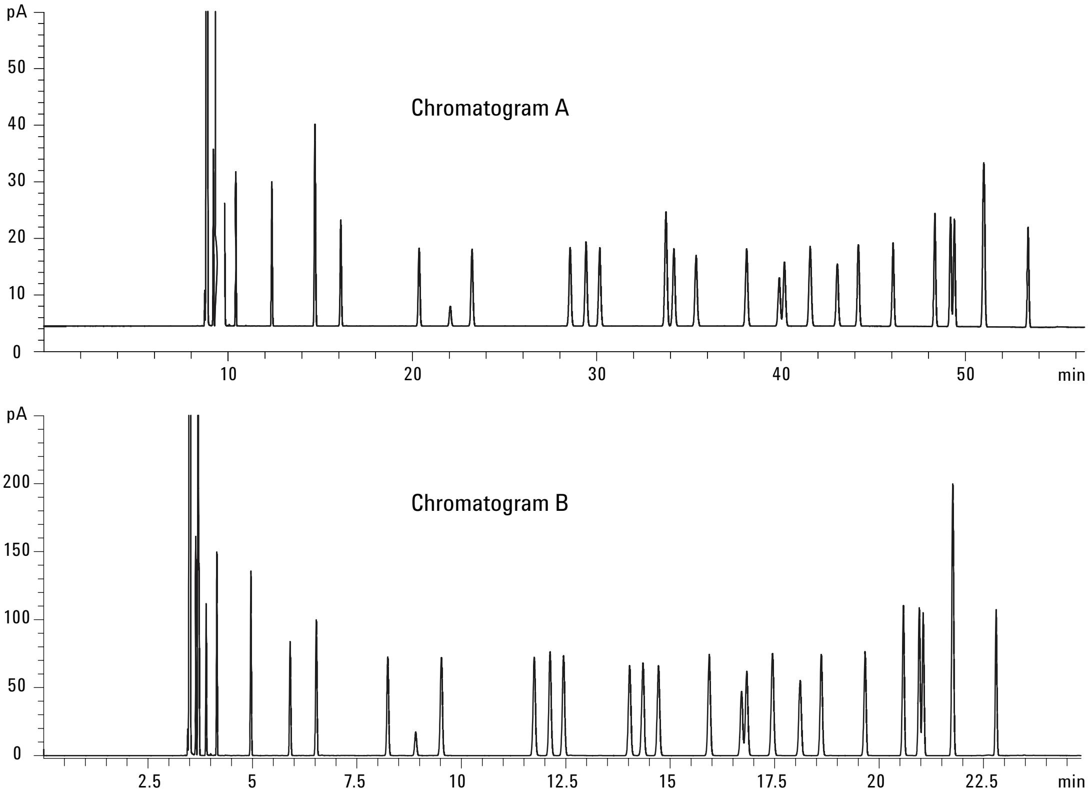
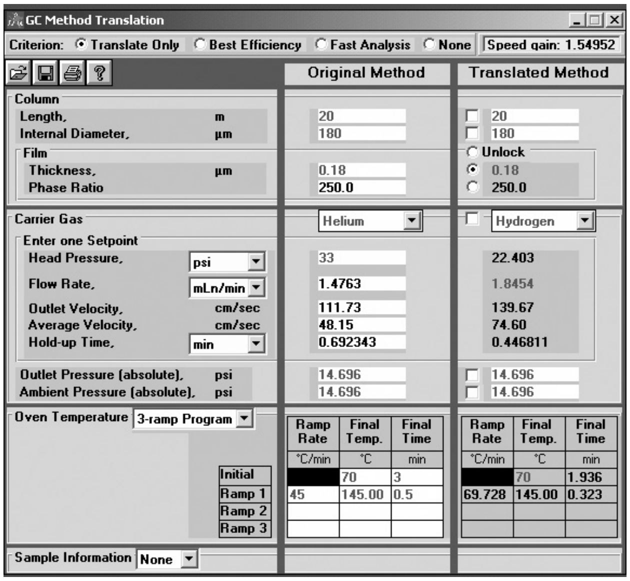


Figure 5. **Comparison of unified aromatic solvent analysis using nitrogen and helium carrier gases with a 60 m × 0.32 mm × 0.5 µm HP-INNOWax column. 5a. Nitrogen carrier gas (Method 4). 5b. Helium carrier gas (Method 1).**

Hydrogen vs. Helium Carrier Gas

A faster analysis can be achieved by switching the carrier gas from helium to hydrogen on the same coumn. Method 3 was translated to Method 5 using the method translation software (see Figure 6); the detailed experimental condition is provided in Table 7. As shown in Figure 7, the total run time was decreased from 5 to 3 minutes by changing the carrier gas from helium to hydrogen while keeping the peaks well separated.


GC Method Translation

Criterion: ● Translate Only ○ Best Efficiency ○ Fast Analysis ○ None Speed gain: 1.54952

		Original Method	Translated Method
Column			
Length,	m	20	☐ 20
Internal Diameter,	µm	180	☐ 180
Film			○ Unlock
Thickness,	µm	0.18	● 0.18
Phase Ratio		250.0	○ 250.0
Carrier Gas		Helium	☐ Hydrogen
Enter one Setpoint			
Head Pressure,	psi	33	22.403
Flow Rate,	mLn/min	1.4763	1.8454
Outlet Velocity,	cm/sec	111.73	139.67
Average Velocity,	cm/sec	48.15	74.60
Hold-up Time,	min	0.692343	0.446811
Outlet Pressure (absolute),	psi	14.696	☐ 14.696
Ambient Pressure (absolute),	psi	14.696	☐ 14.696

Oven Temperature 3-ramp Program

	Original Ramp Rate °C/min	Original Final Temp. °C	Original Final Time min	Translated Ramp Rate °C/min	Translated Final Temp. °C	Translated Final Time min
Initial		70	3		70	1.936
Ramp 1	45	145.00	0.5	69.728	145.00	0.323
Ramp 2						
Ramp 3						

Sample Information None

Figure 6. **Method translation software input screen for a hydrogen carrier.**

Table 7. **Experimental Conditions for Unified Aromatic Solvents Method Using Hydrogen Carrier Gas (Method 5)**

Column	HP-INNOWax, 20 m × 0.18 mm × 0.18 µm
Carrier gas	Hydrogen at 22.00 psi constant pressure mode
Inlet	Split/splitless at 250 °C 100:1 split ratio
Oven temp	70 °C (2 min); 70 °C/min to 145 °C (0.5 min)
Detector	FID at 250 °C
Data acquisition rate	At 50 Hz
Injection size	0.2 µL

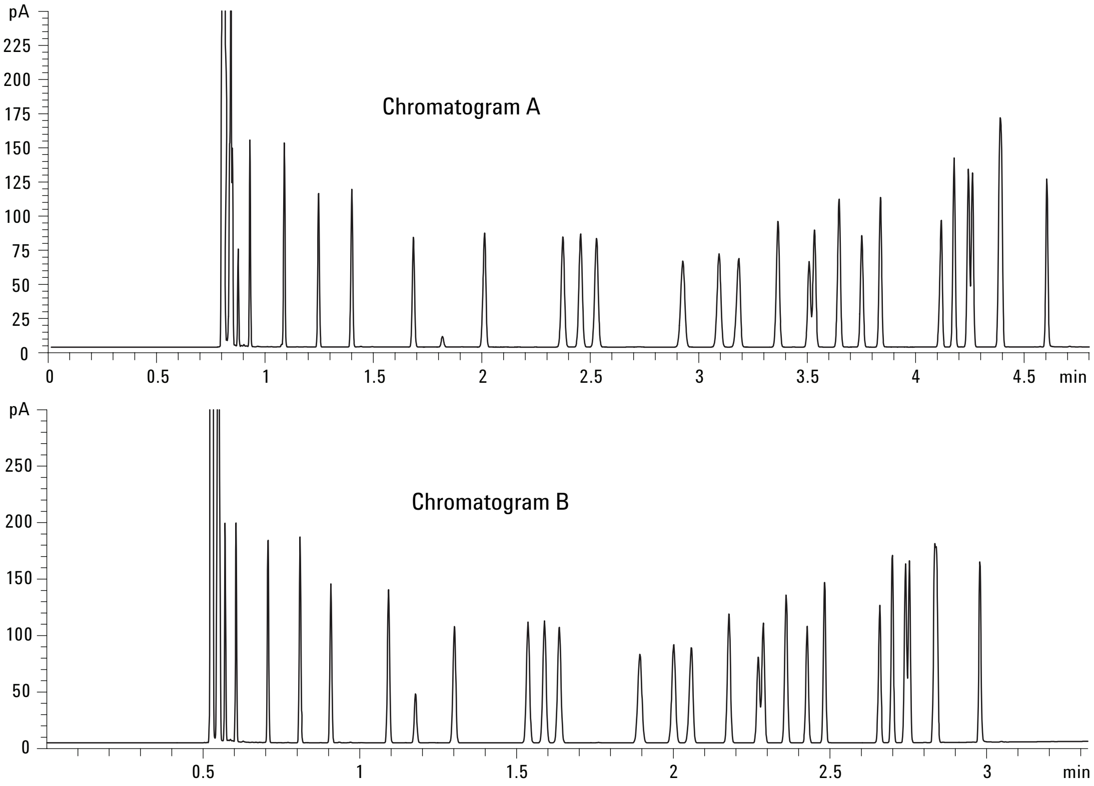


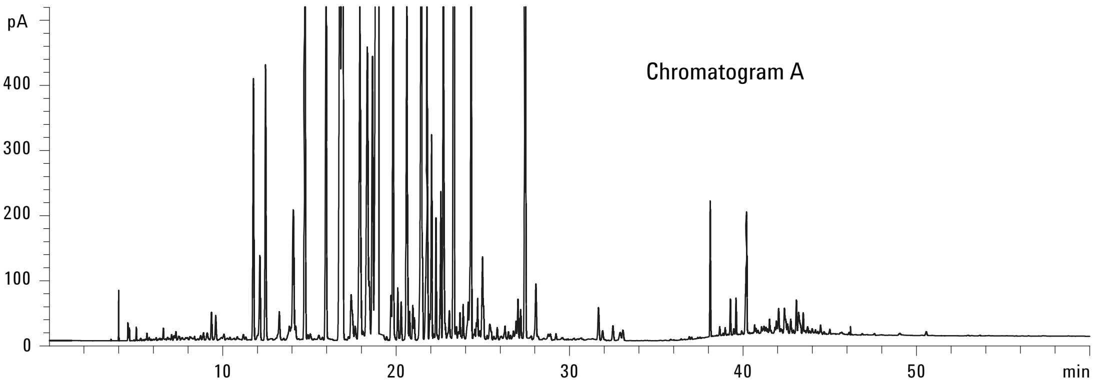
Figure 7. **Comparison of unified aromatic solvent analysis using helium and hydrogen carrier gases with a 20 m × 0.18 mm × 0.18 µm HP-INNOWax column. 7a. Helium carrier gas (Method 5). 7b. Hydrogen carrier gas (Method 3).**

Complex Matrix Sample

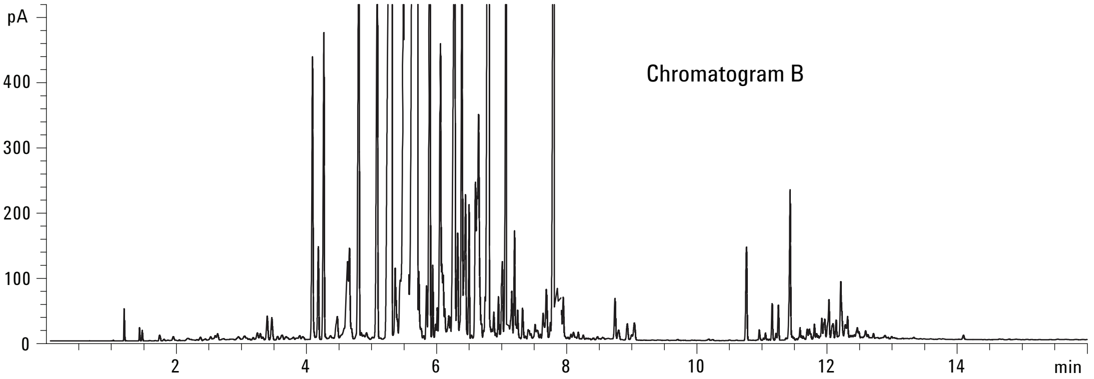
To validate the practicality of fast GC application using high-efficiency GC columns, a real aromatic solvent sample offered by a large-scale integrated petrochemical company was analyzed using the same experimental conditions as those for the standards (Methods 1, 2, and 3); the chromatograms are provided in Figures 8a, 8b, and 8c. A detailed comparison of the center sections is also provided in Figures 8d and 8e.

Although the analysis time is a bit longer with Method 2 compared to Method 3, the overall resolution obtained is slightly better for Method 2 (see Figures 8e and 8f). On the other hand, all the key compounds, including benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, propylbenzene, and a-methylstyrene, were well separated with all three methods.

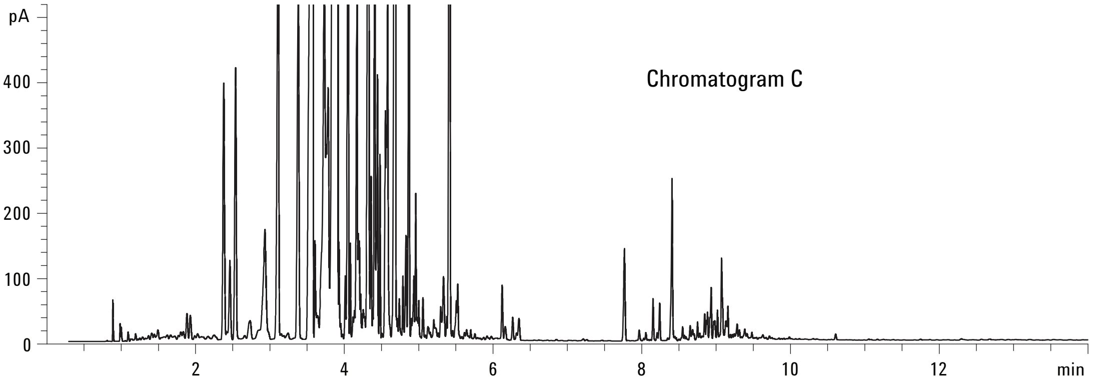
For complex matrix samples, a balance between speed and resolution must be selected according to the laboratory goals. In this case, it demonstrates that a complex matrix sample can be separated well on a high-efficiency 0.18 mm id GC column, where a more than 3x improvement in run time was accomplished compared to a 0.32 mm id column using a helium carrier.



Column	HP-INNOWax, 60 m × 0.32 mm × 0.50 µm
Carrier gas	Helium at 20.00 psi constant pressure mode
Inlet	Split/splitless at 250 °C; 50:1 split ratio
Oven temp	75 °C (10 min); 3 °C/min to 100 °C (0 min); 10 °C/min to 145 °C (12.17 min), 25 °C/min to 220 °C (22 min)
Detector	FID at 250 °C
Injection size	0.2 µL



Column	HP-INNOWax, 20 m × 0.18 mm × 0.18 µm
Carrier gas	Helium at 25.00 psi constant pressure mode
Inlet	Split/splitless at 250 °C; 150:1 split ratio
Oven temp	50 °C (2 min); 15 °C/min to 90 °C (0 min); 20 °C/min to 145 °C (3 min), 80°C/min to 220 °C (8 min)
Detector	FID at 250 °C
Injection size	0.2 µL



Column	HP-INNOWax, 20 m × 0.18 mm × 0.18 µm
Carrier gas	Helium at 33.00 psi constant pressure mode
Inlet	Split/splitless at 250 °C; 150:1 split ratio
Oven temp	70 °C (3 min); 45 °C/min to 145 °C (3 min), 80 °C/min to 220 °C (8 min)
Detector	FID at 250 °C
Injection size	0.2 µL

Figure 8. Comparison of real aromatic solvent sample separations (a) and (d) Method 1, (b) and (e) Method 2, and (c) and (f) Method 3.

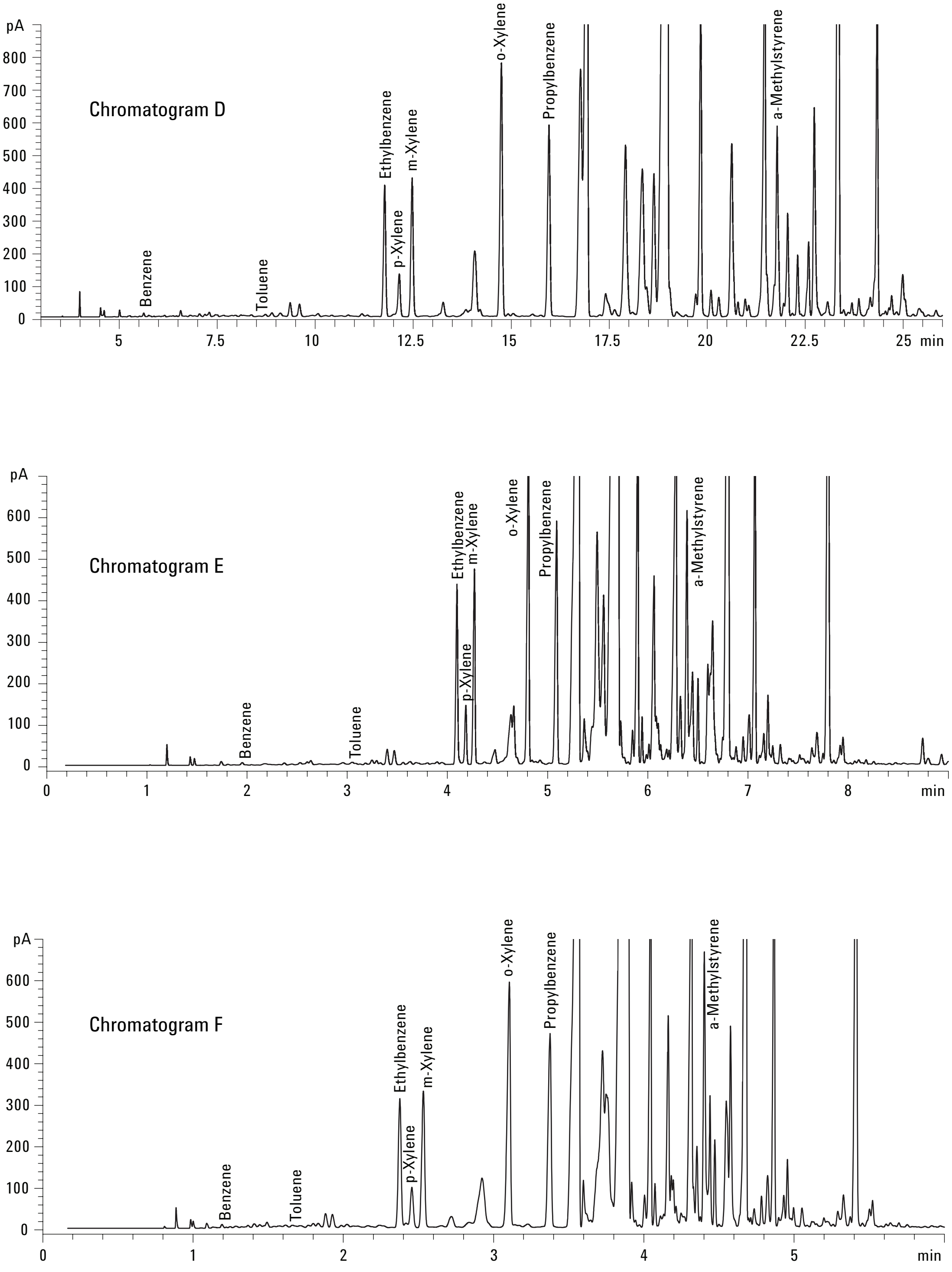


Figure 8. **Comparison of real aromatic solvent sample separations (a) and (d) Method 1, (b) and (e) Method 2, and (c) and (f) Method 3. (continued)**

Evaluation of Individual ASTM Calibration Standards

To evaluate the applicability of high-efficiency GC columns on individual ASTM calibration standards, experiments were carried out with Methods 1 and 3, respectively, on a 7890 gas chromatography system. All standards were prepared as outlined by the ASTM methods.

D2306 – Standard Test for C8 Aromatic Hydrocarbons

Concentration of ASTM D2306 standard calibration mix is quite high. It is therefore a challenge regarding the capacity of the high-efficiency 0.18 mm id column. The workaround is to inject a small volume with a high split ratio. In this experiment, the injection size was 0.2 µL and the split ratio was 600:1. As shown in Figure 9, the run time for the high-efficiency GC column was about 4.5 times shorter than that of the traditional one. The resolution is acceptable in spite of the high concentration of the calibration standard (see Table 8).

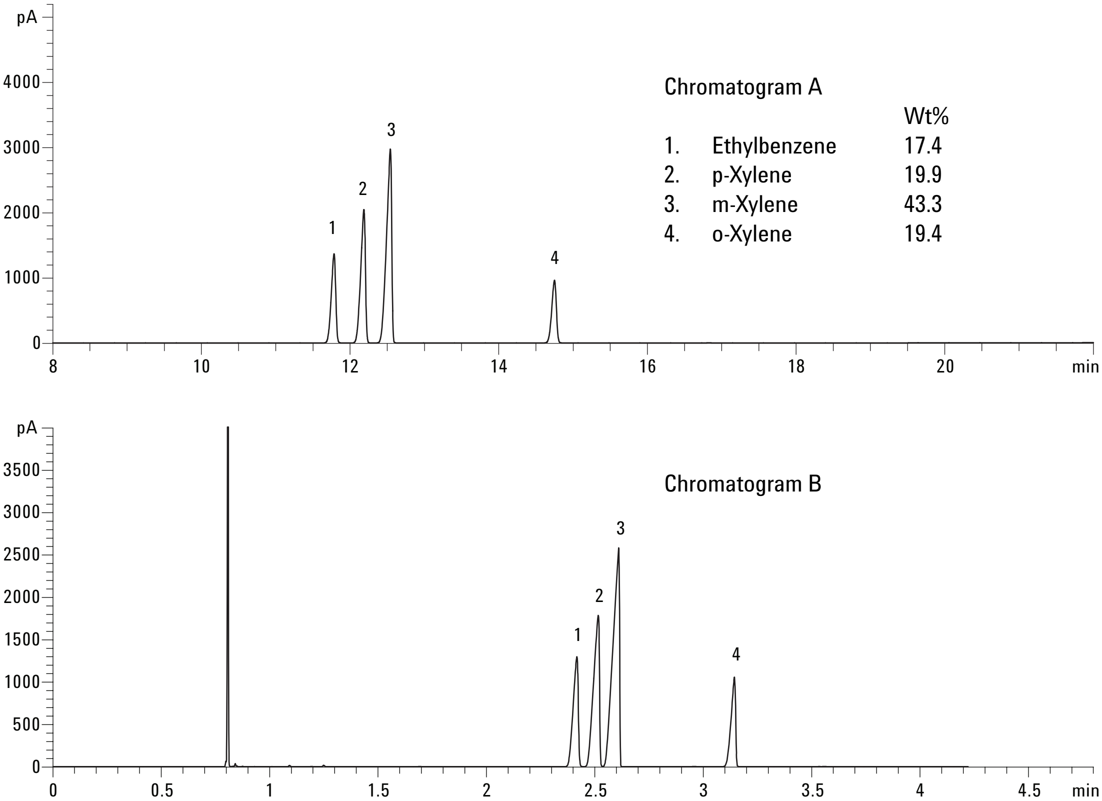


Figure 9. ASTM D2306 C8 aromatic hydrocarbon quantitative calibration standards (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (method 3).

Table 8. Comparison of Resolution Under Different Experimental Condition

Compound	Ethylbenzene/p-xylene	p-Xylene/m-xylene	m-Xylene/o-xylene
Method 1	3.52	2.86	18.11
Method 3	2.10	1.73	11.20

D2360 – Standard Test for Trace Impurities in Monocyclic Hydrocarbons

The standard calibration mix specified by D2360 was prepared in p-xylene. Injection size for this run was 0.2 µL and the split ratio was 200:1.

Similar resolution was obtained for the compounds of interest (Figure 10), except for the sample run time being decreased from 21.05 minutes (Method 1) to 4.28 minutes (Method 3).

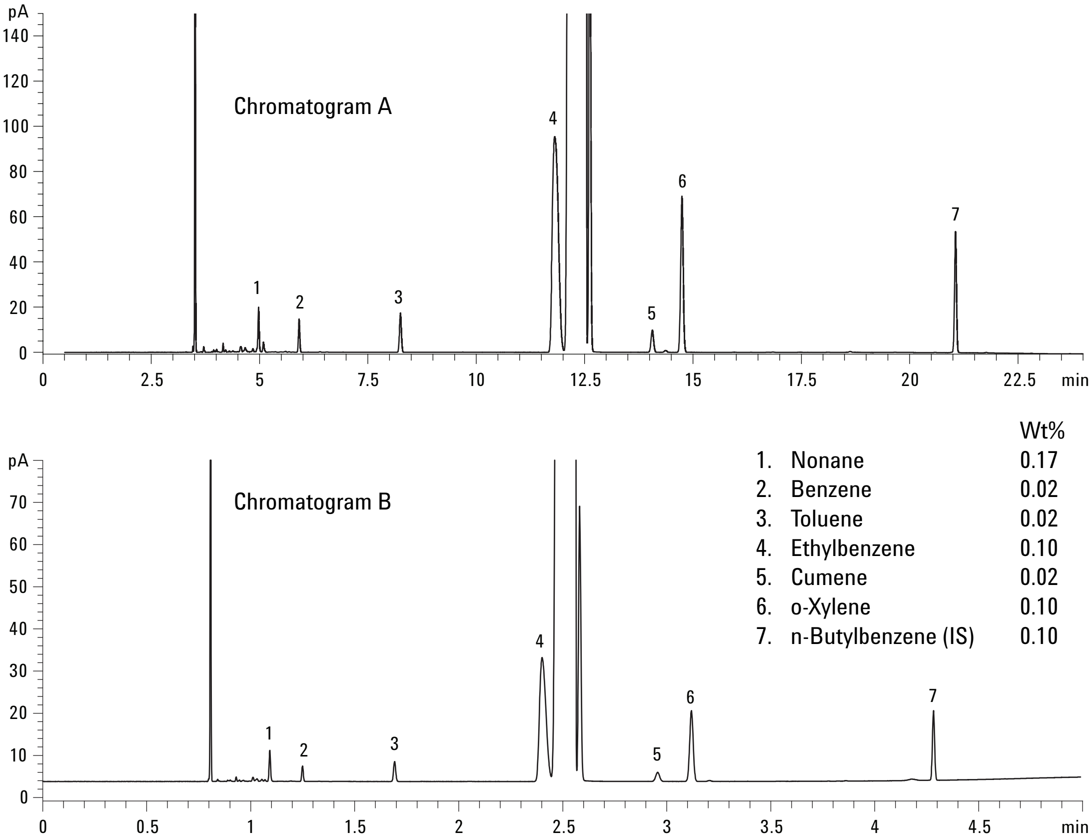
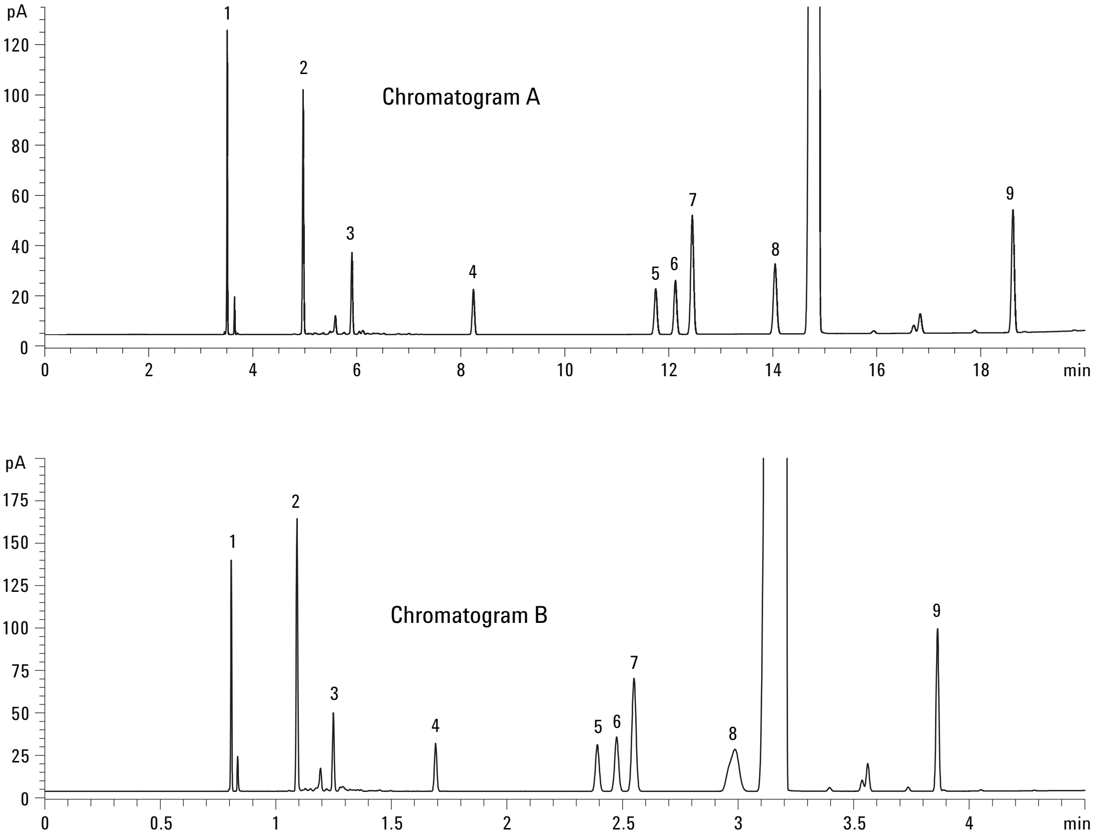


Figure 10. ASTM D2360 monocyclic hydrocarbon quantitative calibration standard run (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (Method 3).

D3797 – Standard Test Method for Analysis of o-Xylene

Figure 11 shows the chromatograms of the D3797 calibration standard. Injection size for this run was 0.2 µL and the split ratio was 100:1.

The broadening of the cumene peak was due to the reverse solvent effect of the overloaded o-xylene peak. This was also observed in the original ASTM D3797 method [4]. Comparison of the chromatograms in Figure 11 indicates that the D3797 calibration standard can be separated well on a high-efficiency 0.18 mm id GC column without loss of resolution.



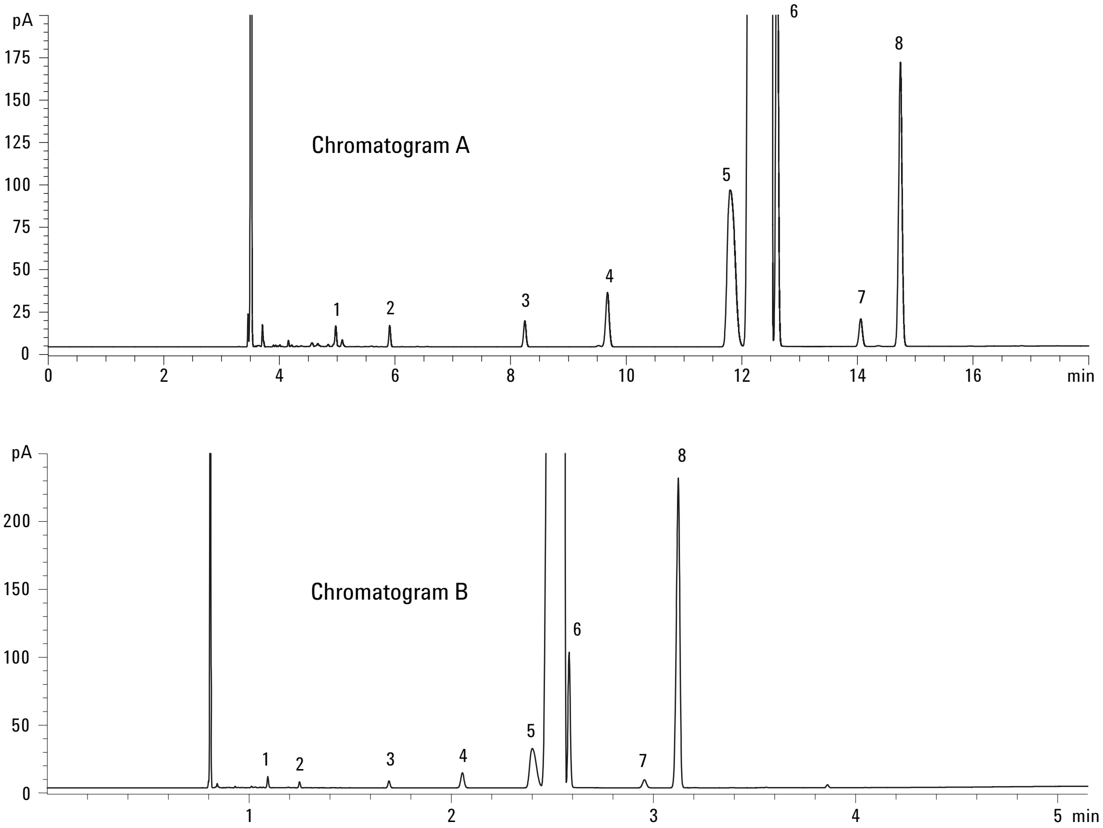
	Wt%		Wt%
1. Isooctane (IS)	0.05	6. p-Xylene	0.21
2. Nonane	0.21	7. m-Xylene	0.42
3. Benzene	0.20	8. Cumene	0.31
4. Toluene	0.21	9. Styrene	0.12
5. Ethylbenzene	0.21		

Figure 11. o-Xylene standard run (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (Method 3).

D3798 – Standard Test Method for Analysis of p-Xylene

This test method covers the determination of known hydrocarbon impurities in p-xylene and the measurement of p-xylene purity by GC. It is generally used for the analysis of p-xylene of 99% or greater purity.

Figure 12 shows the chromatograms of the D3798 calibration standard. Injection size for this run was 0.2 µL and the split ratio was 100:1. The original ASTM D3798 method specifies that the valley points between the large p-xylene peak and the ethylbenzene and m-xylene contaminants should be less than 50% of the contaminants' peak height. Excellent separation was obtained for the critical compounds (Figure 13) with great reproducibility (Figure 14) when using a high-efficiency GC column.



	Wt%		Wt%
1. Nonane	0.01	5. Ethylbenzene	0.10
2. Benzene	0.02	6. m-Xylene	0.20
3. Toluene	0.01	7. Cumene	0.01
4. Undecane (IS)	0.08	8. o-Xylene	0.10

Figure 12. p-Xylene standard run (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (Method 3).

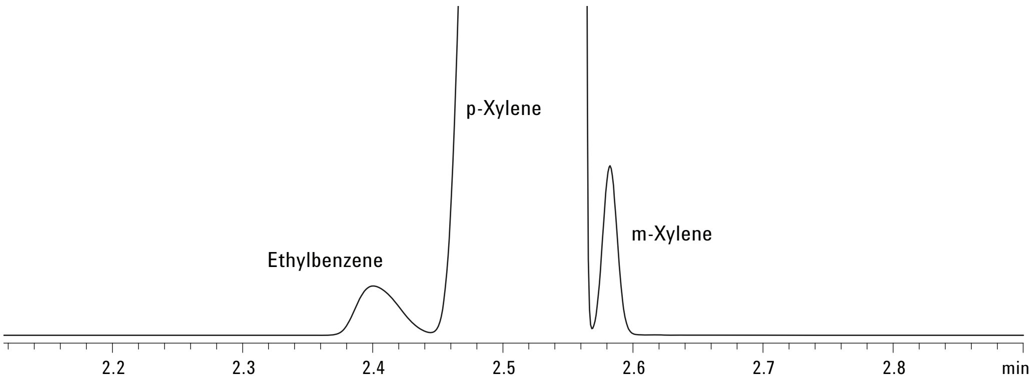


Figure 13. Expanded view from Figure 7 shows excellent separation of m-Xylene peak from p-Xylene peak using the fast GC method.

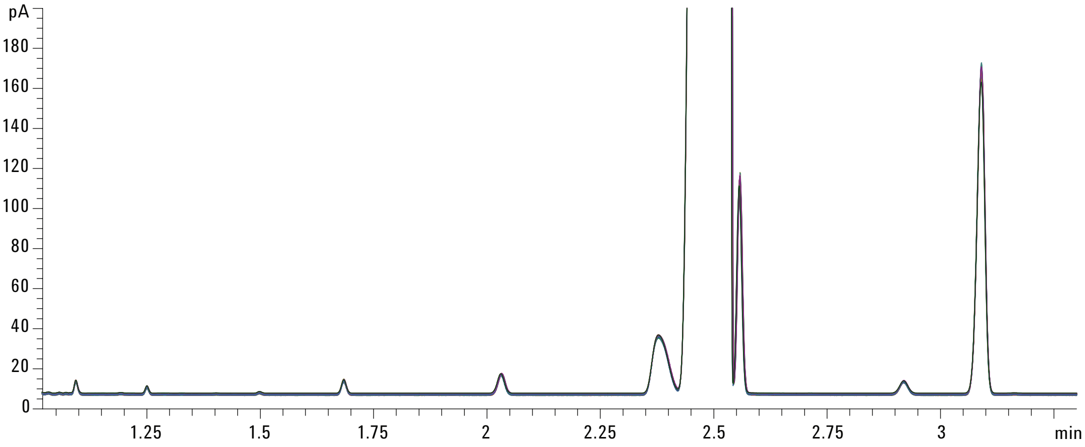


Figure 14. D3798 standard 30th run overlaid using a high-efficiency GC column.

D4492 – Standard Test for Analysis of Benzene

This test method determines the normally occurring trace impurities in, and the purity of, finished benzene. It is applicable for aromatic impurities from 0.001 to 0.010 weight % in benzene. Injection size for this run was 0.2 µL and the split ratio was 50:1.

Figure 15 compares the chromatograms of the D4492 calibration standard with Methods 1 and 3, where good separation of the D4492 calibration standards can be achieved with a high-efficiency column but with 80% saving on analysis time.

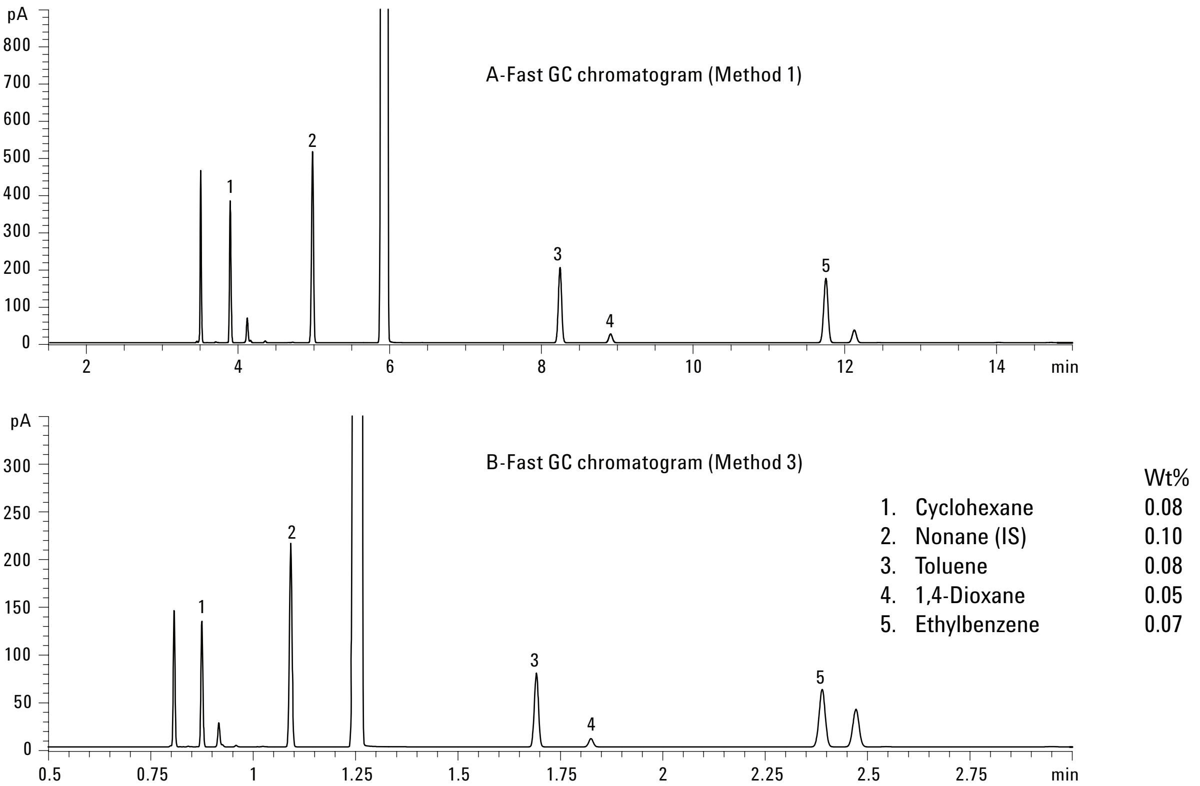


Figure 15. ASTM D4492 benzene quantitative calibration standard run (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (Method 3).

In summary, the analysis time for Method 3 is on average 5x shorter than that for Method 1 when working with the calibration standard samples.

Conclusions

Fast GC applications can significantly improve laboratory productivity by decreasing analysis time. This application showcases the practicality of high-efficiency GC columns in daily aromatic solvent analysis and the associated time savings achieved with these columns. By using high-efficiency GC columns with smaller inner diameters and shorter column lengths as well as an appropriate carrier gas (for example, helium or hydrogen), higher sample throughput and lower cost per sample is achievable [5] for chemical and petrochemical laboratories.

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Agilent Technologies

Investigation of the Unique Selectivity and Stability of Agilent GS-OxyPLOT Columns

Application

Gas Chromatography

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Abstract

The stationary phase of a GS-OxyPLOT column is a proprietary, salt deactivated adsorbent. GS-OxyPLOT columns show unique selectivity to oxygenated hydrocarbons, excellent stability and reproducibility, long column lifetime, and a wide application range.

Introduction

The determination of oxygenated hydrocarbons in different sample matrices is very important for the petrochemical industry, because oxygenates directly influence product quality. Presence of such oxygenates may cause the catalysts to be poisoned and deactivated, resulting in more downtime and higher costs. ASTM has developed several methods for analysis of oxygenates, such as ASTM D7059, D4815, and D5599. The oxygenates include ethers, esters, ketones, alcohols, and aldehydes.

Methanol is one of the oxygenates that often present in light hydrocarbon streams. For example, it is added to natural gas and production of crude oil to prevent hydration of hydrocarbons during transportation via pipelines. Therefore, it is important to accurately measure the content of methanol from light hydrocarbons at different concentrations, including at trace levels.

To achieve this, a new porous layer open tubular (PLOT) capillary column, the GS-OxyPLOT column, was used. The stationary phase of the GS-OxyPLOT is a proprietary, salt deactivated adsorbent with a high chromatographic selectivity for low molecular weight oxygenated hydrocarbons, while having virtually no interactions with saturated hydrocarbon solutes [1].

Using Capillary Flow Technology, such as backflush or Deans switch, GS-OxyPLOT columns can provide a turnkey solution for the analysis of trace level oxygenate impurities in complex matrices, such as motor fuels, crude oil, and gaseous hydrocarbon [2]. Meanwhile, a GS-OxyPLOT column can be used as a single analytical column to separate oxygenates for some samples. In this application, methanol was set as an example to investigate the performance of the GS-OxyPLOT column.

Experimental

The experiments were performed on an Agilent 7890A GC system and a 6890N GC system equipped with split/splitless capillary inlet, flame ionization detector (FID), and Agilent 7683 Automatic Liquid Sampler (ALS). The split/splitless inlets were fitted with long-lifetime septa (Agilent p/n 5183-4761) and spilt/splitless injection liners (Agilent p/n 5183-4711). Injections were done using 10-μL syringes (Agilent p/n 9301-0714). A glass indicating moisture trap (Agilent p/n LGMT-2-HP), an oxygen trap (Agilent p/n BOT-2), and a hydrocarbon trap (Agilent p/n 5060-9096) were installed. Agilent ChemStation was used for all instrument control, data acquisition, and data analysis.

Results and Discussion

Analysis of Normal Hydrocarbons and Methanol

A mixture of normal hydrocarbons and methanol was prepared with the following approximate concentrations %(w/w): 34.8% n-pentane, 12.8% n-hexane, 1.8% n-heptane, 1.9% n-octane, 2.1% n-nonane, 3.9% n-decane, 2.1% n-undecane, 9.8% n-dodecane, 11.8% n-tridecane, 4.7% n-tetradecane, 2.4% n-pentadecane, 4.5% n-hexadecane, 2.4% n-heptadecane, 1.0% n-octadecane, 0.9% n-eicosane, 0.9% n-docosane, 1.1% n-tetracosane, and 0.8% methanol.

The analytical conditions are summarized in Table 1. The normal hydrocarbons and methanol analysis was performed on a GS-OxyPLOT column (Agilent p/n 115-4912). The GC chromatogram is shown in Figure 1.

Table 1. Conditions for Normal Hydrocarbons and Methanol Analysis

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm (Agilent p/n 115-4912)
Carrier gas	Helium, constant flow mode, 40 cm/s @ 50 °C
Inlet	Split/splitless at 325 °C
Split ratio	80:1
Oven temperature	50 °C (2 min); 10 °C/min to 290 °C (2 min)
Post-run	300 °C (2 min)
Detector	FID at 325 °C
Injection size	0.2 µL

In Figure 1, the GS-OxyPLOT column shows unique retention characteristics for methanol. The lower boiling point hydrocarbons were not strongly retained on the stationary phase and eluted through the FID very rapidly. The methanol eluted after n-C14, allowing it to be quantified without any interference from the hydrocarbon matrix, and making it feasible for trace-level methanol analysis in a range of hydrocarbon streams.

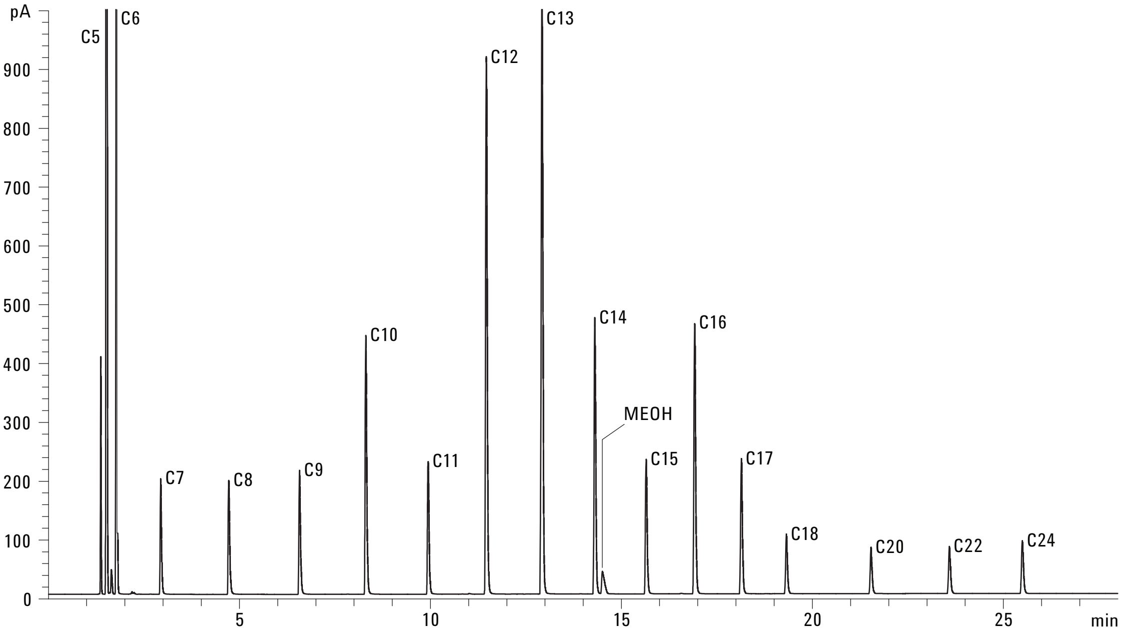

Figure1. Analysis of methanol and normal hydrocarbons on a GS-OxyPLOT column, 10 m × 0.53 mm × 10 µm.

In addition, the baseline was quite smooth, even when the oven temperature was up to 290 °C. GS-OxyPLOT has an upper temperature limit of 350 °C and exhibits virtually no bleed, making it widely applicable for long-term reliable analysis.

Analysis of Alcohols

A mixture containing a range of primary alcohols from methanol to lauryl alcohol was analyzed on a GS-OxyPLOT column using a temperature-programmed method. Table 2 lists conditions for alcohols separation, and the resulting chromatogram is shown in Figure 2.

Sample

The sample had an approximate concentration (v/v) of 1% methanol, ethanol, propanol, butanol, amyl-alcohol, heptanol, octanol, nonanol, decyl alcohol, and lauryl alcohol in toluene.

As can be seen in Figure 2, all of the alcohols are separated and eluted with good peak shape within an analysis time of 15 min. In this experiment, oven temperature was set up to 300 °C. Thanks to its advanced dynamic coating process, Agilent's GS-OxyPLOT stationary phase exhibits virtually no detector spiking due to particle generation from the phase coating [3].

Due to the high viscosity of alcohols, especially decyl alcohol and lauryl alcohol, it is necessary to wash the needle after each injection in case of carryover problems.

Table 2. Conditions for Alcohols Analysis

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm
Carrier Gas	Helium, constant flow mode, 40 cm/s at 150 °C
Inlet	Split/splitless at 325 °C
Split ratio	50:1
Oven temperature	150 °C (0 min); 10 °C/min to 300 °C (5 min)
Detector	FID at 325 °C
Injection size	0.2 µL

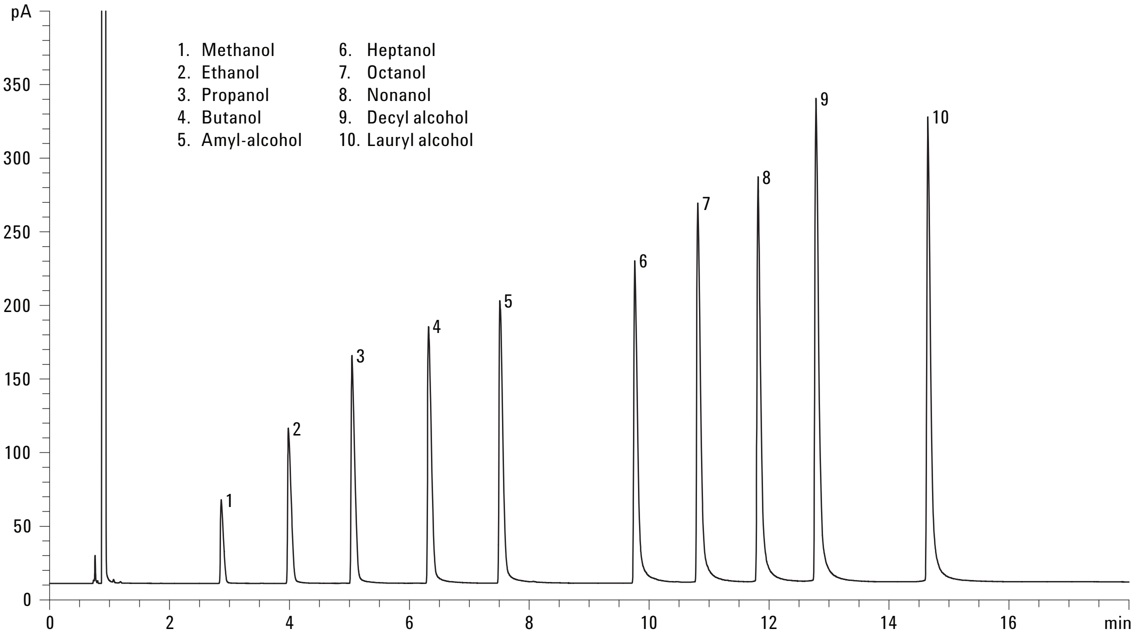

Figure 2. Separation of alcohols using GS-OxyPLOT, 10 m × 0.53 mm × 10 µm.

Influence of Temperature on the Selectivity of GS-OxyPLOT

To polar stationary phases, the temperature has a direct influence on the selectivity. GS-OxyPLOT offers extremely high polarity. The analysis of normal hydrocarbons and methanol demonstrated that methanol elutes after n-C14. Using a mixture containing methanol, n-tetradecane, and n-pentadecane, isothermal Kovats retention indices were tested at isothermal oven temperatures of 150, 200, 220 and 250 °C, respectively (Table 3). The relationship between Kovats retention indices and oven temperature is shown in Table 4.

Table 3. Conditions for Kovats Retention Indices Test

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm
Carrier gas	Helium, constant flow mode, 30 cm/s at 150 °C
Inlet	Split/splitless at 250 °C 100:1 split ratio
Oven temperature	150, 200, 220, and 250 °C, respectively; isothermal
Detector	FID at 250 °C
Injection size	0.2 µL

Table 4. Kovats Retention Indices and Oven Temperature (n > 3)

Oven temp.	150 °C	200 °C	220 °C	250 °C
LOT1	1419	1418	1418	1413
LOT2	1420	1421	1419	1417

Retention index, Ix, was calculated using the following equation:

$$Ix = 100n + 100[\log(t_x) - \log(t_n)]/[\log(t_{n+1}) - \log(t_n)]$$

Where t_n and t_{n+1} are retention times of the reference n-alkane hydrocarbons eluting immediately before and after chemical compound X; t_x is the retention time of compound X. Here compound X is methanol, the reference n-alkane hydrocarbons are n-tetradecane and n-pentadecane, respectively.

Table 4 shows good repeatability of Kovats rentention indices for two different lots of GS-OxyPLOT columns. The retention index for methanol only changed by less than 10 index units over 100 °C temperature difference. Therefore, when the oven temperature changes from 150 to 250 °C, it has little influence on the selectivity of GS-OxyPLOT.

Influence of Moisture on GS-OxyPLOT

Some PLOT columns can adsorb water, which can lead to changes in retention times and selectivity for analytes. Therefore, column performance will be influenced greatly in the presence of water. Although cumbersome solvent-extraction procedures can be performed before injection, injecting sample that contains water is, in some cases, unavoidable.

From a GC point of view, water is a less-than-ideal solvent. The problems associated with water include large vapor expansion volume, poor wet ability and solubility in many stationary phases, detector problems, and perceived chemical damage to the stationary phase. In order to test the effect of water, a GS-OxyPLOT column that had gone through about 1,500 runs was tested before and after injecting 100% aqueous samples.

Water has a large vapor expansion volume; the vapor volume of water (assuming a 1-µL injection) can easily exceed the physical volume of the injection liner (typically 200 to 900 µL). The volume for the liner used in this experiment (Agilent p/n 5183-4711) is 870 µL, so the injection volume was set as 0.2 µL. Table 5 lists the conditions for the moisture testing, and the resulting chromatograms are shown in Figure 3.

Table 5. Conditions for Moisture Test

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm
Carrier gas	Helium, constant flow mode, 38 cm/s at 150 °C
Inlet	Split/splitless at 300 °C 15:1 split ratio
Oven temperature	150 °C isothermal, post-run: 300 °C (5 min)
Detector	FID at 300 °C, H2:45mL/min, air: 400 mL/min, makeup: 30 mL/min
Injection size	0.2 µL
Sample	0.1% n-Dodecane, Methyl tert-butyl ether, n-Tridecane, Iso-Butyraldehyde, n-Tetradecane, Methanol, Acetone, and n-Pentadecane

As shown in Figure 3, the area of n-pentadecane remained the same before and after 100 injections of water. However, compared with the area before injecting water, the area of methanol (peak 6) decreased by 50%, and the area of acetone (peak 7) decreased by14.4% after 100 injections of water (see Table 6). It demonstrated that water can affect the activity of GS-OxyPLOT, especially for the analysis of those relatively low molecular weight oxygenated compounds, such as methanol and acetone.

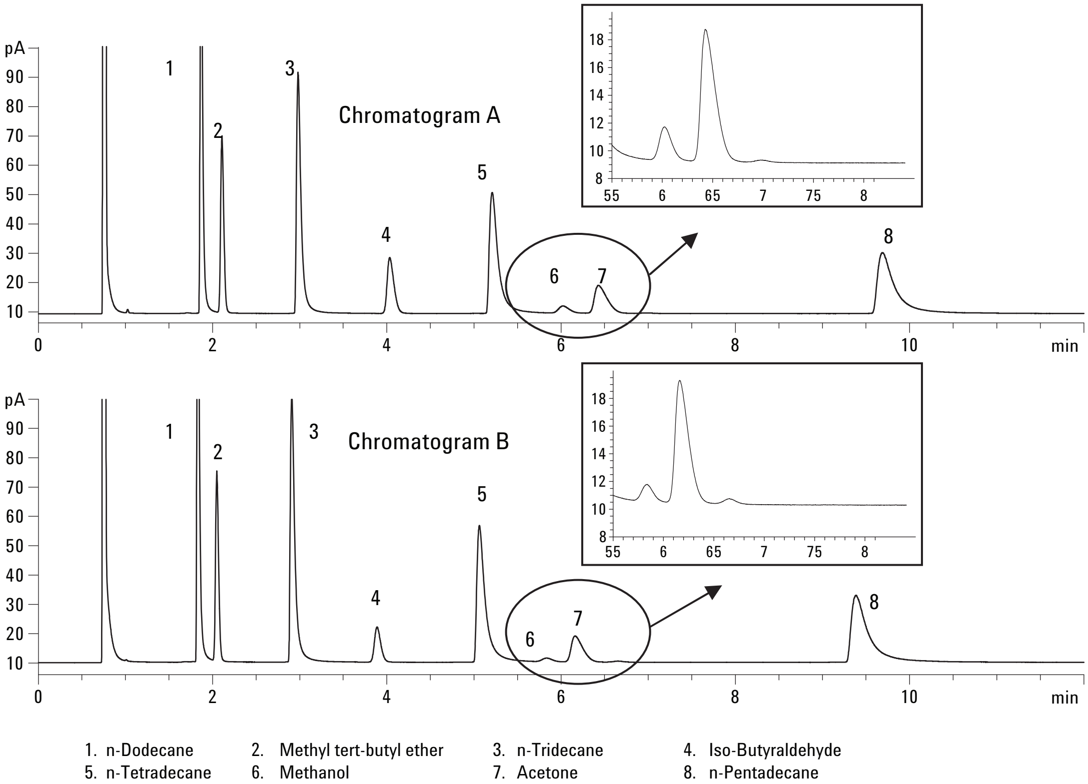

Figure 3. Comparison of test mixture separation before (A) and after (B) 100 injections of water.

As for retention times and column efficiency, they are not strongly influenced. After 100 injections of water, the retention time of C15 changed from 9.689 min to 9.384 min, and the column efficiency of C15 changed from 14,792 to 14,781.

Condition the column at 300 °C for two hours, followed by 12 hours at 250 °C. As shown in Figure 4 and Table 6, it is obvious that GS-OxyPLOT phase can be regenerated by conditioning.

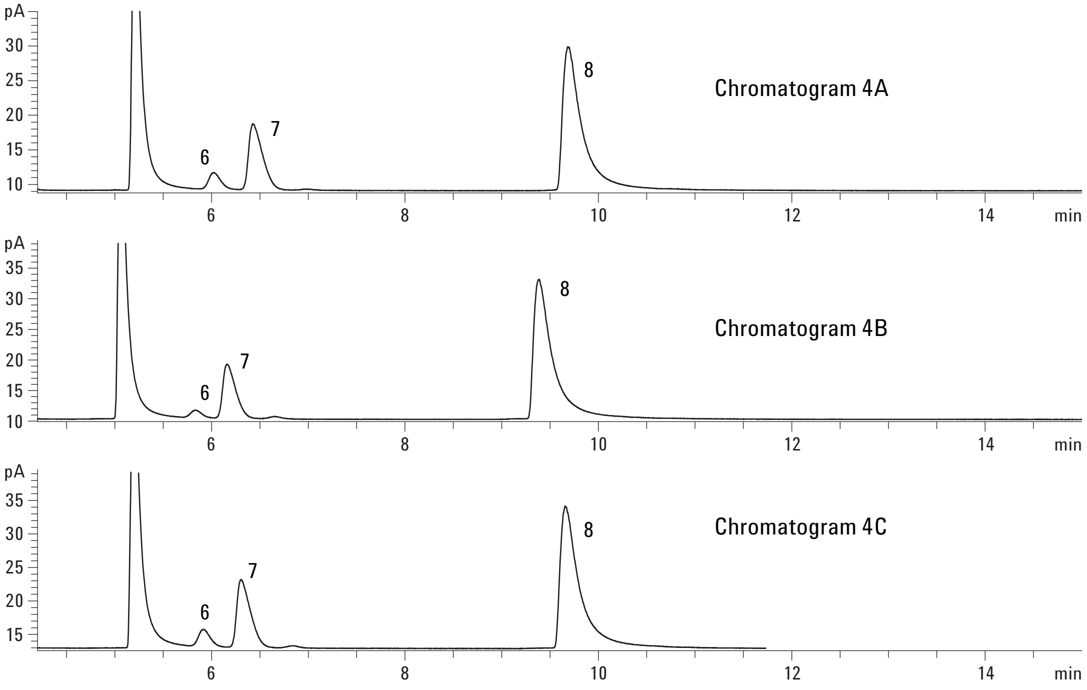

Figure 4. Expanded view shows comparison of test mixture separation on GS-OxyPLOT.
4A. Before injection of water. 4B. After 100 injections of water. 4C. After conditioning the column.

Table 6. Comparison of Test Mixture Separation

	Methanol			Acetone			n-Pentadecane		
	Before injection of water	After 100 injections of water	After conditioning column	Before injection of water	After 100 injections of water	After conditioning column	Before injection of water	After 100 injections of water	After conditioning column
RT (min)	6.022	5.835	5.915	6.429	6.160	6.305	9.689	9.384	9.658
Area	20.23	9.18	20.88	94.53	80.92	98.07	277.79	287.7	287.9
Plates	11887	12920	11616	9532	10357	9573	14792	14781	15100

After conditioning the GS-OxyPLOT column, the peak area and retention time reproducibility were determined. Figure 5 and Table 7 show excellent RT precision, lower than 0.6% over five test mixture runs on this GS-OxyPLOT column. The peak area has a relative standard deviation (RSD%) below 2.5%. It proved that column performance can be restored via conditioning.

Determination of Methanol

The following analysis of methanol followed ASTM D7059 [4]: “Standard Test Method for Determination of Methanol in Crude Oils by Multidimensional Gas Chromatography.” Methanol was determined by gas chromatography with FID using internal standard method with GS-OxyPLOT column.

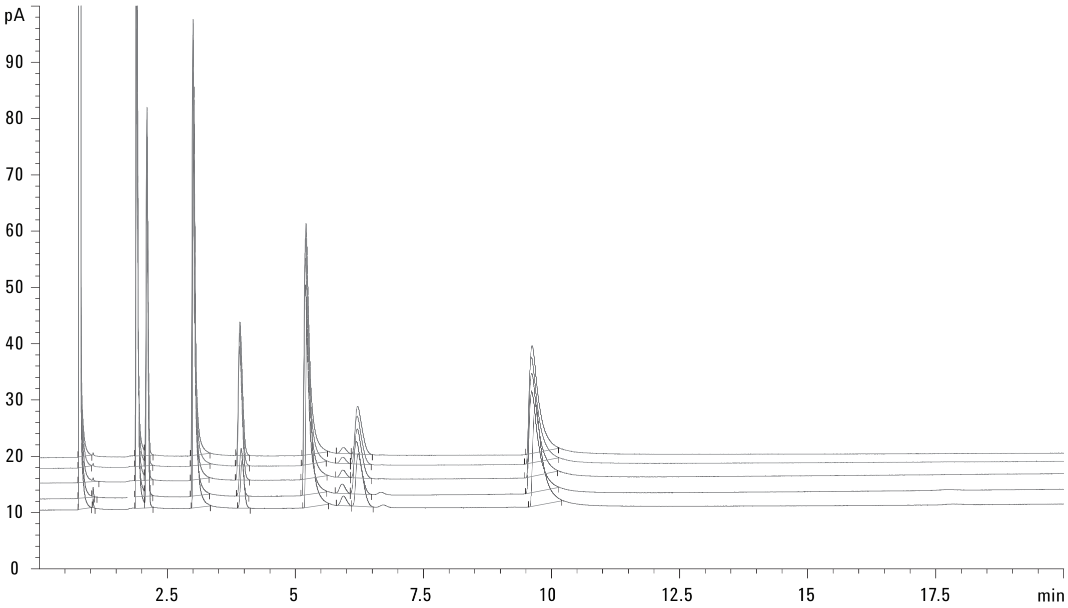

Figure 5. Fifth run overlaid using GS-OxyPLOT (after conditioning column).

Table 7. Peak Area Reproducibility and Retention Time Reproducibility on GS-OxyPLOT (after conditioning column)

Compound (by eluted order)	Dodecane	MTBE	Tridecane	Iso-Butyraldehyde	Tetradecane	MeOH	Acetone	n-C15
Area RSD% (N = 5)	1.18	1.58	1.59	2.49	1.15	2.12	1.98	1.82
RT RSD% (N = 5)	0.18	0.12	0.26	0.55	0.29	0.16	0.19	0.33

Reagents and Materials

Carrier gas, Helium, > 99.95% purity
Methanol, > 99.9% purity
1-propanol, > 99.9% purity, and containing < 500 ppm methanol
Toluene, > 99.9% purity, and containing < 0.5 ppm methanol

A set of calibration standards 5, 25, 125, 250, 500, 1,000 and 1,500 ppm (m/m) of methanol, and each containing 500 ppm (m/m) of 1-propanol internal standard, were prepared in toluene.

The calibration standard solutions should be stored in tightly sealed bottles in a dark place below 5 °C.

Linearity

Under the conditions listed in Table 8, the methanol calibration standards were analyzed. The linearity is shown by plotting the response ratio of methanol and internal standard 1-propanol against their amount ratio (see Figure 6). For methanol, good linearity was gained ranging from 5 to 1,500 ppm. The correlation r^2 value for the calibration curve is higher than 0.999.

Figure 7 and Figure 8 are chromatograms of methanol at a level of 5 ppm and 1500 ppm, respectively. At a relatively high concentration of 1500 ppm, methanol still could get a sharp peak. The limit of quantification (LOQ) was calculated to be 1 ppm using the chromatogram of 5 ppm methanol.

Table 8. System Settings for the Calibration Curve

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm
Carrier gas	Helium, constant flow mode, 50 cm/s at 150 °C
Inlet	Split/splitless at 250 °C 10:1 split ratio
Oven temperature	150 °C (3 min); 20/min to 300 °C (5 min)
Detector	FID at 325 °C
Injection size	1 µL

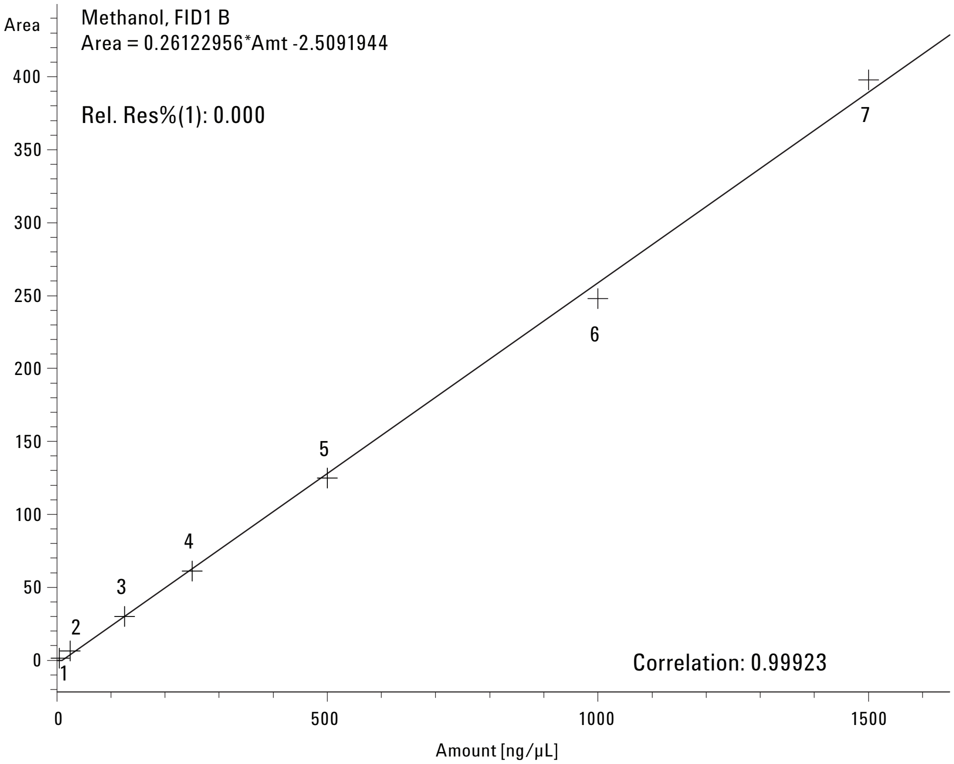

Figure 6. The calibration curve of methanol in toluene.

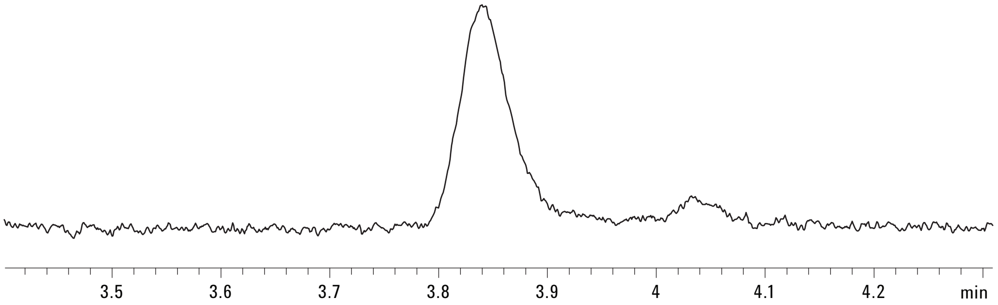

Figure 7. Test mixture of 5 ppm methanol in toluene.

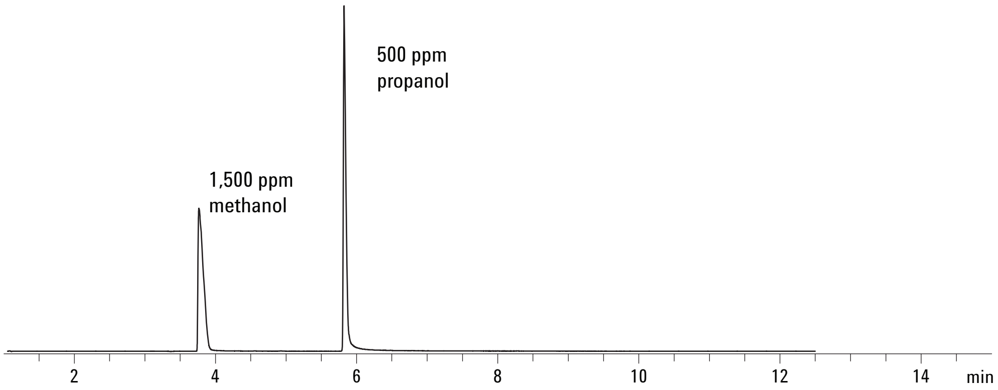

Figure 8. Test mixture of 1,500 ppm methanol in toluene.

Repeatability

The reproducibility of the GS-OxyPLOT is given in Table 9. Those values were obtained by the replicate analysis of different methanol levels (25, 125, and 1,500 ppm) in different days. The injection was done by ALS with RSD no less than 3% either intraday or interday analysis, which was very low for this type of determination.

Life Span

Under the conditions in Table 5, a mixture was analyzed with a GS-OxyPLOT column which went through 1,500 injections of methanol. It shows that the column has a long lifetime. The GS-OxyPLOT column still has good resolution for each compound and high efficiency of 1,482 plates per meter for n-pentadecane (see Figure 9).

Table 9. Relative Standard Deviations Intraday and Interday at Different Levels (25, 125, and 1,500 ppm) of Methanol

Day	25 ppm (average)	RSD (%)	125 ppm (average)	RSD (%)	1,500 ppm (average)	RSD (%)
D 1	25.2	0.46	123.9	0.45	1507.3	0.55
D 2	25.3	1.53	123.2	0.79	1494.4	0.45
D 3	24.4	0.36	125.4	1.71	1523.5	0.35
D 4	25.9	1.06	123.0	0.90	1537.8	0.51
D 5	23.9	0.44	121.1	0.76	1502.4	1.03
Stand. dev.	0.7		1.70		17.4	
Average	24.97		123.6		1513.1	
RSD (%)	2.8		1.37		1.15	

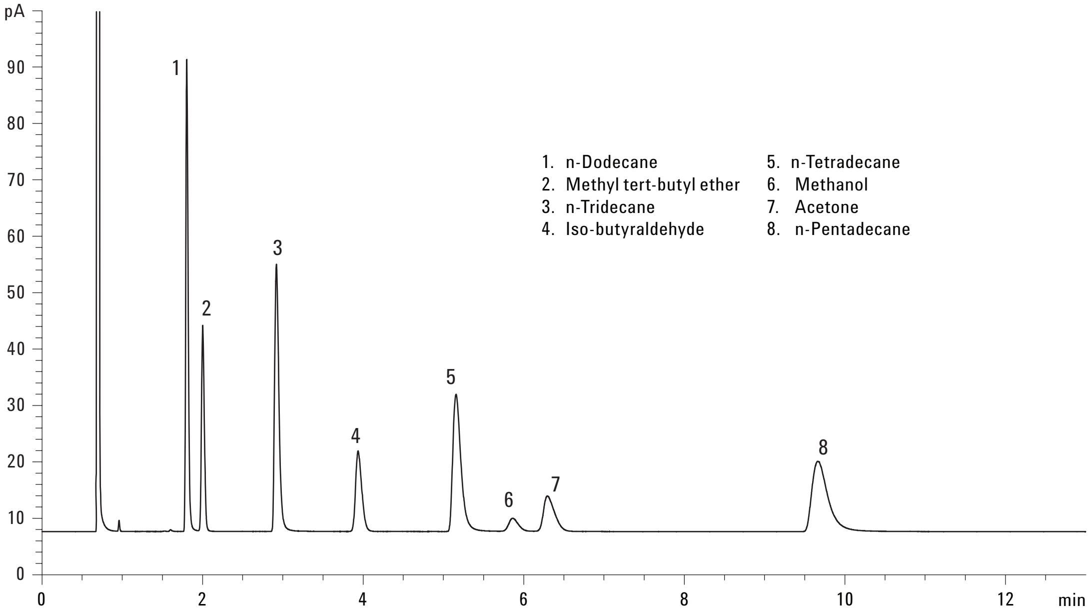

Figure 9. Chromatogram of performance mixture after 1,500 injections.

Conclusions

GS-OxyPLOT provides good retention and selectivity for oxygenated compounds. Normal alkanes up to C24 and primary alcohols up to lauryl alcohol can elute from GS-OxyPLOT within its program temperature maximum limit of 350 °C. Methanol elutes after n-C14 with retention index higher than 1,400; the retention index is quite stable from 150 to 250 °C, allowing methanol to be measured at low levels in a wide range of hydrocarbon streams.

Methanol has to be measured usually at specs as low as 5 ppm. From 5 to 1,500 ppm, it shows good linearity on GS-OxyPLOT. And the column has proven extremely stable with long lifetime.

GS-OxyPLOT can tolerate a little amount of water in samples, and column performance can be restored via conditioning.

GS-OxyPLOT can be used for a single-column system or in multidimensional GC systems. It offers a unique solution for the analysis of oxygenates in the chemical and petrochemical industries.

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Agilent Technologies

Detection of Sulfur Compounds According to ASTM D5623 in Gasoline with Agilent's Dual Plasma Sulfur Chemiluminescence Detector (G6603A) and an Agilent 7890A Gas Chromatograph

Application

Hydrocarbon Processing

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Abstract

Sulfur components in gasoline samples are detected utilizing ASTM D 5623 with an Agilent 7890A GC configured with Agilent 355 dual plasma sulfur chemiluminescence detector (DP SCD). The 355 SCD response is linear, equimolar, and provides a linear range from 0.1 to 10 ppm. The coelution of hydrocarbon and sulfur peaks does not present a problem for the detector. The detection limits of sulfur compounds in gasoline are down to 20 ppb, while no quenching was found in the gasoline sample analysis.

Introduction

Gas chromatography with sulfur chemiluminescence detection (SCD) provides a rapid and highly specific means to identify and quantify various sulfur compounds that may be present in petroleum feed stocks and products, such as gasoline.

Frequently, petroleum feeds and products contain varying amounts and types of sulfur compounds. Many sulfur compounds can be corrosive to equipment, can inhibit or destroy catalysts employed in downstream processing, and can impart undesirable odors to products. The ability to speciate sulfur compounds in various petroleum liquids is useful in controlling sulfur compounds in finished products and is frequently more important than the ability to simply measure total sulfur content alone.

The SCD burner easily mounts on the 6890 and 7890A GCs, and incorporates features for easier and less frequent maintenance. The DP technology harnesses the power of dual flame plasma combustion, optimizing combustion of the sample matrix and formation of sulfur monoxide (SO).

The 355 DP SCD response is inherently linear, equimolar, and far less susceptible to hydrocarbon interference. These advantages eliminate the need for linearizing data or determining separate response factors for individual sulfur compounds. Furthermore, hydrocarbons are virtually invisible to the DP SCD. The coelution of hydrocarbon and sulfur peaks does not show quenching. Frequent column changes are required for analysis of various hydrocarbon products by flame photometric detectors (FPD) to avoid serious quenching and inaccurate results. ASTM Method D5623 utilizes the sulfur chemiluminescence detector (SCD) for the detection of sulfur compounds in gasoline.

Experimental

An Agilent 7890A GC configured with split/splitless inlet (Sulfinert-treated), 7683B autosampler, and Agilent 355 DP SCD were used. The sulfur standards in toluene and iso-octane (10:90) were purchased from Supelco (Bellefonte, PA). The component information is in Table 1.

Table 1. Sulfur Standards Components

	Components	Formula	Concentration (ppm) (w/w)
1	Ethyl mercaptan	CH_3CH_3SH	11.62
2	Dimethyl sulfide	$(CH_3)_2S$	11.92
3	Carbon disulfide	C_2S	17.84
4	Isopropyl mercaptan	$(CH_3)_2CHSH$	34.32
5	T-butyl mercaptan	$(CH_3)_3CSH$	11.28
6	n-propyl mercaptan	$CH_3CH_2CH_2SH$	5.93
7	Methylethyl sulfide	$CH_3CH_2SCH_3$	11.87
8	Thiophene	C_4H_4S	14.81
9	Sec-butyl mercaptan	$CH_3CH_2CH(SH)CH_3$	23.26
10	n-butyl mercaptan	$CH_3(CH_2)_3SH$	5.89
11	Dimethyl disulfide	CH_3SSCH_3	14.75
12	2-methyl thiophene	C_5H_6S	14.29
13	3-metyl thiophene	C_5H_6S	21.35
14	Diethyl disulfide	$(C_2H_5)_2S_2$	27.99
15	Benzo(b)thiophene	C_8H_6S	40.49

NIST Standard Reference Material 2299, Sulfur in Gasoline, was used. The total sulfur in gasoline is 13.6 ± 1.5 µg/g based on analyses by isotope dilution thermal ionization mass spectrometry (ID-TIMS). Homogeneity testing was performed using X-ray fluorescence spectrometry.

Experimental Conditions

7890A GC Conditions

Front inlet	Split/splitless (Sulfinert-treated capillary inlet system)
Heater	275 °C
Pressure	10.951 psi
Septum purge flow	3 mL/min
Mode	Split
Gas saver	20 mL/min after 2 min
Split ratio	10 :1
Split flow	15 mL/min
Oven	30 °C (1 min) 10 °C/min 250 °C (1 min)
Column	HP-1 30 m × 0.32 mm × 4 µm (P/N 19091Z-613)

SCD Conditions – Agilent G6603A

Burner temperature	800 °C
Vacuum of burner	372 torr
Vacuum of reaction cell	5 torr
H_2	40 mL/min
Air	53 mL/min

Results and Discussion

Several commercially available sulfur detectors are available for the determination of sulfur compounds in various matrices. When compared to flame photometric detection (FPD), pulsed flame photometric detection (PFPD), atomic emission detection (AED), and inductively coupled plasma-mass spectrometry (ICP-MS), the SCD shows the best performance based on stability, cost, and quantification. [2,3]

With DP technology, the performance of Agilent 355 SCD has been further enhanced, for unsurpassed stability, selectivity, and lack of quenching. Table 2 lists the DP SCD stability at different sulfur levels.

Table 2. Repeatability of Sulfur Compounds at Different Concentrations (Refer to Table 1 for peak identification.)

	1	2	3	4	5	6	7	8	10	11	12	13	14	15
Con. ppm	1.16	1.79	1.78	3.42	1.13	0.59	1.19	3.80	0.59	1.47	1.43	2.14	2.80	4.0
RSD (%)	2.8	3.6	3.1	1.9	3.0	2.7	3.9	3.9	2.9	2.1	2.2	2.9	0.4	3.7
Con. ppm	0.12	0.18	0.18	0.34	0.11	0.06	0.12	0.38	0.06	0.15	0.14	0.21	0.28	0.4
RSD (%)	5.7	7.4	3.4	3.7	6.6	4.8	5.7	4.8	8.0	4.0	3.3	4.7	7.3	3.1

Correlation coefficients of the tested sulfurs over three orders of magnitude were better than 0.99 (R^2). Table 3 shows the linearity of each sulfur compound. Figure 1 shows the chromatogram of sulfurs in a hydrocarbon matrix without interference (1 to approximately 2 µg/kg).

Table 3. Linear Ranges of Tested Sulfurs (Refer to Table 1 for peak identification.)

Analytes	Concentration Range	Linearity (R^2)
1	0.1ppm to 10ppm	0.9975
2	0.1ppm to 10ppm	0.9982
3	0.1ppm to 10ppm	0.9991
4	0.1ppm to 10ppm	0.9992
5	0.1ppm to 10ppm	0.9995
6	0.1ppm to 10ppm	0.9996
7	0.1ppm to 10ppm	0.9998
8/9	0.1ppm to 10ppm	0.9998
10	0.1ppm to 10ppm	0.9994
11	0.1ppm to 10ppm	0.9999
12	0.1ppm to 10ppm	0.9997
13	0.1ppm to 10ppm	0.9995
14	0.1ppm to 10ppm	0.9997
15	0.1ppm to 10ppm	0.9999

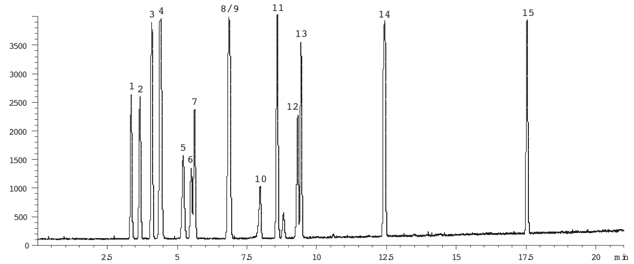

Figure 1. Chromatogram of sulfur standard in hydrocarbon matrix. (Refer to Table 1 for peak identification.)

The data in Table 4 illustrate the sensitivity (S/N) of 355 SCD for trace-level analysis (approximately 20 ng/kg) of sulfurs in a hydrocarbon matrix. Figure 2 shows the chromatogram of trace sulfurs, which also indicates no interferences in the analysis.

Table 4. Sulfur Sensitivity (Refer to Table 1 for peak identification.)

Peak No.	1	2	3	4	5	6	7	8/9	10	11	12	13	14	15
S/N	2.0	2.5	5.0	4.6	1.8	1.6	2.4	5.0	1.5	3.6	2.0	4.6	3.2	5.2

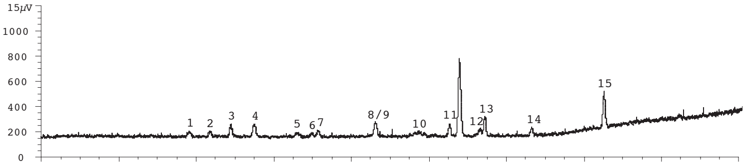

Figure 2. Chromatogram of sulfurs at trace levels (20 ng/g). (Refer to Table 1 for peak identification.)

Gasoline Samples Analysis

NIST Standard Reference Material 2299 was detected on an Agilent SCD and the mass concentration of total sulfur in sample was calculated by summing the sulfur content of all sulfur components (known and unknown) in the sample to arrive at its total sulfur value as recommended by ASTM 5623.

Figure 3A shows the chromatogram of the sulfur standard and Figure 3B shows the chromatogram of the standard gasoline sample. The total amount of sulfur is calculated by summing all the peak areas in Figure 3B and quantitated as thiophene 11.8 µg/g of total sulfur with an RSD 2.7% (n = 5) was calculated in the gasoline sample. This was within the specified range of 13.6 ± 1.5 µg/g.

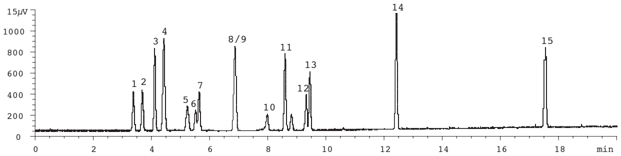

Figure 3A. Chromatogram of sulfur standard.

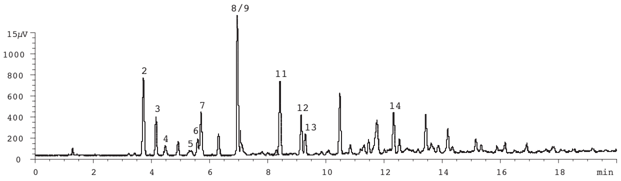

Figure 3B. Chromatogram of gasoline standard sample. (Refer to Table 1 for peak identification.)

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Conclusions

The Agilent DP SCD is used for the detection of sulfur compounds in a complex hydrocarbon matrix. The results show that the DP SCD has linear response to sulfur compounds without quenching, yielding MDLs down to 20 ng/g. This solution is available as an Agilent preconfigured system; please refer to Agilent SP1 7890-0365 for ordering information.

References

1. ASTM 5623: Standard test method for sulfur compounds in light petroleum liquids by gas chromatography and sulfur selective detection
2. Roger L. Firor and Bruce D. Quimby, “Analysis of Trace Sulfur Compounds in Beverage-Grade Carbon Dioxide,” Agilent Technologies publication 5988-2464EN
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Agilent Technologies

Fast Hydrocarbon and Sulfur Simulated Distillation Using the Agilent Low Thermal Mass (LTM) System on the 7890A GC and 355 Sulfur Chemiluminescence Detector

Application Note

Hydrocarbon Processing

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Abstract

A fast multielement simulated distillation method (SimDis) based on Low Thermal Mass (LTM) column technology is described. The LTM system technology using resistive heating allows rapid temperature programming with extremely fast column cooldown. Significantly shortened analytical cycle times as compared to conventional air bath GC ovens are achieved. The method combines hydrocarbon SimDis with an FID with sulfur SimDis using the Agilent 355 sulfur chemiluminescence detector (SCD) in a series configuration. The results show that the LTM method produces a run time for both hydrocarbon and sulfur boiling point distribution at least six times shorter than the conventional ASTM D2887 procedure [1]. The results agree with the specification in ASTM D2887 for the reference gas oil checkout sample.

Introduction

Sulfur and carbon simulated distillation provide meaningful information to optimize refining processes and demonstrate compliance with petroleum product specifications. To meet the increasing needs for greater productivity, a fast sulfur and carbon SimDis method was developed using LTM technology. LTM technology was developed by RVM Scientific and acquired by Agilent Technologies in 2008 [2]. The Agilent 7890A system is designed to work with the LTM column module components to heat and cool the column very efficiently to significantly shorten analytical cycle times as compared to conventional air bath GC oven techniques involving much higher thermal mass. Aside from selectivity, temperature programming is an extremely useful feature of gas chromatography. When appropriate column dimensions and flow rates are choosen, high program rates (such as, 200 °C/min) can be used to great advantage. Agilent's method translation software can be useful in this regard [3]. For example, as temperature program rates increase, a corresponding increase in column flow rate should also be considered to achieve more optimal overall system performance. The system (except external power supply) is built into a replacement GC oven door, which is mounted as an add-on to an Agilent 7890A GC. The method described here combines hydrocarbon SimDis with sulfur selective SimDis using an FID and an SCD in series with simultaneous acquisition of both signals.

Experimental

This two-channel SimDis application uses the Agilent 7890A GC configured with a high-temperature programmable temperature vaporizer (HT-PTV) inlet and an SCD mounted in series with an FID by using a special adapter. A 5-inch format LTM column module is used for the analysis. Samples, such as boiling point (BP) calibration C5-C40, polywaxes, and resids, that are too viscous or waxy to sample with a syringe are heated to approximately 80 °C for a few minutes before injection.

The SimDis application software can process one or two channels of signal data (FID and SCD) from the GC ChemStation. The software is based on four modules: Browse, Setup, SimDis, and Report. Each module provides specific functions to rapidly perform multielement SimDis calculations. For example, the Setup module allows you to assign the files to use for BP Calibration, Blank, and QC reference. The detailed GC conditions used are listed in Table 1.

Table 1. Gas Chromatographic Conditions

HT-PTV inlet	
Temperature	350 °C
Split ratio	30:1
Injection volume	0.1 µL
7890/LTM	
Column (LTM)	DB-1 5 m × 320 mm × 1 µm
LTM temperature program	45 to 350 °C at 150 °C/min, hold 1 min (GC oven: 300 °C, held for duration)
Column flow (He)	Ramp pressure: 18 psi to 42 psi at 11.8 psi/min
FID temperatures	350 °C
H_2 flow	40 mL/min
Air flow	400 mL/min
Make up (N_2)	40 mL/min
Data rate	5 Hz
SCD	
Burner temperature	800 °C
Vacuum of burner	324 Torr
Vacuum of reaction cell	11.6 Torr
H_2	40 SCCM
Air	8.3 SCCM
Data rate (AIB)	5 Hz
LTM system	G6578A, bundle for 1-channel 5-inch modules

Processing Two-Channel Data in the SimDis Software

The Agilent SimDis System enables the use of gas chromatography to determine the boiling point range distribution and percent recovery of petroleum fractions. The SimDis software allows for reports to be generated in two ways: automated and manual. Both require the user to first manually set a blank, calibration, and optional QC reference chromatogram. When working with dual channels, the SimDis software requires that each channel be labeled by the detector type rather than the defaults used by the GC ChemStation. Since the SCD operates off the analog input board (AIB), its signal begins with "AIB." For this reason, the Post-Run command macro SCDnamer.mac must be run to rename the signal file. The macro renames the AIB2B.ch channel as SCD1.ch. If the channel name is not corrected, the software will switch the FID and SCD channels during analysis, giving faulty results. The macro code to do this is shown below. It assumes that the AIB is in the rear position (B).

```
! SCDNamer call this as a post run command when an SCD is installed

! it renames the dual channel AIB2B.ch to SCD1.ch to allow simdis to properly calibrate

NAME SCDNamer

! This macro renames the SCD files named as AIB2B.ch to SCD1.ch
if filestat(mode,dadatapath$+dadatafile$+"\AIB2B.CH")=1
```

```
rename dadatapath$+dadatafile$+"\AIB2B.ch",dadatapath$+dadatafile$+"\SCD1.ch"

print "File Renamed"

else

print "No AIB2B File found"

endif

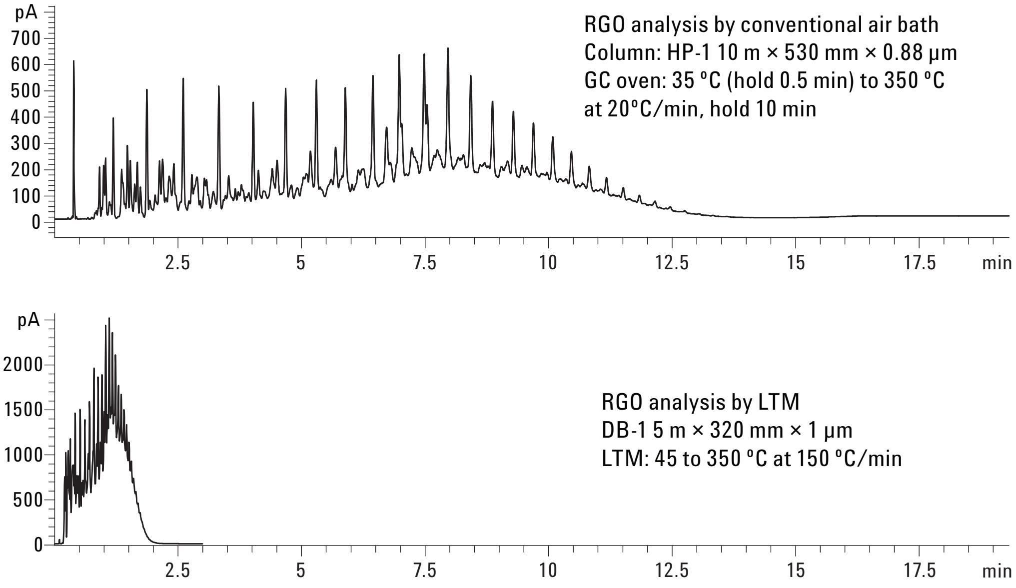
RETURN

ENDMACRO
```

Under the Setup tab of SimDis, select the default chromatograms to be used for the calculation. All desired solvent masking should be done here. The calibration run should have major carbon peaks identified; this can be done with an imported calibration table from ChemStation or manually in SimDis. The QC reference should have concentrations and dilution factors entered. Now enter the SimDis pane and set the parameters to be used. Do not include the solvent peak in the calculations and account for the baseline and noise using a zeroing method. In order to get proper percent recovery values make sure Normalize to 100% is not selected and a proper dilution factor is entered. Set the settings as default. For automation, enter ChemStation and select SimDis > Setup > Use SimDis Defaults under Data Analysis and select a report to generate after each run. For manual operation, select the desired chromatogram under the Report pane in SimDis and enter the report pane to view and print results.

Results and Discussion

The LTM column module employes a unique direct resistive heating technology using ceramic-insulated heating wire where contact with the capillary column is maximized. This is packaged in a very low mass assembly. Accurate and precise temperature sensing is possible by incorporating the temperature sensor with the capillary GC column. This technology greatly reduces GC analytical cycle times, addressing demands for greater productivity. The result for the D2887 reference gas oil (RGO) shows that the run time using LTM is less than 2.5 minutes, or about six times faster compared to conventional ASTM D2887 procedures. The SimDis results agree with the specifications of ASTM D2887 with excellent repeatability (see Table 2). The upper chromatogram in Figure 1 shows the D2887 RGO analysis by conventional air bath GC oven and the lower chromatogram shows RGO by LTM GC. The run time is about 2.5 minutes and 15 minutes for LTM and conventional air bath GC, respectively.



RGO analysis by conventional air bath
Column: HP-1 10 m × 530 mm × 0.88 µm
GC oven: 35 °C (hold 0.5 min) to 350 °C
at 20°C/min, hold 10 min

RGO analysis by LTM
DB-1 5 m × 320 mm × 1 µm
LTM: 45 to 350 °C at 150 °C/min

Figure 1. Comparison of RGO analysis by LTM and air bath GC ovens.

Table 2. RGO SimDis Results with the LTM System

	ASTM D2887 Values		Observed Value												
	BP, °C	**Allowable difference**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Average**	**Difference**	**RSD%**
IBP	115	7.6	112	113	112	113	112	113	112	113	112	113	112.5	2.5	0.47
10%	176	4.1	173	174	173	174	173	174	173	174	173	174	173.5	2.5	0.30
20%	224	4.9	220	220	220	220	220	220	220	220	220	220	220	4	0.00
30%	259	4.7	254	255	255	255	255	255	255	255	255	255	254.9	4.1	0.12
40%	289	4.3	285	286	285	287	285	286	285	286	286	286	285.7	3.3	0.24
50%	312	4.3	309	310	309	310	309	309	309	309	309	309	309.2	2.8	0.14
60%	332	4.3	329	330	329	330	329	330	329	329	329	329	329.3	2.7	0.15
70%	354	4.3	350	352	351	352	351	352	351	352	351	352	351.4	2.6	0.20
80%	378	4.3	375	376	375	377	375	376	375	376	375	376	375.6	2.4	0.19
90%	407	4.3	404	405	405	406	404	406	404	405	404	405	404.8	2.2	0.19
FBP	475	11.8	474	475	475	476	475	476	475	475	475	475	475.1	–0.1	0.12

A mixture of C5 through C40 n-alkanes with known boiling points which are used for establishing the correlation between RT (min) and BP (°C) can be separated in less than 2.5 minutes with repeatability in retention time better than 0.1 percent relative standard deviation (RSD). Table 3 shows RT stability with RSD of approximately 0.02 to 0.15 percent (C40) using a rapid temperature program of 150 °C/min ramped from 45 to 350 °C. These results indicate a lack of cold spots and temperature nonuniformity in the LTM column module. Figure 2 is an overlay of five consecutive runs of the C5 to C40 calibration mixture.

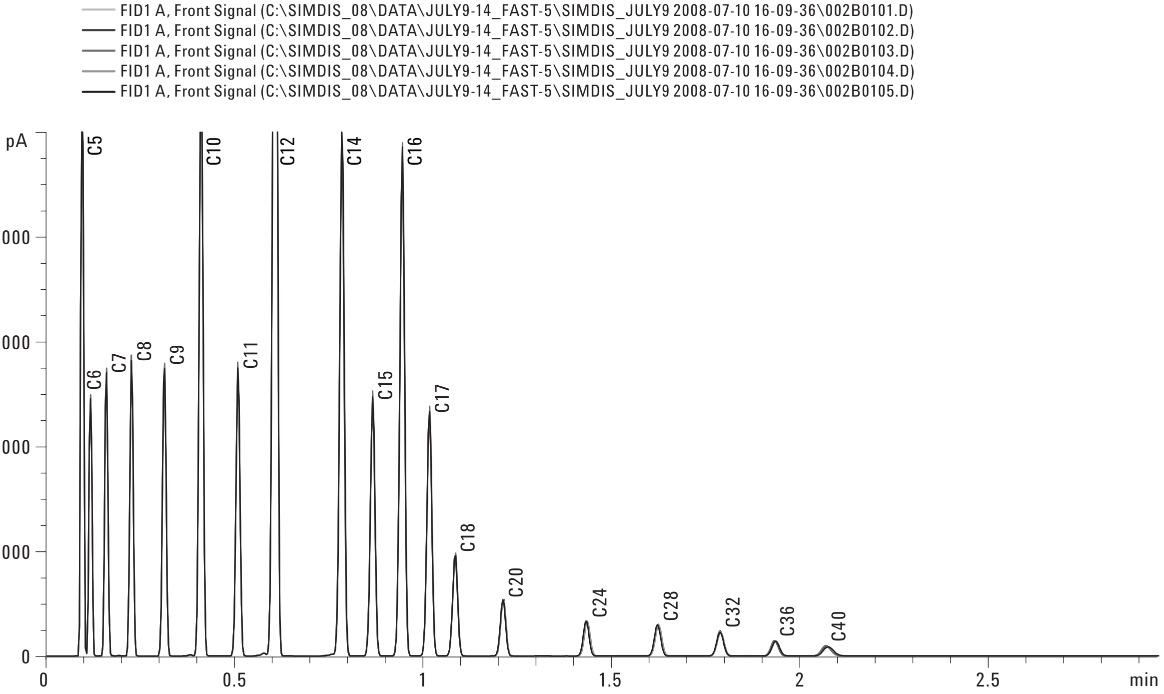


Figure 2. Overlays of five consecutive runs of the C5 to C40 calibration mixture. Chromatographic overlay shows outstanding repeatability. LTM: 45 to 350 °C at 150 °C/min.

Table3. Retention Time Repeatability of C5 to C40 Calibration Mixture (n = 5)

	1	2	3	4	5	Average	SD	RSD%
C5	0.09766	0.09760	0.09766	0.09763	0.09764	0.09764	2.33E-05	0.024
C6	0.11999	0.11992	0.11994	0.11989	0.11993	0.11994	3.67E-05	0.031
C7	0.16285	0.16274	0.16270	0.16263	0.16270	0.16272	8.07E-05	0.050
C8	0.23072	0.23051	0.23045	0.23036	0.23045	0.23050	0.000135	0.059
C9	0.31908	0.31883	0.31877	0.31867	0.31874	0.31882	0.000158	0.049
C10	0.41803	0.41775	0.41779	0.41777	0.41780	0.41783	0.000117	0.028
C11	0.51730	0.51707	0.51711	0.51716	0.51719	0.51717	8.61E-05	0.017
C12	0.61713	0.61688	0.61723	0.61716	0.61721	0.61712	0.000138	0.022
C14	0.79706	0.79676	0.79746	0.79707	0.79733	0.79714	0.000271	0.034
C15	0.87963	0.87964	0.88004	0.87985	0.88009	0.87985	0.000216	0.025
C16	0.95952	0.95940	0.95986	0.95941	0.95966	0.95957	0.000192	0.020
C17	1.03290	1.03263	1.03314	1.03279	1.03257	1.03281	0.000225	0.022
C18	1.10255	1.10190	1.10250	1.10236	1.10201	1.10226	0.00029	0.026
C20	1.23235	1.23131	1.23203	1.23151	1.23060	1.23156	0.000676	0.055
C24	1.45819	1.45721	1.45683	1.45772	1.45470	1.45693	0.001348	0.093
C28	1.65011	1.64884	1.64878	1.65001	1.64698	1.64895	0.001261	0.076
C32	1.81666	1.81587	1.81535	1.81739	1.81562	1.81618	0.000834	0.046
C36	1.96355	1.96259	1.96200	1.96611	1.96522	1.96389	0.001738	0.088
C40	2.10071	2.10110	2.10021	2.10619	2.10665	2.10297	0.003168	0.151

This work combines hydrocarbon SimDis with sulfur selective SimDis using an SCD mounted over the FID for simultaneous dual detector aquisition. In this configuration, about 20% of the FID exhaust gases enter the SCD burner, reducing sensitivity to 1/5 observed in an SCD-only configuration. This series configuration provides more than enough sensitivity for SimDis. A sample with known sulfur concentration is used as a QC reference (external reference sample) to calibrate response factors (RFs) for the sulfur channel needed for calculation of total sulfur. Sulfur linearity of the LTM method was checked by injecting the standard mixture at different concentration levels, ranging from 100 to 1,500 ng/µL (ppm). The calibration curve is displayed in Figure 3, giving a correlation coefficient above 0.999.

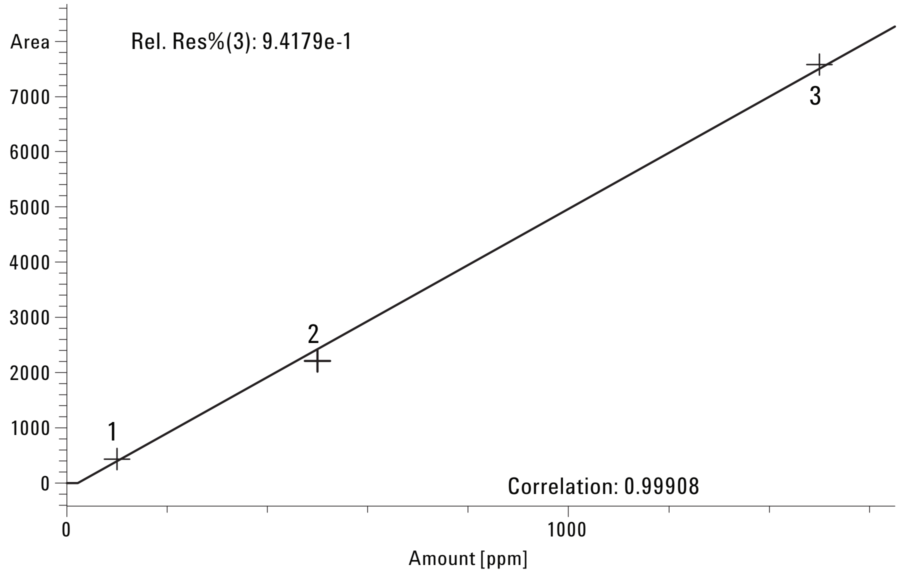


Figure 3. Linearity of sulfur with the SCD and LTM system.

A high-sulfur light cycle oil (LCO) sample was analyzed. Data were processed for hydrocarbon and sulfur simulated distillation, yielding excellent repeatability as shown in Table 4. The RSD is less than 0.4 percent for hydrocarbon and 0.5 percent except that of FBP for sulfur. The average total sulfur is 260.8 ppm with an RSD of 4.83 percent. Figure 4 shows the chromatograms for sulfur (top) and carbon (bottom).

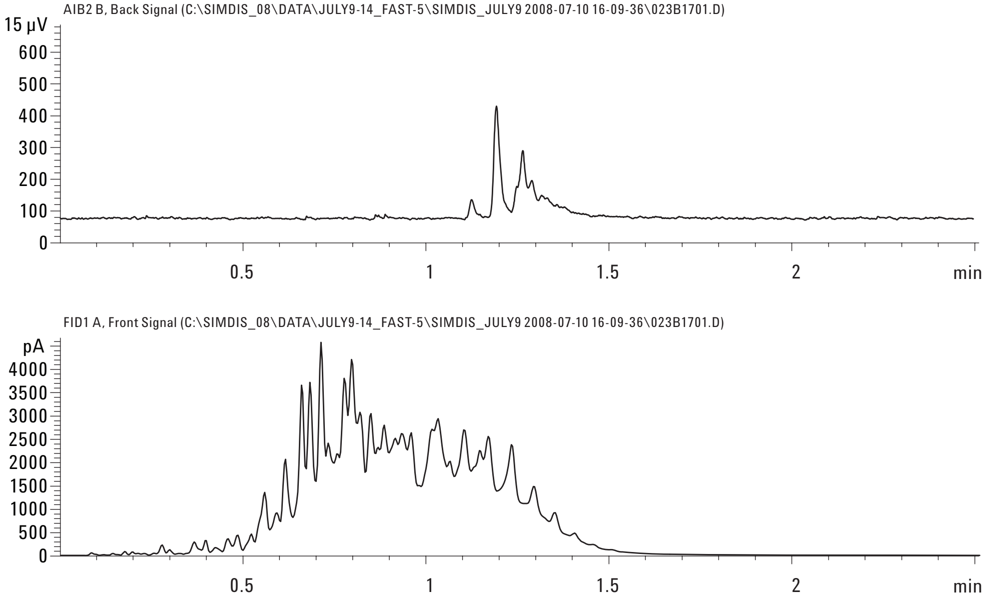


Figure 4. Chromatograms for sulfur and carbon. Sulfur top chromatogram.

Table 4. Hydrocarbon and Sulfur SimDis Results for Light Cycle Oil

						Hydrocarbon SimDis						
						BP, ºC					**Average**	**RSD%**
IBP	139	140	139	140	140	139	140	139	140	139	139.5	0.38
10%	222	223	222	223	223	222	223	222	224	223	222.7	0.30
20%	235	236	235	236	236	235	236	235	236	235	235.5	0.22
30%	249	250	249	250	250	249	250	249	250	249	249.5	0.21
40%	262	262	262	262	262	262	262	262	262	262	262.0	0.00
50%	276	277	277	277	277	277	277	276	277	277	276.8	0.15
60%	293	294	293	294	294	293	294	293	294	293	293.5	0.18
70%	308	309	308	309	309	308	309	308	309	308	308.5	0.17
80%	326	326	326	326	327	326	326	326	326	326	326.1	0.10
90%	347	347	347	347	347	347	347	347	347	347	347.0	0.00
FBP	411	411	411	412	413	412	412	412	412	412	411.8	0.15
						Sulfur SimDis						
						BP, ºC						
IBP	319	320	318	319	320	319	318	319	319	318	318.9	0.22
10%	334	334	334	334	334	334	334	334	334	334	334.0	0.00
20%	335	335	335	335	336	335	335	335	335	335	335.1	0.09
30%	337	337	337	337	337	337	337	337	337	337	337.0	0.00
40%	341	340	343	341	340	345	344	342	341	342	341.9	0.50
50%	349	349	349	349	349	350	349	349	349	349	349.1	0.09
60%	352	351	352	351	352	352	351	352	351	352	351.6	0.14
70%	355	354	355	355	355	355	355	355	355	355	354.9	0.08
80%	361	358	360	360	359	360	360	359	359	360	359.6	0.22
90%	368	365	367	367	366	369	368	367	367	367	367.1	0.30
FBP	399	384	385	386	383	407	392	384	395	395	391.0	2.05
Total sulfur (ppm)	260	237	255	262	252	281	273	254	263	273	260.8	4.83

Conclusions

A fast dual detector (FID and SCD in series) simulated distillation method using an LTM system on the 7890A GC provides a cycle time improvement over conventional systems of about 6X.

The SimDis result for ASTM D2887 RGO shows that the LTM system is equivalent to that of air-bath GCs. Results agree with the RGO specification of ASTM D2887 with RSDs of 0.12 to 0.47 percent across the reported percent off range. Wide boiling range hydrocarbons (C5 to C40 BP calibration mixtures) also show very good RT stability with RSD of 0.02 to 0.15 percent using a rapid column module temperature program of 150 °C /min ramped from 45 to 350 °C and sample injection using the HT-PTV. Sulfur linearity of the LTM/SCD system reveals an excellent correlation coefficient, above 0.999. SimDis of a high sulfur LCO sample shows an RSD of less than 0.4 percent for hydrocarbon and 0.5 percent except that of FBP for sulfur. The average total sulfur is 260.8 ppm, with an RSD of 4.83 percent.

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Dual Channel Simulated Distillation of Carbon and Sulfur with the Agilent 7890A GC and 355 Sulfur Chemiluminescence Detector

Application Note

Hydrocarbon Processing

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Abstract

Two-channel simulated distillation by gas chromatography (GC) for both hydrocarbons and sulfur is described. The method utilizes a 7890A GC configured with a high-temperature programmable temperature vaporizer (HT-PTV) inlet and a sulfur chemiluminescence detector (SCD) mounted in series with a flame ionization detector (FID) by use of a special mounting adapter. A simulated distillation (SimDis) software program provides an easy-to-use solution for sulfur and hydrocarbon simulated distillation. The data show that observed boiling point (BP) values agree with the ASTM D2887 consensus BP values within the allowable differences. The system also demonstrates very good repeatability for both hydrocarbon and sulfur SimDis. An example of a light cycle oil (LCO) analyzed according to D2887 is also included.

Introduction

Sulfur and hydrocarbon simulated distillation results provide meaningful information to optimize refining processes and ensure compliance with petroleum product specifications. A previous application note [1] describes a 6890 GC based system for hydrocarbon simulated distillation by ASTM D2887 [2]. Now with the highly selective Agilent Sulfur Chemiluminescence Detector (SCD), sulfur simulated distillation is possible. This 7890A GC based simulated distillation system consists of acquiring and analyzing simultaneously the specific detector data for hydrocarbon (FID) and sulfur (SCD).

Experimental

This two-channel SimDis application uses the Agilent 7890A GC configured with a high-temperature programmable temperature vaporizer (HT-PTV) inlet, and an SCD mounted onto an FID using a special adapter. Detailed GC conditions used are listed in Table 1.

Table 1. 7890A Gas Chromatographic Conditions (1) D2887, (2) D7213

HT-PTV inlet typical temperature programs	(1) 225 to 350 °C (hold 15 min) at 200 °C/ min to 225 °C at 100 °C /min (2) 50 to 420 °C (hold 15 min) at 200 °C /min to 50 °C at 100 °C /min
Split ratio	(1) 4:1 for diluted sample, 20:1 for nondiluted sample (2) 1:1
Injection volume	(1) 0.1 µL (2) 0.5 to 1 µL
Column	(1) HP-1 10 m × 530 mm × 0.88 µm (19095z-021) (2) DB-HT-SimDis 5 m × 530 mm × 0.15 µm (145-1001)
Column flow (He)	(1) 13 mL/min, constant flow mode (2) 16 mL/min, constant flow mode
FID temperatures	(1) 350 °C (2) 400 °C
H_2 flow	40 mL/min
Air flow	400 mL/min
Make up (N_2)	40mL/min
SCD	
Burner temperature	800 °C
Vacuum of burner	324 torr
Vacuum of reaction cell	11.6 torr
H_2	40 SCCM
Air	8.3 SCCM
Oven programs	(1) 35 °C (hold 0.5 min) to 350 °C at 20 °C/min , hold 10 min (2) 40 to 420 °C at 20 °C/min , hold 6 min
Data acquisition rate	5 Hz typical

SimDis Software

The processes of SimDis analysis include: blank analysis for baseline subtraction, calibration for establishing the relationship between boiling point and retention time (RT), validation for verifying both the chromatographic conditions and calculations in the method, and sample analysis. The Agilent SimDis software divides these functions under separate tabs that make navigation and data processing straightforward. The software is based on four modules: Browse, Setup, SimDis, and Report. For example, the Setup module allows you to configure the files to use for BP calibration, blank selection, and QC reference. Partial integration with the GC ChemStation sequence makes automated data analysis possible.

Processing Two Signals

The software can process one or two channels of signal data (FID and SCD for example) from GC ChemStation data files. When working with dual channels, the SimDis software requires that each channel be labeled by the detector type rather than the defaults used by the GC ChemStation. Since the SCD operates off the analog input board (AIB), its signal begins with "AIB." For this reason, the post-run command macro SCDnamer.mac must be run to rename the signal file. The macro renames the AIB2B.ch channel as SCD1.ch. If the channel name is not corrected, the software will switch the FID and SCD channels during analysis, giving faulty results. The macro code to do this is shown below. It assumes the AIB is in the rear position (B).

```
!===========================================
! SCDNamer call this as a post run command when an SCD is
installed
! it renames the dual channel AIB2B.ch to SCD1.ch to allow
simdis to
! properly calibrate
!===========================================
NAME SCDNamer
! This macro renames the SCD files named as AIB2B.ch to
SCD1.ch
if filestat(mode,dadatapath$+dadatafile$+"\AIB2B.CH")=1
rename dadatapath$+dadatafile$+"\AIB2B.ch",dadata-
path$+dadatafile$+"\SCD1.ch"
print "File Renamed"
else
print "No AIB2B File found"
endif
RETURN
ENDMACRO
```

Results and Discussion

Calibration

A calibration mixture containing a series of known n-alkanes can be used for establishing the relationship between BP and RT. C5 to C40 is used for ASTM D2887, and Polywax 500 dissolved in toluene is used to calibrate ASTM D7213 [3]. Since both are too viscous or waxy at ambient temperature to sample with a syringe, they need to be heated manually to approximately 80 °C before injection. RT repeatability is key for consistent correlation of BP and RT. Figure 1 and Figure 2 show overlays of consecutive runs of C5 to C40 and Polywax 500, respectively. Tables 2 and 3 show repeatability for both RT and area.

Polywax 500 Sample Preparation

Place approximately 80 mg of Polywax 500 in a 2-mL vial. Add about 1.5 mL toluene followed by the addition of a suitable mixture of n-paraffins from C5 to C18 (Agilent SimDis calibration No.2). The final concentration should be approximately one part of (C5–C18) to 20 parts of toluene. Initially heat the solution to 80 °C to dissolve the Polywax 500.

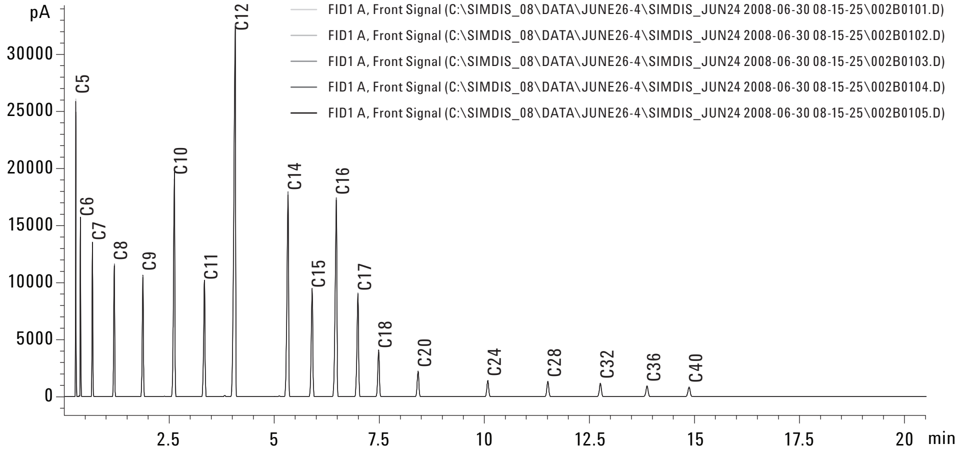


Figure 1. Overlay of five consecutive runs of C5 to C40 calibration mix, vial heated to 80 °C for 3 min prior to injection. GC conditions are listed in Table 1, items (1).

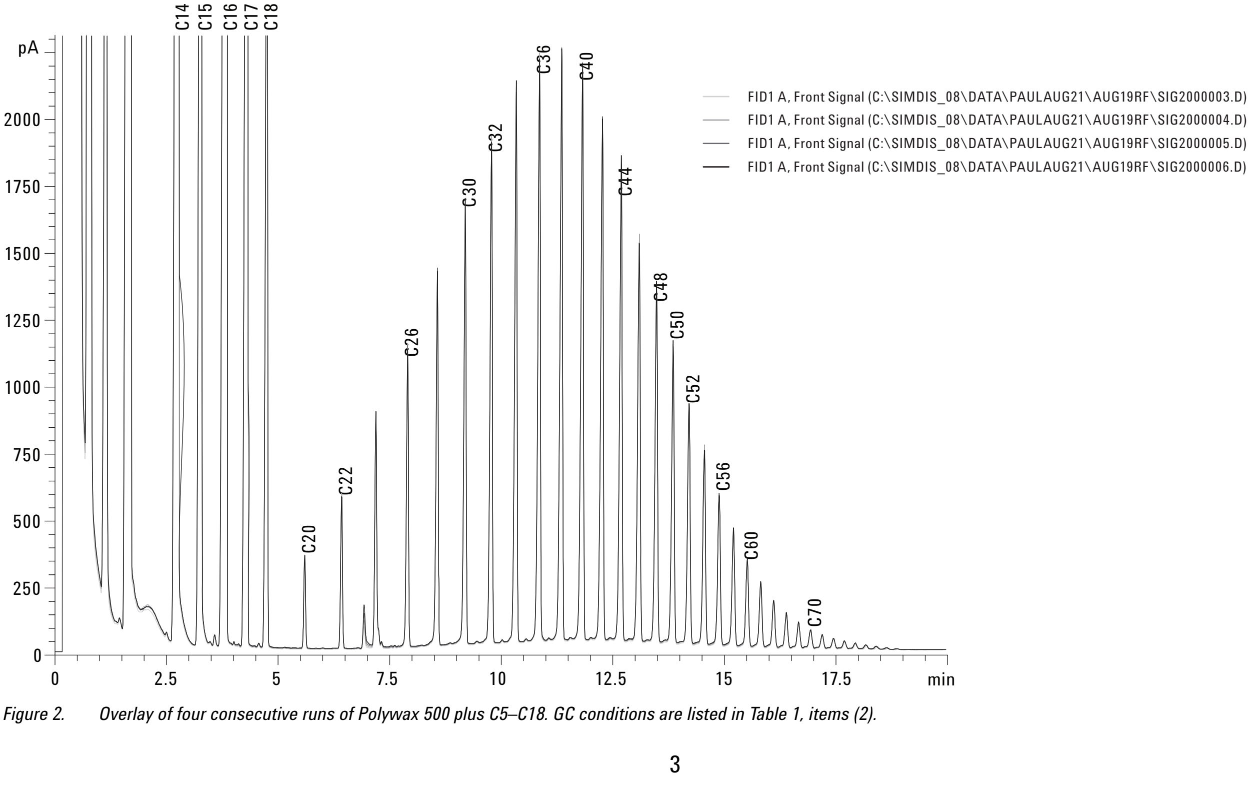


Figure 2. Overlay of four consecutive runs of Polywax 500 plus C5–C18. GC conditions are listed in Table 1, items (2).

Table 2. Repeatability for C5 to C40, n = 10

	Retention Time			Area		
	Average	**STDEV**	**RSD%**	**Average**	**STDEV**	**RSD%**
C5	0.275	0.000	0.06	19870	126	0.64
C6	0.388	0.000	0.09	14020	83	0.60
C7	0.673	0.001	0.17	16527	108	0.65
C8	1.192	0.002	0.16	18693	81	0.43
C9	1.874	0.002	0.12	20383	107	0.53
C10	2.622	0.003	0.10	43561	280	0.64
C11	3.338	0.002	0.07	22730	158	0.69
C12	4.068	0.002	0.05	94289	714	0.76
C14	5.327	0.002	0.03	48149	393	0.82
C15	5.902	0.002	0.03	24268	199	0.82
C16	6.477	0.001	0.02	49175	408	0.83
C17	6.991	0.001	0.02	24448	201	0.82
C18	7.485	0.000	0.00	10552	84	0.80
C20	8.424	0.001	0.01	6187	53	0.86
C24	10.083	0.000	0.00	4293	17	0.40
C28	11.512	0.001	0.01	4288	45	1.06
C32	12.762	0.002	0.01	3988	66	1.66
C36	13.874	0.001	0.01	3407	66	1.94
C40	14.874	0.002	0.01	3238	69	2.14

Table3. Repeatability of Polywax 500 Plus C5 to C18, n = 10

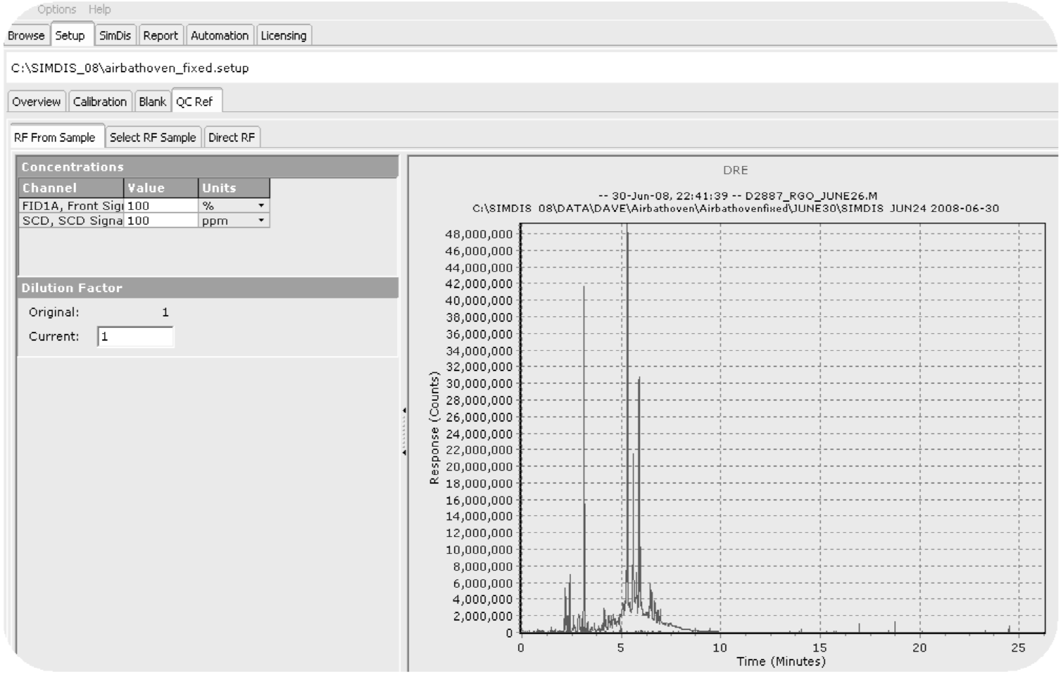
	Retention Time			Area		
	Average	**STDEV**	**RSD%**	**Average**	**STDEV**	**RSD%**
C14	2.769	0.002	0.07	49126	953	1.94
C15	3.278	0.002	0.05	24337	469	1.93
C16	3.847	0.002	0.05	49304	948	1.92
C17	4.311	0.002	0.05	24597	470	1.91
C18	4.753	0.001	0.03	11374	218	1.92
C20	5.596	0.001	0.01	952	17	1.80
C22	6.424	0.001	0.01	1635	30	1.81
C26	7.904	0.001	0.01	3615	62	1.71
C32	9.783	0.001	0.01	6856	105	1.53
C36	10.858	0.001	0.01	8418	137	1.63
C40	11.823	0.001	0.01	8432	128	1.52
C44	12.690	0.002	0.01	7037	137	1.95
C48	13.480	0.001	0.01	5288	104	1.98
C52	14.208	0.001	0.01	3677	67	1.83
C60	15.512	0.001	0.01	1353	19	1.40
C70	16.931	0.002	0.01	273	5	1.92

QC Reference

A QC reference sample is the basis for quantifying total sulfur and allows the direct entry of response factors for calculation based on total area and user-entered concentrations of sulfur. In this application, a diesel sample (SDF-1X-4, AccuStandard, Inc., New Haven, CT) with a sulfur concentration of 100 µg/g is used as the QC external reference for calibration of response factors for the SCD channel. This is needed for calculation of total sulfur in the sample. Figure 3 shows the graphic pane from the SimDis software for of the QC reference.

Reference Gas Oil Analysis

To meet the requirements of ASTM D2887, the reference gas oil (RGO) sample analysis must be performed to verify both the chromatographic performance and the calculation algo-



C:\SIMDIS_08\airbathoven_fixed.setup

Concentrations

Channel	Value	Units
FID1A, Front Sig	100	%
SCD, SCD Signa	100	ppm

Dilution Factor

Original: 1

Current: 1

Figure 3. QC reference setup. GC conditions are listed in Table 1, items (1).

rithms involved in this test method. Figure 4 shows the chromatograms of RGO for both the hydrocarbon and sulfur channels. Tables 4 and 5 show the results for six runs of RGO analysis. The data show that observed BP values agree with the ASTM D2887 consensus BP values within the allowable differences and with good repeatability.

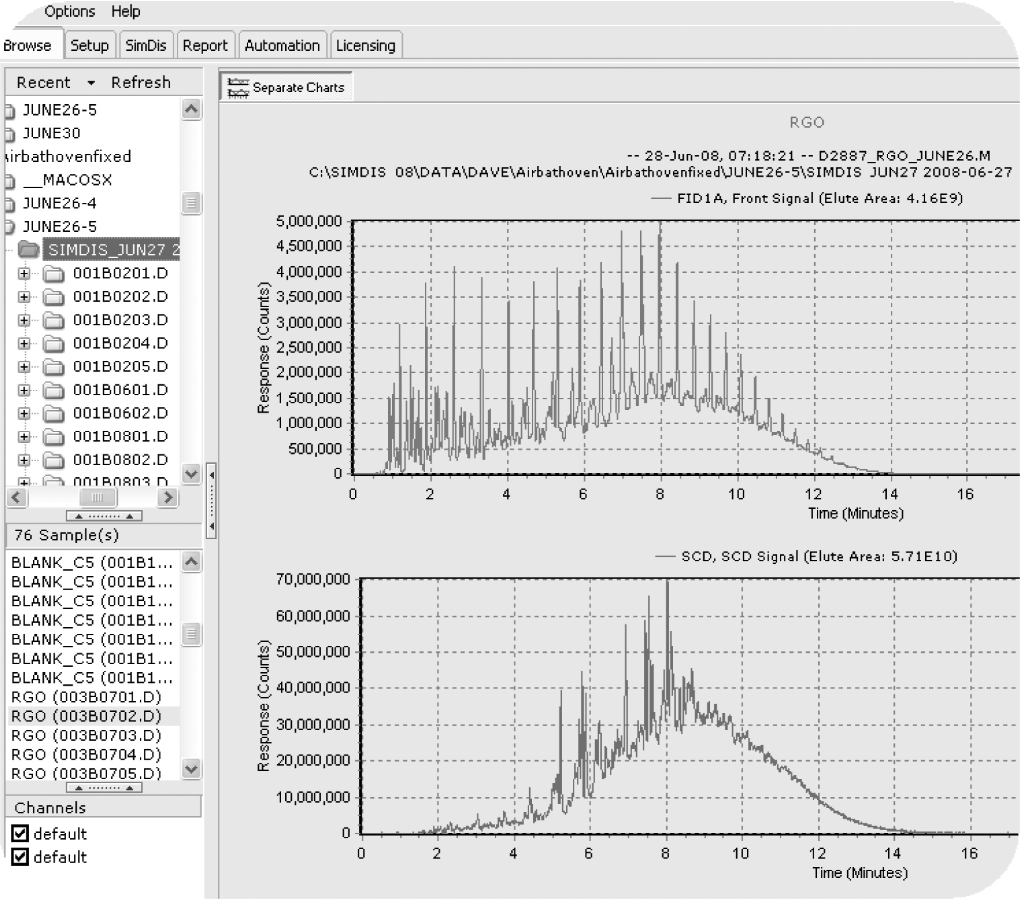


Figure 4, Chromatograms of RGO for hydrocarbon and sulfur channels. GC conditions are listed in Table 1, items (1).

Table 4. Hydrocarbon SimDis Results for Reference Gas Oil (Six runs shown.)

ASTM D2887 Values											
OFF %	**BP, ºC**	**Allowable Difference**	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**Difference**	**RSD%**
IBP	115	7.6	114	114	114	114	114	114	114	1	0.00
10%	176	4.1	174	174	174	174	174	174	174	2	0.00
20%	224	4.9	223	223	223	223	223	223	223	1	0.00
30%	259	4.7	258	258	258	258	258	258	258	1	0.00
40%	289	4.3	287	287	287	287	287	287	287	2	0.00
50%	312	4.3	311	311	311	311	311	311	311	1	0.00
60%	332	4.3	330	330	330	330	330	330	330	2	0.00
70%	354	4.3	352	352	351	352	352	352	352	2	0.12
80%	378	4.3	376	376	376	376	376	376	376	2	0.00
90%	407	4.3	405	405	405	405	405	405	405	2	0.00
FBP	475	11.8	471	471	471	471	471	471	471	4	0.00

Table 5. Sulfur SimDis Results for Reference Gas Oil, BP in °C

OFF%	1	2	3	4	5	6	Average	STDEV	RSD%
IBP	168	169	169	167	165	169	168	1.60	0.95
10%	265	265	265	265	265	265	265	0.00	0.00
20%	293	293	293	293	293	293	293	0.00	0.00
30%	314	314	314	314	314	314	314	0.00	0.00
40%	329	330	330	330	330	330	330	0.41	0.12
50%	344	344	344	344	344	345	344	0.41	0.12
60%	359	359	359	360	360	360	360	0.55	0.15
70%	376	376	377	377	377	377	377	0.52	0.14
80%	396	396	396	397	397	398	397	0.82	0.21
85%	408	408	408	409	409	409	409	0.55	0.13
90%	422	422	423	423	424	424	423	0.89	0.21
FBP	495	495	495	499	499	501	497	2.66	0.53

Light Cycle Oil Analysis

To illustrate repeatability, chromatographic overlays are shown in Figures 5a and 5b for an LCO sample. Tables 6 and 7 list the results for hydrocarbon and sulfur SimDis, respectively. The average total sulfur content calculated is 248 ppm with 3.5% RSD.

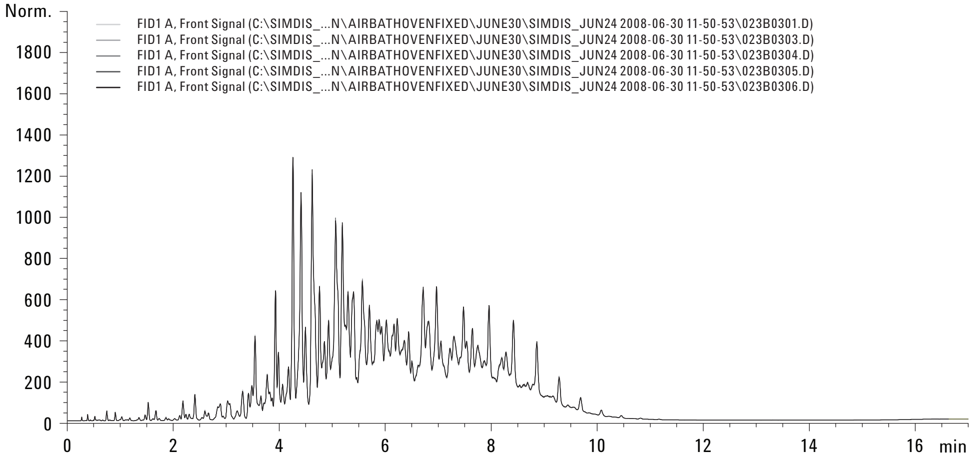


Figure 5a. Carbon SimDis of LCO. Five-run overlay.

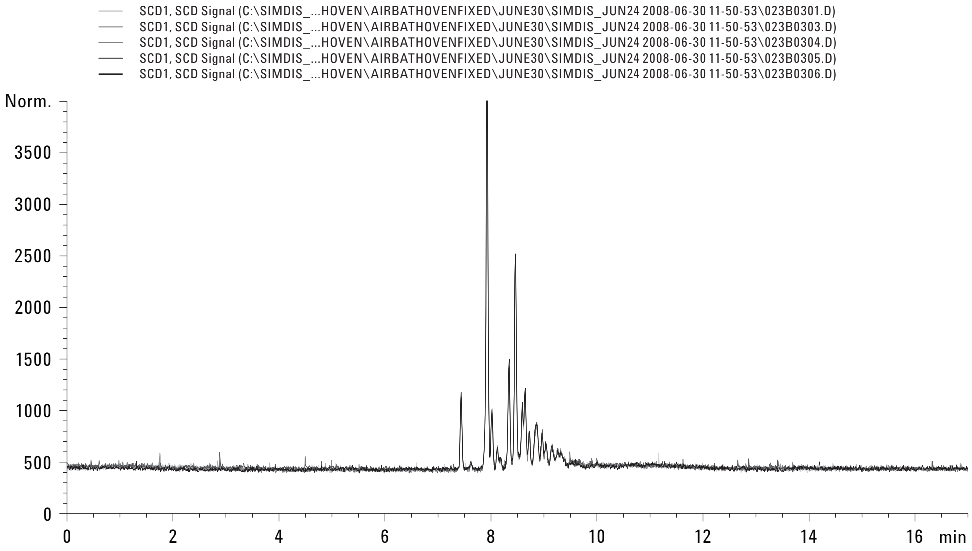


Figure 5b. Sulfur SimDis of LCO. Five-run overlay.

Table 6. Carbon SimDis Results for LCO, BP in °C

OFF%	**1**	**2**	**3**	**4**	**5**	**Average**	**SD**	**RSD%**
IBP	141	140	140	140	139	140	0.71	0.51
10%	221	221	221	221	221	221	0.00	0.00
20%	233	233	233	233	234	233	0.45	0.19
30%	247	247	247	247	247	247	0.00	0.00
40%	260	260	261	260	261	260	0.55	0.21
50%	274	275	275	275	275	275	0.45	0.16
60%	291	292	292	292	292	292	0.45	0.15
70%	306	307	307	307	307	307	0.45	0.15
80%	324	324	324	324	324	324	0.00	0.00
90%	344	344	344	344	344	344	0.00	0.00
FBP	391	391	391	391	392	391	0.45	0.11

Table 7. Sulfur SimDis Results for LCO, BP in °C

OFF%	**1**	**2**	**3**	**4**	**5**	**Average**	**SD**	**RSD%**
IBP	314	314	314	314	314	314	0.00	0.00
10%	328	329	328	328	328	328	0.45	0.14
20%	329	329	329	329	329	329	0.00	0.00
30%	329	329	329	329	329	329	0.00	0.00
40%	332	332	332	332	332	332	0.00	0.00
50%	342	342	342	342	342	342	0.00	0.00
60%	345	345	345	345	345	345	0.00	0.00
70%	347	347	346	346	347	347	0.55	0.16
80%	351	351	350	350	351	351	0.55	0.16
90%	359	359	357	359	358	358	0.89	0.25
FBP	375	375	371	374	371	373	2.05	0.55
Sulfur, ppm	254	250	240	238	258	248	8.62	3.48

Conclusions

This new SimDis procedure utilizes a 7890A GC configured with the HT-PTV inlet, and an SCD mounted in series with an FID. The Agilent SimDis software is capable of processing both FID and SCD data channels, providing a solution for hydrocarbon and sulfur simulated distillation.

Sulfur simulation distillation has been demonstrated using the Agilent 355 sulfur chemiluminescence detector. With a selectivity over carbon of approximately 10^6 , reliable boiling point distributions of sulfur in petroleum fractions can be obtained.

References

1. C. Wang and R. Firor, "Simulated Distillation System for ASTM D2887," Agilent Technologies, publication 5989-2726EN
2. ASTM D2887-06 a,"Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography," Annual Book of Standards, Volume 05.01, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA
3. ASTM D 7213-05, "Standard Test Method for Boiling Point Distribution of Petroleum Distillates from 100 °C to 615 °C by Gas Chromatography," Annual Book of Standards, Volume 05.04, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA

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Agilent Technologies

Analysis of Trace Hydrocarbon Impurities in Benzene by Agilent 7820A Gas Chromatograph

Chunxiao Wang and Wenmin Liu

Application Brief

HPI

Knowledge of impurities in benzene provides critical quality control information where benzene is either produced or used in a manufacturing process. ASTM D4492 [1] was used for analyzing these impurities, including nonaromatics containing up to nine carbon atoms, toluene, C8 aromatics, and 1,4-dioxane. The Agilent 7820A gas chromatograph offers an efficient and easy-to-use platform for the analysis of benzene and may other aromatic solvents. For this application, an Agilent 7820A GC is configured with a split/splitless capillary inlet and a flame ionization detector (FID). Agilent EZChrom Elite Compact software is used to control the 7820A GC and provide data acquisition/data analysis. The Agilent 7820A GC supports an automatic liquid sampler (ALS), allowing fully unattended operation – from injection all the way through final reporting.

Experimental

Table 1. Typical GC Conditions

Inlet settings	250 °C, Split ratio: 100:1 to 30:1
Injection volume	0.5 µL
Column	HP-INNOWax 60 m × 0.32 µm × 0.5 µm
Column flow (He)	2.6 mL/min (21.8 at 75 °C), constant flow mode
Oven temperature program	For impurities in benzene: 75 °C (10 min); 3 °C/min to 100 °C For aromatic solvent: 75 °C (10 min); 3 °C/min to 100 °C 10 °C/min to 145 °C
FID setting	
Temperature	250 °C
H2 flow	40 mL/min
Air flow	400 mL/min
Make up (N2)	25 mL/min
Data acquisition rate:	20 Hz

Highlights

- An easy-to-use, single-column method for benzene as well as a wide range of aromatic solvent purity analyses meets the chromatographic requirements of 10 separate ASTM methods. Therefore fewer GCs, stock columns, and supplies are required to analyze many different types of samples.
- EPC control and automatic injection ensures excellent repeatability for both retention time and peak area.
- The wide dynamic response range of the FID enables a quantitative analysis of samples containing both very high and very low concentrations in a single run.

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Discussion

The Agilent 7820A GC with full electronic pneumatics control (EPC) on all inlets and detectors ensures good repeatability and also makes it fast and easy to set and to save the pressures and flows. Figure 1 shows the chromatograms of the D4492 calibration standard. Excellent repeatability for retention time with RSD of approximately 0.03 to 0.01% and peak area with RSD of about 1.6% are shown in Table 2.

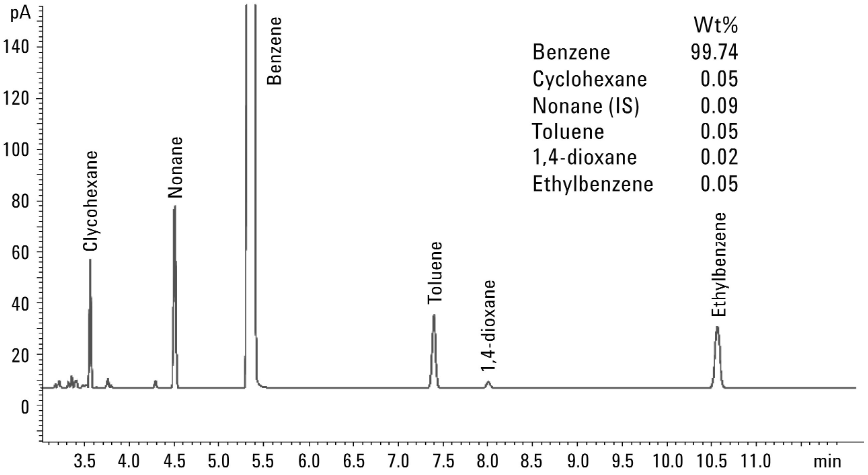


Figure 1. ASTM D4492 benzene calibration standard. *Oven temperature program: 75 °C (10 min); 3 °C/min to 100 °C. Sample size: 0.5 µL, Split ratio: 100:1.*

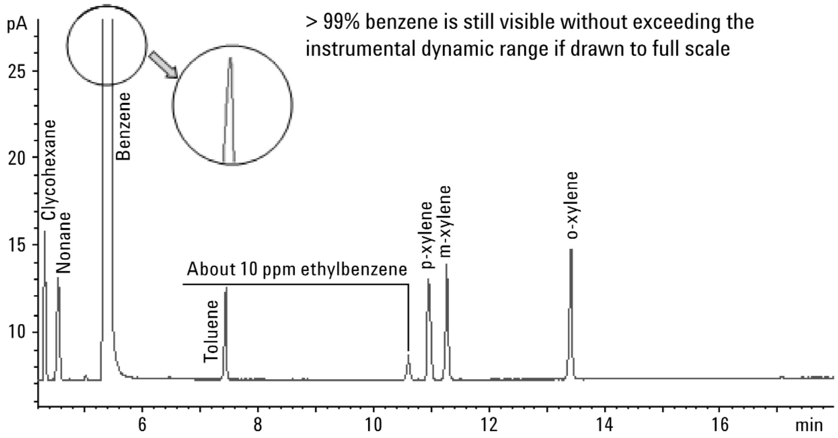
Table 2. Repeatability–ASTM D4492 Benzene Calibration Standard (11 runs) with First Run Included

	Cyclohexane	**Nonane**	**Bezene**	**Toluene**	**1,4-dioxane**	**Ethylbenzene**
			Peak Area			
1	430130	861450	900088289	590385	56288	689141
2	425791	848159	888131170	581775	55693	677502
3	437496	874885	915251703	599534	57071	698269
4	439204	879141	918796665	601857	57355	701225
5	438646	876346	917995860	601138	57056	700462
6	436941	876809	914994185	599823	57743	699919
7	423567	844923	885230656	580241	55487	675473
8	420259	843030	878870585	577475	55392	673593
9	422665	844761	883243038	579572	55419	675665
10	430741	865226	901189833	591633	56211	691217
11	431032	865007	901921807	592037	56118	691200
Mean:	430588	861794	900519436	590497	56348	688515
Std Dev:	6852	14298	14909746	9406	837	11061
%RSD:	1.59	1.66	1.66	1.59	1.49	1.61

Table 2. ***Repeatability–ASTM D4492 Benzene Calibration Standard (11 runs) with First Run Included*** *(Continued)*

	Cyclohexane	Nonane	Bezene	Toluene	1,4-dioxane	Ethylbenzene
			Retention Time			
1	3.562	4.503	5.369	7.397	8.003	10.561
2	3.562	4.504	5.371	7.398	8.005	10.563
3	3.562	4.504	5.371	7.398	8.007	10.565
4	3.561	4.503	5.370	7.398	8.006	10.563
5	3.561	4.503	5.370	7.398	8.006	10.563
6	3.561	4.503	5.369	7.398	8.007	10.563
7	3.561	4.503	5.369	7.398	8.006	10.563
8	3.561	4.503	5.369	7.398	8.006	10.563
9	3.561	4.504	5.370	7.398	8.006	10.563
10	3.563	4.506	5.372	7.400	8.007	10.567
11	3.563	4.506	5.372	7.400	8.009	10.565
Mean:	3.562	4.504	5.370	7.398	8.006	10.564
Std Dev:	0.0008	0.0012	0.0012	0.0009	0.0015	0.0016
%RSD:	0.02	0.03	0.02	0.01	0.02	0.01

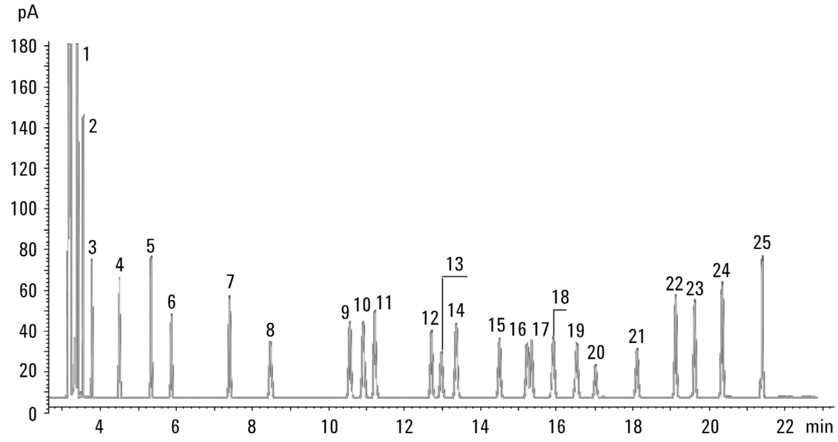
The FID has a very wide dynamic response range due to its full digital path. This enables a quantitative analysis of samples containing very high and very low concentrations in a single run. Figure 2 shows that trace impurities spiked in benzene, trace level (10 ppm) ethyl benzene, and > 99% benzene can be quantitative analyzed in a single run.



> 99% benzene is still visible without exceeding the instrumental dynamic range if drawn to full scale

Figure 2. ***Analysis of trace impurities spiked in benzene.*** *Oven temperature program: 75 °C (10 min); 3 °C/min to 100 °C. Sample size: 0.5 µL, Split ratio: 30:1.*

This system is also chromatographically suitable for a wide range of aromatic solvent samples according to 10 different ASTM aromatics methods as mentioned in reference 2. An n-hexane solution was prepared containing 0.1 wt% of aromatic solvents and impurities specified by the 10 ASTM methods for the analysis; the chromatographic overlay of 11 runs demonstrates outstanding repeatability as shown in Figure 3.



1. Heptane
2. Cyclohexane
3. Octane
4. Nonane
5. Benzene
6. Decane
7. Toluene
8. Undecane
9. Ethylbenzene
10. p-xylene
11. m-xylene
12. Cumene
13. Dodecane
14. o-xylene
15. Propylbenzene
16. p-ethyltoluene
17. m-ethyltoluene
18. t-butylbenzene
19. s-butylbenzene
20. Styrene
21. Tridecane
22. Diethylbenzene
23. n-butylbenzene
24. a-methylstyrene
25. Phenyacetylene

Figure 3. Chromatographic overlay of 11 runs of aromatic solvent specified by 10 ASTM methods.
Oven temperature program: 75 °C (10 min); 3 °C/min to 100 °C, 10 °C/min to 145 °C.
Sample size: 0.5 µL, Split ratio: 100:1.

References

1. ASTM D4492-98, "Standard Test Method for Analysis of Benzene by Gas Chromatography," Annual Book of Standards, Volume 06.04, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA
2. James D. McCurry, "A Unified Gas Chromatography Method for Aromatic Solvent Analysis," Agilent Technologies publication 5988-3741EN

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Agilent Technologies

Automated Preparation of Simulated Distillation Samples for ASTM Methods D2887, D7213, D7398 and D6352 using a Dual Tower 7693A and Tray System

Application Note

Hydrocarbon Processing

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Abstract

A dual tower 7693A and tray system installed on the 7890A Gas Chromatograph was used for preparation of hydrocarbon calibration standards, solvent blanks, and actual petroleum samples for the purpose of analysis by simulated distillation (SimDis). The front tower is equipped with a 5 or 10 µL syringe while the back tower is equipped with a 250 or 500 µL syringe. A 150 sample tray with heater and mixer/barcode reader is also used. Procedures are described for sample preparation for ASTM D2887, D7213, D7398 and D6352. The Multimode Inlet, G3510, operated in a temperature programmed split mode was used for all samples.

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Introduction

Sample and calibration standard preparation for various simulated distillation methods is normally a manual process requiring dilution, mixing, and heating. Many procedures use volatile toxic solvents such as carbon disulfide. ASTM method D2887 commonly uses CS_2 for sample dilution while D6352 may use CS_2 or toluene for polywax calibration standard preparation. Sample heating is required for many of these procedures. Using the automation capabilities of the 7693A tower and tray system improves lab safety as well when working with CS_2 and other solvents by avoiding manual handling and uncontrolled heating of mixtures.

Experimental

For all experiments, the 7890A GC was equipped with dual 7693A towers and tray. The front tower used a standard 5 or 10 µl syringe and the rear tower was equipped with the optional large syringe carriage with either a 250 or 500 µL syringe. Sample prep procedures were done on the rear tower and sample injection occurred on the front tower. The 7890A was configured with the multimode inlet operated in temperature programmed split mode. Detection was with FID. In addition, two 7890A oven systems were used. The first configuration used the conventional air bath oven and the second used the Low Thermal Mass (LTM) system. Instrumental parameters for various configurations are listed in Table 1.

Table 1. 7890A SimDis parameters

LTM System for D2887	
LTM module	5M × 0.32 mm × 0.50 µm DB1, 5 inch format
7890A oven	300 °C isothermal
Inlet	Multimode, 270 °C (0 min) to 355 °C at 200 °C/min
Liner	Single taper with glass wool, 5183-4647
Split ratio	20:1
Pressure program (Inlet)	8 psi (0 min) – 42 psi (0.9 min) at 14 psi/min
LTM program	40 °C (0 sec) to 350 °C (30 sec) at 100 °C/min
Standard System for D2887	
Column	10M × 0.53 mm × 3.0 µm D2887
Oven	40 °C (0 min) to 350 °C (5 min) at 15 °C/min
Inlet	Multimode, G3510, 50 °C (0 min) to 330 °C (4 min) at 200 °C/min
Liner	Single taper with glass wool, 5183-4647
Split	4 to 1
Flow	3.2 psig at 40 °C, constant flow mode
7890A system for D7213 and D7398 (Polywax 500 calibration)	
LTM	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis 5-inch LTM format
Oven	LTM configuration, 7890A oven 325 °C isothermal, module 40 °C (0 min) to 400 °C (30 sec) at 50 °C/min
Inlet	Multimode, 270 °C (0 min) to 400 °C (3 min) at 300 °C/min
Split ratio	4 to 1 and 10 to 1
Pressure program	2.5 psi (0 min) to 9.5 psi (1.0 min) at 1 psi/min
Standard Air Bath Oven	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis
Oven program	40 °C (0 min) to 400 °C (5 min) at 15 °C/min
Inlet	Multimode, 210 °C (0 min) to 400 °C (10 min) at 200 °C/min
Split ratio	4 to 1
Flow	15 mL/min, constant flow mode
7890A system for D6352 (Polywax 655 calibration)	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis
Oven program	40 °C (0 min) to 430 °C (5 min) at 15 °C/min
Inlet	Multimode, 250 °C (0 min) to 430 °C (hold until end of run) at 200 °C/min
Split ratio	4 to 1
Flow	16 mL/min, constant flow mode
7693A System	
Front tower	5 or 10 µL syringe, G4513A
Back tower	250 or 500 µL syringe, G4521A syringe carriage
Tray	150 sample capacity with heater and mixer/barcode reader, G4520A
Inlet	G3510 Multimode, CO_2 cooled
ChemStation	B.04.01
7890A firmware	A.01.10 or greater

Discussion

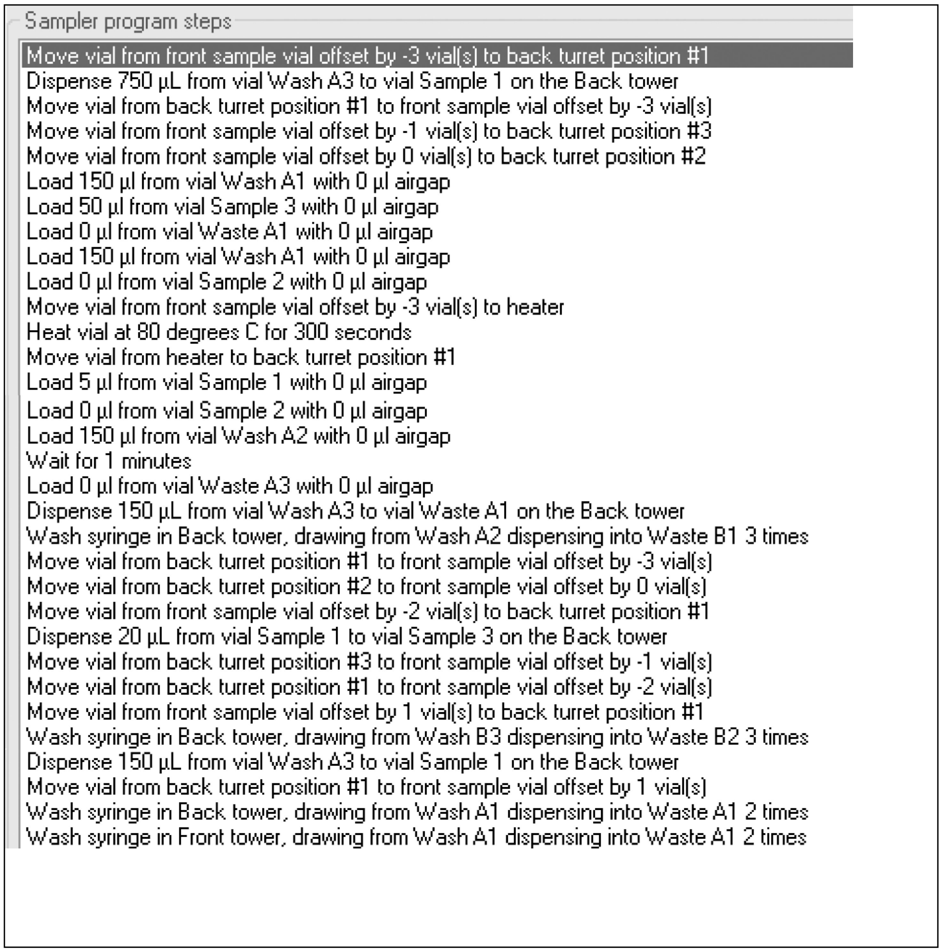
A typical sample preparation program for D2887 setup is shown in Table 2. This illustrates just one way to program preparation of the calibration standard, reference gas oil (RGO), and blank that are necessary to set up a system for routine analyses. The commands can be assembled in other ways to produce the same end result. The following vials and tray locations are used with this program.

Tray position 1	Calibration mix, 0.5 µL of C5 to C40, Agilent part number 5080-8716
Tray position 2	1 mL RGO, Agilent part number 5060-9086
Tray position 3 to 5	Empty vials with 100 µL inserts, Agilent part number 5188-6592

When the procedure is complete, vial 3 will be the prepared RGO for injection, vial 4 will be the prepared calibration mix for injection, and vial 5 will be a CS_2 blank. Next, a three-line sequence is set up that starts with vial 4 (calibration mix). Vial 4 is run with the ChemStation method set with this procedure active, then vial 3 (RGO) and vial 5 (CS2 blank) are run using the same method but with the prep procedure inactive (unchecked in ChemStation's 7890A Injector Program pane under edit 7890A Parameters parameters menu because these samples are already prepared from the method in the first line of the sequence table). For all three samples, the core ChemStation method performs a sample preheat at 80 °C and a sample mix at 500 rpm for 20 seconds before injection. Lastly, the calibration, prepared RGO, and blank vials are fitted with 100 µL inserts so that the solvent amounts used for the procedure are minimized. Please note that when these inserts are used, mixing should be limited to speeds of approximately 500 rpm to avoid "spilling" liquid over the top of the insert into the bottom of the 2-mL vial.

Preparation of polywax standards for the higher temperature SimDis method is always challenging due to their low solubility. Solvents such as CS_2 and toluene are commonly used, and

Table 2. Sample prep procedure for D2887



Move vial from front sample vial offset by -3 vial(s) to back turret position #1
Dispense 750 µL from vial Wash A3 to vial Sample 1 on the Back tower
Move vial from back turret position #1 to front sample vial offset by -3 vial(s)
Move vial from front sample vial offset by -1 vial(s) to back turret position #3
Move vial from front sample vial offset by 0 vial(s) to back turret position #2
Load 150 µl from vial Wash A1 with 0 µl airgap
Load 50 µl from vial Sample 3 with 0 µl airgap
Load 0 µl from vial Waste A1 with 0 µl airgap
Load 150 µl from vial Wash A1 with 0 µl airgap
Load 0 µl from vial Sample 2 with 0 µl airgap
Move vial from front sample vial offset by -3 vial(s) to heater
Heat vial at 80 degrees C for 300 seconds
Move vial from heater to back turret position #1
Load 5 µl from vial Sample 1 with 0 µl airgap
Load 0 µl from vial Sample 2 with 0 µl airgap
Load 150 µl from vial Wash A2 with 0 µl airgap
Wait for 1 minutes
Load 0 µl from vial Waste A3 with 0 µl airgap
Dispense 150 µL from vial Wash A3 to vial Waste A1 on the Back tower
Wash syringe in Back tower, drawing from Wash A2 dispensing into Waste B1 3 times
Move vial from back turret position #1 to front sample vial offset by -3 vial(s)
Move vial from back turret position #2 to front sample vial offset by 0 vial(s)
Move vial from front sample vial offset by -2 vial(s) to back turret position #1
Dispense 20 µL from vial Sample 1 to vial Sample 3 on the Back tower
Move vial from back turret position #3 to front sample vial offset by -1 vial(s)
Move vial from back turret position #1 to front sample vial offset by -2 vial(s)
Move vial from front sample vial offset by 1 vial(s) to back turret position #1
Wash syringe in Back tower, drawing from Wash B3 dispensing into Waste B2 3 times
Dispense 150 µL from vial Wash A3 to vial Sample 1 on the Back tower
Move vial from back turret position #1 to front sample vial offset by 1 vial(s)
Wash syringe in Back tower, drawing from Wash A1 dispensing into Waste A1 2 times
Wash syringe in Front tower, drawing from Wash A1 dispensing into Waste A1 2 times

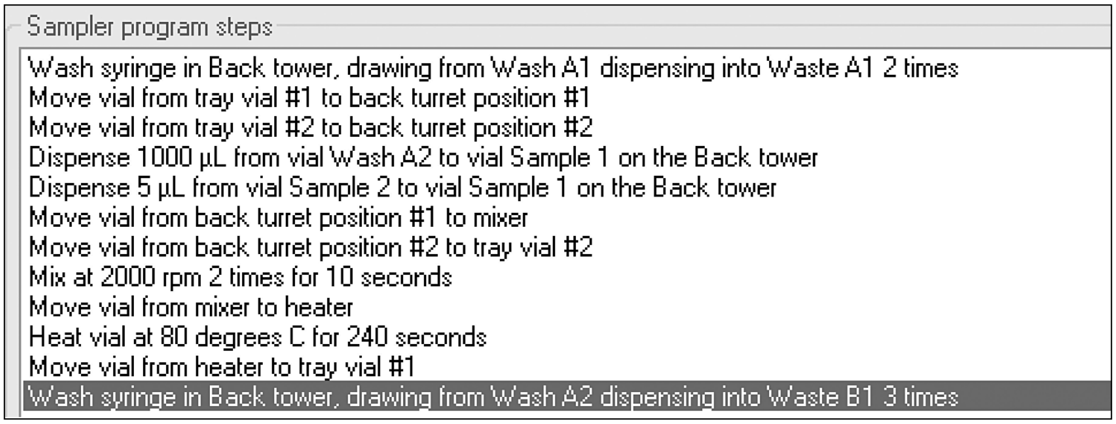
heating of the solvent/polywax vial is required just prior to injection. This entire procedure can be automated with the 7693A tower and tray system. The basic procedure for Polywax 500 is as follows:

- Place approximately 80–100 mg of Polywax 500 in a 2-mL vial and seal
- Add 125 µL of a C20/toluene solution to the polywax vial
- Add 1.25 mL of toluene to the polywax-C20 vial
- Mix the vial
- Heat the vial at 80 °C for 4 min
- Return to tray
- Heat one final time (3 min. typical) just prior to injection

Table 3 shows the basic prep procedure using a dual tower/tray system automating the steps shown above. The only manual step is adding the solid polywax to Vial 1. Vial 2 contains a C20/toluene mixture. Preparation of this sample could be automated as well. This procedure is applicable to D7213 SimDis and D7398 (Boiling Range Distribution of Fatty Acid Methyl Esters).

A resulting chromatogram from injection of the prepared Polywax 500 vial (vial 1) is shown in Figure 1. A symmetric distribution of the polywax fragments with good resolution to C80 can be seen.

Table 3. Preparation of Polywax 500



Wash syringe in Back tower, drawing from Wash A1 dispensing into Waste A1 2 times
Move vial from tray vial #1 to back turret position #1
Move vial from tray vial #2 to back turret position #2
Dispense 1000 µL from vial Wash A2 to vial Sample 1 on the Back tower
Dispense 5 µL from vial Sample 2 to vial Sample 1 on the Back tower
Move vial from back turret position #1 to mixer
Move vial from back turret position #2 to tray vial #2
Mix at 2000 rpm 2 times for 10 seconds
Move vial from mixer to heater
Heat vial at 80 degrees C for 240 seconds
Move vial from heater to tray vial #1
Wash syringe in Back tower, drawing from Wash A2 dispensing into Waste B1 3 times

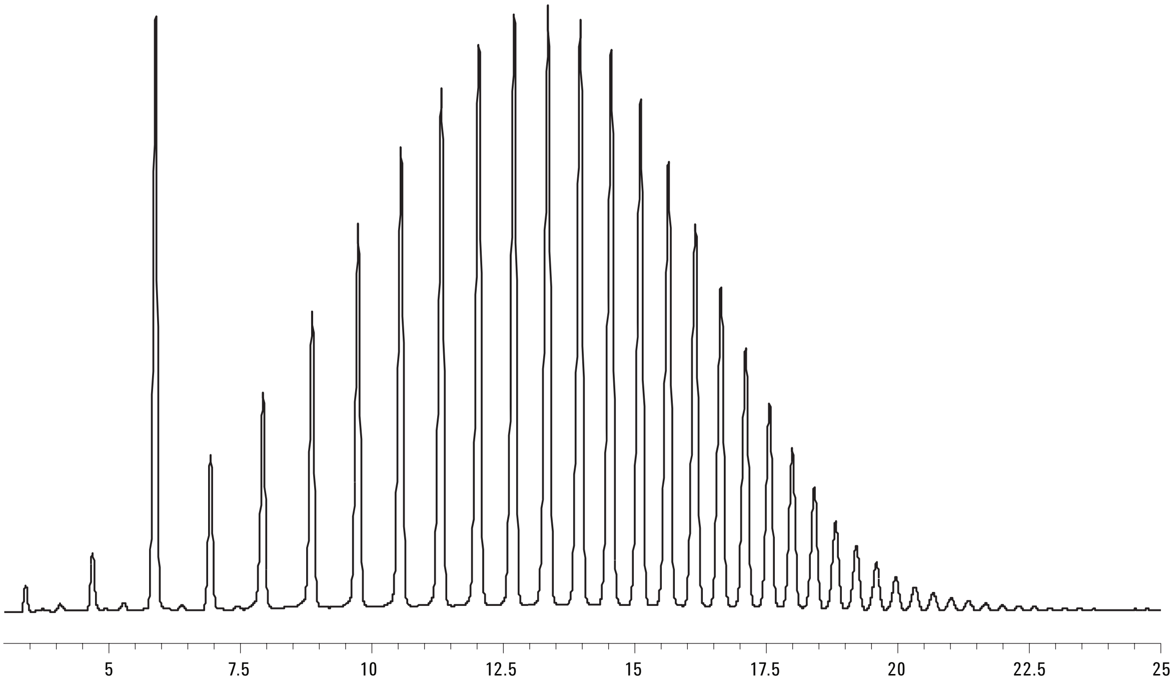


Figure 1. Polywax 500 with C20 marker. Multimode inlet with 7890A oven.

The preparation program for Polywax 655 is essentially the same as shown above for Polywax 500 except that heating is extended to 6 minutes, for better dissolution. Then just prior to injection, the prepared vial is heated for another 3 minutes. In the chromatogram shown below in Figure 2, a small amount (5 µL) of C5-C18 mix was added to the Polywax 655/ toluene solution as part of the automated procedure.

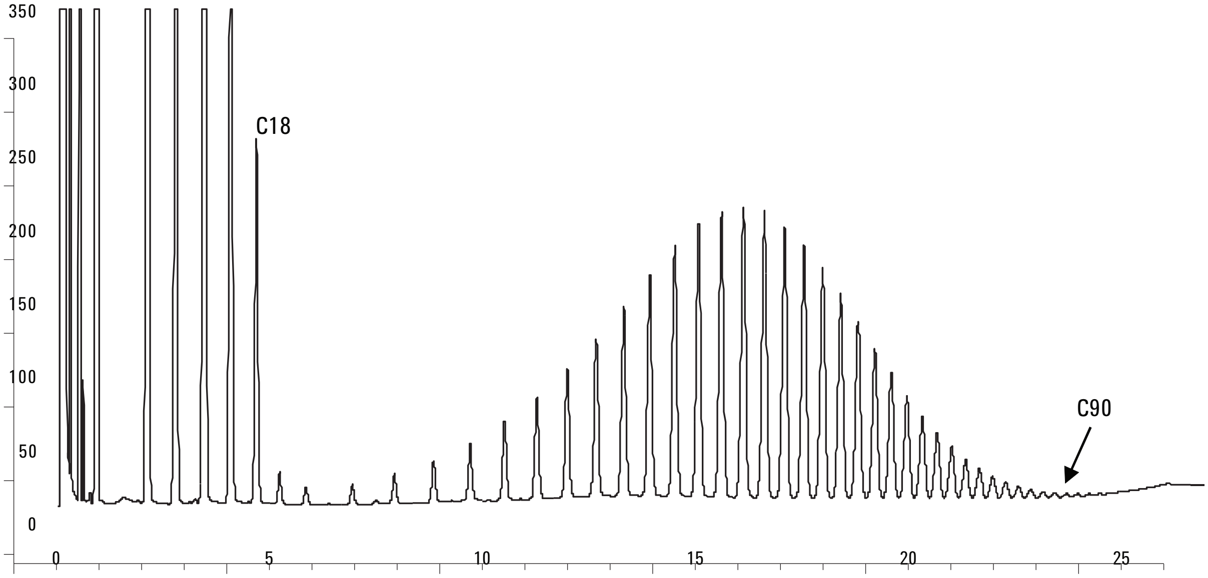


Figure 2. Chromatogram of Polywax 655.

The chromatogram was produced with the multimode inlet used in temperature-programmed split mode. Good definition of polyethylene fragmented to C110 is shown in Figure 3 where the last 5 minutes of the chromatogram are enlarged to show detail. Producing this detail out to C110 is extremely difficult for most chromatographic systems. The 7890A/7693A system produces excellent results with this sample.

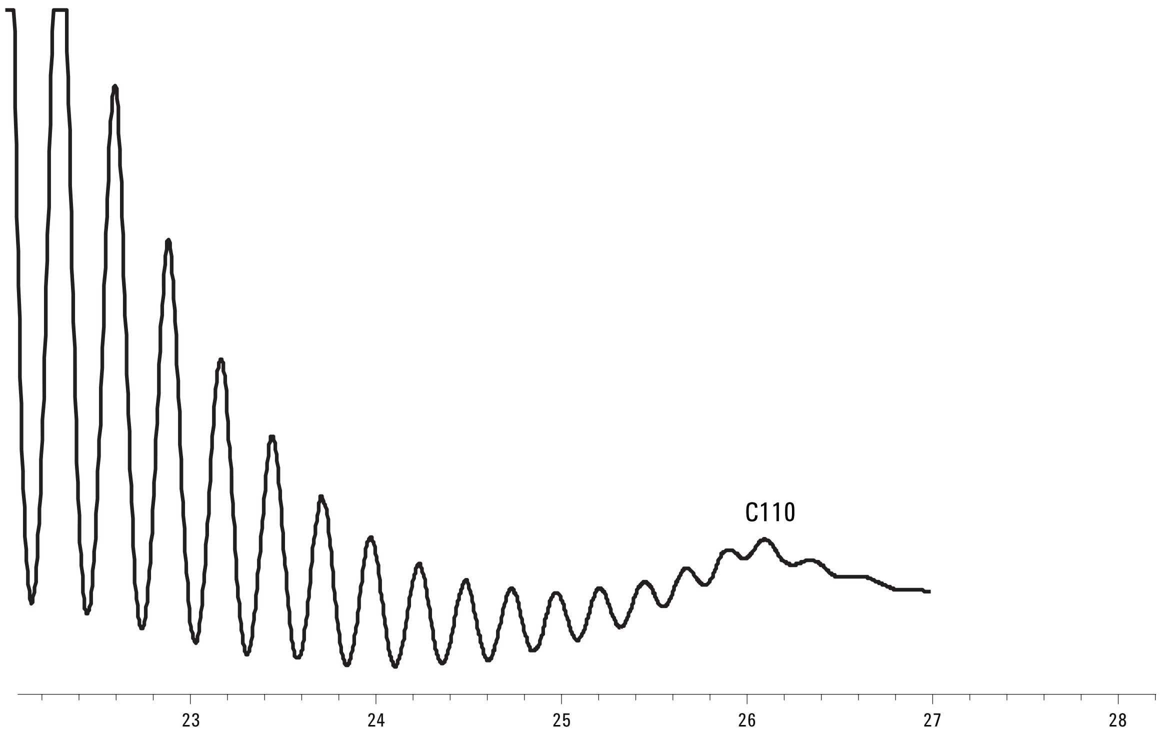


Figure 3. Polywax 655 to C110. Multimode inlet program: 150 °C (0 min) to 430 °C (hold until end of run) at 200 °C/min. 7890A oven: 40 °C (0 min) to 430 °C (5 min) at 15 °C/min. 3 µL injection. Solvent is toluene.

Reproducibility of the sample preparation steps is excellent as seen in Figure 4, for the dilution of a heavy vacuum gas oil sample (HVGO). The program steps that were followed to produce these chromatograms are given in Table 4. The back tower equipped with a 500-µL syringe, was used for sample preparation and the front tower with a 5-µL syringe was used for sample injection. Carbon disulfide was used for sample dilution. This program assumes a sequence is run using vial 2. Vial 1 is the stock HVGO sample that is first prepared by adding 0.5 g of the oil to a 2-mL vial. This material is extremely viscous and cannot be drawn into a syringe. Therefore the program performs a fully automated two-stage dilution prior to injection.

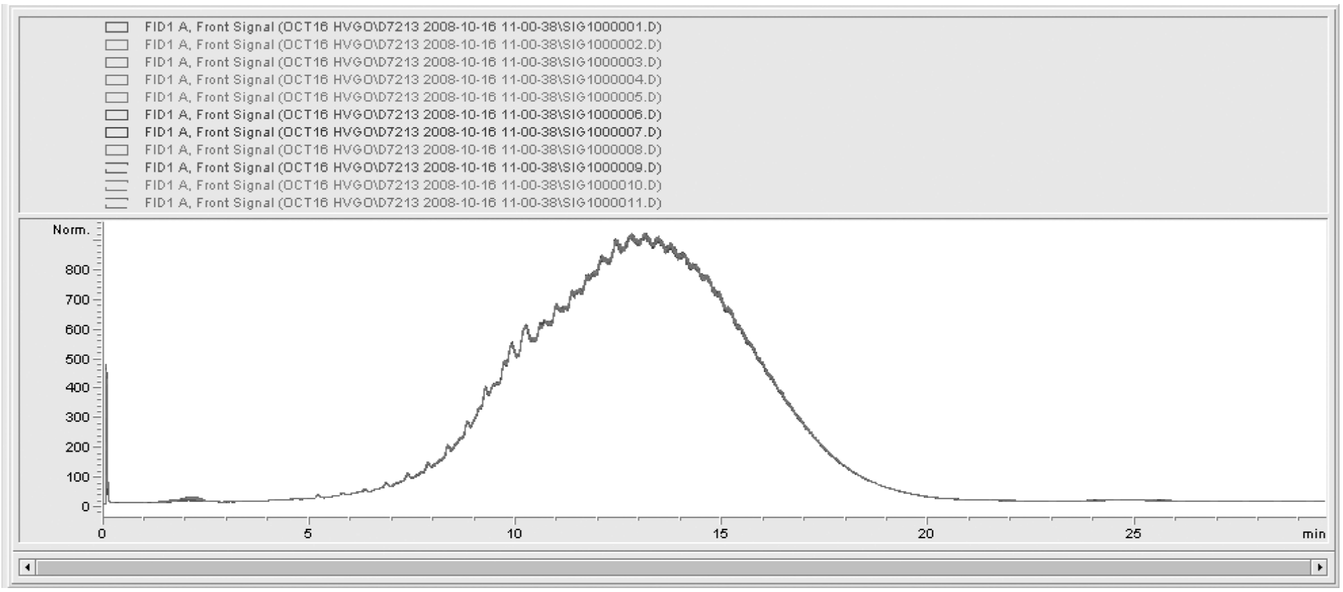
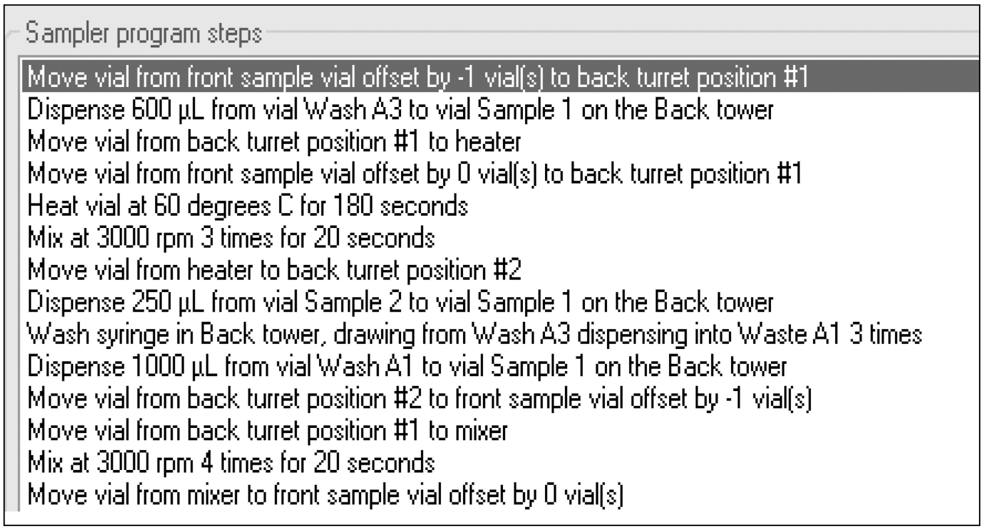

FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000001.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000002.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000003.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000004.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000005.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000006.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000007.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000008.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000009.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000010.D)
FID1 A, Front Signal (OCT16 HVGO\D7213 2008-10-16 11-00-38\SIG1000011.D)

Figure 4. Overlay of 11 runs of HVGO, each prepared using 7693A towers and tray.

Table 4. Preparation of HVGO for injection. CS_2 is used as the solvent.



Move vial from front sample vial offset by -1 vial(s) to back turret position #1
Dispense 600 µL from vial Wash A3 to vial Sample 1 on the Back tower
Move vial from back turret position #1 to heater
Move vial from front sample vial offset by 0 vial(s) to back turret position #1
Heat vial at 60 degrees C for 180 seconds
Mix at 3000 rpm 3 times for 20 seconds
Move vial from heater to back turret position #2
Dispense 250 µL from vial Sample 2 to vial Sample 1 on the Back tower
Wash syringe in Back tower, drawing from Wash A3 dispensing into Waste A1 3 times
Dispense 1000 µL from vial Wash A1 to vial Sample 1 on the Back tower
Move vial from back turret position #2 to front sample vial offset by -1 vial(s)
Move vial from back turret position #1 to mixer
Mix at 3000 rpm 4 times for 20 seconds
Move vial from mixer to front sample vial offset by 0 vial(s)

Conclusions

Difficult sample preparation procedures that are commonly used for petroleum and fuel samples can be easily automated with the 7693A tower and tray system for the 7890A and the 6890A. The system is particularly well suited for preparation of polywax calibration samples that are used for higher temperature methods. Tasks such as mixing, solid dissolution, dilution, heating, and internal standard addition are easily accomplished.

Chromatographic performance is enhanced through use of the multimode inlet. Using standard split injection liners, good sample capacity without carryover and with minimal discrimination of wide boiling samples is seen. The inlet was used in the temperature-programmed split mode for this work. Cryo cooling was not used, however, cryo can be used optionally to shorten inlet cool down between runs if desired.

For samples that fall within the boiling point range of D2887, D7213, and D7398, the Low Thermal Mass (LTM) system can be used to shorten typical analysis cycle times by 30 to 50% [1]. The high temperature method D6352 requires the standard 7890A oven.

The sample prep procedures listed here represent just one way of accomplishing a given task. Given the commands available with the system, there are many variants that will lead to the same end result.

Reference

1. C. Wang, R. Firor, and P. Tripp, "Fast Hydrocarbon and Sulfur Simulated Distillation Using the Agilent Low Thermal Mass (LTM) System on the 7890A GC and 355 Sulfur Chemiluminescence Detector," November 2008, Agilent Technologies publication 5990-3174EN.

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Agilent Technologies

Achieving Lower Detection Limits Easily with the Agilent Multimode Inlet (MMI)

Application Note

All Industries

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Abstract

This application note discusses three injection techniques: hot splitless, cold splitless, and solvent vent mode available on the Multimode Inlet. The cold splitless and solvent vent mode injections allow analysts to achieve a lower detection limit by making large volume injections (LVI). A total ion chromatogram overlay of 40-ppb pesticide standards from 2-µL hot splitless, 10-µL cold splitless and 25-µL solvent vent illustrates the improvement in signal-to-noise ratios using LVI.

Agilent Technologies

Introduction

A growing number of analysts are exploring large volume injection (LVI) techniques to improve existing analyses. With traditional liquid injection techniques in capillary gas chromatography, most inlets and columns can only handle 1 – 2 µL at a time. Attempts to increase the injection volume can lead to broadened and distorted analyte peaks, large and long solvent peak tails, and saturated or damaged detectors.

The purpose of increasing the injection volume is normally to improve detection limits in trace analysis. By introducing more of the sample to the system, the mass of analyte reaching the detector will be proportionally increased, resulting in larger peak areas and peak heights. If the baseline noise is constant, larger peak heights mean greater signal to noise ratios and lower system detection limits. An additional benefit of LVI is the ability to reduce the amount of sample originally processed. By injecting 10 – 100 times more volume of processed sample and concentrating it in the inlet, the sample preparation can start with 10 – 100 times smaller sample volume and still achieve the same mass of analyte on column. Another advantage of using LVI (solvent vent) is the decrease in solvent that actually reaches the detector. Usually, only 10 – 30% of the injection solvent actually enters the column and makes it to the detector.

LVI can be applied to injection volumes ranging from a few microliters up to 1 mL or more. In most LVI approaches, the sample solvent is evaporated and removed from the inlet system before the analytes are transferred to the separation column. In this way, LVI is similar to nitrogen evaporation or rotary evaporation of the solvent, with the added benefit of being performed in the GC inlet rather than in a fume hood. Analytes that would be lost during nitrogen evaporation may be retained in the inlet and successfully analyzed via LVI. Furthermore, the LVI process can be automated and is reproducible. As in the other evaporation techniques, the LVI approach is a function of the solvent type, the inlet temperature, the vent flow of evaporation gas, and the analyte boiling point. In addition, the inlet pressure during evaporation and the inlet liner have an impact on the rate of solvent removal and analyte recovery. These parameters will be discussed in this application note.

Experimental

MMI Operational Modes

The Agilent Multimode Inlet (MMI) uses the same liners and consumables as a standard split/splitless inlet, making it compatible with existing hot split and splitless methods. Its operational modes include: Hot Split/Splitless (also in pulsed mode), Cold Split/Splitless (also in pulsed mode), Solvent Vent and Direct mode.

Hot Splitless (for 1 – 3 µL injections)

For most analysts considering LVI, their current methods are using hot splitless injection. This proven and reliable sample introduction technique has worked well for almost 40 years; however, it does present some challenges to the sample integrity and to the method developer. First, the inlet must be hot enough to flash vaporize the solvent and analytes so that the resulting vapor cloud can be transferred to the column. The inlet liner volume must be sufficiently large to contain this vapor cloud. If the liner volume is too small, the vaporized sample can overflow the liner and reach reactive surfaces, leading to analyte loss. In addition, the pressure wave generated by the vaporized sample can push back against the incoming carrier gas and enter sensitive pressure and flow control systems. Using the Agilent pressure/flow calculator [1], a 1-µL injection of acetone into an inlet at 240 °C and 14.5 psig expands to 288 µL of gas. Most inlet liners for standard split/splitless inlets have a nominal volume of 1 mL. An increase of injection volume to only 3.5 µL under these conditions creates a vapor cloud of 1 mL which could easily overflow the inlet liner.

Hot splitless injection also creates a challenging environment for thermally unstable or labile analytes. Compounds such as the organochlorine pesticides DDT and endrin can rearrange to form breakdown compounds. This process is accelerated with the inlet temperatures normally used to analyze them. Effective chemical deactivation of the liner can minimize analyte breakdown. However, high inlet temperatures can decrease the lifetime of deactivated liners.

Another challenge created by hot splitless injection is the opportunity for needle fractionation or analyte discrimination. The needle temperature increases as the sample is being transferred from the syringe to the inlet because the needle is in contact with the septum. The rise in needle temperature can cause the solvent to "boil" away and deposit high boiling analytes inside the needle. To avoid this fractionation problem, some analysts load a solvent plug into the syringe first and then draw up the desired sample volume (available in 7693A Automatic Liquid Sampler). The thought is that the solvent plug will wash any deposits into the inlet. An effective way to address this problem is to make a high speed injection. This minimizes the time the needle is in contact with the septum and the time the sample touches the needle. Even with these issues, hot splitless injection is a well-accepted technique. An alternative technique, such as cold splitless can address these concerns and improve the analysis results.

Cold Splitless (for 1 – 10 µL injections)

MMI's versatile temperature programmability allows it to perform cold split and splitless analyses. In cold splitless mode, the MMI is cooled to a temperature below the normal boiling point of the sample solvent so that when the sample is injected, no vaporization takes place. The injection is simply a liquid transfer from the syringe to the inlet. Once the syringe is removed from the inlet, the inlet is heated to vaporize the sample and transfer it to the column. The solvent vaporizes first and moves to column, allowing analyte focusing to take place as in normal hot splitless injections. The analytes subsequently vaporize and move to the column. The main advantage is that the analytes vaporize at the lowest possible inlet temperature, rather than at a constant high temperature. This minimizes thermal degradation while still allowing a wide range of analytes to vaporize. Cold splitless operations also do not thermally stress the liner as harshly as hot splitless does, prolonging its usable life. Cold splitless can also extend the amount of sample that can be injected in some cases. If a slow inlet temperature program is used, the solvent can be vaporized slowly and will not overflow the liner volume. As long as the analytes can be refocused on the column, slow inlet temperature programs cause no detrimental effects to the chromatography.

Solvent Vent (for 5 – 1000 µL injections)

The solvent vent mode is the method which enables MMI to do LVI of more than 5 µL. In solvent vent mode, the inlet is kept at a low initial temperature during sample injection. Pneumatically, the inlet is in split mode with a low inlet pressure. The flow of gas through the inlet liner and out to vent removes the evaporating solvent. The sample is injected slowly so that the incoming liquid is deposited on the liner wall and the solvent evaporates at a similar rate. Once the entire sample has been injected, the inlet switches to a splitless mode for analyte transfer. The inlet is then heated to vaporize the concentrated sample and any remaining solvent and the vapor is transferred to the column. After a sufficient period to ensure the sample transfer, the inlet is then switched to a purge mode to allow any remaining material in the inlet liner to be vented. During the sample injection and solvent venting period, the GC oven has been held at an appropriate temperature to allow the solvent to refocus the analytes on the column. When this refocusing is complete, the oven is then programmed to perform the separation.

LVI Method Development

An effective procedure for developing an LVI method on a MMI is to run the existing method first to determine peak areas for a small volume injection. Such results serve as a baseline for evaluating the LVI method performance. The next step is to switch to the solvent vent mode with a slightly larger injection volume (for example, 2 to 5 times larger). By comparing the resulting peak areas and accounting for the increased injection volume, the analyte recovery can be calculated and conditions can be further optimized.

Backflush

A traditional bakeout step for removing late eluters can be very time consuming for samples with complicated matrices, even as long as the analysis time. Capillary flow devices (in this case, a purged ultimate union) provide backflush [2, 3] capability. "Backflush" is a term used for the reversal of flow through a column such that sample components in the column are forced back out the inlet end of the column. By reversing column flow immediately after the last compound of interest has eluted, the long bake-out time for highly retained components can be eliminated. Therefore, the column bleed and ghost peaks are minimized, the column will last longer, and the MS ion source will require less frequent cleaning. The split vent trap may require replacement more frequently than usual.

Instrument Parameters

GC	Agilent 7890A
MS	Agilent 5975C MSD
Column	HP-5MS UI, 15 m × 0.25 mm × 0.25 µm (19091S-431UI), from inlet to purged union
MMI	Constant pressure (~18 psi), chlorpyrifos-methyl RT locked to 8.297 min, 2 psi at post run for backflush
MMI liner	Double taper deactivated, Helix (5188-5398)
Septum purge	3 mL/min
Purged Union	4 psi; 70 psi at post run for backflush
Restrictor	0.7 m × 0.15 mm deactivated fused silica tubing (from purged union to MSD)
Syringes	10 µL, for splitless injections (5181-3354) 50 µL, for solvent vent mode (5183-0318)
ALS	Agilent 7693A
MS parameters	
Solvent delay	2.5 min
Gain factor	1
Mass range	44–550
Threshold	0
Samples	2
Tune file	atune.u

Oven

Initial temperature	70 °C
Initial hold time	1 min
Rate 1	50 °C/min
Temperature 1	150 °C
Hold time	0 min
Rate 2	6 °C/min
Temperature 2	200 °C
Hold time	0 min
Rate 3	16 °C/min
Temperature 3	280 °C
Hold time	5 min
Total runtime	20.933 min
Post run	5 min (for backflush)
Oven post run temp	280 °C

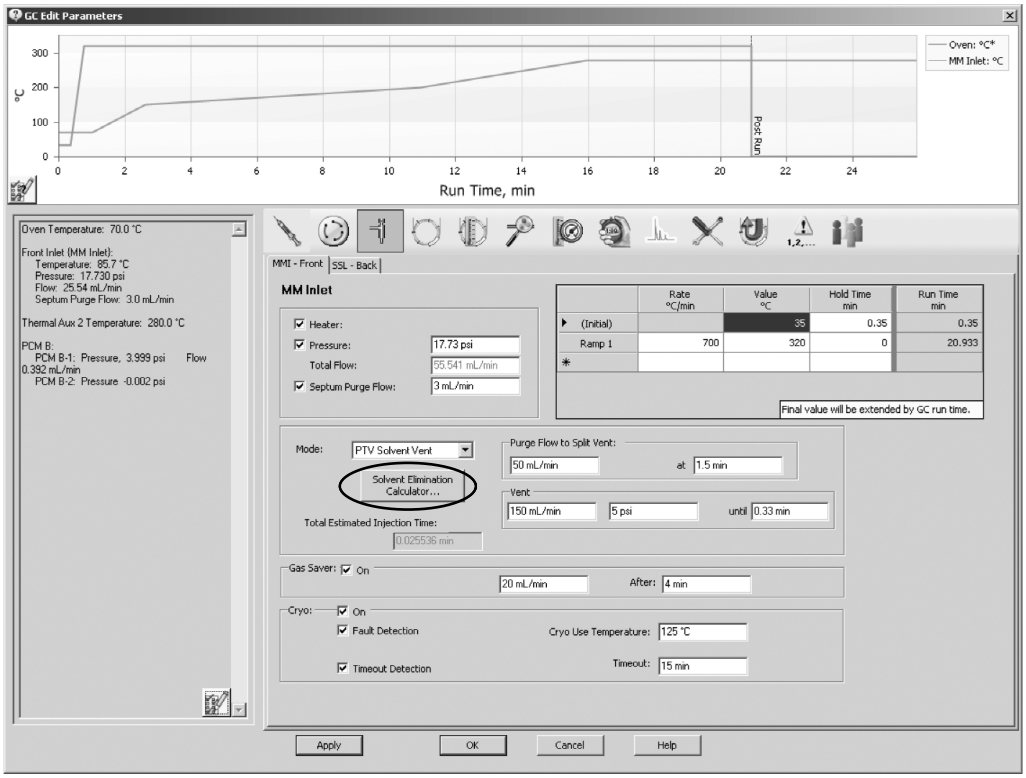
Sample: 40-ppb pesticide standards in acetone (for a list of compounds, see Figure 5).

Multimode Inlet (MMI)

Parameter	Hot Splitless	Cold Splitless	Solvent Vent
Initial temperature	280 °C	30 °C	35 °C
Initial time	–	0.01 min	0.35 min
Rate 1	–	700 C/min	700 °C/min
Final temperature	–	320 °C	320 °C
Vent flow	–	–	150 mL/min
Vent pressure	–	–	5 psig
Vent time	– –	– –	0.33 min (from calculator, Figure 3)
Purge time	0.75 min	1.25 min	1.5 min
Purge flow	50 mL/min	50 mL/min	50 mL/min
Injection volume	2 µL	10 µL	25 µL
Injection speed	Fast –	Fast –	75 µL/min (from calculator, Figure 3)
Cryo	–	On (liquid CO_2)	On (liquid CO_2)
Cryo fault detection	–	On	On
Cryo use temperature	–	125 °C	125 °C
Time out detection	–	On (15 min)	On (15 min)

The parameters for the 25-µL Solvent Vent injection were determined with the Solvent Elimination Calculator integrated in the ChemStation. This calculator was designed to help determine reasonable starting conditions for LVI methods. When the MMI is put into the PTV Solvent Vent mode, an additional button appears in the inlet screen, shown in Figure 1.

In the first screen of the Solvent Elimination Calculator (Figure 2), the sample solvent and desired injection volume are selected and entered. The calculator "knows" the syringe currently installed and will only allow 50% of that volume to be injected at once. Larger injection volumes can be entered into the calculator but the injection volume will not be downloadable. The calculator also requests the boiling point of the earliest eluting analyte, as this allows the initial inlet temperature to be selected. If the boiling point is unknown, the temperature should be left at 150 °C as this will work for a wide range of analytes.



Oven Temperature: 70.0 °C

Front Inlet {MM Inlet}:
Temperature: 85.7 °C
Pressure: 17.730 psi
Flow: 25.54 mL/min
Septum Purge Flow: 3.0 mL/min

Thermal Aux 2 Temperature: 280.0 °C

PCM B:
PCM B-1: Pressure, 3.999 psi Flow 0.392 mL/min
PCM B-2: Pressure -0.002 psi

MM Inlet

☑ Heater:
☑ Pressure: 17.73 psi
Total Flow: 55.541 mL/min
☑ Septum Purge Flow: 3 mL/min

	Rate °C/min	Value °C	Hold Time min	Run Time min
(Initial)		35	0.35	0.35
Ramp 1	700	320	0	20.933
*				

Final value will be extended by GC run time.

Mode: PTV Solvent Vent

Solvent Elimination Calculator...

Total Estimated Injection Time: 0.025536 min

Purge Flow to Split Vent: 50 mL/min at 1.5 min

Vent: 150 mL/min 5 psi until 0.33 min

Gas Saver: ☑ On 20 mL/min After: 4 min

Cryo: ☑ On
☑ Fault Detection
Cryo Use Temperature: 125 °C
☑ Timeout Detection
Timeout: 15 min

Figure 1. Multimode Inlet "Solvent Elimination Calculator" imbedded in ChemStation for easy method development.

Welcome to the Solvent Elimination Calculator!

Please supply the following information.

If you don't know the first analyte boiling point, leave it at 150 °C.

Solvent: acetone

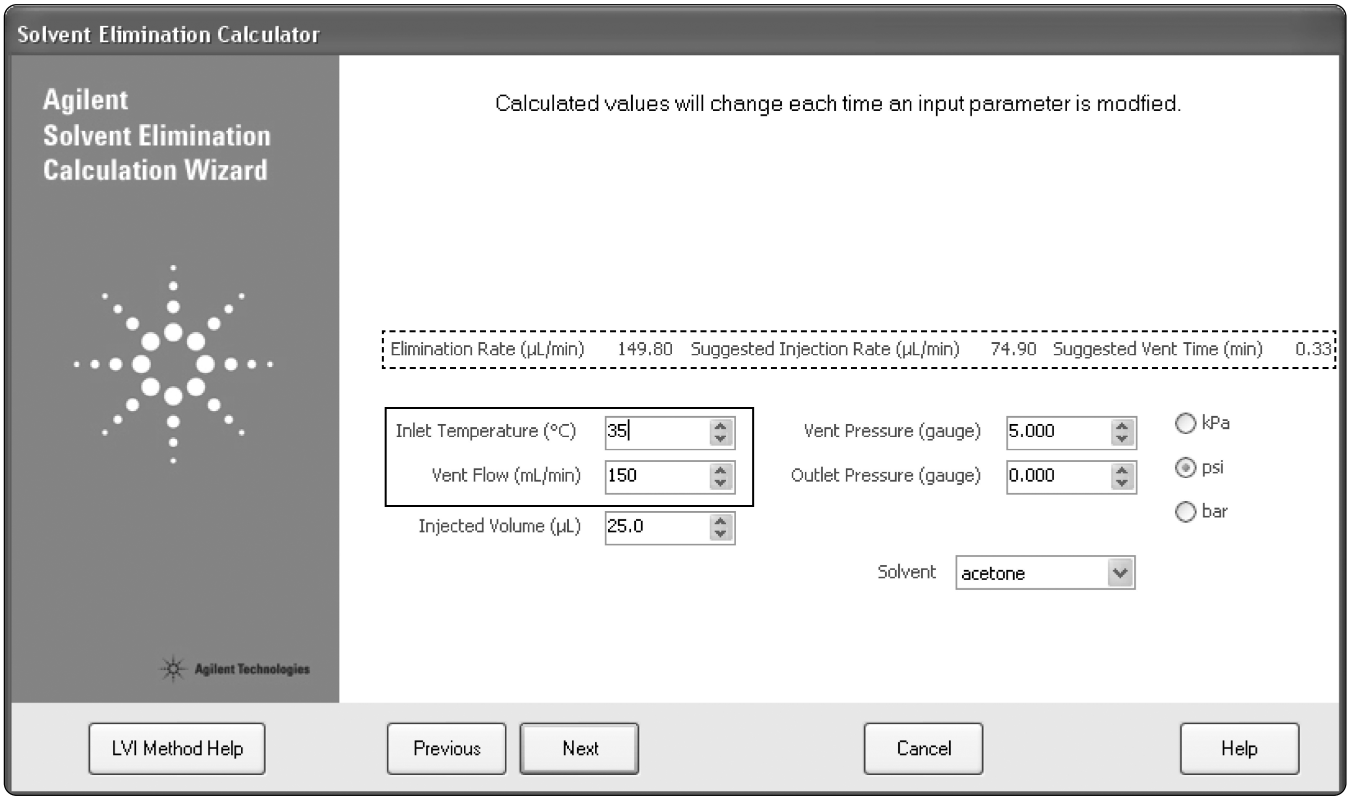
Injection Volume (uL): 25 µL

Boiling Point of first eluting analyte (°C): 150 °C

Figure 2. Select solvent of choice and enter the injection volume to start the calculation.

Figure 3 shows the calculation screen. The calculator uses an initial set of inlet conditions to determine the solvent elimination rate according to fundamental theory [4]. This "Elimination Rate" does not account for other factors (for example, local cooling due to solvent evaporation) specific to LVI and is normally faster than that determined from practical experience. The "Suggested Injection Rate" does consider these factors and is designed to leave a small amount of solvent in the liner at the end of the venting period. This solvent serves as a liquid "trap" for the more volatile analytes and promotes their recovery. The "Suggested Vent Time" is determined by dividing the injection volume by the "Suggested Injection Rate."

Several variables for determining elimination rate can be set by the user in the lower portion of the window. A small change in inlet temperature has a significant impact on elimination rate. Vent flow has a linear effect such that a decrease by a factor of two in vent flow gives an equal decrease in elimination rate. As the vent pressure decreases, the elimination rate increases. Bear in mind that the vent pressure also impacts the amount of solvent that reaches the column during venting. As the vent pressure is increased, more solvent is loaded onto the column before the analytes are transferred. Finally, the type of solvent, specifically its normal boiling point, has a substantial impact on the elimination rate.



Calculated values will change each time an input parameter is modfied.

Elimination Rate (µL/min) 149.80 Suggested Injection Rate (µL/min) 74.90 Suggested Vent Time (min) 0.33

Inlet Temperature (°C) 35

Vent Flow (mL/min) 150

Injected Volume (µL) 25.0

Vent Pressure (gauge) 5.000

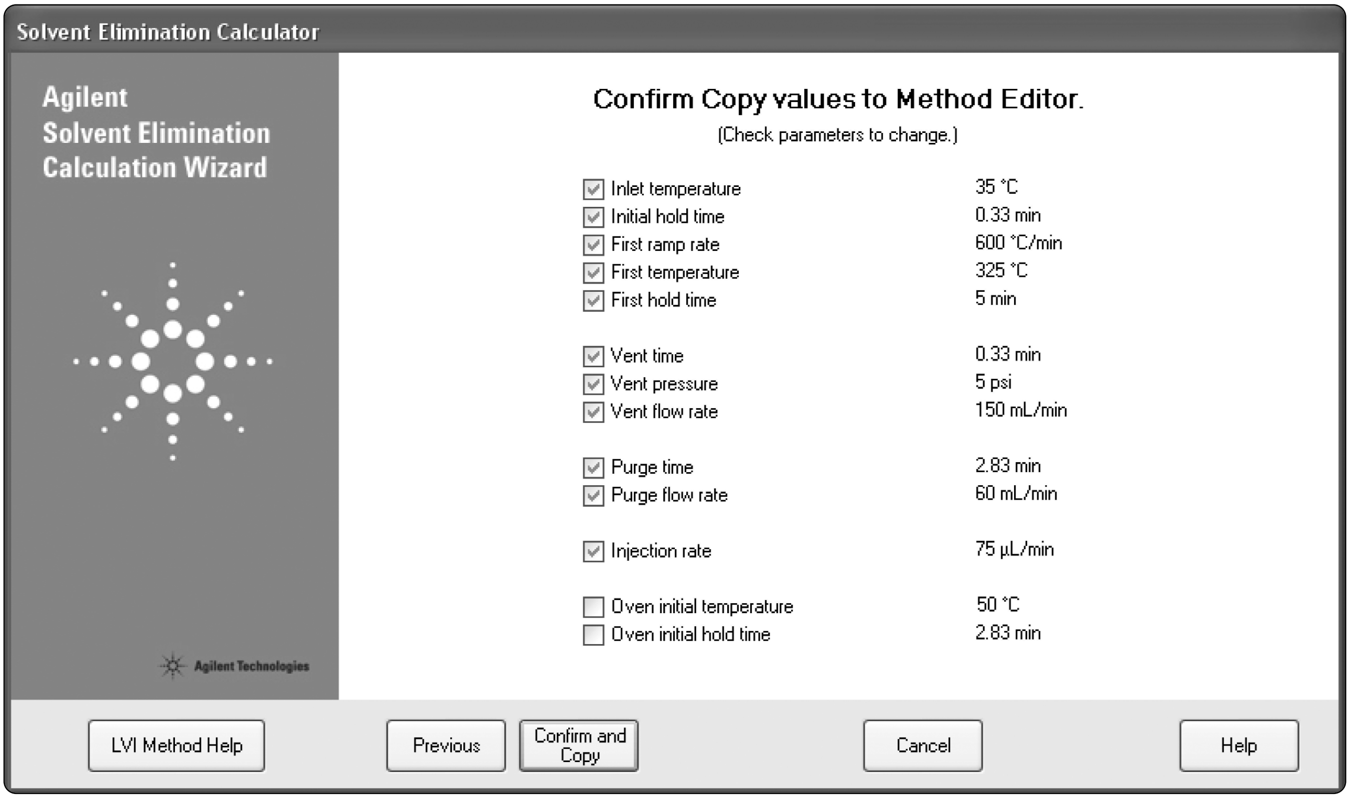
Outlet Pressure (gauge) 0.000

○ kPa
● psi
○ bar

Solvent acetone

Figure 3. The calculator calculates the injection rate and vent time according to the selected inlet temperature and vent flow.

The download screen in Figure 4 shows all of the method changes that are downloaded to the edit parameters screen. The check boxes allow the user to accept (by checking) or reject any of these parameters. The oven initial temperature and hold times are not automatically checked in case the current method requires these values to be unchanged (for example, a Retention Time Locked method).



Confirm Copy values to Method Editor.

(Check parameters to change.)

☑ Inlet temperature 35 °C
☑ Initial hold time 0.33 min
☑ First ramp rate 600 °C/min
☑ First temperature 325 °C
☑ First hold time 5 min

☑ Vent time 0.33 min
☑ Vent pressure 5 psi
☑ Vent flow rate 150 mL/min

☑ Purge time 2.83 min
☑ Purge flow rate 60 mL/min

☑ Injection rate 75 µL/min

☐ Oven initial temperature 50 °C
☐ Oven initial hold time 2.83 min

Figure 4. Confirm values suggested by the Calculator and download to ChemStation.

Results and Discussion

Figure 5 compares the responses of a 40-ppb standard solution from three injection modes.

The bottom total ion chromatogram (TIC) is a typical 2-µL hot splitless injection. Some of the 40-ppb pesticides are barely visible (80 pg each on column). The middle TIC is from a 10-µL cold splitless injection. The MMI starting temperature was 30 °C. In this TIC, the on column amount for each analyte is 400 pg. Lastly, the top TIC is from a 25-µL solvent vent injection with MMI starting temperature at 35 °C. In this TIC, the signal-to-noise ratio is significantly better than the TIC from hot splitless injection (bottom TIC), as noted in the Introduction section. The peak shape and resolution are maintained, even with the 25-µL injection volume. This implies that the solvent was mostly eliminated during the injection.

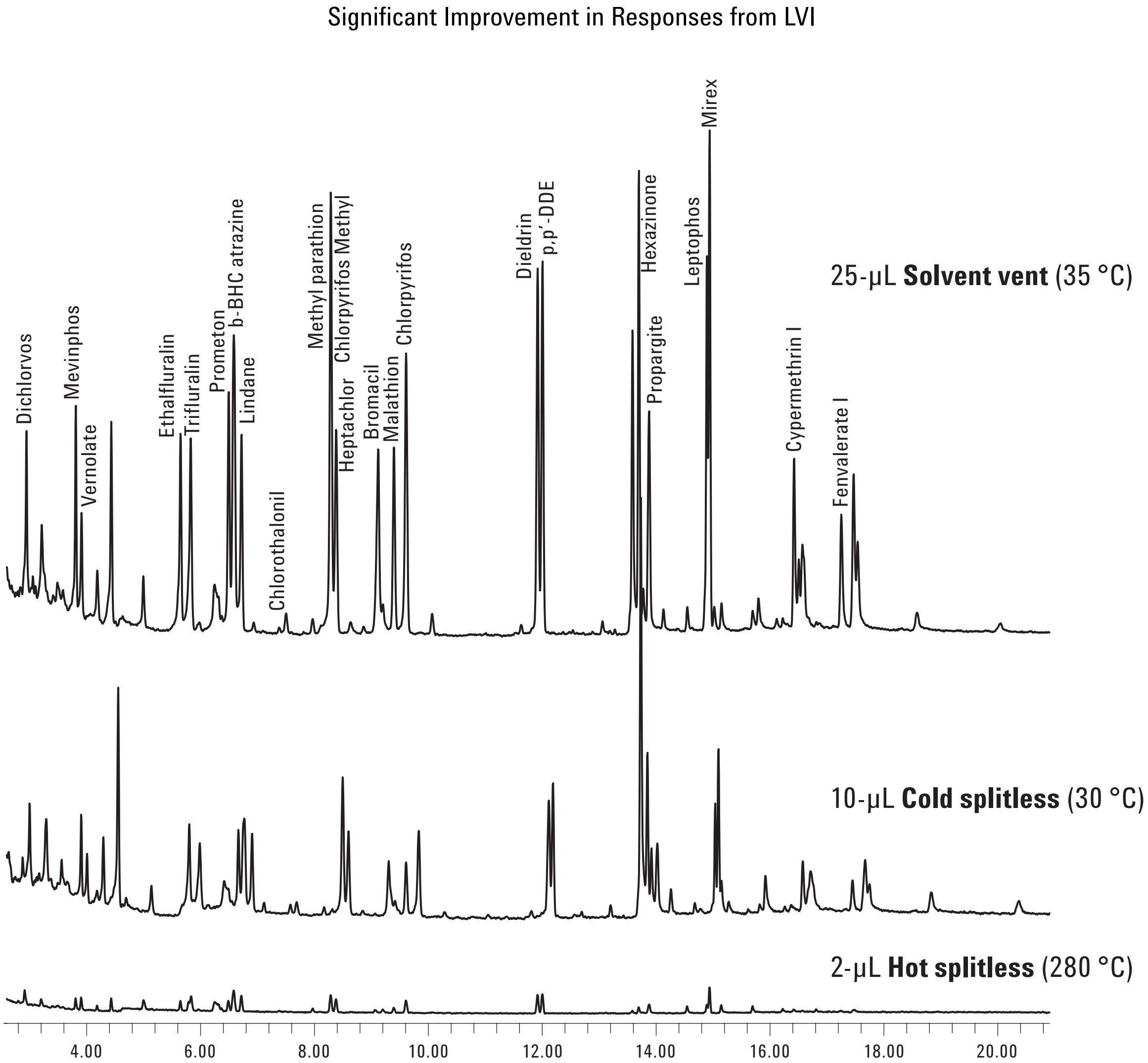


Figure 5. Overlay of total ion chromatograms (TICs) from three injection modes, plotted on the same scale.

Conclusion

The new Agilent Multimode Inlet (MMI) has the same form factor and uses the same consumables (for example, liners, o-rings and septa) as the existing split/splitless inlet, allowing existing hot splitless methods to be replicated. In addition, the temperature programmability permits both cold splitless and large volume injection (LVI) methods for improved detection limits. An integrated Solvent Elimination Calculator provides a complete set of initial conditions for easy LVI method development. The application results show a significant signal-to-noise improvement (lower detection limits) comparing the 25-µL solvent vent injection to the 2-µL hot splitless injection.

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1. Agilent Pressure/Flow Calculator Included in the Instrument Utility DVD, available with each gas chromatograph and MMI accessory kit.
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3. Matthew Klee, "Simplified Backflush Using Agilent 6890 GC Post Run Command," Agilent Technologies publication, 5989-5111EN, June 2006.
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Agilent Technologies

Analysis of Permanent Gases and Light Hydrocarbons Using Agilent 7820A GC With 3-Valve System

Application Note

HPI

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Highlights

- Agilent 7820A GC 3-valve system provides a low-cost but powerful platform for analysis of permanent gases and light hydrocarbons.
- Full electronic pneumatics control (EPC) provides an easy-to-use operation for the end user and ensures excellent repeatability for both retention time and peak area.
- This application work can also be used as a reference in the analysis of natural gas, petroleum gas, synthesis gas, purified gas, water gas, blast furnace gas, stack gas, and so on.

Abstract

A new economical solution is provided to test permanent gases and light hydrocarbons. An Agilent 7820A Gas Chromatograph equipped with three valves, a flame ionization detector (FID), and a thermal conductivity detector (TCD), is configured for analysis of permanent gases and light hydrocarbons. The TCD channel with packed columns is used to measure H_2,CO_2,O_2, N_2,CH_4 and CO. A capillary column (Al_2O_3 PLOT: 50 m × 0.53 mm) is used to measure all hydrocarbons (C1~C6) including CH_4.

Agilent Technologies

Introduction

Analysis of permanent gases and light hydrocarbons has been widely employed in the petrochemical, chemical and energy industries. These permanent gases, such as O_2, N_2, CH_4, CO, and CO_2 are the common target compounds in natural gas, petroleum gas, synthesis gas, purified gas, water gas, blast furnace gas, stack gas, and so on. Understanding the concentrations of these components is important for petrochemical, chemical and energy industrial processes. The 7820A 3-valve system offers an easy-to-use and powerful platform for the analysis of these kinds of samples.

This work illustrates one typical application of the 7820A 3-valve system for the analysis of permanent gases and light hydrocarbons.

Experimental

Three valves were used in this 7820A system: six-port gas sampling, ten-port gas sampling with back-flush to vent, and another six-port column isolation. The valve diagram and columns configuration are shown in Figure 1. Normally, the valve sample loops are connected in series for simultaneous dual-channel injection. Valve control is handled by EZChrom Elite compact software. Chromatographic conditions and valve time events are listed in Tables 1 and 2.

Table 1. Gas Chromatographic Conditions

Sample loop size	0.25 mL
FID channel flow	5 mL/min
FID temp	300 °C
FID channel carrier	N_2
Capillary splitter temp	200 °C
Split ratio	25:1
TCD channel flow	30 mL/min
TCD temp	250 °C
TCD channel carrier	He
Valve box temp	120 °C
Oven program	45 °C (6 min) >180 °C (2.25 min) at 20 °C/min

Table 2. Time Events

Events	**Time (min)**
Valve 1 ON*	0.01
TCD Negative Polarity ON	0.6
TCD Negative Polarity OFF	1.4
Valve 2 ON	1.7
Valve 1 OFF*	2.5
Valve 2 OFF	3.2

*Time events of valve 3 are the same as valve 1.

A fixed gas mix standard, (Jiliang Standard Gas Inc., Shanghai), was used in this application test. The components and concentrations are listed in Table 3.

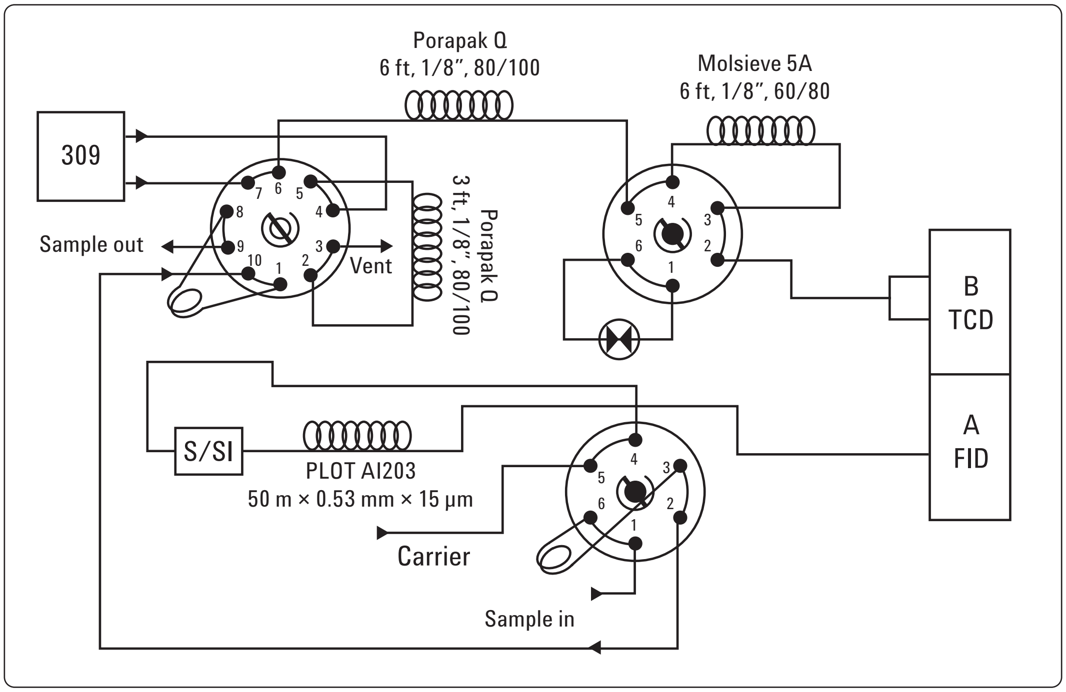

Figure 1. Valve diagram for dual-channel natural gas analysis.

Table 3. Concentrations of the Standard Gases

Components	H_2	O_2	N_2	CO	CO_2	CH_4	C_2H_6	C_3H_8	iC_4	nC_4	iC_5	nC_5	nC_6
Conc. (%)	6.09	3.00	9.97	1.99	3.48	71.92	2.00	0.99	0.11	0.10	0.12	0.12	0.11

Results

Chromatograms

Chromatograms for the FID and TCD channels of standard gas are shown in Figures 2 and 3. Hydrocarbons from C1 to C6 are separated by a PLOT Al_2O_3 column in approximately 15 minutes. For natural gas samples containing hydrocarbons higher than C6, the final temperatures of the oven program can be modified to 220 °C for the elution of hydrocarbons up to C11.

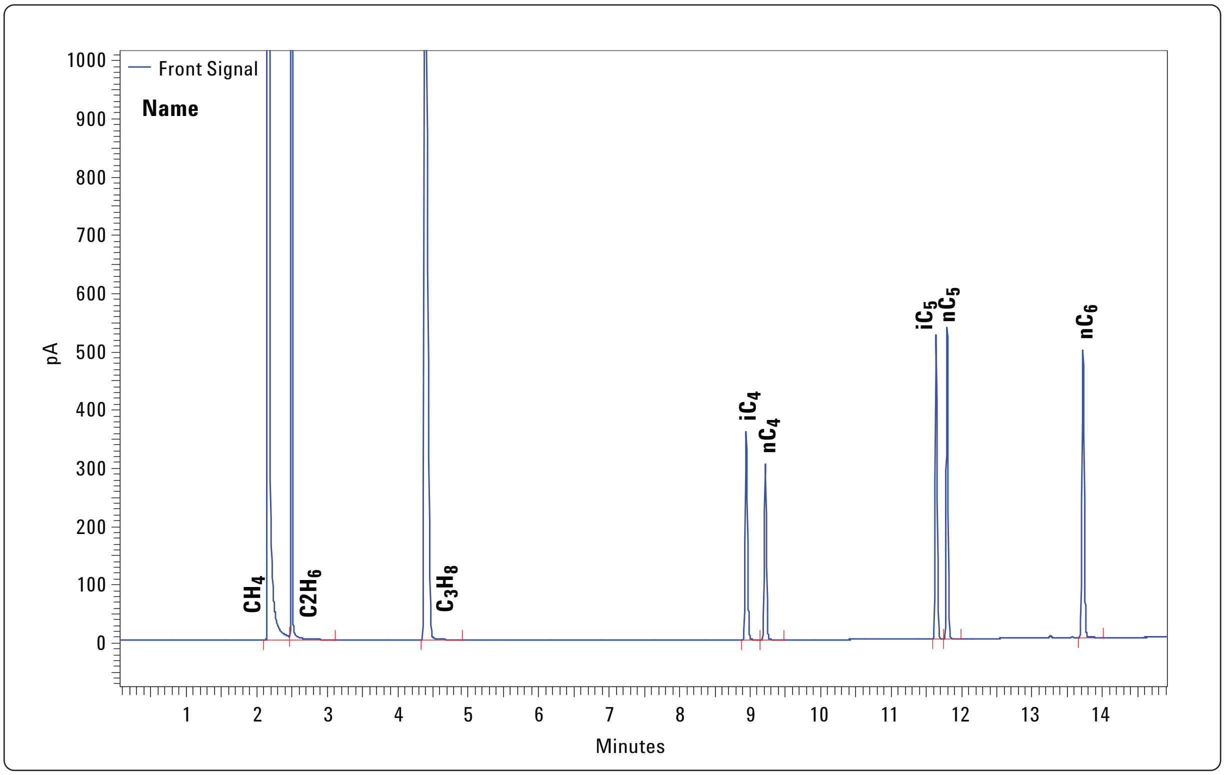

Figure 2. FID Channel chromatogram of CH_4, C_2H_6, C_3H_8, iC_4, nC_4, iC_5, nC_5, and nC_6.

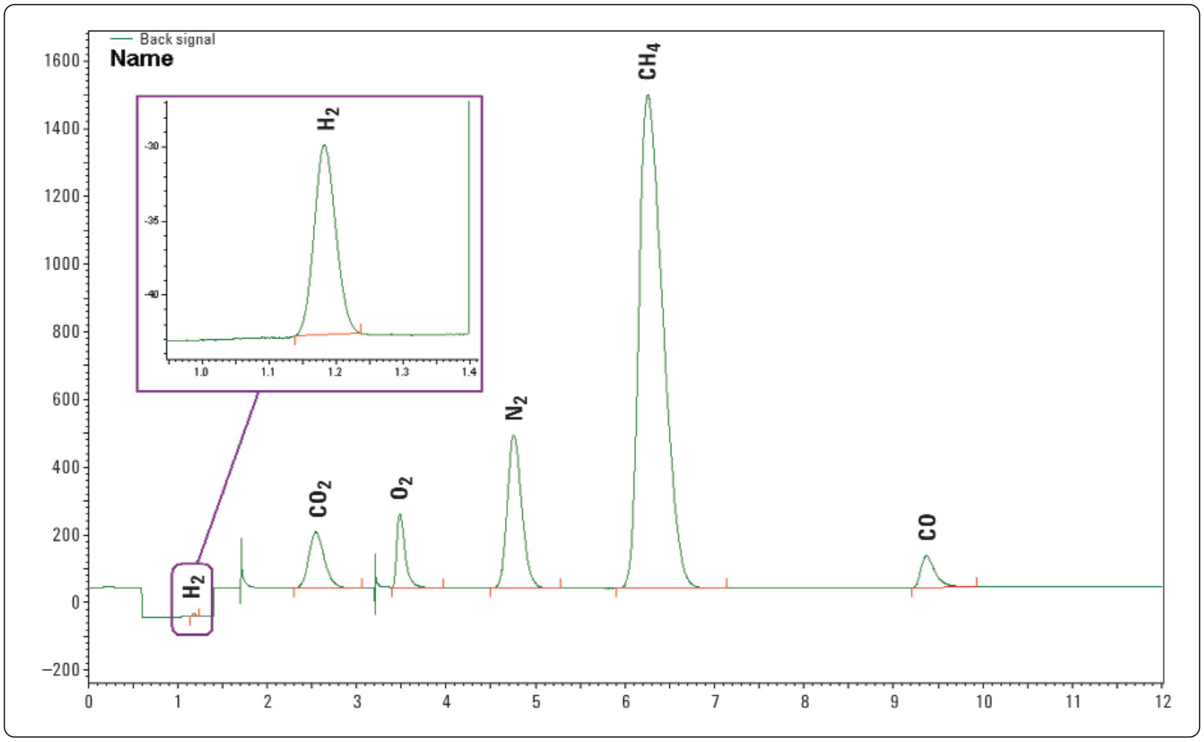

Figure 3. TCD Channel chromatogram of H_2, O_2, CO_2, N_2, CH_4, CO.

Linearity

The mixed standard was dynamically diluted to five different lower-concentration levels for calibration. The linearity results of all the permanent gas components are listed in Table 4.

Table 4. Linearity Results of TCD Channel

%	H_2	CO_2	O_2	N_2	CH_4	CO
Level 1	0.305	0.174	0.150	0.500	3.596	0.100
Level 2	0.609	0.348	0.300	0.997	7.192	0.199
Level 3	1.523	0.870	0.750	2.493	17.98	0.498
Level 4	3.045	1.740	1.500	4.985	35.96	0.995
Level 5	6.090	3.480	3.000	9.970	71.92	1.990
R^2	0.999	0.999	0.998	1.000	0.999	0.999

Repeatability

The relative standard deviations (RSD) for all hydrocarbon components were lower than 0.8% by using split injection on the FID channel. This was due to the full electronic pneumatics control (EPC) from injector to detector on 7820A. Results of the TCD channel also show excellent repeatability (Table 5). Component concentrations were 0.305%, 0.174%, 0.15%, 0.5%, 3.596%, and 0.1%, respectively for H_2, CO_2, O_2, N_2, CH_4, and CO.

Table 5. TCD Channel Repeatability

Runs	H_2	CO_2	O_2	N_2	CH_4	CO
1	10389	753601	137865	2180997	10904896	370250
2	10630	750304	142332	2191591	10947696	378184
3	10498	749748	140281	2156911	10926314	379868
4	10595	745289	139133	2168986	10822886	374996
5	10358	744909	140300	2172639	10826691	371749
RSD%	1.15	0.49	1.18	0.6	0.53	1.09

Low Level Permanent Gases

Another standard gas cylinder (Jiliang Standard Gas Inc., Shanghai) was tested by the 7820A 3-valve system to check low level response and repeatability. Figure 4 shows the chromatogram of the low level permanent gas mix and Figure 5 shows the overlapped chromatograms of five runs. Chromatogram conditions and concentrations of each compound are listed as follows:

Carrier gas:	He	
Sample loop:	1 mL	
Oven:	45 °C (6 min) >180 °C (2.25 min) at 20°C/min	
TCD:	250 °C	
1.	CO_2	200 ppm
2.	O_2	176 ppm
3.	N_2	Balance gas
4.	CH_4	810 ppm
*	Signal of valve switching	

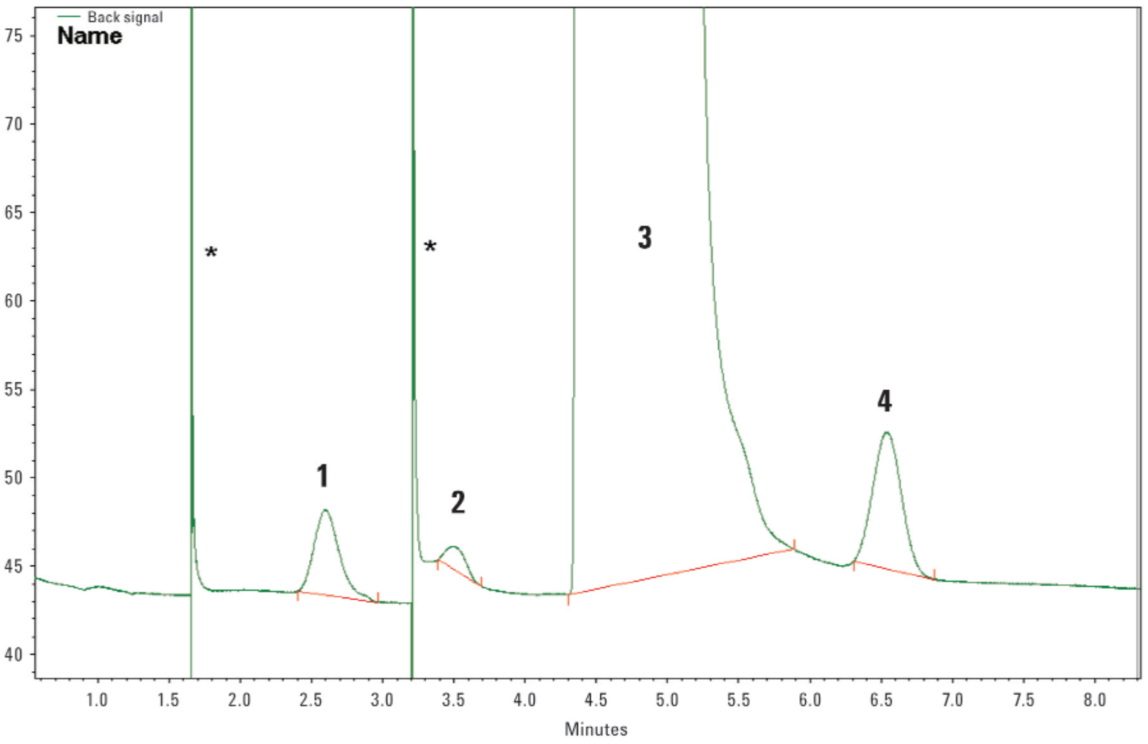

Figure 4. *Chromatogram of low level permanent gas standard mix.*

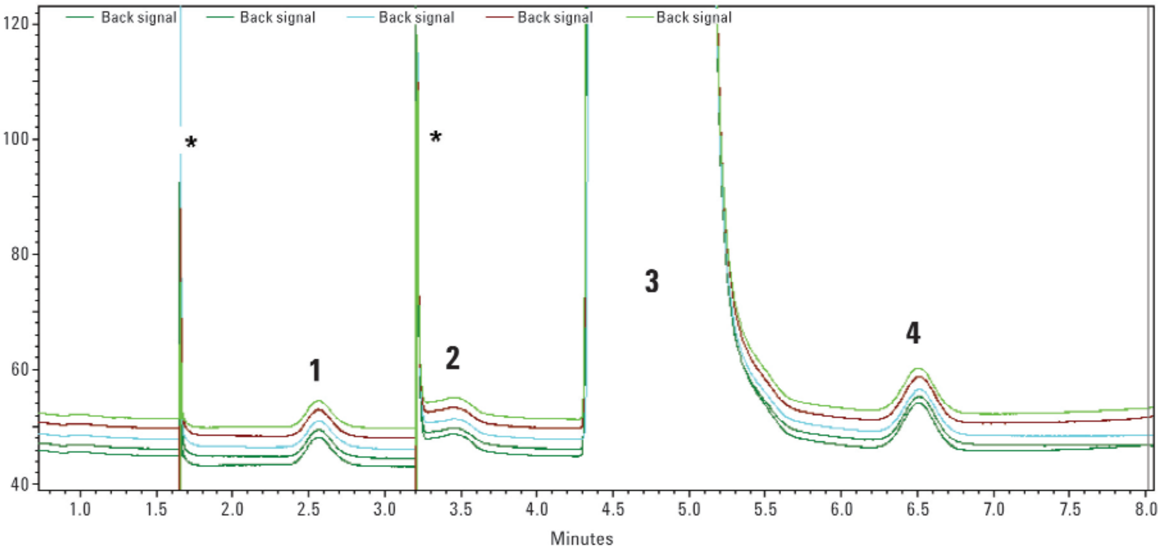

Figure 5. *Overlapped chromatograms of five runs.*

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Agilent Technologies

Meeting the Requirements of EN12916:2006 (IP391/07) Using Agilent 1200 Series HPLC Systems

Application Note

Hydrocarbons

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Abstract

The performance of diesel fuel is predominantly determined by its ignition quality. This parameter is known as the Cetane number. The Cetane number describes the volume % Cetane (hexadecane) present in a mixture of Cetane and 1-Methylnaphthalene. Generally, in order to provide the best performance and lifetime of an engine, the amount of aromatics in diesel should be as low as possible. For the analysis of non-aromatics and aromatics in diesel fuel and petroleum distillates boiling in the range 150 °C to 400 °C, there exists an IP Method (391/07), which uses HPLC with refractive index detection. The two compound classes (aromatics and non-aromatics) are separated using normal phase HPLC and a column which has little affinity for non-aromatic but pronounced selectivity for aromatic hydrocarbons [1]. Recent growth in biodiesel production created a demand for analysis of petrodiesel and petrodiesel/ biodiesel blends. In this method revision, fatty acid methyl esters (FAME) originating from biodiesel sources must elute after a tetra-aromatic marker peak, chrysene, which facilitates improved accuracy of large PAH molecules without interference from FAME. The refractive index detector is used because this detector responds to both non-aromatic and aromatic hydrocarbons.

About Standard Method IP391/07

"This European Standard specifies a test method for the determination of the concentration of mono-aromatic, di-aromatic and tri+-aromatic hydrocarbons in diesel fuels that may contain fatty acid methyl esters (FAME) up to 5 % (v/v) and petroleum distillates in the boiling range from 150 °C to 400 °C. The polycyclic aromatic hydrocarbon content is calculated from the sum of di-aromatic and tri+-aromatic hydrocarbons and the total content of aromatic compounds is calculated from the sum of the individual aromatic hydrocarbon types. Compounds containing sulfur, nitrogen and oxygen may interfere in the determination; mono-alkenes do not interfere, but conjugated di-alkenes and polyalkenes, if present, may do so.

The precision statement of the test method has been established for diesel fuels with and without FAME blending components, with a mono-aromatic content in the range from 6 % (m/m) to 30 % (m/m), a di-aromatic content from 1 % (m/m) to 10 % (m/m), a tri+-aromatic content from 0 % (m/m) to 2 % (m/m), a polycyclic aromatic content from 1 % (m/m) to 12 % (m/m), and a total aromatic content from 7 % (m/m) to 42 % (m/m)." [2]

This method, also known as EN12916:2006, is an official method of the Energy Institute (United Kingdom, www.energyinst.org.uk) which maintains IP (Institute of Petroleum) standards since their acquisition of the IP. Earlier IP391 revisions are similar to ASTM D-6591-06 and include a column backflush-capable instrument configuration and analysis scheme. This requirement was discontinued in the current IP391/07 revision due to erroneous reporting of tri+aromatic hydrocarbons when FAME were present. The main IP391 changes from earlier revisions include the elimination of the backflushing valve, allowing compatibility with biodiesel/petrodiesel fuel blends (up to 5% v/v FAME) and modifications to calibrants to improve data accuracy.

The various methods associated with middle distillate fuel analysis are shown in Table 1.

Table 1. Middle Distillate Fuel Analysis Methods

IP method and revision	Method overview	Special parameters	ASTM method	Comments
IP391/07	150-400 °C diesel fuel petro/bio blends up to B-5	No backflush, amino and/or cyano column	No current equivalent available	Same as method EN12916:2006 *MAH, DAH, Tri+AH are reported
IP436/01	50-300 °C aviation fuel, kerosene	No backflush, amino and/or cyano column	D-6379-04	MAH and DAH reported not for samples with Tri+AH
IP548/06	150-400 °C diesel fuel	Backflush required, amino and/or cyano column	D-6591-06	MAH, DAH, Tri+AH reported FAME interferes with result

*MAH – monoaromatic hydrocarbon, DAH –- diaromatic hydrocarbon, Tri+AH – tri and higher ring aromatic hydrocarbons

Equipment and Conditions

LC:	Agilent 1200 Series LC including
G1312B:	Binary pump, used isocratically with pump head seals for normal phase, Agilent p/n 0905-1420
G1367C:	Autosampler with needle wash
G1316C:	Thermostatted column compartment
G1362A:	Refractive index detector
Software:	Agilent ChemStation with version B.04.01 software
Columns:	ZORBAX NH_2 4.6 mm × 150 mm, 5 µm (p/n 883952-708) and ZORBAX SB-CN 4.6 mm × 150 mm, 5 µm (p/n 883975-905) connected in series using 0.12 × 70 mm ss connector tubing, Agilent p/n G1316-87303
Mobile phase:	n-heptane, HPLC grade
Flow rate:	1 mL/min
Injection volume:	10 µL
Oven temperature:	25 °C
Detection:	Refractive index

Sample preparation

Samples and standards were prepared according to Standard Method IP391/07, using heptane as the diluent. Final quantitative results were reported using Agilent IP391/07 standard mixtures (p/n 5190-0485 system calibration standards SCS1 and SCS2, and p/n 5190-0484 quantitative calibration standards A-D).

Results and Discussion

The first step in implementing of IP391/07 is the analysis of calibrants that establish overall separation selectivity and resolution, and confirmation of the elution order of the calibrant components. (Sections 8.6, 8.7, 8.9 IP391/07). Figure 1 shows the results of running these calibrants on the Agilent system.

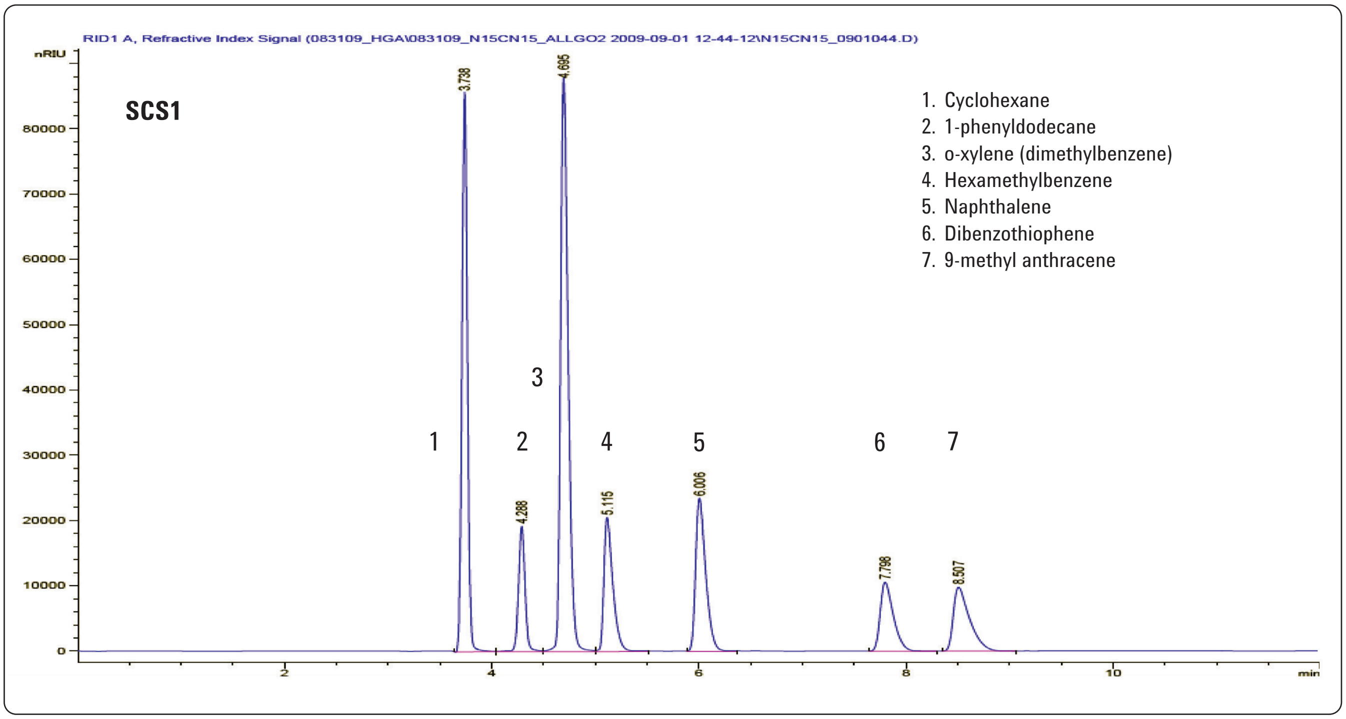


Figure 1. Standard chromatogram of SCS1.

The system calibration standard 1 (SCS1) determines selectivity and retention data for the saturate and aromatic markers used for method acceptance criteria. The SCS1 also determines retention time grouping parameters for sample reporting. Resolution between cyclohexane and o-xylene (1,2-dimethylbenzene) is part of the method specification and must conform to a minimum and maximum value.

System calibration standard 2 (SCS2) establishes the selectivity for components present in petro/bio diesel blends, demonstrating that there is no interference with tri+aromatic components by FAME. Petro/bio fuel blends require longer analysis time to elute all FAME peaks before the next analysis is begun. This applies whether there is an interest in quantifying the FAME or not. When FAME is present in the sample, but does not need to be quantified, it is possible to reduce analysis time by programming the flow rate through the column to increase with time. This will rapidly wash FAME components from the column.

The method requirements state that chrysene, a tetra-aromatic marker peak, must elute with or before the first FAME peak. As shown in Figure 2, the selected operating conditions provide ample separation of the chrysene from the first FAME peak (C16:0 and C18:0 partially resolved).

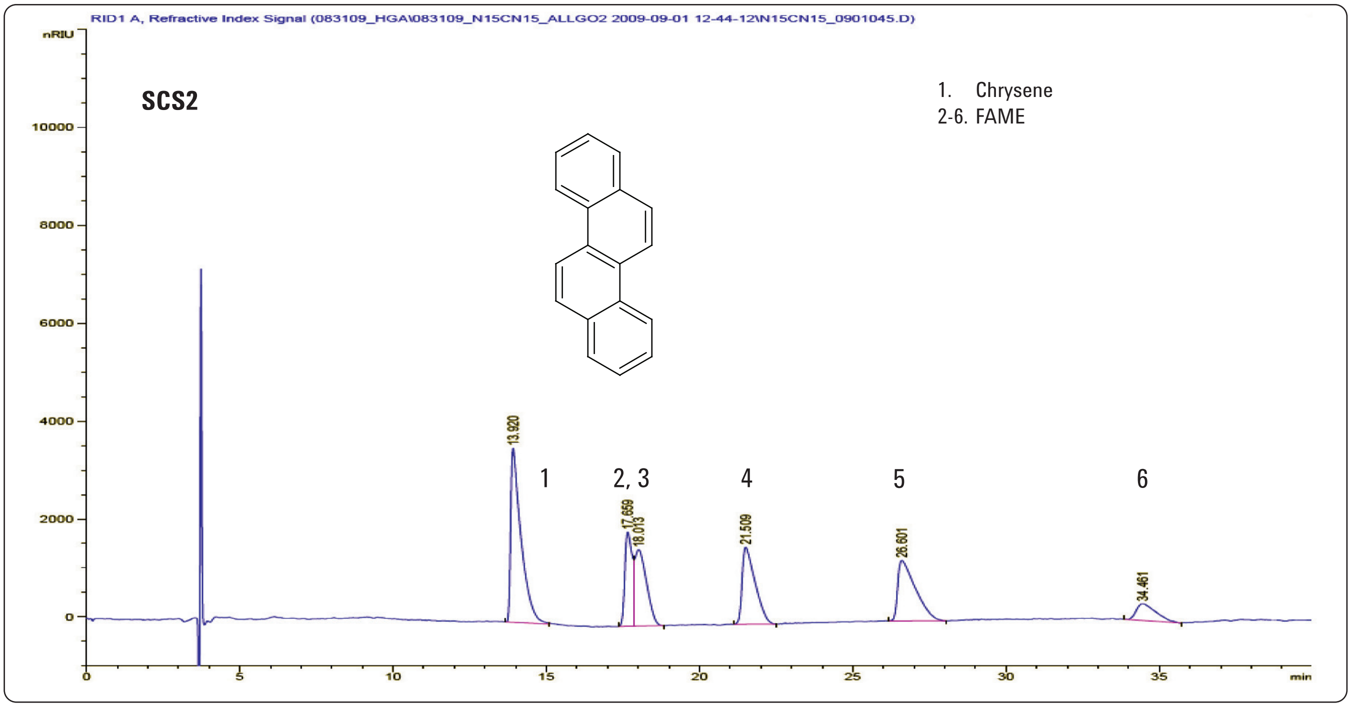


Figure 2. *Standard chromatogram of SCS2.*

With a genuine fuel sample, in this case retail quality petrodiesel, we can see greater complexity and overlapping of the various compound class regions (Figure 3). Within the method definitions there are specific "cut" points defining the grouping to be performed in the quantitative reports. These are calculated from retention and peak width data in SCS1.

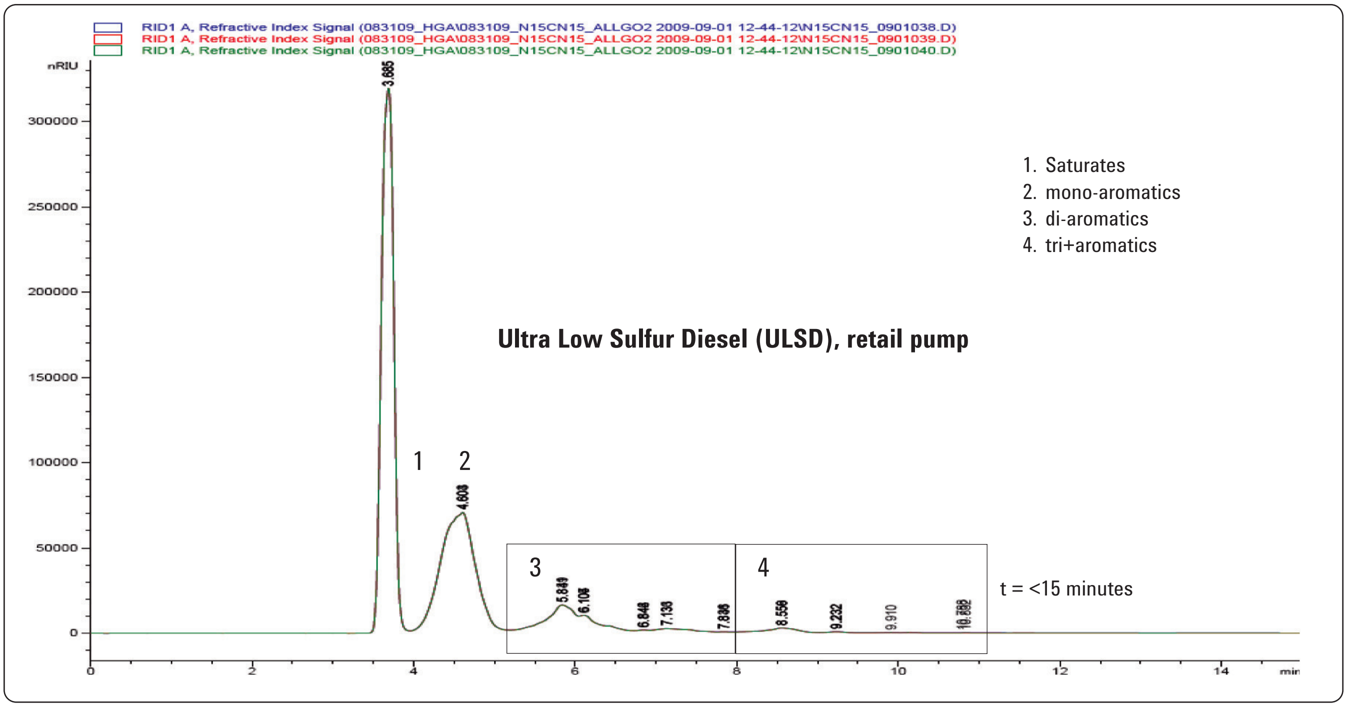


Figure 3. *Petroleum diesel sample showing cut points for the various compound groups typically present in these samples.*

Results and Discussion

Method Performance

As with most official methods, there are specific performance criteria that allow qualification of the separation system and its subsequent use for reporting quantitative results of diesel fuel analysis.

- 6.4 Column system, consisting of a stainless steel HPLC column(s) packed with a commercial 3 µm, 5 µm or 10 µm amino-bonded (or amino/cyano-bonded) silica stationary phase meeting the resolution requirements given in 8.6, 8.7 and 8.9.
- 8.6 Ensure the components of the SCS1 are eluted in the order: cyclohexane, phenyldodecane, 1,2, dimethylbenzene, hexamethylbenzene, naphthalene, dibenzothiophene and 9-methylanthracene.
- 8.7 Ensure that baseline separation is obtained between all components of the SCS1.
- 8.9 Ensure that the resolution between cyclohexane and 1,2 dimethylbenzene is between 5.7 and 10. [calculated as described in 11.2]
- 11.2 Column Resolution

Calculate the resolution, R, between cyclohexane and 1,2 dimethylbenzene using the following equation.

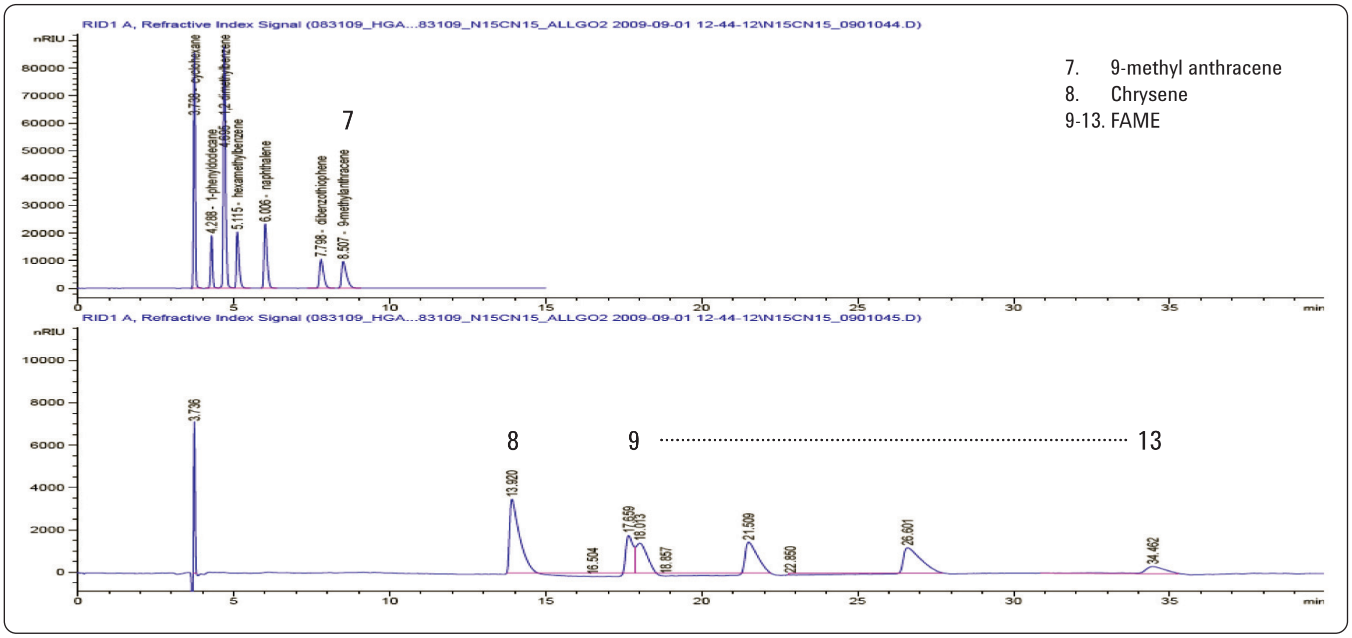
$$R = \frac{2(t3-t1)}{1.699(y1+y3)} \qquad \begin{array}{l}\text{(difference in retention time)}\\ \text{(averaging of peak widths)}\end{array}$$

Name	Ret Time [min]	Resolution	W hh [min]	Cut ref
1. Cyclohexane	3.738	–	0.0558	t1
2. 1-phenyldodecane	4.288	–	0.0648	t2
3. 1,2-dimethylbenzene	4.695	8.57	0.0756	t3

- 8.11 Ensure the retention time peak of chrysene is higher than the ... 9-methylanthracene peak....and check that the chrysene peak elutes just before or with the first peak of FAME.

In Figure 4, we see that there is distinct separation between the markers specified in section 8.11 of the method. With this information in hand, it is possible to proceed to the evaluation of calibration standards.

- 9.4 R = >0.999, Intercept <0.01 g/100 mL)



7. 9-methyl anthracene
8. Chrysene
9-13. FAME

Figure 4. Stack plot of SCS1 and SCS2 showing proof for section 8.11.

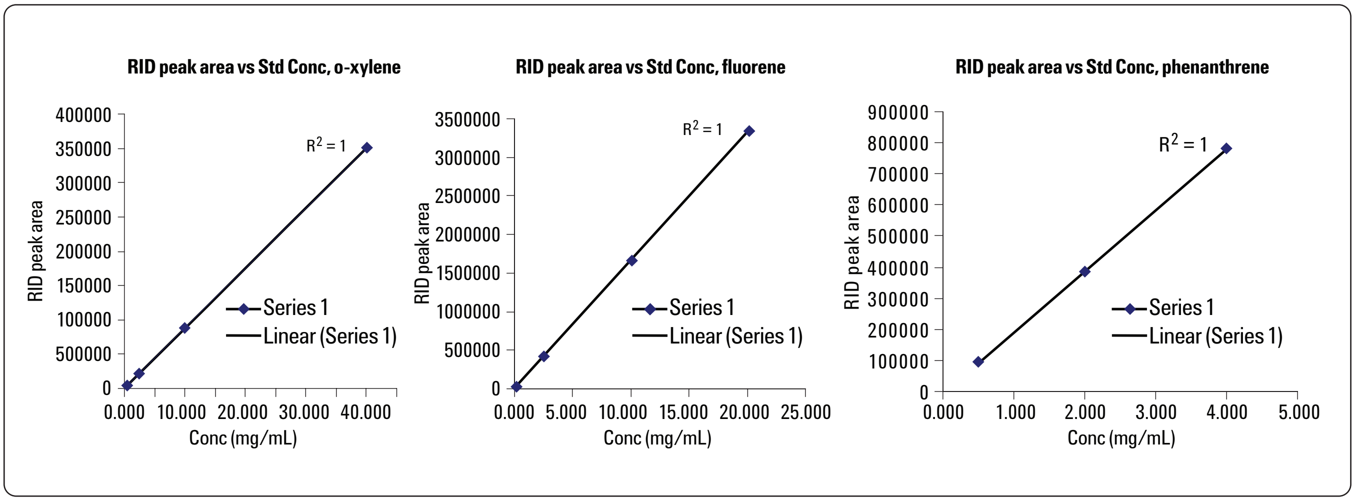


Figure 5. Calibration plots for o-xylene, fluorene and phenanthrene, the three components of the four calibration levels specified in the method.

In the calculated results, all calibration plots exceed linearity of 0.9999 and have calculated intercepts well below 0.01 g/100 mL, the method specification of section 9.4.

Retention time and peak area precision can be found in Table 2, in which we see that the overall performance of the method is excellent.

Table 2. Retention Time and Peak Area Precision

Calibrant A

Analyte	R.T. Avg, n=3	R.T. Std dev	R.T. RSD%	Area Avg, n=3	Area Std dev	Area RSD%
Xylene	4.57	0.003	0.06	3.54E+06	5829.9	0.16
Fluorene	6.82	0.004	0.05	3.38E+06	2500.5	0.07
Phenanthrene	8.32	0.004	0.04	8.05E+05	594.03	0.07

Calibrant B

Analyte	R.T. Avg, n=3	R.T. Std dev	R.T. RSD%	Area Avg, n=3	Area Std dev	Area RSD%
Xylene	4.65	0.001	0.02	9.23E+05	636.28	0.07
Fluorene	6.95	0.001	0.02	1.70E+06	1731.17	0.10
Phenanthrene	8.44	0	0.00	4.00E+05	473.79	0.12

Calibrant C

Analyte	R.T. Avg, n=3	R.T. Std dev	R.T. RSD%	Area Avg, n=3	Area Std dev	Area RSD%
Xylene	4.70	0.002	0.03	2.24E+05	474.36	0.21
Fluorene	7.15	0.002	0.03	4.29E+05	507.38	0.12
Phenanthrene	8.62	0.002	0.02	1.00E+05	291.04	0.29

Calibrant D

Analyte	R.T. Avg, n=3	R.T. Std dev	R.T. RSD%	Area Avg, n=3	Area Std dev	Area RSD%
Xylene	4.72	0.001	0.02	4.45E+04	321.90	0.72
Fluorene	7.36	0.002	0.02	1.70E+04	145.91	0.86
Phenanthrene	8.70	0.002	0.02	3.80E+04	551.43	1.45
Average RSD% All Runs			**0.029**			**0.355**

Results for Specific Petrodiesel and Petro/ Biodiesel Blends

Various samples were collected from local commercial and retail fuel delivery points. An overlay of four samples is shown in Figure 6.

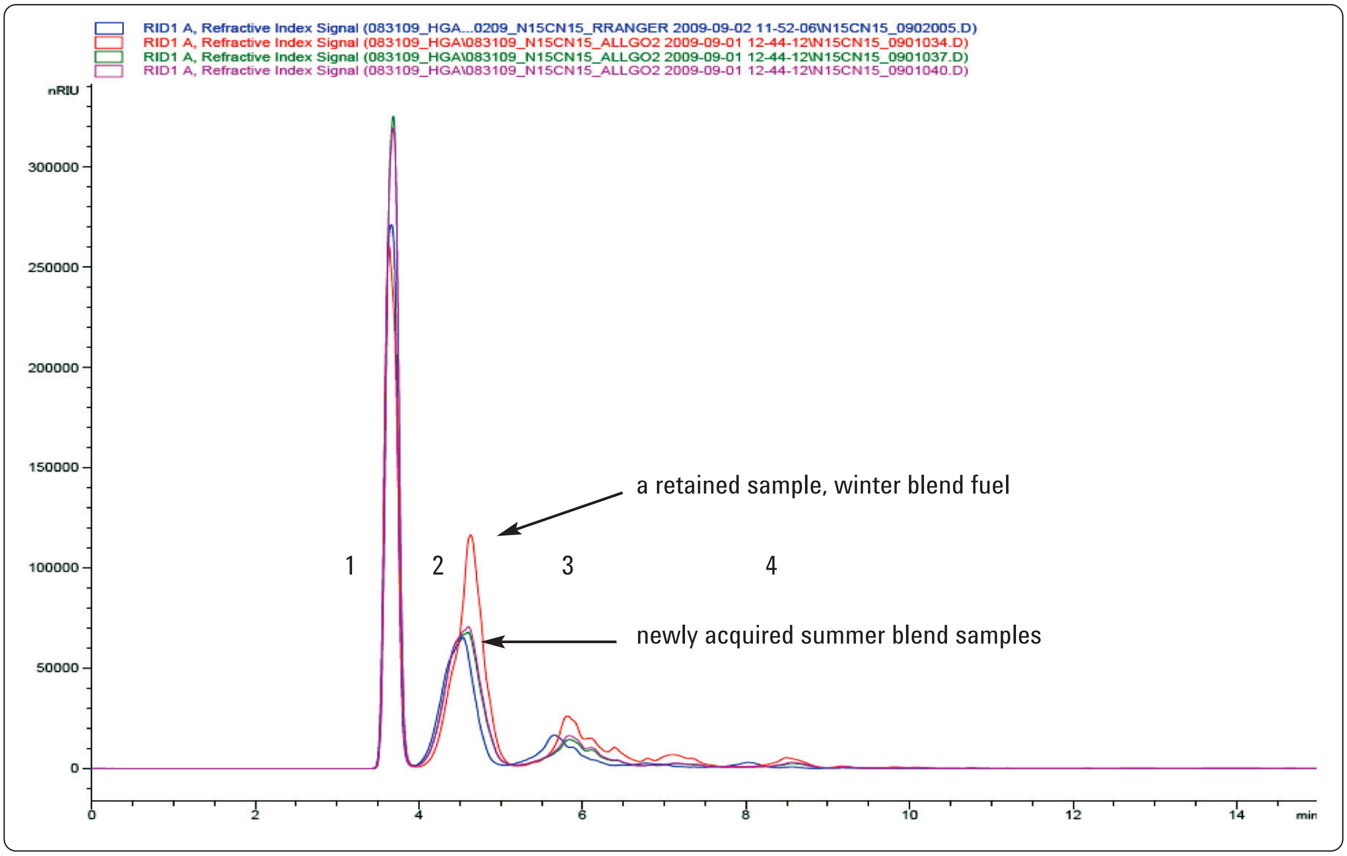


Figure 6. Overlay of four samples.

Results (n=3 each sample) and precision data are reported in Table 3, where vendor 4 results are n=3 based on one sampling of each of the three B-11 biodiesel delivery points (commercial heavy truck, commercial auto/light truck and retail auto/light truck).

Table 3. Results (n=3 each sample) and Precision Data for Four Vendors.

Vendor	Group	Avg, n=3		RSD%	Std dev
1	MAH	36.0	g/100 mL	0.06	0.022
	DAH	8.4	g/100 mL	0.09	0.008
	Tri+AH	1.2	g/100 mL	2.78	0.033
2	MAH	28.5	g/100 mL	0.05	0.016
	DAH	4.8	g/100 mL	0.48	0.023
	Tri+AH	0.6	g/100 mL	3.24	0.020
3	MAH	29.0	g/100 mL	0.07	0.021
	DAH	5.3	g/100 mL	0.37	0.020
	Tri+AH	0.7	g/100 mL	6.81	0.047
4	MAH	24.7	g/100 mL	5.06	1.252
	DAH	5.1	g/100 mL	3.38	0.174
	Tri+AH	0.7	g/100 mL	4.58	0.033

Because of very low level response and broadenend peaks, it is much more difficult to get high precision for the tri+aromatic hydrocarbons group of components. If no biodiesel components are present, it would be practical to consider using Method IP548/01, which uses a backflush valve to elute the tri+aromatic hydrocarbons group as a single peak via the backflush configuration.

Ruggedness and Stability of the IP391/07 Method

As with most normal phase methods the column is susceptible to the adsorption of highly polar components which can affect overall separation performance. Water present in samples or the mobile phase also adsorbs into the column and somewhat predictably causes reduced elution times for all sample components. Using a high quality HPLC grade mobile phase is essential, and the user may consider using a drying agent such as molecular sieve to dehydrate the mobile phase. While this is often done by adding molecular sieve to the solvent container, it is also possible and preferable to prepare a high pressure compatible column with pre-washed drying agent and placing it inline between the pump and injector.

Conclusion

The performance of the Agilent 1200 Series HPLC with normal phase separation and refractive index detection meets or exceeds the requirements of IP391/07 within the range of samples defined in the method. The user should take care identifying samples of petrodiesel that may contain biodiesel components to ensure adequate analysis time before proceeding to the next analytical run.

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Fast analysis of polyaromatic hydrocarbons using the Agilent 1290 Infinity LC and Eclipse PAH columns

Application Note

Environmental

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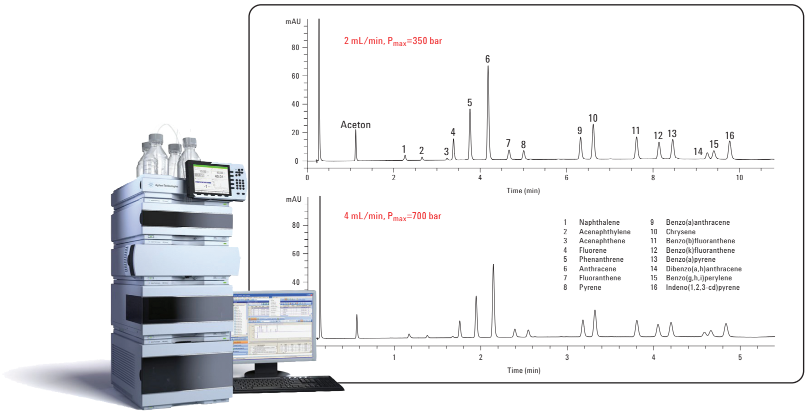

The Agilent 1290 Infinity LC has a broader power range (the combination of pressure and flow capabilities) than any other commercially available system. This is extremely useful for method transfer from one (U)HPLC to the Agilent 1290 Infinity LC system and allows the analyst to develop methods that are impossible to run on these other systems.

The flow and pressure capabilities are illustrated by a separation of 16 polyaromatic hydrocarbons (PAHs) at high pressure and flow rate. At 2 mL/min, the analysis time is approximately 11 min. Doubling the flow rate and gradient speed allows the sample to be analyzed in 5.5 min with a maximum pressure of 700 bar. The combination of high flow (4 mL/min) and pressure is useful in this case to increase the sample throughput. The separation of the PAHs is shown in Figure 1.

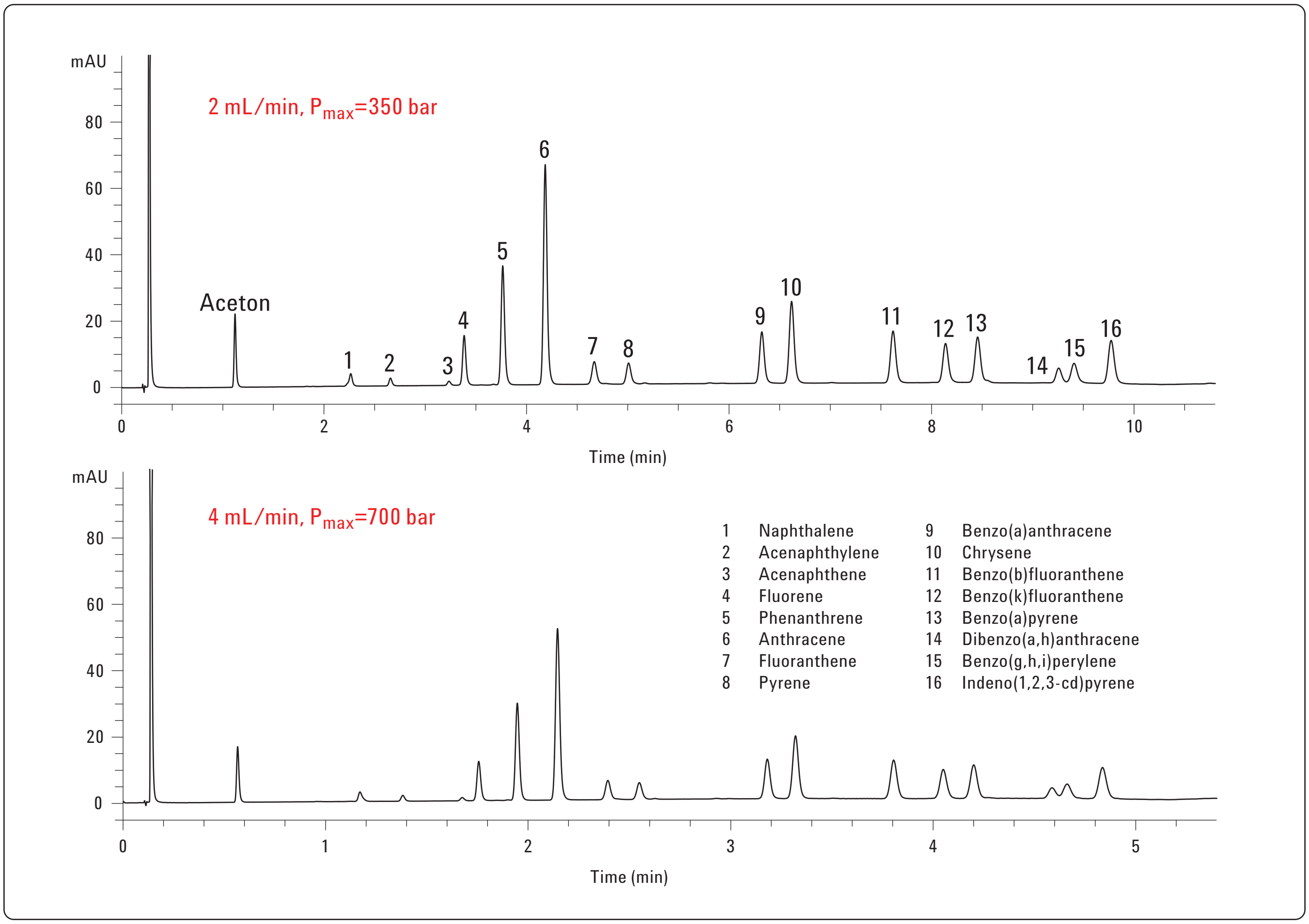

Figure 1
Analysis of 16 PAHs on the 1290 Infinity LC. Sample: standard solution of 16 PAHs, 50 µg/mL each.

Configuration:			
• G4220A	1290 Infinity Binary Pump with Integrated Vacuum Degasser		
• G4226A	1290 Infinity Autosampler		
• G1316C	1290 Infinity Thermostatted Column Compartment		
• G4212A	1290 Infinity Diode Array Detector		
Method:			
Column:	ZORBAX Eclipse PAH 4.6 mm × 50 mm, 1.8 µm		
Mobile phase:	A = water, B = acetonitrile		
Flow rate and gradient:	2 mL/min	0–0.33 min	40% B
		0.33–10 min	40–100% B
	4 mL/min	0–0.17 min	40% B
		0.17–5 min	40–100% B
Injection volume:	0.2 µL		
Detector:	Sig = 254/10 nm, Ref = off, 40 Hz		
Temperature:	25 °C		

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Agilent Technologies

Prefractionator for Reliable Analysis of the Light Ends of Crude Oil and other Petroleum Fractions

Application Note

Hydrocarbon Processing

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Abstract

A precolumn backflush system based on capillary columns using midpoint pressure control is described. Midpoint backflush is made possible with a Capillary Flow Technology (CFT) purged union controlled by an AUX EPC channel on the Agilent 7890A GC system. The key application discussed is prefractionation of crude oil that provides a high resolution separation of the C4 to C12 cut. A general backflush method using Polywax 500 is presented to illustrate the backflush concept.

Introduction

The concept of backflushing in gas chromatography has been a mainstay of many petrochemical and gas analysis applications for over 40 years. Most use some implementation of a packed or micropacked precolumn connected to a mechanical valve. The analytical separation can then be done with either a packed or capillary column while the precolumn is backflushed to vent. Now precolumn backflush can be implemented in capillary only systems using either a standard split/splitless inlet or multimode inlet (MMI). Any application where sample components elute (or in some cases never elute) after the last compound of interest is a good candidate for a backflush implementation.

Process engineers and chemists working in the petroleum industry often have a need to analyze in detail the lighter fraction of a wide boiling raw material or feedstock. While GC is always the separation method of choice for petroleum and petrochemical samples, real limitations exist concerning the boiling point range or maximum carbon number that can be accommodated by a given capillary column. Many petroleum materials contain high boilers that can never elute. Analysis time can also be an issue even for compatible samples and columns because heavy material may require 60 minutes or longer to elute from the column. Now, the analysis of wide range petroleum material such as crude oils can be easily optimized, providing a high resolution time optimized separation for only the fraction required.

Crude oil analysis serves as an excellent example. A detailed analysis of the hydrocarbons in the C4 to C12 fraction is extremely valuable to the process engineer looking for the best method of refining the material. It is also valuable for determining the crude oil's value. Typically prefractionator or precolumn backflush GC configurations are based on packed precolumns and mechanical valves that can require specialized inlets. These systems require frequent maintenance, can suffer from poor thermal control, and are not optimized for high resolution separations. Agilent offers a unique solution based on a simple in-oven Capillary Flow Technology (CFT) device, the Purged Union (p/n G3186-60580). An MMI, AUX module, and FID complete the required hardware on the Agilent 7890A GC system. The configuration is compatible with all GC detectors including the MSD.

Experimental

A diagram of the basic system is shown below in Figure 1. The MMI is used in temperature programmed split mode to assist with cleaning out the liner during backflush while an AUX channel controls analytical column flow. Injection is handled by the 7693A Tower and Tray system where basic sample prep (mixing, dilution, and heating) is used for automated sample prep.

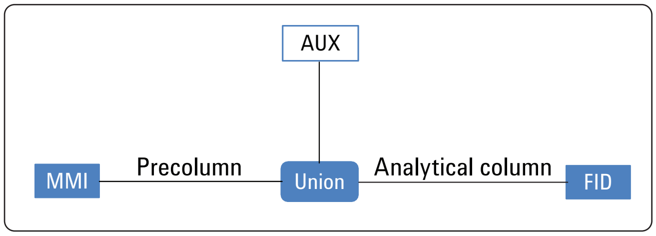


Figure 1. Basic precolumn backflush configuration with purged union.

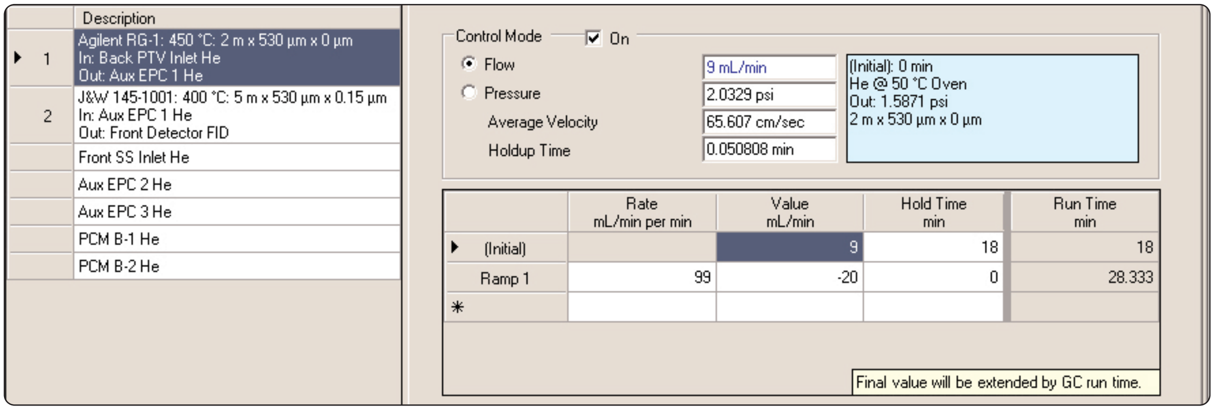
Parameters for crude oil analysis of C4 to C12/C13

Sample:	Various crude oils
Inlet:	Multimode, 250:1 split
Inlet program:	250 °C (0.3 min) to 425 °C (60 min) at 200 °C/min
Oven program:	35 °C (10 min) to 160 °C (1 min) at 1 °C/min then 15 °C/min to 240 °C
Column 1:	2 m × 0.32 mm deactivated retention gap
Column 1 Flow:	0.9 mL/min in constant flow mode
Column 2:	100 m x 0.25 mm, 0.5 µm DB-Petro
Column 2 Flow:	1.2 mL/min in constant flow mode
Backflush after C12:	1.3 min approx.

Parameters for wide boiling range generic method

Sample:	Polywax 500
Inlet:	MMI, 10:1 split
Inlet program:	350 °C (0 min) to 425 °C (20 min)
Oven program:	50 °C (0 min) to 355 °C (5 min) at 15 °C/min
Column 1:	1 m x 0.53 mm deactivated retention gap
Column 1 Flow:	9 mL/min
Column 2:	5 m x 0.53 mm × 0.15 µm DB-HT
Column 2 Flow:	12 mL/min
Backflush times:	Various

The general procedure for precolumn backflush can be illustrated using a wide boiling range sample such as Polywax 500 (PW 500) where backflushing at specific carbon numbers can be easily accomplished. Setup panes for the PW500 analysis are shown in Figures 2A and 2B for precolumn and analytical column, respectively. Note that backflush is triggered by programming a rapid pressure drop at the inlet to the precolumn, which is the MMI in this example. First, defining the inlet and outlet sources for the columns is critical. The inlet to the precolumn is the MMI and the outlet an Aux channel. For the analytical column, the inlet is the Aux and FID the outlet.



	Description
▸ 1	Agilent RG-1: 450 °C: 2 m x 530 µm x 0 µm In: Back PTV Inlet He Out: Aux EPC 1 He
2	J&W 145-1001: 400 °C: 5 m x 530 µm x 0.15 µm In: Aux EPC 1 He Out: Front Detector FID
	Front SS Inlet He
	Aux EPC 2 He
	Aux EPC 3 He
	PCM B-1 He
	PCM B-2 He

Control Mode ☑ On

● Flow: 9 mL/min

○ Pressure: 2.0329 psi

Average Velocity: 65.607 cm/sec

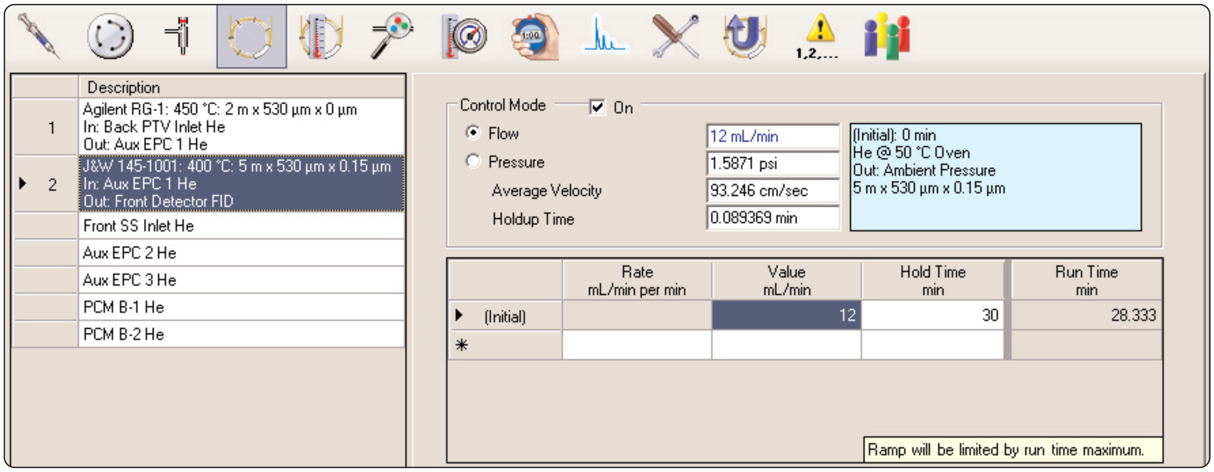
Holdup Time: 0.050808 min

(Initial): 0 min
He @ 50 °C Oven
Out: 1.5871 psi
2 m x 530 µm x 0 µm

	Rate mL/min per min	Value mL/min	Hold Time min	Run Time min
▸ (Initial)		9	18	18
Ramp 1	99	-20	0	28.333
*				

Final value will be extended by GC run time.

Figure 2A. Precolumn flows. Backflush starts at 18 min in this example.



	Description
1	Agilent RG-1: 450 °C: 2 m x 530 µm x 0 µm In: Back PTV Inlet He Out: Aux EPC 1 He
▸ 2	J&W 145-1001: 400 °C: 5 m x 530 µm x 0.15 µm In: Aux EPC 1 He Out: Front Detector FID
	Front SS Inlet He
	Aux EPC 2 He
	Aux EPC 3 He
	PCM B-1 He
	PCM B-2 He

Control Mode ☑ On

● Flow: 12 mL/min

○ Pressure: 1.5871 psi

Average Velocity: 93.246 cm/sec

Holdup Time: 0.089369 min

(Initial): 0 min
He @ 50 °C Oven
Out: Ambient Pressure
5 m x 530 µm x 0.15 µm

	Rate mL/min per min	Value mL/min	Hold Time min	Run Time min
▸ (Initial)		12	30	28.333
*				

Ramp will be limited by run time maximum.

Figure 2B. Analytical column flow set at 12 ml/min for the entire run.

Note that at certain backflush times, only part of the last hydrocarbon is transferred to the analytical column. This occurs because individual compounds will be spread out and distorted on the precolumn. Backflush times can usually be fine tuned to make a clean cut with the polyethylene fragments that make up PW500 since they occur at even carbon numbers only (Figure 3).

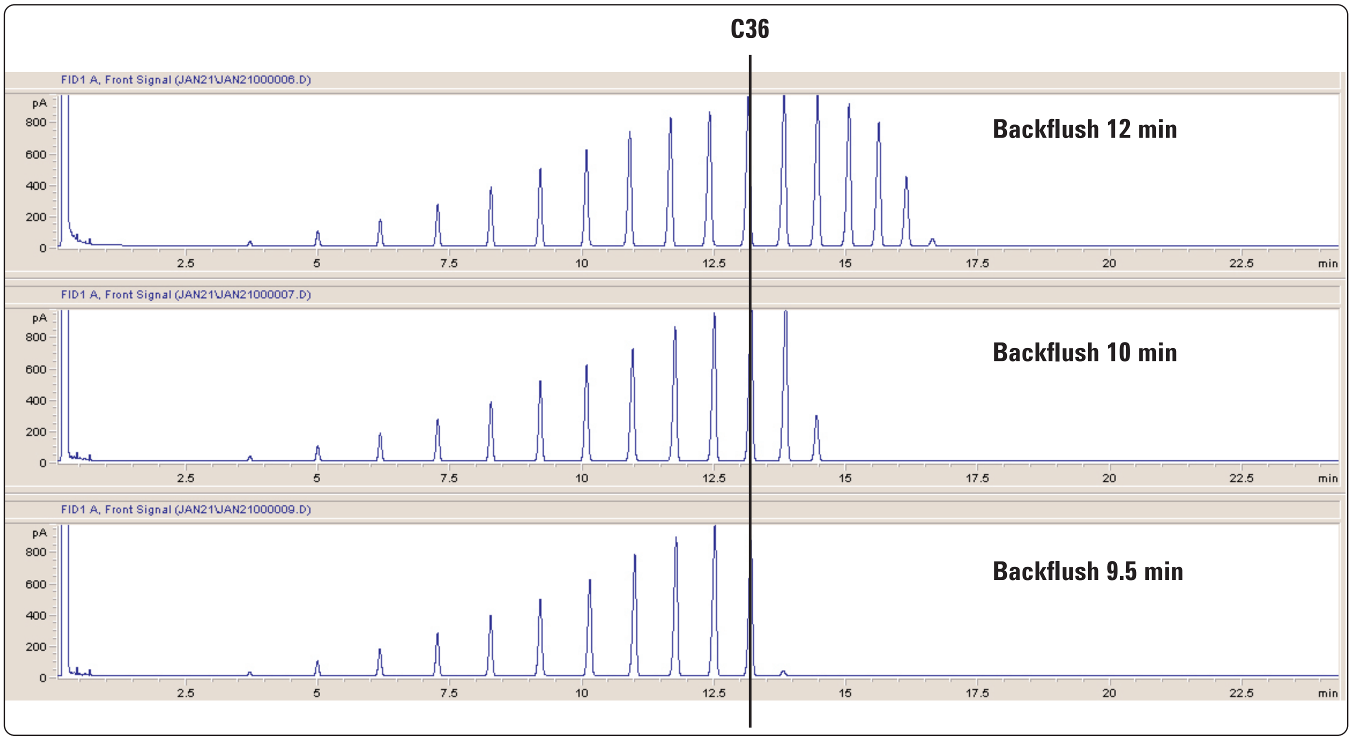


Figure 3. Polywax 500 chromatograms at three backflush times.

A plot of backflush time versus carbon number can be constructed as shown in Figures 4A and 4B. While a polynomial curve fit is best (Figure 4A), a linear regression will give a very good prediction of an appropriate backflush time at any desired carbon number (Figure 4B). The equation

BF Time = (Carbon number – 5.56)/3.68

can be used to give very close to ideal times for the columns and conditions stated here. Any change in the parameters would require a new equation. When developing a new applicatin three to four points would be enough to establish the relationship between carbon number and backflush time using an appropriate test mixture. This is easily done using a ChemStation sequence for fast method optimization.

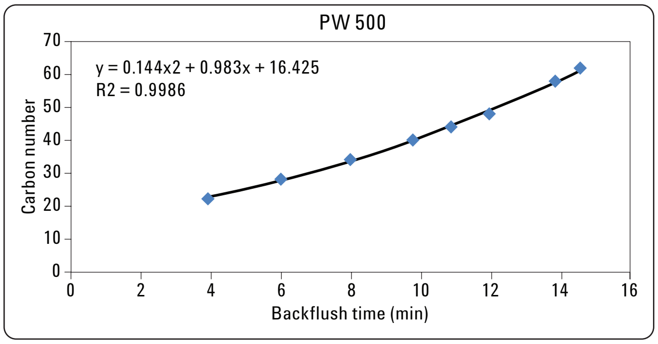


Figure 4A. Polynomial fit.

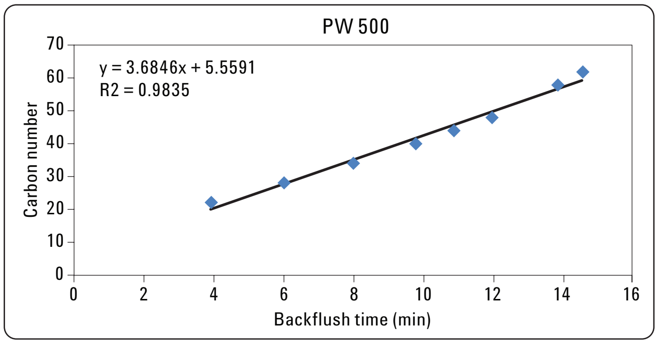


Figure 4B. Linear regression.

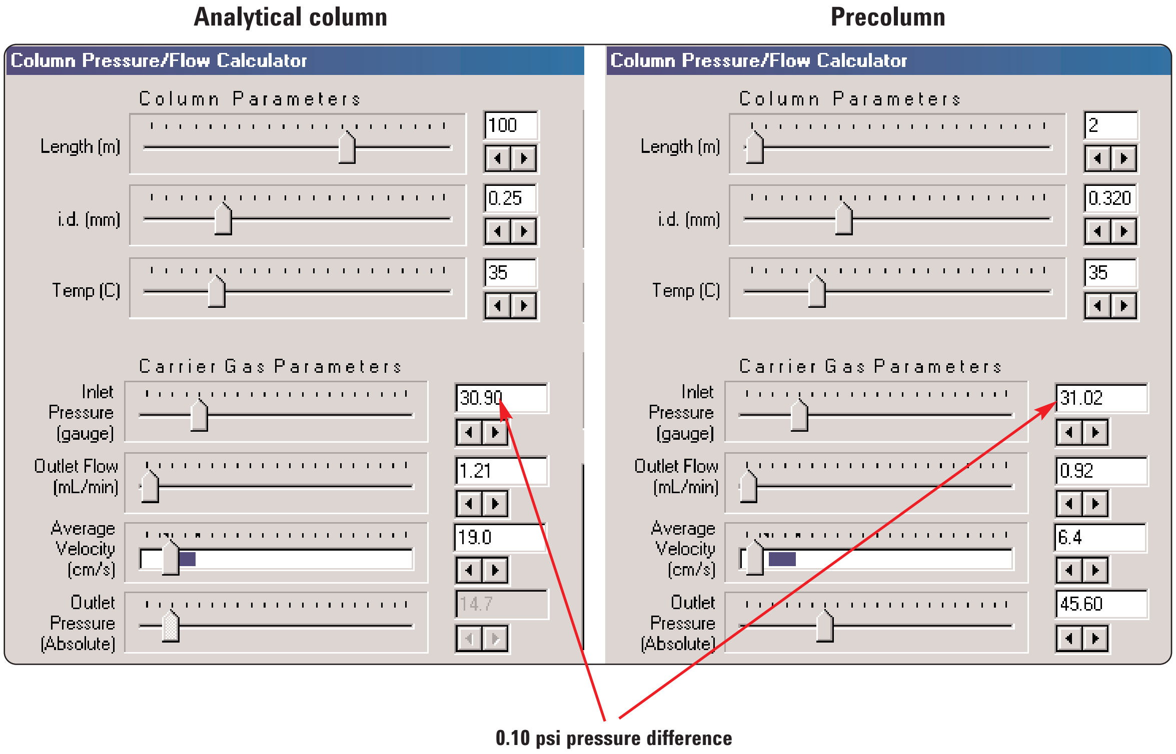
Discussion

Crude oil analysis is used as an example to show system setup and typical results. The precolumn usually consists of a short piece of deactivated fused silica, and the analytical column is chosen to provide sufficient separation power for the application. The columns used for crude oil analysis are 2 m × 0.32 mm deactivated retention gap, and 100 m × 0.25 mm × 0.50 µm DB-PETRO for the pre and analytical columns, respectively. Many possibilities exist for choice of pre and analytical columns for customizing the system for a particular application. Attention must be given to the pressure differential between the inlet and aux to assure stable operation when choosing columns and conditions. Differences less than 0.1 psig must be avoided.

To begin system setup, the EPC channels must first be zeroed. This is necessary because the pressure difference between the MMI pressure and the Aux pressure may be as small as 0.1 psig. This can be seen in Figure 5 where the flow calculator is used to determine the flow settings for the crude oil prefractionation system. Flow calculator software can be downloaded from the Agilent web site. [1]

Next the "Quick swap" PID constants need to be uploaded to the Aux channel. This is done with the LMD Update Utility Tool for the 7890A. Flow or pressure is set first for the analytical column controlled by an Aux channel, then Flow or pressure is set for the precolumn controlled by the MMI. As a general rule, the precolumn flow should be set between 70% and 85% of the analytical column flow.

Fine tuning the backflush time is easily done by running a sequence of several methods with a slightly different backflush time in each using a mix of hydrocarbons from C5 to C17 (p/n 5080-8769). A given hydrocarbon will elute from the uncoated precolumn at a lower temperature than it would from the analytical column. Exactly how much lower is highly dependent on the phase ratio of the analytical column. Therefore it is best to start with a relatively quick backflush and then adjust the time upwards to allow all of the desired boiling point range to pass into the analytical column for separation. As shown in Figure 6, the area of the C13 peak increases as the backflush time is lengthened. The final desired backflush time is reached once the area becomes constant (BF = 1.30 min).



	Analytical column	Precolumn
Length (m)	100	2
i.d. (mm)	0.25	0.320
Temp (C)	35	35
Inlet Pressure (gauge)	30.90	31.02
Outlet Flow (mL/min)	1.21	0.92
Average Velocity (cm/s)	19.0	6.4
Outlet Pressure (Absolute)	14.7	45.60

0.10 psi pressure difference

Figure 5. Pressure and flow setting for the analytical column (left pane) and precolumn (right pane).

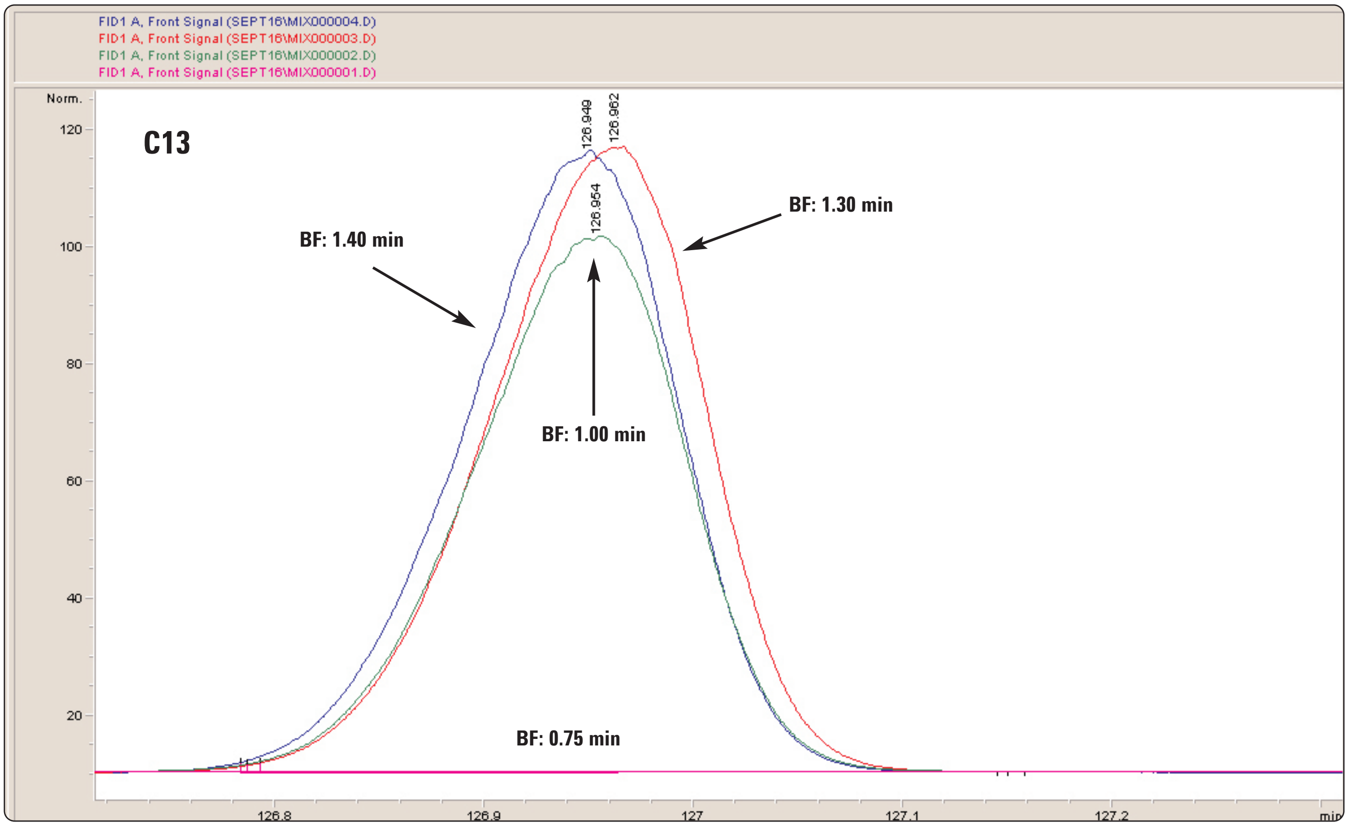
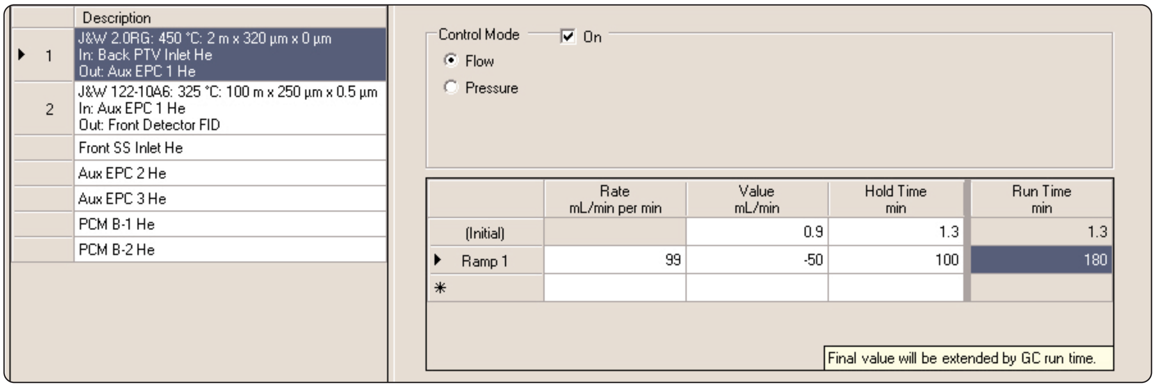


Figure 6. Fine tuning backflush time for ending transfer at C13. Trace at baseline: BF = 0.75 min, Peak at height of 100pa: BF = 1.00 min, Peaks at 117 pa: BF = 1.3 min and 1.4 min.

Easily Protect the Analytical Column with Backflush

Without backflush, a crude oil sample would contaminate and render the 100 m column useless. Setting the system to perform a backflush of the precolumn after approximately C12 has transferred to the 100 m column allows a high resolution separation to occur while the heaver fraction of the crude oil is backflushed through the MMI's split vent. The MMI is also programmed to 425 °C to assist in cleaning the inlet liner during backflush. A single taper liner with glass wool is used (Agilent p/n 5183-4647). ChemStation screens showing setup conditions for the pre and analytical columns are shown in Figures 7A and 7B, respectively.



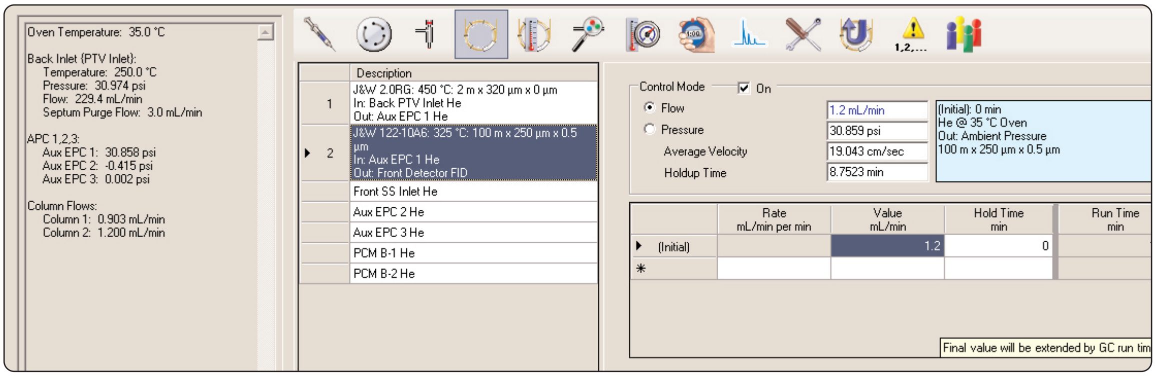
	Description
1	J&W 2.0RG: 450 °C: 2 m x 320 µm x 0 µm In: Back PTV Inlet He Out: Aux EPC 1 He
2	J&W 122-10A6: 325 °C: 100 m x 250 µm x 0.5 µm In: Aux EPC 1 He Out: Front Detector FID
	Front SS Inlet He
	Aux EPC 2 He
	Aux EPC 3 He
	PCM B-1 He
	PCM B-2 He

Control Mode ☑ On
● Flow
○ Pressure

	Rate mL/min per min	Value mL/min	Hold Time min	Run Time min
(Initial)		0.9	1.3	1.3
Ramp 1	99	-50	100	180
*				

Final value will be extended by GC run time.

Figure 7A. Precolumn set to backflush at 1.3 min.



Oven Temperature: 35.0 °C

Back Inlet {PTV Inlet}:
Temperature: 250.0 °C
Pressure: 30.974 psi
Flow: 229.4 mL/min
Septum Purge Flow: 3.0 mL/min

APC 1,2,3:
Aux EPC 1: 30.858 psi
Aux EPC 2: -0.415 psi
Aux EPC 3: 0.002 psi

Column Flows:
Column 1: 0.903 mL/min
Column 2: 1.200 mL/min

	Description
1	J&W 2.0RG: 450 °C: 2 m x 320 µm x 0 µm In: Back PTV Inlet He Out: Aux EPC 1 He
2	J&W 122-10A6: 325 °C: 100 m x 250 µm x 0.5 µm In: Aux EPC 1 He Out: Front Detector FID
	Front SS Inlet He
	Aux EPC 2 He
	Aux EPC 3 He
	PCM B-1 He
	PCM B-2 He

Control Mode ☑ On
● Flow 1.2 mL/min
○ Pressure 30.859 psi
Average Velocity 19.043 cm/sec
Holdup Time 8.7523 min

(Initial): 0 min
He @ 35 °C Oven
Out: Ambient Pressure
100 m x 250 µm x 0.5 µm

	Rate mL/min per min	Value mL/min	Hold Time min	Run Time min
(Initial)		1.2	0	
*				

Final value will be extended by GC run tim

Figure 7B. ChemStation panes for configuring backflush and column flow.

Note that precolumn flow (0.9 mL/min) is set to approximately 80% of the analytical column flow. This is a good general rule to follow for method development. The same control mode should be set for both columns, either pressure or flow. Under the conditions used, setting the backflush time at 1.3 min allows up to C12 to pass into the analytical column. A 0.32 mm id precolumn is used instead of one with the same diameter as the analytical column simply because it has more sample capacity and therefore less peak distortion. Peak capacity will be largely dependent on surface area in uncoated retention gaps.

Four crude oils with prefractionation up to approximately C12 are shown in Figure 8. The resulting detailed C4-C12 hydrocarbon analysis provides valuable information to help the process chemist develop the best refining strategy. This system could be coupled with DHA software to provide comprehensive peak identification. The information could also be combined with crude oil simulated distillation for a complete GC sample characterization.

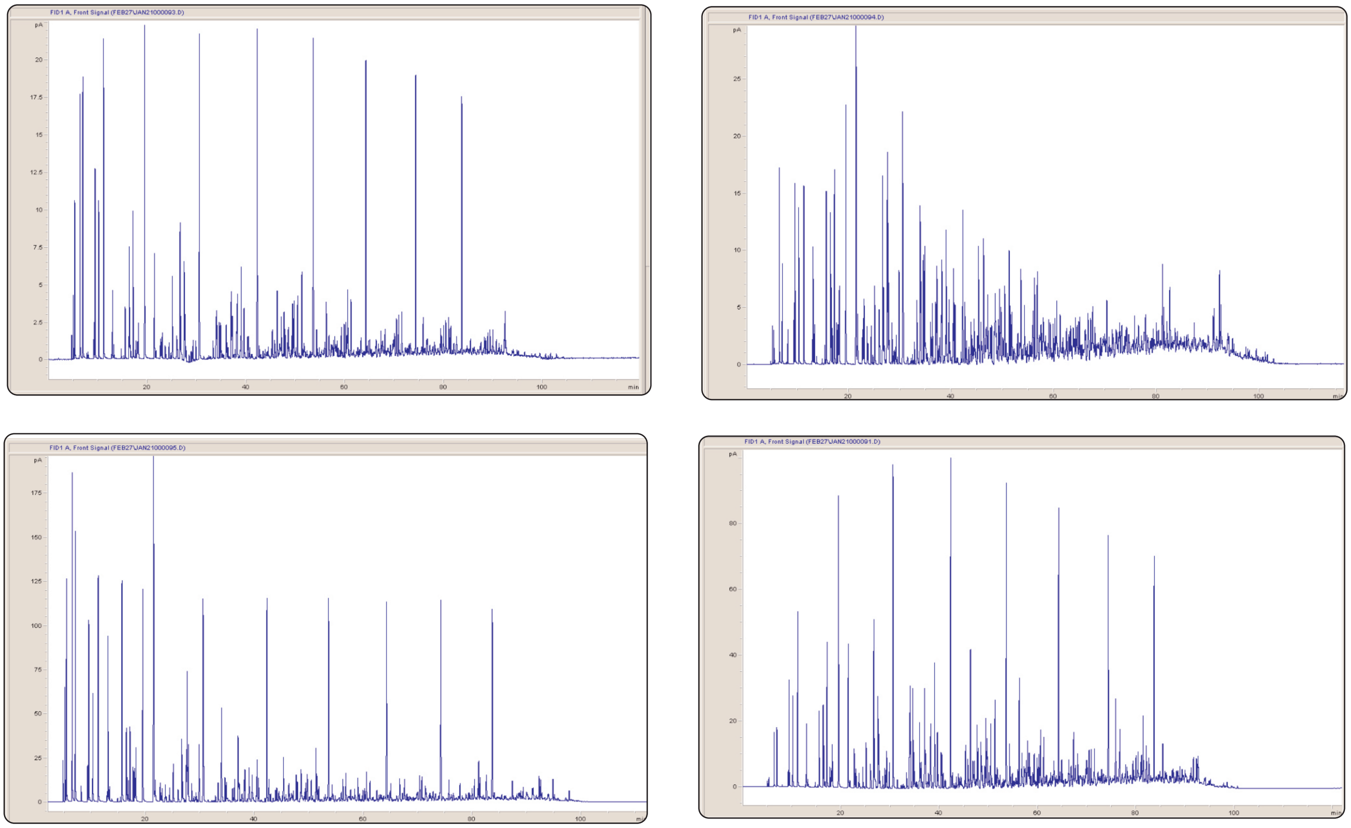


Figure 8. *Four crude oils from different regions. Backflushed between C12 and C13.*

Backflush With no Traces of High Molecular Weight Contamination

Figure 9 shows 12 consecutive injections of crude oil and analysis of the C4 to C12 fraction on the DB-Petro column. Retention time repeatability is better than 0.002 min and the baselines show no signs of variability from residual material. This indicates a clean and complete backflush of each run. Typically a liner change should be made after approximately 50 to 75 crude oil injections to be conservative.

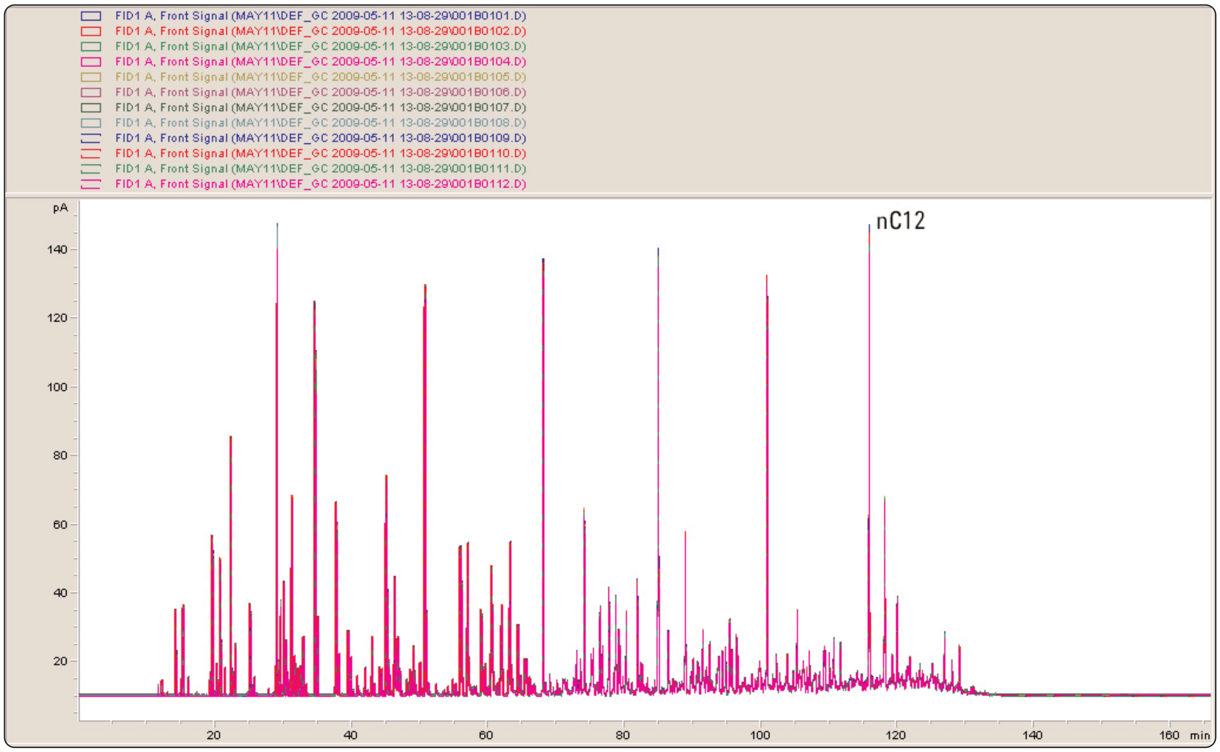


Figure 9. Overlay of twelve runs of crude oil backflushed between C12 and C13.

Conclusions

First and foremost, the system allows GC analysis of many wide molecular weight range samples that otherwise could not be injected without damaging the column or detector. Midpoint pressure control allows the analytical column to run at the desired flow while the precolumn is backflushed during the run. Further, the use of an uncoated precolumn transfers the desired compounds at a low temperature. This has the added benefit of faster backflushing of the heavier material. However, coated precolumns can also be used, and in some applications the use of a thin stationary phase will be advantageous. Columns will have longer lifetimes with improved retention time stability. Many combinations of pre and analytical columns can be used to address just about any GC application where light or early eluting material needs to be separated from heavier material that should not be introduced to an analytical column for either time savings or column protection. Example applications include additives in fuels and biodiesel analysis.

The configuration is compatible with the MSD as high carrier flows to the detector do not occur during backflush. In most cases, even a diffusion pump system can be used since the analytical column is usually of high resolution and the column flow during backflush will be low.

The Agilent 7890A GC system with precise and stable electronic pneumatic control enables midpoint backflush with a variety of column lengths, stationary phases and internal diameters. The CFT purged union designed for leak-free connections, superior inertness, and lack of unswept volumes yields chromatographic performance identical to single column systems.

References

1. Flow Calculator sofware: www.agilent. com/chem/flowcalculator

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Agilent Technologies

Simultaneous Analysis of Greenhouse Gases by Gas Chromatography

Application

Environmental

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Abstract

Two analytical methods based on the Agilent 7890A GC system are developed for simultaneous analysis of methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O) in air samples. Each system has its own features to meet different requirements of greenhouse gases analyses. Both systems can easily be expanded to determine sulfur hexafluoride (SF_6). Results from both methods demonstrated high sensitivity and excellent repeatability for the required analyses.

Agilent Technologies

Introduction

Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are considered the main greenhouse gases in the Earth's atmosphere. These gases trap heat in the atmosphere and affect the temperature of the Earth. Continuous measurement of these gases provides meaningful information to track greenhouse gas emission trends and help in the fight against climate change. On January 1, 2010, the U.S. Environmental Protection Agency will require large emitters of heat-trapping emissions to begin collecting greenhouse gas data under a new reporting system [1].

Two different configurations of Agilent 7890A GC systems have been developed for greenhouse gas analysis. These systems can also be used for other samples such as soil gases analysis or plant breathing studies where the analytes of interest contain gases such as CH_4, N_2O and CO_2 [2].

Method 1: SP1 7890-0468

An Agilent 7890A GC system is configured with a single channel using two detectors (FID and micro-ECD) for the analysis of CO_2, CH_4, N_2O, and SF_6 in air samples. Low concentrations of CO_2 can be analyzed by a methanizer with an FID.

Method 2: SP1 7890-0467

An Agilent 7890A GC is configured with two separate channels using three detectors (FID, TCD and micro-ECD) for the analysis of CO_2, CH_4, N_2O, and SF_6 in air samples. CO_2 can be analyzed at wide concentration levels. High levels of CO_2 can be analyzed by TCD and low concentrations can be analyzed by a methanizer with an FID.

A dynamic blending system is used to prepare the low level calibration standards using N_2 as a diluent.

Experimental and Results

Method 1: SP1 7890-0468

This system has three valves and two detectors using 1/8-in stainless steel packed columns (HayeSep Q 80/100). The methanizer/FID combination is used to measure low levels of CH_4 and CO_2, while the micro-ECD detects N_2O. The valve diagram is shown in Figure 1. The system can be modified to use a 6-port valve instead of a 10-port for automated headspace sampling. The typical GC conditions for Method 1 are listed in Table 1.

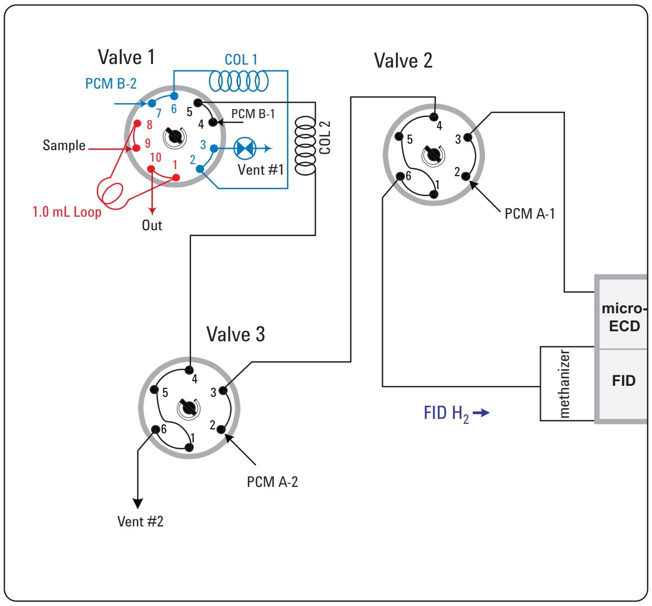

Figure 1. Configuration for SP1 7890-0468.

Table 1. Typical GC Conditions for Greenhouse Gas Analysis using Method 1

7890A GC	
Valve temperature:	100 °C
Oven temperature:	60 °C
Post run at oven temperature of 110 °C for 2 minutes is recommended	
Methanizer Temperature:	375 °C
Sample loop:	1 mL
Column 1, 2 flow (N_2):	21 mL/min (at 60 °C), constant pressure
FID	
Temperature :	250 °C
H_2 flow:	48 mL/min
Air flow:	500 mL/min
Make-up (N_2):	2 mL/min
micro-ECD	
Temperature :	350 °C
Make-up, 5% methane in Argon ($Ar/5\%CH_4$):	2 mL/min
Concentration of Gas Sample Standards	
CH_4:	20.18 ppm v
CO_2:	376.4 ppm v
N_2O:	3.27 ppm v

Figure 2 illustrates a chromatogram of gas sample standards using Method 1. The sample is injected into a short HayeSep Q (column 1) which separates the components including air, CO2 and CH4 from water. All analytes after N2O are backflushed to vent 1. Air (O2) should be directed away from the methanizer and micro-ECD and vented through vent 2. CO2 is converted to CH4 through the methanizer and measured by FID as shown in Figure 2B. After CO2 elutes from column 2, the effluent is introduced to micro-ECD for measuring N2O as shown in Figure 2A.

A repeatability study with 21 consecutive analyses was performed with results tabulated in Table 2. Excellent peak area repeatability for the analysis of CH_4, CO_2, and N_2O standards was observed with this configuration.

Table 2. Repeatability for Greenhouse Gas Standards (n=21, Excluding the First Run)

Name	Average (Area)	STDVE	RSD%
CH_4	149.26	0.29	0.20
CO_2	2779.04	17.16	0.62
N_2O	8253.96	11.06	0.13

To improve the sensitivity of micro-ECD, Ar-5% CH_4 is recommended as the make-up gas, which can lower the detection of N_2O to approximately 32 ppb with the good signal-to-noise (S/N) ratio as shown in Figure 3. The injected standard is prepared by dynamic blending with a 100-times dilution.

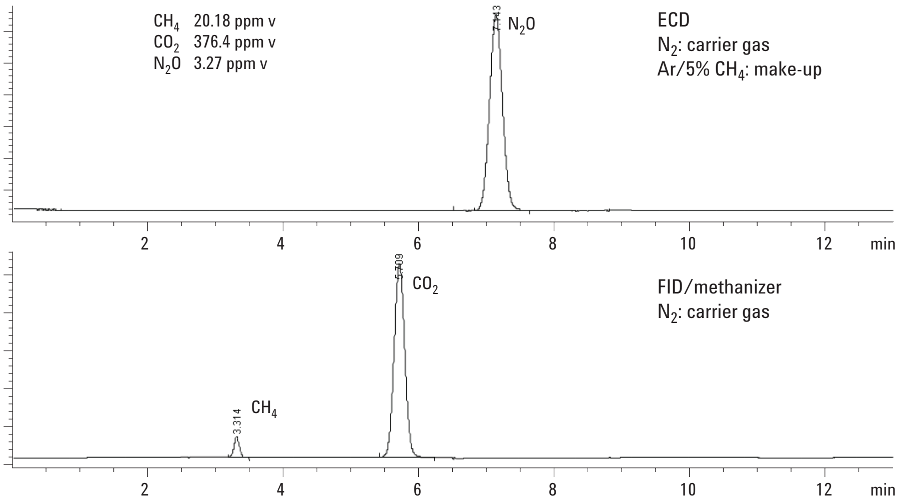

Figure 2. Analysis of greenhouse gases standards using Method 1.

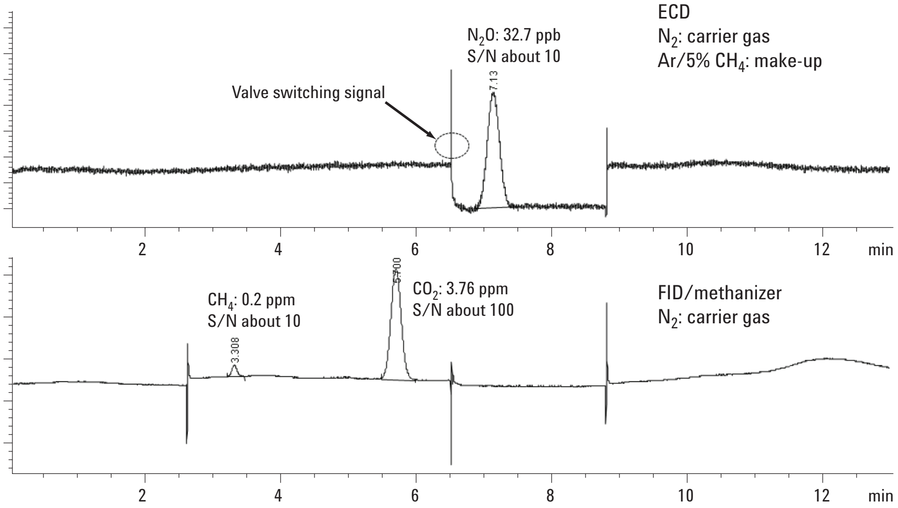

Figure 3. Chromatogram using Method 1 for CH_4, CO_2, and N_2O standards with a 100-times dilution.

The same configured system was used to analyze real samples. In this experiment, laboratory air is analyzed with Method 1. The chromatogram is shown in Figure 4. The measured concentrations of N_2O, CH_4, and CO_2 are 473 ppb, 2.7 ppm, and 380 ppm respectively.

The system can easily include the analysis of SF_6 by delaying the backflush time (valve 1) to allow SF_6 to elute into column 1 (precolumn). Figure 5 shows the chromatogram of SF_6 at approximately 0.5 ppb with a 1-mL sample size. The 0.5 ppb SF_6 standard is prepared by dynamic blending with 200 times dilution of the standard (original standard of SF_6 is 100 ppb).

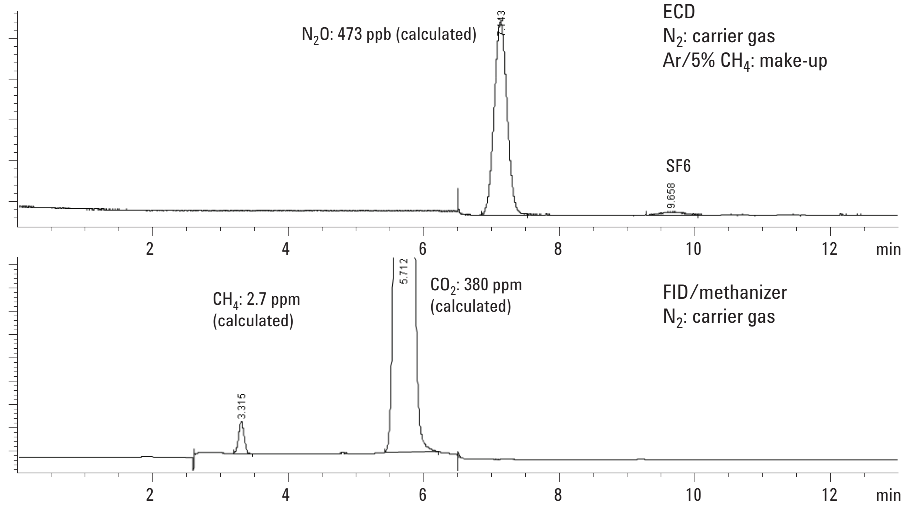

Figure 4. Chromatogram of real sample (laboratory air).

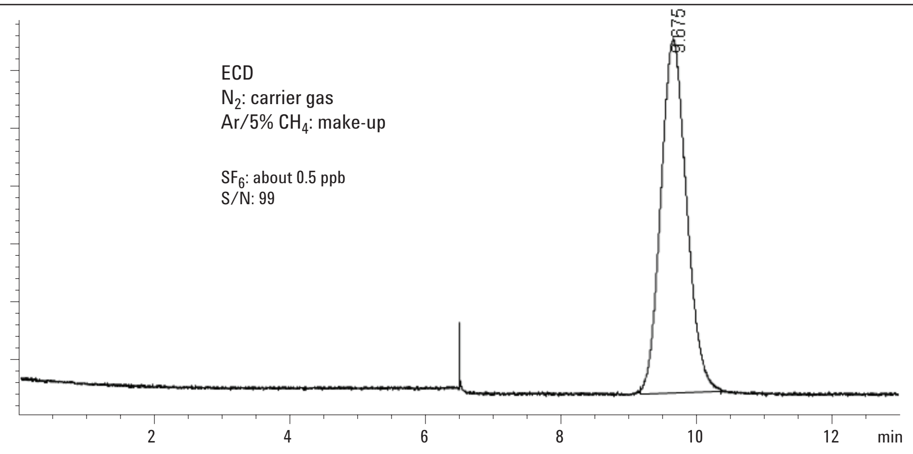

Figure 5. Chromatogram of SF_6 standard at approximately 0.5 ppb.

Method 2: SP1 7890-0467

This system consists of two separate channels with 1/8-in stainless steel packed columns (HayeSep Q 80/100). The first channel employs two valves with TCD and FID. The TCD and methanizer-FID are connected in series to measure CH_4 and CO_2. This channel provides the flexibility for CO_2 in varying levels. Low level CO_2 can be converted to CH_4 through the methanizer and measured by FID. The system is flexible depending on the requirements. The TCD can be used for high concentrations of CO_2. If only higher levels of CO_2 (higher than 50 ppm) analysis is required, the methanizer can be removed. This channel can be expanded to include O_2 and N_2 analysis by adding an additional Molsive column.

Another micro-ECD channel with two valves is dedicated to measuring N_2O and SF_6. Precolumns (column 1 and 2) direct heavier components (mainly water) to be backflushed to vent 1 and vent 4. O_2 should be excluded from the methanizer and micro-ECD and vented through vent 2 and vent 3. A typical plumbing diagram for this setup is shown in Figure 6. Typical GC conditions for Method 2 are listed in Table 3.

Table 3. Typical GC conditions for Greenhouse Gas Analysis Using Method 2

Valve temperature:	100 °C
Oven temperature:	60 °C
Post run at oven temperature of 110 °C for 2 min is recommended	
Sample loop:	1 mL
Column 1, 2 flow (He):	21 mL/min (at 60 °C), constant pressure
Column 3, 4 flow (N_2):	21 mL/min (at 60 °C), constant pressure
FID	
Temperature:	250 °C
H_2 flow:	48 mL/min
Air flow:	500 mL/min
Make-up (N_2):	2 mL/min
TCD	
Temperature:	200 °C
Reference flow:	40 mL/min
Make-up:	2 mL/min
micro-ECD	
Temperature:	350 °C
Make-up, Ar/5% CH_4:	2 mL/min
Methanizer Temperature :	375 °C

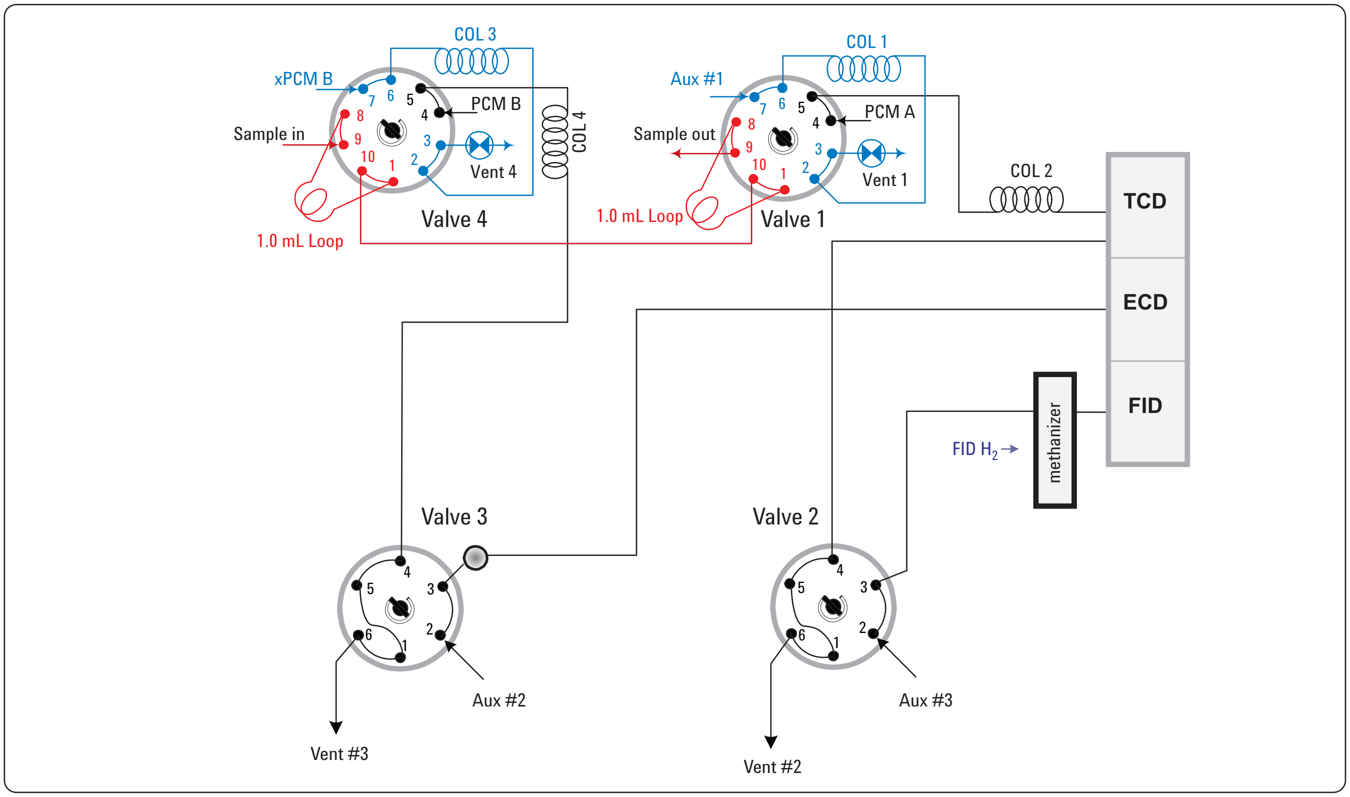

Figure 6. Valve configuration for Method 2.

Results obtained for greenhouse gases (N_2O, CH_4, CO_2 and SF_6) by Method 2 are equivalent to those obtained by Method 1. In addition, with this setup, high levels of CO_2 can now be measured by the third detector, TCD. The dynamic blending system is also used for Method 2 to prepare the low level standards. Table 4 shows very good repeatability of peak areas for the analysis of the greenhouse gas standards.

Table 4. Repeatability for Greenhouse Gas Standards (n=20, Excluding the First Run)

Name	Average (Area)	STDVE	RSD%
CH_4	151.61	0.64	0.42
CO_2(FID)	2788.51	14.72	0.53
N_2O	7467.92	13.91	0.19
CO_2(TCD)	186.00	0.80	0.43

Real sample (laboratory air) is analyzed with Method 2. The chromatogram is shown in Figure 7. The concentrations of N_2O, CH_4 and CO_2 measured are 441 ppb, 2.2 ppm and 398 ppm respectively.

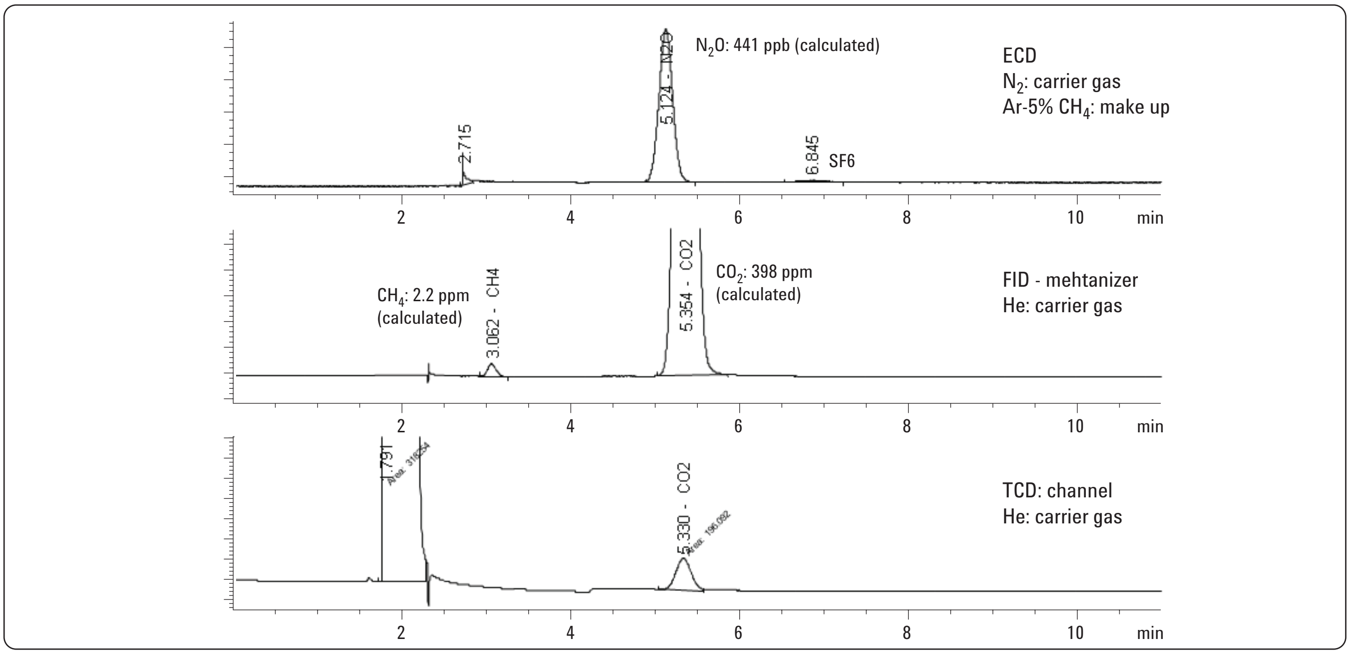

Figure 7. Chromatogram for real sample (laboratory air) using Method 2.

Conclusion

Two Agilent 7890A GC systems have been developed to meet the different requirements for simultaneous analyses of greenhouse gases including CH_4, CO_2, and N_2O in air samples.

Method 1 (SP1 7890-0468) has a simpler valve configuration and with minor modifications, accomodates autosampling by a headspace sampler.

Method 2 (SP1 7890-0467) has two separate channels with three detectors and can achieve even faster results. The separate channels increase flexibility to make the valve switching time less critical and the method easier to set up. The use of the third TCD allows measurement of a wide concentration range of CO_2 (0.2 ppm to 20%).

Results obtained on both analyzers are the same for greenhouse gases (N_2O, CH_4, CO_2 and SF_6).

References

1. Environmental Protection Agency (EPA), “40 CFR Parts 86, 87, 89 et al. Mandatory Reporting of Greenhouse Gases; Final Rule“.
2. Teri Kanerva, Kristiina Regina, Kaisa Ramo, Katinka Ojanpera, Sirkku Manninen, “Fluxes of N_2O, CH_4 and CO_2 in a meadow ecosystem exposed to elevated ozone and carbon dioxide for three years”, Environmental Pollution 145 (2007) 818-828.
3. European Environment Agency, Manual for the EEA greenhouse gases data viewer.

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Agilent Technologies

High-throughput method development for aldehydes and ketones using an Agilent 1290 Infinity LC system and an Agilent ZORBAX StableBond HD column

Application Note

Environmental

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Abstract

This Application Note describes the development of a fast method for the determination of 13 aldehyde and ketone derivates with the Agilent 1290 Infinity LC system. The method, which used acetone as organic co-solvent separates the analytes within 3.5 minutes.

Introduction

Aldehydes and ketones are important compounds in the chemical industry. One of the most essential aldehydes is formaldehyde because it is used for the production of glued wood and synthetic resin. In addition, formaldehyde is one of the most used disinfectants and preservative agents worldwide. Another relevant aldehyde in the chemical industry is acetaldehyde. This chemical is frequently used as an organic solvent and is an important intermediate product in many industries. For example, acetaldehyde is principally used for the production of acetic acid. In general, aldehydes and ketones with middle carbon chain lengths are used as intermediate products during the production of gum, synthetic resin and plastic products. Therefore, many analytical methods exist for the determination of aldehydes and ketones in different matrices. The majority of these methods use the derivatization with 2,4-dinitrophenylhydrazine yielding the corresponding 2,4-dinitrophenylhydrazone. After that, an HPLC separation with UV detection at 360 nm is then performed.

The introduction of the Agilent 1290 Infinity LC system has improved LC-UV methods in several ways. The pressure of the Agilent 1290 Infinity LC system remains stable as high as 1200 bar at flow rates up to 2 mL/min. This is a significant enhancement in comparison to conventional HPLC systems. The most important advantage of the Agilent 1290 Infinity LC system is the small dwell volume of 125 µL (the volume from the point of mixing solvents A and B up to the column inlet including the autosampler). Because of this very small dwell volume, narrow bore columns can be used to shorten analysis time and reduce organic solvent consumption.

This Application Note focuses on LC method development for the determination of several aldehydes and ketones, as well as the advantages of the Agilent 1290 Infinity LC system.

A commercially available method development software package was used to determine the optimal method parameters. Four basic chromatographic runs were performed to determine the optimal column temperature and solvent gradient. These measurements comprised two linear solvent gradients from 5% to 100% B in 10 and 30 minutes at 20 °C and the same gradients at 40 °C. The measurements were performed on an Agilent ZORBAX StableBond RRHD C18 column (50 mm × 2.1 mm, 1.8 µm) by using acetone as an organic modifier. A method was then developed and experimentally confirmed with high agreement between prediction and experiment.

Experimental

All calculations were performed with Agilent ChemStation software version B.04.02 [65].

LC system

For method development, an Agilent 1290 Infinity LC system was used. The system consists of:

- Agilent 1290 Infinity Binary Pump with integrated degasser (G4220A)
- Agilent 1290 Infinity High Performance Autosampler (G4226A)
- Agilent 1290 Infinity Thermostatted Column Compartment SL (G1316B)
- Agilent 1290 Infinity Diode Array Detector (G4212A)

Analyte mixture

The mixture of aldehyde-2,4-dinitrophenylhydrazones and ketone-2,4-dinitrophenylhydrazones is a certified reference material from Sigma-Aldrich (Catalog No. 47651-U) diluted in acetonitrile. In the mixture, each analyte has a concentration of 30 µg/mL of carbon.

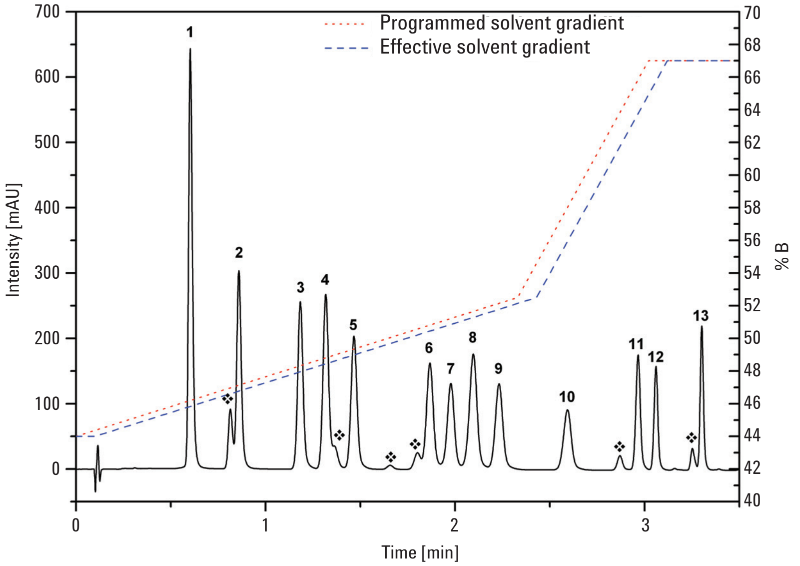
The elution order for all analytes depicted in all figures is:

1. Formaldehyde-2,4-dinitrophenylhydrazone
2. Acetaldehyde-2,4-dinitrophenylhydrazone
3. Acrolein-2,4-dinitrophenylhydrazone
4. Acetone-2,4-dinitrophenylhydrazone
5. Propionaldehyde-2,4-dinitrophenylhydrazone
6. Crotonaldehyde-2,4-dinitrophenylhydrazone
7. Methacrolein-2,4-dinitrophenylhydrazone
8. 2-Butanone-2,4-dinitrophenylhydrazone
9. Butyraldehyde-2,4-dinitrophenylhydrazone
10. Benzaldehyde-2,4-dinitrophenylhydrazone
11. Valeraldehyde-2,4-dinitrophenylhydrazone
12. m-Tolualdehyde 2,4-dinitrophenylhydrazone
13. Hexaldehyde-2,4-dinitrophenylhydrazone

Results and discussion

Figure 1 shows the computer-optimized separation of 13 aldehyde 2,4-dinitrophenylhydrazones and ketone-2,4-dinitrophenylhydrazones on an Agilent ZORBAX StableBond RRHD C18 column within 3.5 minutes. Acetone was used as an organic co-solvent. All peaks are baseline separated with a critical resolution of 1.6 between peak pair 6 and 7. The critical resolution was calculated by the tangent method. The impurities, which are present in the reference material and highlighted by stars were not included in the method development. Figure 1 also shows a comparison of the programmed and effective solvent gradient. Due to a very small dwell volume, there is only a minor difference between the programmed and effective solvent gradients compared to a conventional HPLC system, which exhibits a dwell volume of approximately 1000 µL. This means that at a flow rate of 1.2 mL/min, the programmed solvent gradient reaches the column inlet with a delay of 0.83 minutes, so that the elution of the early-eluting analytes occurs under isocratic conditions. In other words, the elution of the early-eluting analytes cannot be affected by the solvent gradient. Using the Agilent 1290 Infinity LC system with a dwell volume of 125 µL at a flow rate of 1.2 mL/min, the programmed solvent gradient reaches the column inlet after 6.25 seconds and enables fast separations within a few minutes.

The chromatogram shown in Figure 1 is a high pressure application. Due to the applied flow rate of 1.2 mL/min and the 1.8 µm particle packed column, a pressure drop of 1100 bar during the solvent gradient can be observed. Figure 2 shows an overlay of ten consecutive chromatograms, demonstrating the robustness and reproducibility of the develped method.



Chromatographic conditions:

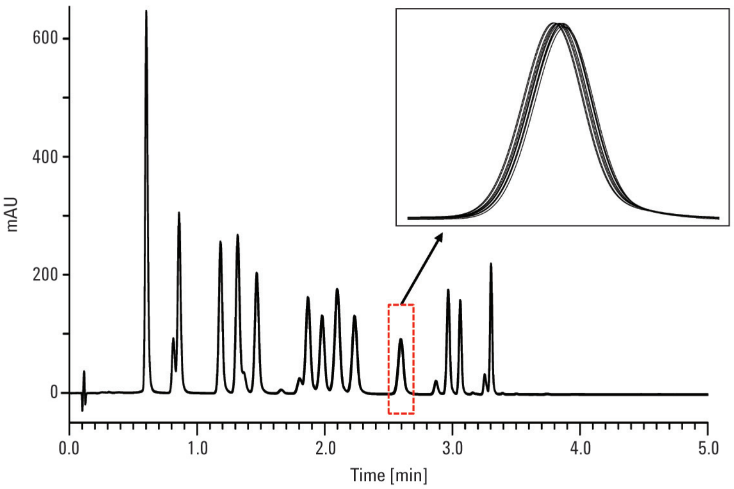
Stationary phase:	Agilent ZORBAX StableBond RRHD C18 (2.1 mm × 50 mm, 1.8 µm)
Mobile phase:	A: deionized water, B: acetone;
Solvent gradient:	0–2.33 min from 44% to 52.5% B, 2.33–3.02 min from 52.5% to 67% B, 3.02–3.50 min isocratic at 67% B;
Flow rate:	1.2 mL/min
Detection:	UV at 360 nm
Injection volume:	1 µL
Temperature:	33.4 °C
Pressure drop:	1100 bar.
Elution order of the analytes:	See experimental section; ❖impurities

Figure 1
Separation of 13 aldehyde-2,4-dinitrophenylhydrazones and ketone-2,4-dinitrophenylhydrazones.

Figure 2 shows that there are virtually no differences among the ten chromatograms. This conclusion is confirmed by the relative standard deviation (RSD) of retention times of the analytes, which ranges between 0.03% and 0.09%.

Conclusion

The Agilent 1290 Infinity LC system is suitable for developing fast HPLC methods. The separation of 13 aldehyde and ketone derivates was completed in around 3.5 minutes, using acetone as an organic modifier in the mobile phase. In addition, the method presented here illustrates that fast HPLC separations are only possible using HPLC systems with small dwell volumes. Finally, we have shown that the Agilent StableBond RRHD C18 column is suitable for separations where the pressure drop is greater than 1100 bar, without loss of separation efficiency.



See Figure 1 for Chromatographic conditions.

Figure 2
Overlay of 10 consecutive chromatograms of the separation of 13 aldehyde-2,4-dinitrophenylhydrazones and ketone-2,4-dinitrophenylhydrazones.

www.agilent.com/chem/1290

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Agilent Technologies

Meeting the requirements of ASTM D 6591-06 (IP548/06) Using Agilent 1200 Series HPLC Systems

Application

Hydrocarbons

Abstract

The performance of diesel fuel is predominantly determined by its ignition quality. This parameter is known as the Cetane number. The Cetane number describes the volume % Cetane (aliphatic hexadecane) present in a mixture of Cetane and (aromatic) 1-Methyl-naphthalene. Generally, in order to provide the best performance and maximize the lifetime of an engine, the amount of aromatics in diesel should be as low as possible. For the analysis of non-aromatics and aromatics in diesel fuel and petroleum distillates boiling in the range of 150 °C to 400 °C, there exists an ASTM Method (D 6591-06), and identical method IP548/06 that uses HPLC with refractive index detection. The two compound classes (aromatics and non-aromatics) are separated using normal phase HPLC and a column that has little affinity for non-aromatic but has pronounced selectivity for aromatic hydrocarbon classes [1]. The refractive index detector is used because this detector responds to both non-aromatic and aromatic hydrocarbons.

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About Standard Method ASTM D 6591-06

"This test method covers a high performance liquid chromatographic test method for the determination of monoaromatic, di-aromatic, tri+-aromatic, and polycyclic aromatic hydrocarbon contents in diesel fuels and petroleum distillates boiling in the range of 150 to 400 °C. The total aromatic content in % m/m is calculated from the sum of the corresponding individual aromatic hydrocarbon types.

NOTE 1—Aviation fuels and petroleum distillates with boiling points that range from 50 to 300 °C are not determined by this test method and should be analyzed by Test Method, D 6379 or another suitable equivalent test method.

- 1.2 The precision of this test method has been established for diesel fuels and their blending components, containing from 4 to 40 % (m/m) mono-aromatic hydrocarbons, 0 to 20 % (m/m) di-aromatic hydrocarbons, 0 to 6 % (m/m) tri+-aromatic hydrocarbons, 0 to 26 % (m/m) polycyclic aromatic hydrocarbons, and 4 to 65 % (m/m) total aromatic hydrocarbons.
- 1.3 Compounds containing sulfur, nitrogen, and oxygen are possible interferents. Mono-alkenes do not interfere, but conjugated di- and poly-alkenes, if present, are possible interferents.
- 1.4 By convention, this standard defines the aromatic hydrocarbon types on the basis of their elution characteristics from the specified liquid chromatography column relative to model aromatic compounds. Quantification is by external calibration using a single aromatic compound, which may or may not be representative of the aromatics in the sample, for each aromatic hydrocarbon type. Alternative techniques and methods may classify and quantify individual aromatic hydrocarbon types differently.
- 1.5 Fatty Acid Methyl Esters (FAME), if present, interfere with tri+-aromatic hydrocarbons. If this method is used for diesel containing FAME, the amount of tri+-aromatics will be overestimated."[2]

This method, also known as IP548/06, is an official method of the American Society of Testing Methods (United States, www.astm.org). The method requires a column backflush-capable instrument configuration and analysis scheme, and is similar to other hydrocarbon group analysis methods. Because of this similarity, with respect to mobile phase and detection strategy, the instrument configuration is readily adaptable to those other methods.

The various methods associated with middle distillate fuel analysis are shown in Table 1.

Equipment and Conditions

LC:	Agilent 1200 Series LC
Binary pump:	G1312B used isocratically with pump head seals for normal phase, Agilent p/n 0905–1420
Autosampler:	G1367C with needle wash
Therm. Column Compartment:	G1316C with 6 port 2 position switching valve
Refractive Index Detector:	G1362A
Software:	Agilent ChemStation with version B.04.02 software
Columns:	Agilent ZORBAX NH_2 4.6 × 250 mm, 5 µm (p/n 880952-708)
Mobile Phase:	n-heptane, HPLC grade
Flow Rate:	1 ml/min
Injection Volume:	10 µl
Oven Temperature:	20 °C
Detection:	Refractive index

Sample preparation

Samples and standards were prepared according to guidance published in the method, using heptane as the diluent. System qualification and final quantitative results were reported using Agilent ASTM D 6591-06 standard mixtures (p/n 5190-0483 system performance solution SPS, and p/n 5190-0482 quantitative calibrant solutions A-D, respectively).

Table 1. Fuel Analysis Methods

IP Method and Revision	Method Overview	Special Parameters	ASTM Method	Comments
IP391/07	150-400 °C diesel fuel petro/bio blends up to B-5	no backflush, amino and/or cyano column	No current equivalent available	same as method EN12916:2006 *MAH, DAH, Tri+AH are reported
IP436/01	50-300 °C aviation fuel, kerosene	no backflush, amino and/or cyano column	D-6379-04	MAH and DAH reported not for samples with Tri+AH
IP548/06	150-400 °C diesel fuel	backflush required, amino and/or cyano column	D-6591-06	MAH, DAH, Tri+AH reported FAME interferes with result

*MAH – monoaromatic hydrocarbon, DAH – diaromatic hydrocarbon, Tri+AH – tri and higher ring aromatic hydrocarbons

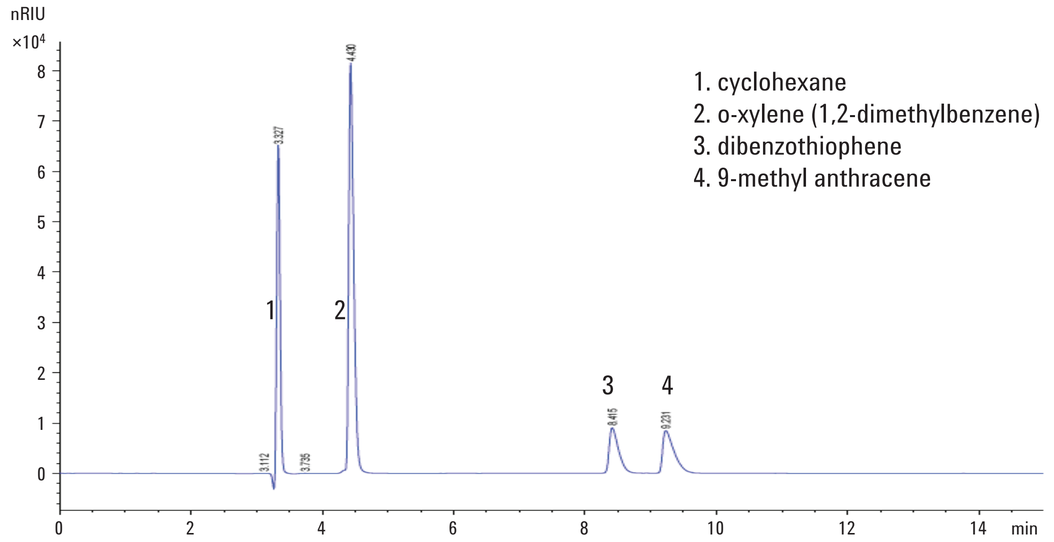


Figure 1. Standard chromatogram of system performance solution (SPS).

Results and Discussion

The first steps in method implementation are to analyze a system performance solution (SPS) that establishes overall separation selectivity and resolution, and to establish the event time table for column backflushing during the analysis. (Sections 9.4 and 9.6 of the method). Figure 1 illustrates the results of running the performance solution on the Agilent system without a backflush event.

The SPS is used to determine selectivity and retention data for the saturate and aromatic markers that are used for method acceptance criteria. It is also used to determine the backflush time for eluting tri+aromatics as a single peak.

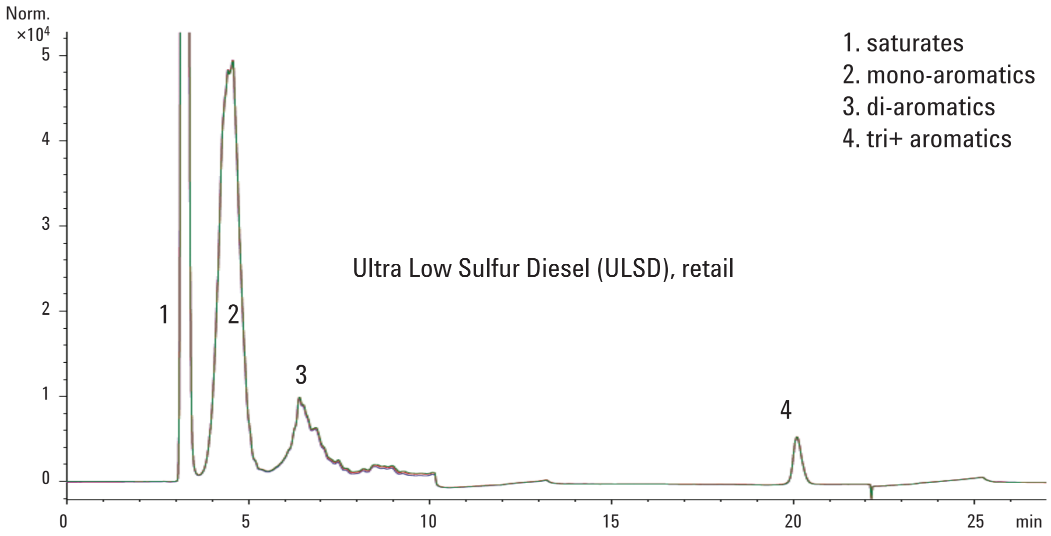


Figure 2. Petroleum diesel sample, n=3 overlay, showing cutpoints for the various compound groups typically present in these samples.

Resolution between cyclohexane and o-xylene (1,2-dimethylbenzene) is part of the method specification and must attain a minimum value of 5.

With a genuine fuel sample, in this case retail quality petrodiesel, greater complexity and overlapping of the various compound class regions are evident. Within the method definitions there are specific "cutpoints" defining the grouping to be performed in the quantitative reports. Manual peak integration is specified in the method for setting the baseline, and inserting valley drop points.

Results and Discussion

Method Performance

As with most official methods, there are specific performance criteria that allow qualification of the separation system and its subsequent use for reporting quantitative results of diesel fuel analysis.

- 6.4 Column System—Any stainless steel HPLC column(s) packed with an approved amino-bonded (or polar amino/cyano-bonded) silica stationary phase is suitable, provided it meets the resolution requirements laid down in 9.4.3. [2]
- 9.4.1 Ensure that baseline separation is obtained between all components of the SPS.
- 8.9 Ensure that the resolution between cyclohexane and 1,2 dimethylbenzene is at least 5 as described in 9.4.3.
- 9.4.3.1 Column Resolution
  Calculate the resolution, R, between cyclohexane and 1,2 dimethylbenzene using the following equation.

$$R = \frac{2(t2-t1)}{1.699(y1+y2)} \quad \begin{matrix}\text{difference in retention time}\\ \text{averaging of peak widths}\end{matrix}$$

- 10.1.5: R = >0.999, Intercept <0.01 g / 100 ml)

Table 2.

Name	R. Time [min]	width (hh)	Resolution
1. cyclohexane	3.307	0.059	
2. 1,2-dimethylbenzene)	4.477	0.097	8.79
3. dibenzothiophene	8.907	0.186	
4. 9-methyl anthracene (r.t. with backflush)	18.905	0.282	

In Figure 1 there is distinct separation between the markers specified in sections 9.4 and 9.6 of the method. Table 2 confirms the minimum resolution requirement of section 9.4 and shows retention time data obtained with the programmed backflush calculated as defined in section 9.6. With this information, it is possible evaluate calibration standards.

An overlay of calibrant solutions A-D is shown in Figure 3. The backflush time was determined from injections of SPS at the beginning of the analysis sequence.

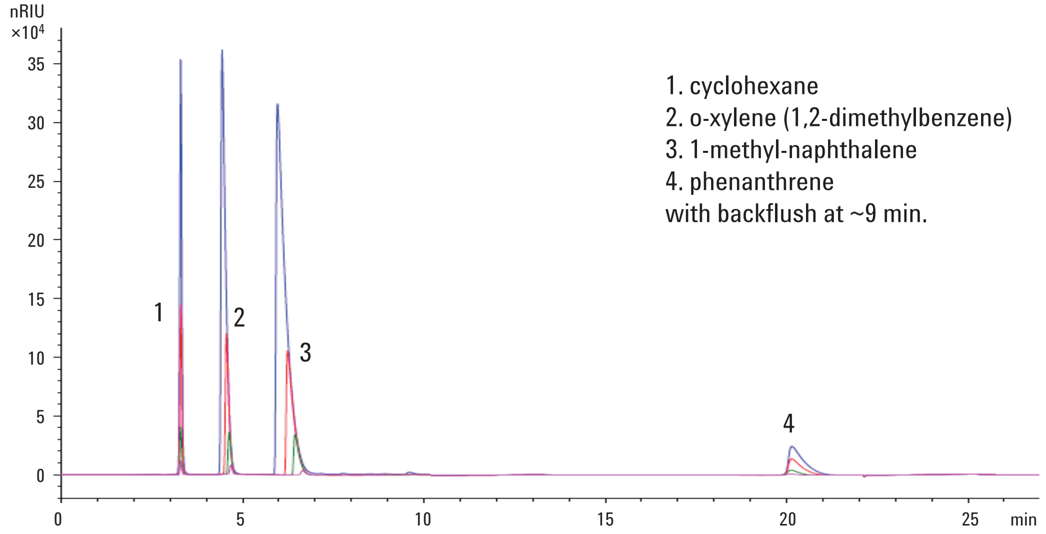


Figure 3. Overlay of calibrant solutions A-D.

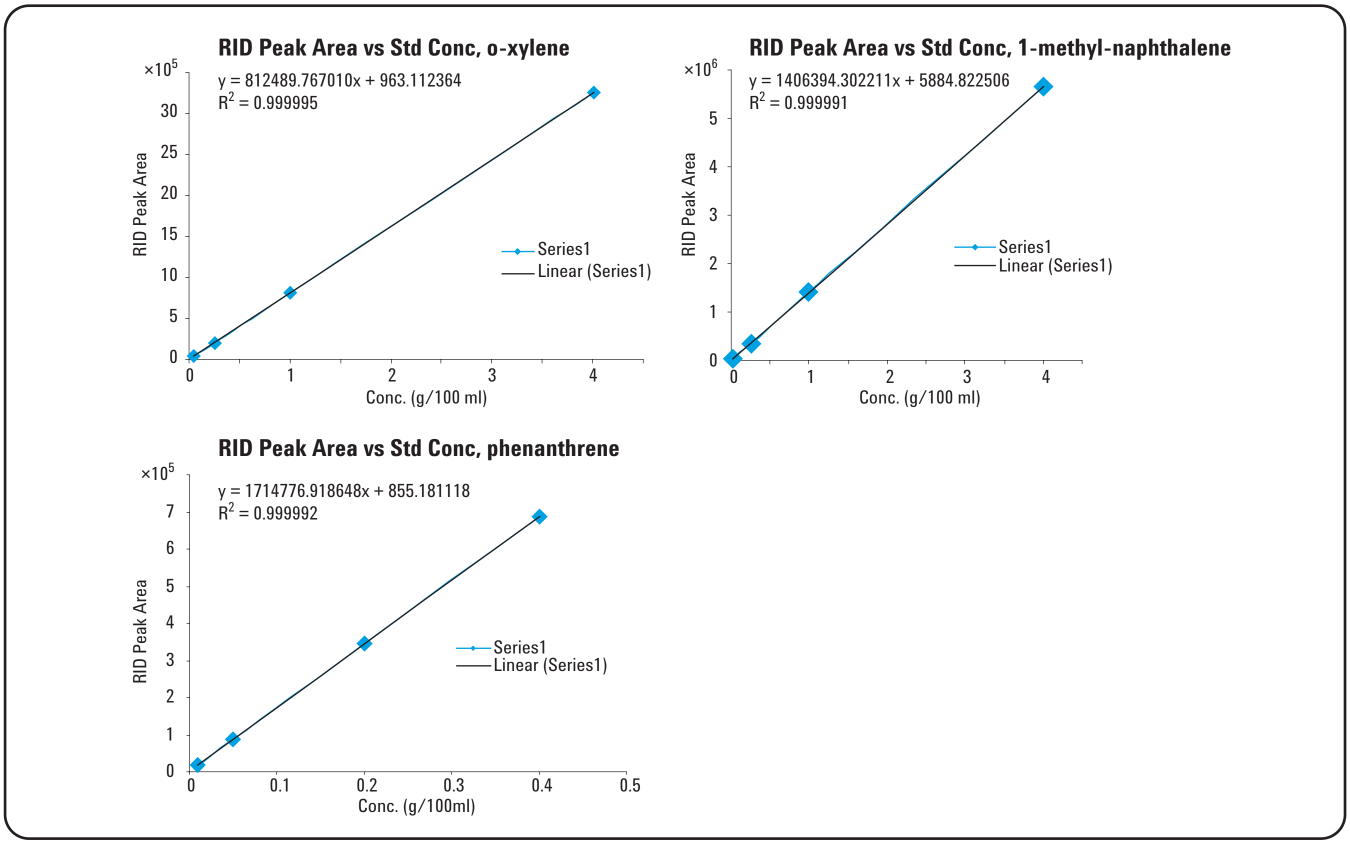


Figure 4. Calibration plots for o-xylene,1-methyl-naphthalene, and phenanthrene which, are the three components of the four calibration levels specified in the method.

In the calculated results, all calibration plots exceed linearity of 0.9999 and have calculated intercepts well below 0.01 g/100 mL, which are the method specifications of section 10.1.5.

Retention time and peak area precision can be found in Table 3, illustrating that the overall performance of the calibration method is excellent.

Table 3. Calibration Precision

Calibrant A

Analyte	RT, Avg, n=3	RT, Stdev	RT, RSD%	Area Avg, n=3	Area Stdev	Area RSD%
xylene	4.44	0.0005	0.01%	3.29E+06	755.9	0.02%
1-Methyl-naphthalene	5.96	0.001	0.02%	5.76E+06	2299.2	0.04%
phenanthrene	20.14	0.0020	0.01%	7.12E+05	8351.8	1.17%

Calibrant B

Analyte	RT, Avg, n=3	RT Stdev	RT, RSD%	Area Avg, n=3	Area Stdev	Area RSD%
xylene	4.55	0.0020	0.05%	8.33E+05	5263.9	0.63%
1-Methyl-naphthalene	6.24	0.0041	0.07%	1.46E+06	14197.7	0.97%
phenanthrene	20.13	0.0023	0.01%	3.55E+05	849.5	0.24%

Calibrant C

Analyte	RT, Avg, n=3	RT Stdev	RT, RSD%	Area Avg, n=3	Area Stdev	Area RSD%
xylene	4.63	0.0017	0.04%	2.06E+05	536.3	0.26%
1-Methyl-naphthalene	6.44	0.0036	0.06%	3.66E+05	1830.7	0.50%
phenanthrene	20.12	0.0040	0.02%	8.87E+04	139.0	0.16%

Calibrant D

Analyte	RT Avg, n=3	RT Stdev	RT, RSD%	Area Avg, n=3	Area Stdev	Area RSD%
xylene	4.67	0.0005	0.01%	4.03E+04	214.7	0.53%
1-Methyl-naphthalene	6.65	0.0020	0.03%	2.96E+04	334.1	1.13%
phenanthrene	20.10	0.0025	0.01%	1.76E+04	176.5	1.00%
Average RSD% All Runs			**0.028%**			**0.555%**

Results for specific petrodiesel and petro/biodiesel blends

Various samples were collected from local commercial and retail fuel delivery points. An overlay of three samples is shown in Figure 5.

Despite some apparent compositional differences among the samples, the general resolution and valley points are consistent. This should ensure relatively straightforward data reduction.

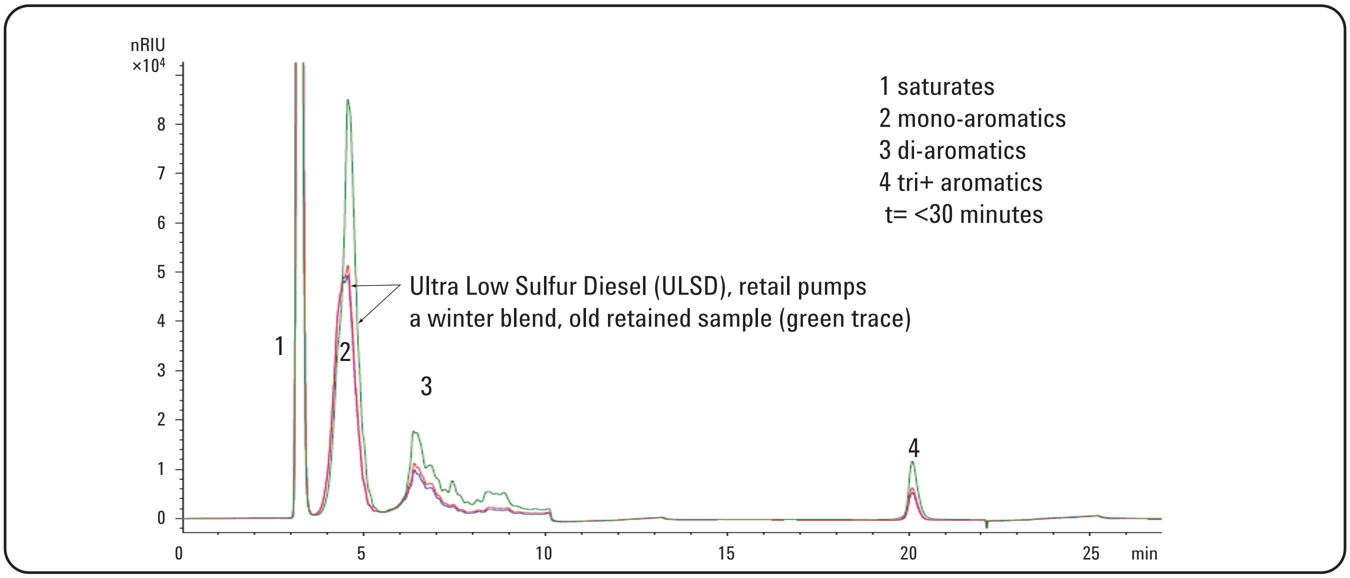
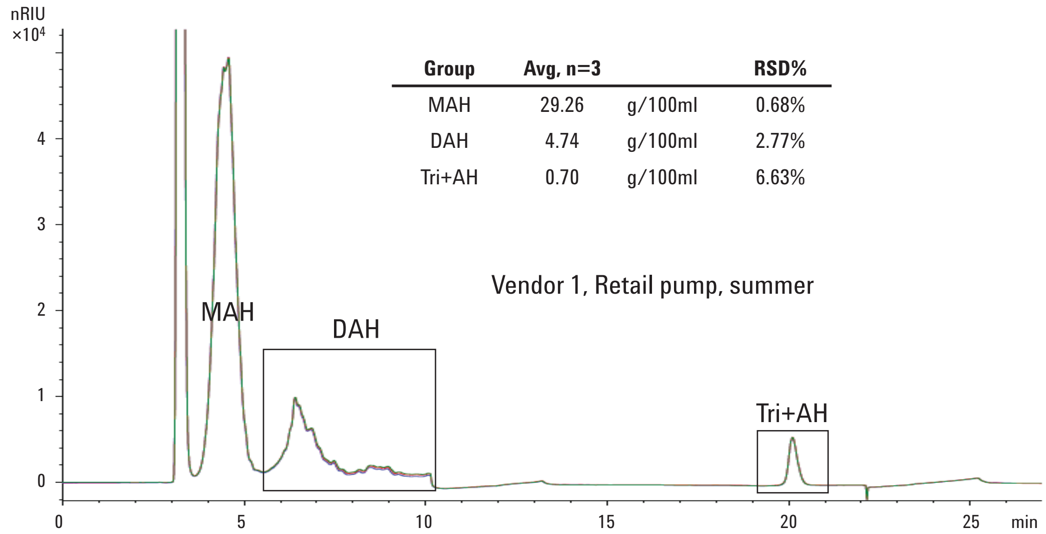
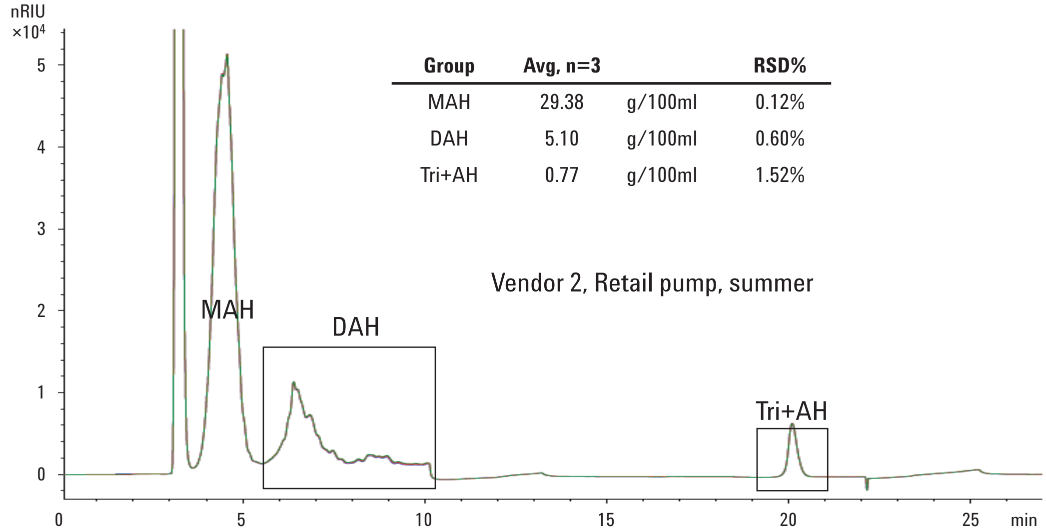


Figure 5. Overlay of three samples.



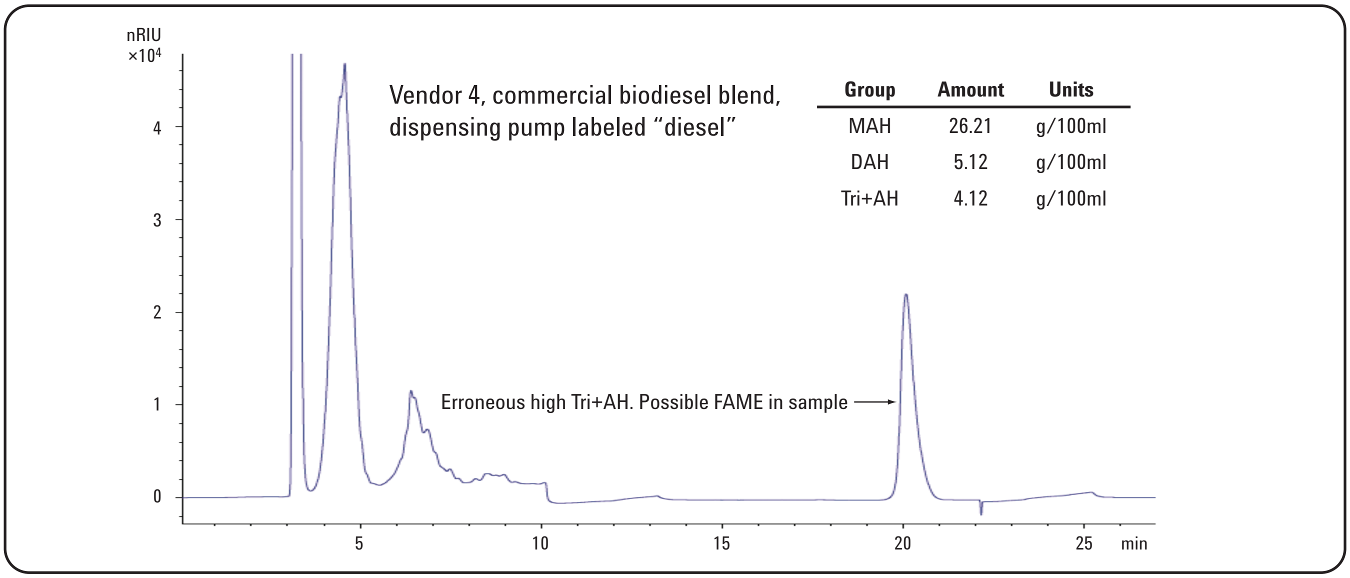
Group	Avg, n=3		RSD%
MAH	29.26	g/100ml	0.68%
DAH	4.74	g/100ml	2.77%
Tri+AH	0.70	g/100ml	6.63%

Figure 6. Results and precision for sample designated "Vendor 1".



Group	Avg, n=3		RSD%
MAH	29.38	g/100ml	0.12%
DAH	5.10	g/100ml	0.60%
Tri+AH	0.77	g/100ml	1.52%

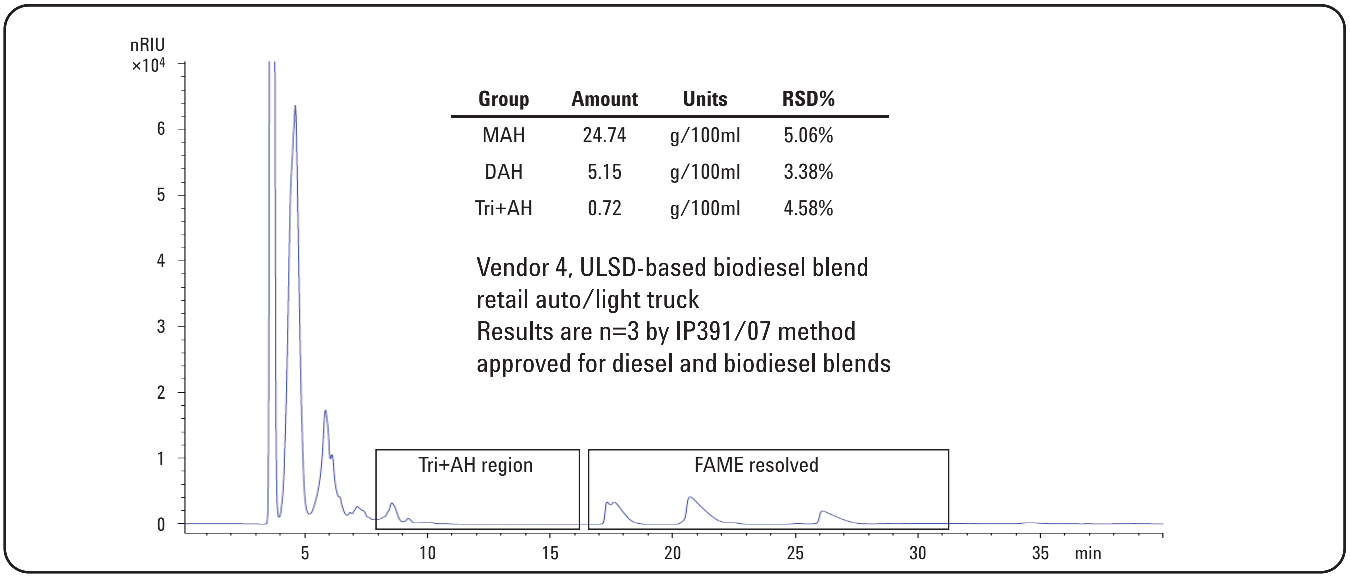
Figure 7. Results and precision for sample designated "Vendor 2".


Vendor 4, commercial biodiesel blend, dispensing pump labeled “diesel”

Group	Amount	Units
MAH	26.21	g/100ml
DAH	5.12	g/100ml
Tri+AH	4.12	g/100ml

Erroneous high Tri+AH. Possible FAME in sample →

Figure 8. *This sample was represented as diesel and was analyzed by the method. Suspiciously high tri+aromatic values compelled an analysis by the alternate, biodiesel approved, method IP391/07.*


Group	Amount	Units	RSD%
MAH	24.74	g/100ml	5.06%
DAH	5.15	g/100ml	3.38%
Tri+AH	0.72	g/100ml	4.58%

Vendor 4, ULSD-based biodiesel blend
retail auto/light truck
Results are n=3 by IP391/07 method
approved for diesel and biodiesel blends

Figure 9. *Analysis of suspect biodiesel sample by IP391/07 conditions confirms the contamination or dispensing pump mislabeling and yields a more expected result for typical diesel motor fuel. For further details on the performance and utility of this method, please refer to Agilent application note 5990-4789EN. [3]*

Ruggedness and Stability of the ASTM D 6591-06 method

As with most normal phase methods the column is susceptible to adsorption of highly polar components that can affect overall separation performance. Water present in samples or mobile phase also adsorb to the column and somewhat predictably cause reduced elution times for all sample components. Using a high quality anhydrous HPLC grade mobile phase is essential, and the user may consider using a drying agent such as molecular sieve to dehydrate the mobile phase. While this is often done by adding molecular sieve to the solvent container, it is also possible and preferable to prepare a high pressure compatible column with prewashed drying agent and placing it inline between the pump and injector.

Conclusion

The performance of the Agilent 1200 Series High Performance LC system with normal phase separation and refractive index detection meets or exceeds the requirements of ASTM D 6591-06 within the range of samples defined in the method. The user should take care to identify samples of petrodiesel containing biodiesel components to ensure adequate analysis modifications are made to prevent erroneous high tri+aromatic values. IP391/07 (EN12916:2006) is required for samples found to contain biodiesel FAME components, and any results showing suspiciously high Tri+aromatics values with ASTM D 6591-06 should be re-analyzed by IP391/07.

References

1. Angelika Gratzfeld-Huesgen, "Analysis of Aromatic Hydrocarbons in Middle Distillates with HPLC using IP Standard Method 391/95", Agilent Application Note, 5965-9044E, 1997.
2. ASTM D 6591-06 "Standard Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection".
3. Michael Woodman and Malgorzata Sierocinska, "Meeting the Requirements of EN12916:2006 (IP391/07) Using Agilent 1200 Series HPLC Systems", Agilent Application Note 5990-4789EN, 2009.

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May 28, 2010
5990-5867EN

Agilent Technologies

Automated Preparation of Simulated Distillation Standards and Samples for ASTM Methods D2887, D7213, D7398 and D6352 using the 7693A System with Easy SamplePrep Software

Application Note

Hydrocarbon Processing

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Abstract

A dual tower Agilent 7693A and tray system installed on the Agilent 7890A GC system is used for the preparation of hydrocarbon calibration standards, solvent blanks, and petroleum samples for analysis by simulated distillation (SimDis). The front tower is equipped with a 5-µL syringe while the back tower is equipped with a 250-µL syringe. A 150 sample tray with heater and mixer/barcode reader is also used. Procedures are described for sample preparation for ASTM D2887, D7213, D7398 and D6352. The Multimode Inlet (MMI), G3510, operated in a temperature programmed split mode is used for all samples. On-line sample preparation programs are constructed using Easy SamplePrep software, an add-on software module for the multitechnique ChemStation.

Introduction

Sample and calibration standard preparation for various simulated distillation methods is normally a manual process requiring dilution, mixing, and heating. Many procedures use volatile toxic solvents such as carbon disulfide. ASTM method D2887 commonly uses CS_2 for sample dilution while D6352 may use CS_2 or toluene for polywax calibration standard preparation. Sample heating, mixing and solvent addition is available with the automation capabilities of the Agilent 7693A tower and tray system. Lab safety is improved by using small quantities of solvents with controlled heating, and mixing in sealed 2-mL vials.

Experimental

The Agilent 7890A GC system was equipped with two Agilent 7693A towers and 150 sample tray. The front tower used a standard 5-µL or 10-µL syringe and the rear tower was equipped with the optional large syringe carriage with a 250-µL syringe. Sample prep procedures were done by manipulating vials in the sample tray and in the tower turrets. Sample injection occurred on the front tower. The Agilent 7890A was configured with the multimode inlet (MMI) operating in temperature programmed split mode. Detection was with FID. Instrumental parameters for various configurations are listed in Table 1.

Discussion

A number of options or paths to construct sample prep programs using the drag and drop icon implementation of Easy SamplePrep software is possible. This discussion will in general illustrate just one possible solution for each procedure. Screen captures are used to detail the steps and advanced syringe settings.

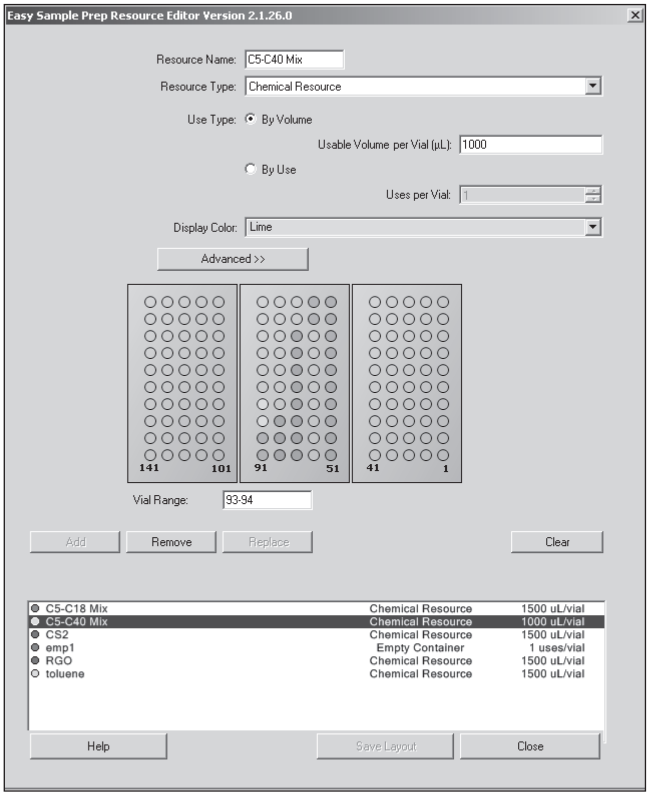
Table 1. Agilent 7890A GC System SimDis Parameters

System for D2887	
Column	10 m × 0.53 mm, 3.0 µm DB-2887
Oven	40 °C (0 min) to 350 °C (5 min) @ 15 °C/min
Inlet	Multimode (MMI), G3510, 100 °C (0 min) to 340 °C (to end of run) @ 250 °C/min
Liner	Single taper with glass wool, No. 5183-4711
Split	4 to 1
Flow	12 mL/min, constant flow mode
System for D7213 and D7398 (Polywax 500 calibration)	
Column	5 m × 0.53 mm, 0.15 µm DB-HT SimDis
Oven Program	35 °C (0 min) to 400 °C (5 min) @ 10 °C/min
Inlet	Multimode (MMI), 100 °C (0 min) to 400 °C (20 min) @ 250 °C/min
Split ratio	5 to 1
Flow	14 mL/min, constant flow mode
Agilent 7890A GC system for D6352 (Polywax 655 calibration)	
Column	5 m × 0.53 mm, 0.15 µm DB-HT SimDis
Oven Program	35 °C (0 min) to 435 °C (2 min) @ 10 °C/min
Inlet	Multimode (MMI), 100 °C (0 min) to 430 °C (hold to end of run) @ 250 °C/min
Split ratio	5 to 1
Flow	15 mL/min, constant flow mode
Agilent 7693A system	
Front tower	5 µL syringe, G4513A
Back tower	250 µL syringe, G4521A syringe carriage
Tray	150 sample capacity with Heater/Mixer/Bar Code Reader, G4520A
ChemStation	B.04.02 SP1
Sample Prep	G7300AA, Easy SamplePrep
Agilent 7890A GC system firmware	A.01.10.3 or greater
Standards and vials	
Calibration mix, C5-C40, No. 5080-8716	
Calibration mix, C5-C18, No. 5080-8768	
RGO, No. 5060-9086	
PW500, No. 5188-5316	
PW655, No. 5188-5317	
Empty vials with 100 µL inserts, No. 5188-6592	
Simulated Distillation Software	
G2887BA	

Two-milliliter vial resources are assigned in user defined tray locations as shown in Figure 1. These are the resources needed for methods D2887, D7213, D6352, and D7398. The polywax standards are handled differently, usually as "Sample (front)" vials when the front tower is used for injection. Resource vials are specified for use by maximum volume extracted or by number of allowed uses. Ensure that appropriate syringe details such as draw and dispense speeds for the handling of a given chemical resource are set. An example of advanced settings for use of CS_2 is shown in Figure 2.

A typical sample preparation program for D2887 setup (blank, calibration, reference gas oil) may consist of a sequence of three methods, each for a specific sample prep and injection. An example sequence is shown in Figure 3. This illustrates preparation of the blank, calibration standard, and reference gas oil (RGO) samples necessary to set up and verify a system for routine analyses.

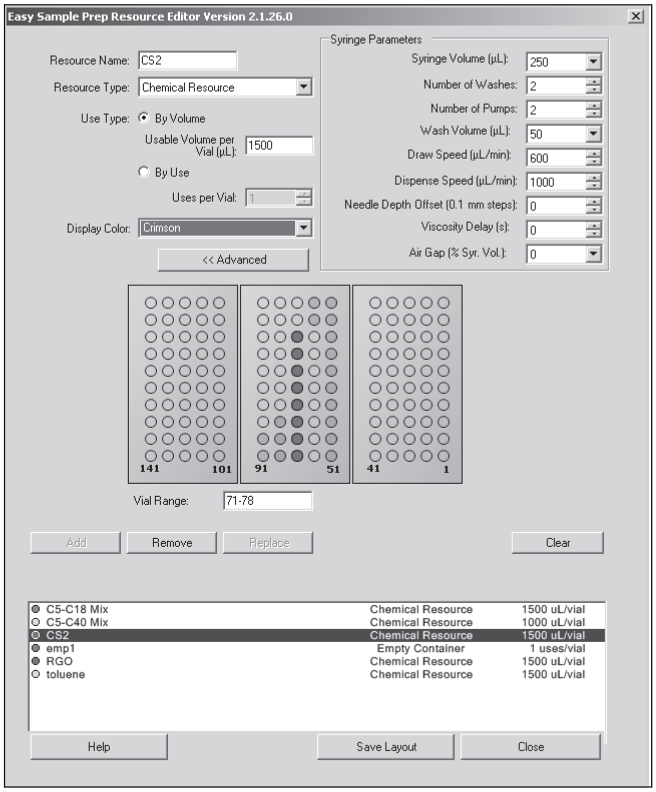
The Easy SamplePrep programs used for methods CS2 BLANK, C5C40 CAL 2887, and RGO 2887 are shown in Figures 4, 5, and 6, respectively. Using three methods in a sequence is convenient since each method has different integration parameters.



Resource Name: C5-C40 Mix
Resource Type: Chemical Resource
Use Type: ● By Volume
Usable Volume per Vial (µL): 1000
○ By Use
Uses per Vial: 1
Display Color: Lime
Vial Range: 93-94

C5-C18 Mix	Chemical Resource	1500 uL/vial
C5-C40 Mix	Chemical Resource	1000 uL/vial
CS2	Chemical Resource	1500 uL/vial
emp1	Empty Container	1 uses/vial
RGO	Chemical Resource	1500 uL/vial
toluene	Chemical Resource	1500 uL/vial

Figure 1. Example resource layout for various simulated distillation procedures. Each resource is assigned a unique color.

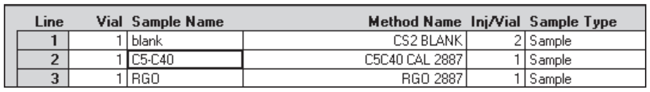


Resource Name: CS2
Resource Type: Chemical Resource
Use Type: ● By Volume
Usable Volume per Vial (µL): 1500
○ By Use
Uses per Vial: 1
Display Color: Crimson
Vial Range: 71-78

Syringe Volume (µL): 250
Number of Washes: 2
Number of Pumps: 2
Wash Volume (µL): 50
Draw Speed (µL/min): 600
Dispense Speed (µL/min): 1000
Needle Depth Offset (0.1 mm steps): 0
Viscosity Delay (s): 0
Air Gap (% Syr. Vol.): 0

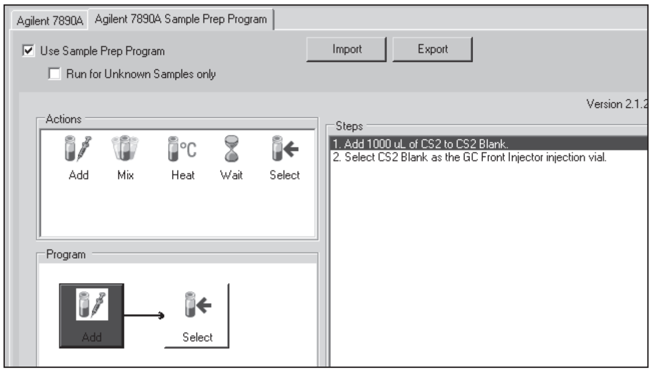
C5-C18 Mix	Chemical Resource	1500 uL/vial
C5-C40 Mix	Chemical Resource	1000 uL/vial
CS2	Chemical Resource	1500 uL/vial
emp1	Empty Container	1 uses/vial
RGO	Chemical Resource	1500 uL/vial
toluene	Chemical Resource	1500 uL/vial

Figure 2. Advanced parameters shown (upper right box) for chemical resource CS2.



Line	Vial	Sample Name	Method Name	Inj/Vial	Sample Type
1	1	blank	CS2 BLANK	2	Sample
2	1	C5-C40	C5C40 CAL 2887	1	Sample
3	1	RGO	RGO 2887	1	Sample

Figure 3. Sequence for setup of D2887. Each method contains the appropriate EasySample Prep procedure.



☑ Use Sample Prep Program

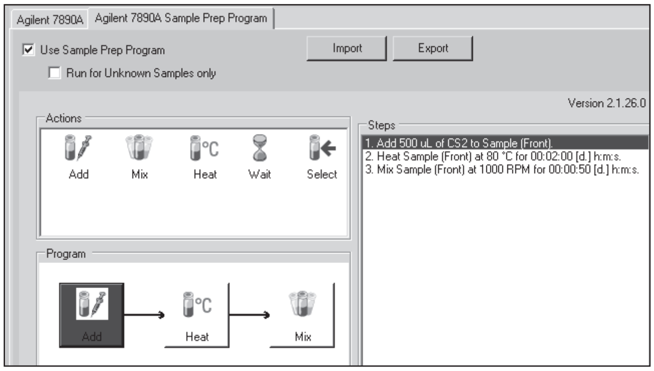
☐ Run for Unknown Samples only

Version 2.1.2

Steps

1. Add 1000 uL of CS2 to CS2 Blank.
2. Select CS2 Blank as the GC Front Injector injection vial.

Figure 4. Easy Sample Prep program for the preparation of a CS_2 blank. An empty tray vial has been assigned the name "CS2 Blank". The select icon indicates that the prepared vial is to be injected.



☑ Use Sample Prep Program

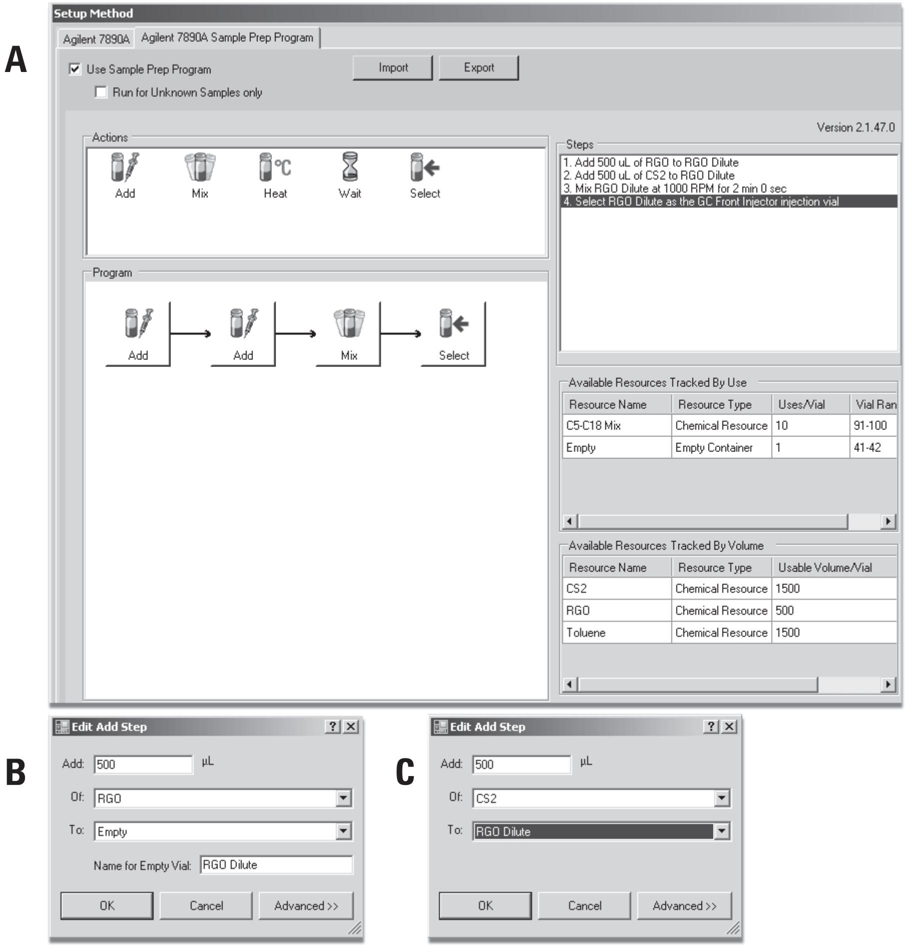
☐ Run for Unknown Samples only

Version 2.1.26.0

Steps

1. Add 500 uL of CS2 to Sample (Front).
2. Heat Sample (Front) at 80 °C for 00:02:00 [d.] h:m:s.
3. Mix Sample (Front) at 1000 RPM for 00:00:50 [d.] h:m:s.

Figure 5. Easy Sample Prep program for preparation and injection of the C5 to C40 calibration mix. The "sample [front]" label defines sequence vials for the front tower.



☑ Use Sample Prep Program

☐ Run for Unknown Samples only

Version 2.1.47.0

Steps

1. Add 500 uL of RGO to RGO Dilute
2. Add 500 uL of CS2 to RGO Dilute
3. Mix RGO Dilute at 1000 RPM for 2 min 0 sec
4. Select RGO Dilute as the GC Front Injector injection vial

Available Resources Tracked By Use

Resource Name	Resource Type	Uses/Vial	Vial Ran
C5-C18 Mix	Chemical Resource	10	91-100
Empty	Empty Container	1	41-42

Available Resources Tracked By Volume

Resource Name	Resource Type	Usable Volume/Vial
CS2	Chemical Resource	1500
RGO	Chemical Resource	500
Toluene	Chemical Resource	1500

B

Add: 500 µL
Of: RGO
To: Empty
Name for Empty Vial: RGO Dilute

C

Add: 500 µL
Of: CS2
To: RGO Dilute

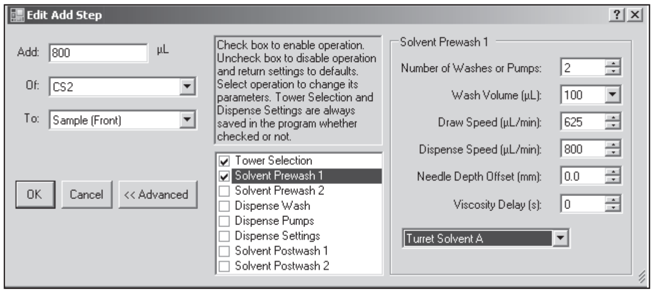
Figure 6a. Easy Sample Prep program for preparation and injection of RGO. An empty tray vial(empty) has been assigned the name "RGO Dilute" during the "Add" step and is selected for injection after prep. "Selected" vials override the vial number given in the sequence table.

Figure 6b. Add steps for RGO and vial naming.

Figure6c. Adding carbon disulfide to the RGO vial.

Upon completion of the sequence, all three prepared vials will have been injected producing data files ready for analysis by simulated distillation software. Note that two blanks are run to ensure both are the same; otherwise, additional blanks should be run. As an alternate setup, the calibration, prepared RGO, and blank vials can be fitted with 100-µL inserts to minimize solvent and resource amounts used for the procedure. Please note that when these inserts are used, limit mixing to speeds of approximately 500 rpm to avoid "spilling" liquid over the top of the insert into the bottom of the 2-mL vial.

Syringe washing is important to incorporate into these programs to avoid contamination or carryover for each vial addition. An example of settings is shown in Figure 7.



Add: 800 µL
Of: CS2
To: Sample (Front)

Check box to enable operation. Uncheck box to disable operation and return settings to defaults. Select operation to change its parameters. Tower Selection and Dispense Settings are always saved in the program whether checked or not.

☑ Tower Selection
☑ Solvent Prewash 1
☐ Solvent Prewash 2
☐ Dispense Wash
☐ Dispense Pumps
☐ Dispense Settings
☐ Solvent Postwash 1
☐ Solvent Postwash 2

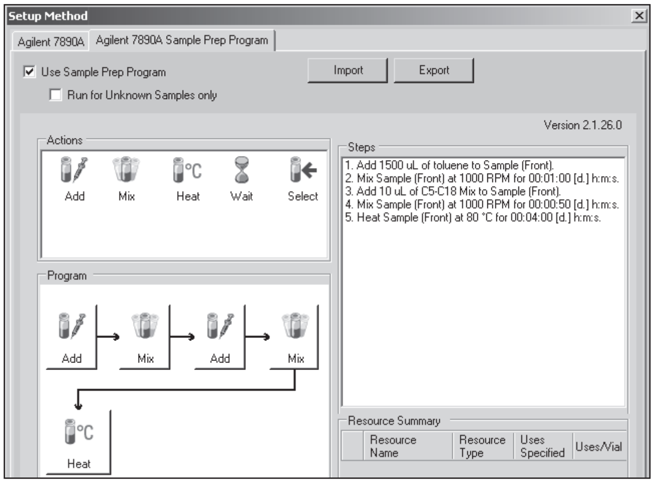
Solvent Prewash 1
Number of Washes or Pumps: 2
Wash Volume (µL): 100
Draw Speed (µL/min): 625
Dispense Speed (µL/min): 800
Needle Depth Offset (mm): 0.0
Viscosity Delay (s): 0
Turret Solvent A

Figure 7. An example using solvent wash vial 1 (5 mL) in the turrent of tower A.

Preparation of polywax standards for the higher temperature SimDis methods can be challenging due to their low solubility. Solvents such as CS_2 and toluene are commonly used. Heating of the solvent/polywax vial is required just prior to injection. This entire procedure can be automated with the Agilent 7693A tower and tray system. The basic procedure for Polywax 655 is as follows:

- Manually place approximately 80 – 100 mg of polywax 500 in a 2 mL vial and seal
- Add 1.5 mL of toluene to the polywax vial
- Add 10 µL of C5-C18 to the polywax-toluene vial
- Mix the vial
- Heat the vial at 80 °C for 4 min.
- Return to tray
- Heat one final time just prior to injection by setting injection/tray parameters in the core ChemStation method

Figure 8 shows the basic prep procedure using a dual tower/tray system automating the steps shown above. The only manual step is adding the solid polywax 500 to Vial 1 (Sample front). This procedure is applicable to D7213 SimDis and D7398 (Boiling Range Distribution of Fatty Acid Methyl Esters).



☑ Use Sample Prep Program
☐ Run for Unknown Samples only

Steps
1. Add 1500 uL of toluene to Sample (Front).
2. Mix Sample (Front) at 1000 RPM for 00:01:00 [d.] h:m:s.
3. Add 10 uL of C5-C18 Mix to Sample (Front).
4. Mix Sample (Front) at 1000 RPM for 00:00:50 [d.] h:m:s.
5. Heat Sample (Front) at 80 °C for 00:04:00 [d.] h:m:s.

	Resource Name	Resource Type	Uses Specified	Uses/Vial

Figure 8. Polywax 500 prep procedure.

A resulting chromatogram for the injection of the prepared PW500 vial (vial 1) is shown in Figure 9. A symmetric distribution of the polyethylene fragments with good resolution to C80 is shown.

The preparation program for Polywax 655 is essentially the same as shown above for PW500 except that heating is extended for 6 minutes typically for dissolution. Prior to injection, the prepared vial is heated for another 3 minutes. Parameters for this second heating step are set under the core ChemStation injection parameter menu item. In the chromatogram shown in Figure 10, a small amount (5 µL) of C_5-C_{18} mix was added to the PW655/toluene solution as part of the automated procedure. This allows calibration starting at C12.

The chromatogram was produced with the multimode inlet set in temperature programmed split mode. Good definition of polyethylene fragments to over C110 are seen in Figure 11. The last 5 minutes of the chromatogram are zoomed to show detail. Producing this detail out to C110 is extremely difficult for any chromatographic system.

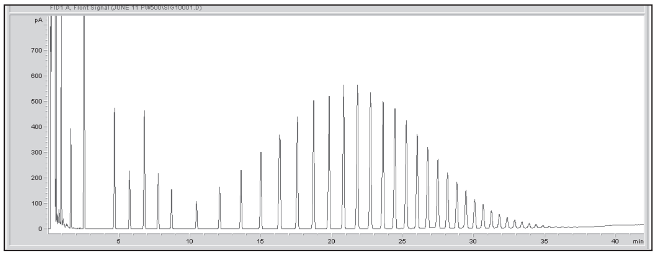


Figure 9. Polywax 500 with C5-C18 added. Multimode inlet, 2.5-µL injection.

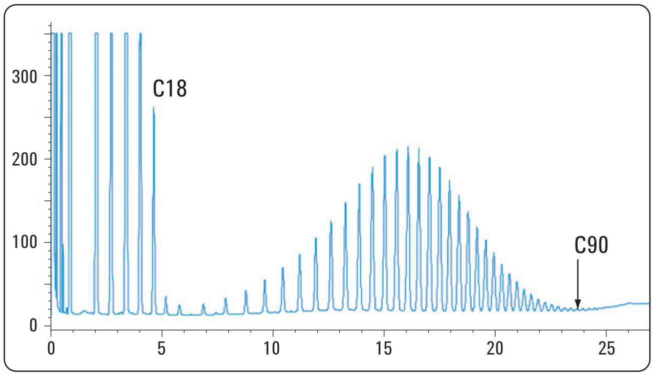


Figure 10. Chromatogram of PW 655.

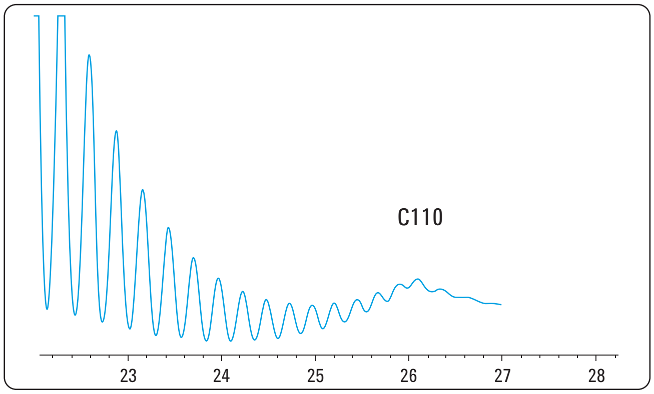


Figure 11. Polywax 655 to C110. Multimode inlet program: 150 °C (0 min) to 430 °C (hold to end of run) @ 200 °C/min. 7890A oven: 40 °C (0 min) to 430 °C (5 min) @ 15 °C/min. 3-µL injection. Solvent is toluene.

Reproducibility of sample preparation steps for the dilution of a heavy vacuum gas oil sample (HVGO) is illustrated in Figure 12. Carbon disulfide was used for sample dilution. Tray vial 1 is the stock HVGO sample, prepared by manually adding 0.5 g of the oil to a 2-mL vial. This material is extremely viscous and cannot be drawn into a syringe without dilution. The program performs a fully automated dilution prior to injection. (Figure 13)

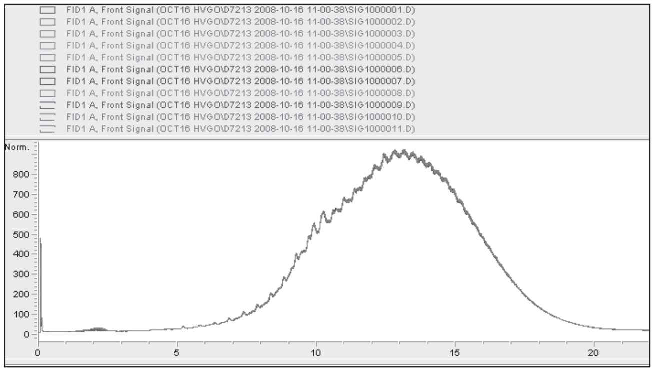


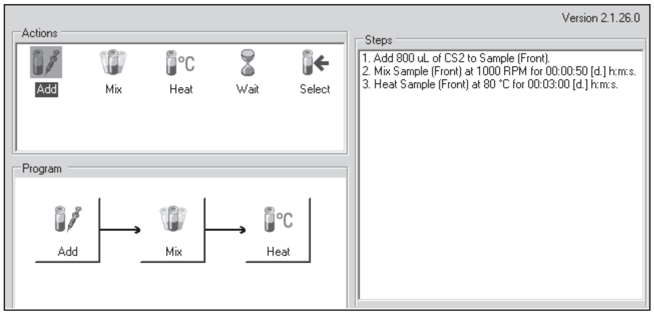
Figure 12. Overlay of 11 runs of HVGO, each prepared by using a Easy Sample Prep program.

Summary

Difficult sample preparation procedures that are commonly used for petroleum and fuel samples can be easily automated on-line with the Agilent 7693A tower and tray system for the Agilent 7890A GC system and Agilent 6890N Network GC system, including A, and Plus models using the Easy SamplePrep add-on software for the multitechnique ChemStation. The system is particularly well suited for preparation of polywax calibration samples used for higher temperature methods. Tasks such as mixing, solid dissolution, dilution, heating, viscosity reduction, and internal standard addition are easily accomplished by assembling icon based instructions. User contact with toxic solvents such as CS_2 is greatly reduced. The software monitors used resources and moves to the next available resource vial as assigned in the resource table when needed.

Chromatographic performance is enhanced through use of the multimode inlet. Using standard split injection liners, good sample capacity without carryover and with minimal discrimination of wide boiling samples is achieved. The inlet was used in the temperature programmed split mode for this work. Cryo cooling was not used, however, carbon dioxide cryo can be used optionally to shorten inlet cool down if desired.

The sample prep procedures listed here represent just one way of accomplishing a given task. Using the icon based commands available with the system, there are many variants that lead to the same end result.



1. Add 800 uL of CS2 to Sample (Front).
2. Mix Sample (Front) at 1000 RPM for 00:00:50 [d.] h:m:s.
3. Heat Sample (Front) at 80 °C for 00:03:00 [d.] h:m:s.

Figure 13. Preparation of HVGO for injection. CS_2 is used as the solvent.

Reference

1. Roger L. Firor, “Automated Preparation of Simulated Distillation Samples for ASTM Methods D2887, D7213, D7398, and D6352 using a Dual Tower 7693A and Tray System”, April 2009, Agilent Technologies publication 5990-3778EN.

www.agilent.com/chem

Printed in the USA
July 29, 2010
5990-6132EN

Agilent Technologies

Analysis of Trace 2-Ethylhexyl Nitrate in Diesel Using Chemiluminescence Detector (NCD)

Application Brief

ChunXiao Wang and Roger Firor

HPI

An increase in the use of fleet diesel vehicles has helped define requirements for diesel fuel for light duty engines. One of these requirements is to recognize the influence of the cetane number on cold start properties, exhaust emissions and combustion noise. Several types of chemicals such as alkyl nitrates, ether nitrates or nitroso compounds have been identified as effective in increasing the cetane number. The most commonly used cetane enhancer is 2-ethylhexyl nitrate (2-EHN). ASTM D4046 standard test method is used for determining the amount of alkyl nitrate added to diesel fuel to judge compliance with specifications covering any alkyl nitrate. This method uses spectrophotometry with a detection range of 0.03 to 0.30 volume percent. The Agilent 7890A GC system configured with a chemiluminescence detector (NCD) provides an alternative method to ASTM D4046 with excellent results. Although the detection of 2-EHN is very difficult because of its low concentration in diesel fuel, a NCD can deliver both the required sensitivity and selectivity as shown in this analysis report.

Experiment

Table 1. Typical GC Conditions

Inlet:	250 °C, Split: 10:1
Column:	HP-5MS, 15 m × 0.32 mm, 0.32 µm, 3.9 mL/min, constant flow:
Oven:	60 °C (2 min), to 280 °C (8 min) at 20 °C/min
NCD	
Temperature:	200 °C
Detector pressure (Torr):	7.7
Dual plasma controller pressure (Torr):	110
Burner temperature:	905 (°C)
Hydrogen flow rate (sccm):	5
Oxidant flow rate (sccm):	10 (oxygen)

Highlights

- High sensitivity in analyzing nitrogen at low ppm levels. The results demonstrate a good signal-to-noise ratio for 2-EHN as nitrogen in diesel at the 1.87 ppm level.
- High selectivity for nitrogen over carbon. Analyzes nitrogen in diesel without suffering from any hydrocarbon interference.
- Linear response simplifies calibration. The results illustrate a linear response to nitrogen (2-EHN) over the concentration range of interest.
- An equimolar response simplifies quantification of unknowns, eliminating the need for determining separate response factors for individual nitrogen compounds.

Agilent Technologies

Results

The Agilent 255 NCD delivers the sensitivity required for analysis of 2-EHN in diesel without hydrocarbon interference.

Figure 1 shows a good signal-to-noise for 2-EHN as nitrogen in diesel at 1.87 ppm. The result also demonstrates the selectivity of the detector showing no response from the diesel hydrocarbon background.

Trace 2-EHN added to diesel fuel can be found in pump diesel and B20 biodiesel. Figures 2 and 3 show chromatograms with nitrogen species in pump diesel and B20 biodiesel, respectively. The concentration determined for 2-EHN as nitrogen is 1.18 ppm and 18.7 ppm respectively. Also, other higher boiling nitrogen species are observed in both pump diesel and B20 biodiesel.

Figure 3 illustrates linear response to nitrogen (2-EHN) over the concentration range of the interest.

The precision for analysis of 2-EHN in pump diesel with an RSD of 1.15% is shown in Table 2.

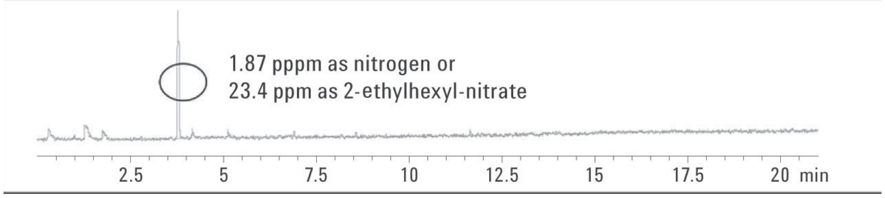


Figure1. Standard sample: 2-EHN at a concentration of 23.4 ppm in diesel (nitrogen free).

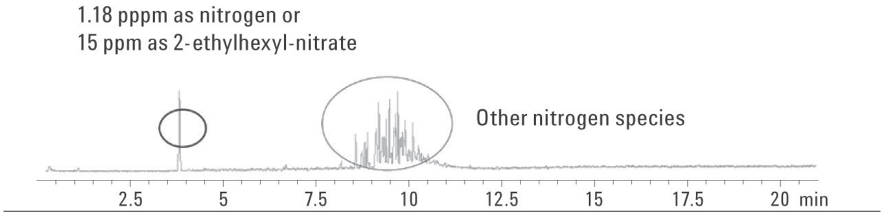


Figure 2. Nitrogen species in pump diesel fuel.

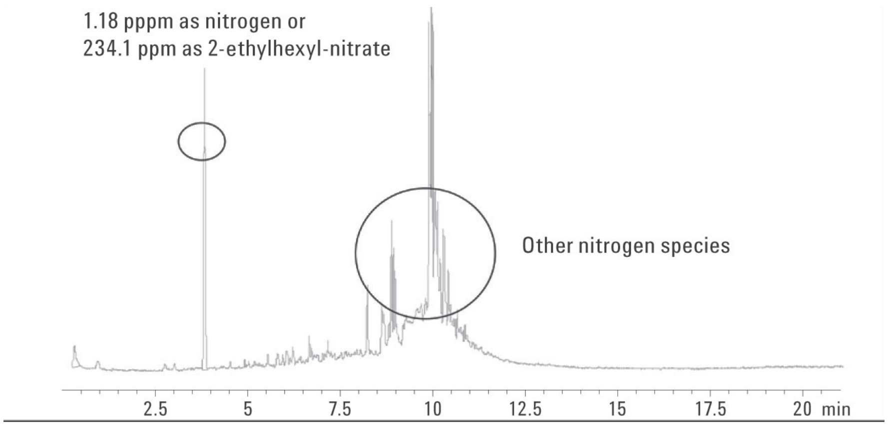
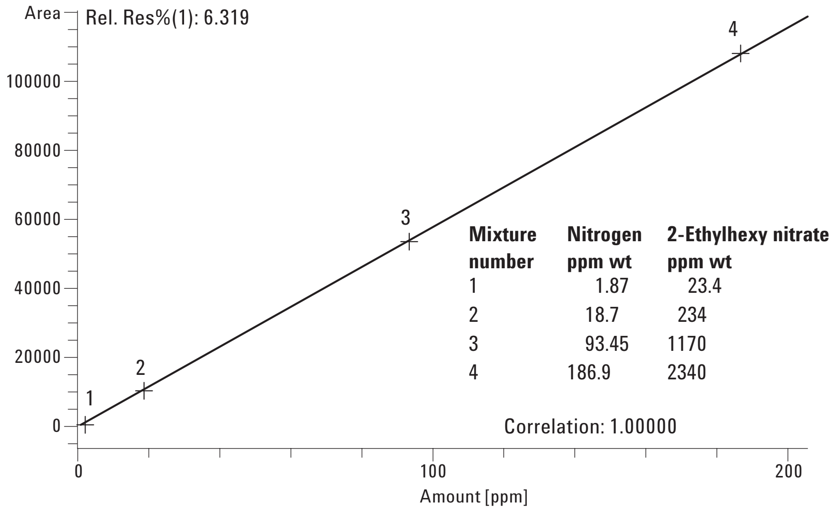


Figure 3. *Nitrogen species in B20 biodiesel.*



Mixture number	Nitrogen ppm wt	2-Ethylhexy nitrate ppm wt
1	1.87	23.4
2	18.7	234
3	93.45	1170
4	186.9	2340

Figure 4. *2-ethylhexyl nitrate calibration.*

Table 2. *Method precision for analysis of 2-ethylhexyl nitrate in pump diesel.*

	Run 1	**Run 2**	**Run 3**	**Run 4**	**Run 5**	**Run 6**	**Average**	**RSD%**
Nitrogen, mg/kg	1.18	1.21	1.19	1.17	1.19	1.18	1.19	1.15

Sample run 6 times

References

1. ASTM D 4046-91(2005), "Standard Test Method for Alkyl Nitrate in Diesel Fuels by Spectrophotometry", Annual Book of Standards, Volume 05.04, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA.
2. Agilent Technical Overview, "Analysis of Trance Nitrogen Species in Benzene," Agilent Technologies publication. 5989-6774EN.

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Evaporation from 2-mL Vials on the Agilent 7696A Sample Prep WorkBench: Septa Unpierced, Septa Pierced with a Syringe Needle, Septa with an Open Hole

Application Note

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Introduction

In the course of sample analysis by gas chromatography, the vial septum may be pierced multiple times before each injection, often with multiple injections. Once the septum is pierced, solvent evaporation from the vial occurs. This usually does not create a reproducibility problem for GC analysis, even with multiple injections, unless the time between runs is an hour or longer. With the Agilent 7696A Sample Prep WorkBench, the number of times a septum is pierced may be greater, and the time before the final sample is analyzed may be much longer than is typical in GC.

Another problem that arises with the Agilent 7696A Sample Prep WorkBench is the need to withdraw large volumes from 2 mL vials. For example, transferring 0.5 mL solvent or sample from one vial to another can create a partial vacuum in the source vial. This results in poor reproducibility because the degree of vacuum varies from vial to vial and the amount of liquid actually transferred also varies. One way to eliminate this problem is to prepierce the septum with a small off-center hole so that no vacuum is created and the syringe needle is still wiped by the septum when withdrawn from the vial.

The evaporation rates of hexane (bp = 70 °C) and isooctane (bp = 100 °C) were measured at ambient temperature for three different septum scenarios to determine the magnitude of the problem. The three scenarios are as follows: a new unpierced septum, a septum prepierced approximately nine times, and a septum cored to prevent vacuum formation. Evaporation from the new, unpierced screw cap vial septa was considered negligible. Evaporation was greater with the septa pierced with a syringe needle and much greater with the cored septa.

Experimental

Hardware

Vials:	2 mL glass screw cap (5182-0714)
Septum caps:	With PTFE/red silicone rubber (5185-5820)

Septum types:

A = new, unpierced
B = pierced approximately 9 times with syringe needle
C = new, cored off-center with a 0.5 mm hole

The type B septa were prepierced with GC injections. The type C septa were cored with a miniature “cork borer” made from a brass tube (1/16” od × 0.035” id). One end was filed to create a sharp inner edge. The holes created were about 0.5 mm id.

Fifteen empty vials plus caps were weighed. Five contained type A septa, five contained type B and five contained type C. Vials were filled with about 1 mL of solvent each, reweighed, and placed in a Agilent 7696 sample tray. Vials were weighed again after 24 and 96 hr at room temperature (23 °C).

Results

The %loss/hr for the different septum types for hexane is:

A = 0
B = 0.3
C = 0.9

The %loss/hr for the different septum types for isooctane is:

A = 0
B = 0.1
C = 0.3

Table 1 lists average evaporation rates from vials with the different septa.

Conclusions

This data provides a rough idea of the effect solvent evaporation has on our preparation results. It is up to the user to determine what level of evaporation can be tolerated based on the specific method and length of time between initial and final samples in the preparation. When a method requires vacuum relief holes in the septa, the transfers should be performed early in the method if possible, and even perhaps as a separate method so that vials can be recapped before significant evaporation occurs.

Table 1. Average Evaporation Rates from Vials with the Different Septa

Solvent: hexane, bp = 70 °C

Septum:	**A**		**B**		**C**	
After:	**%loss**	**%loss/hr**	**%loss**	**%loss/hr**	**%loss**	**%loss/hr**
24hr	0.00	0.00	7.27	0.30	21.06	0.88
96hr	0.03	0.00	29.21	0.30	84.55	0.88

Solvent: isooctane, bp = 100 °C

Septum:	**A**		**B**		**C**	
After:	**%loss**	**%loss/hr**	**%loss**	**%loss/hr**	**%loss**	**%loss/hr**
24hr	0.12	0.01	2.74	0.11	6.84	0.29
96hr	0.65	0.01	11.38	0.12	28.26	0.29

A New, unpierced septa
B Septa prepierced about nine times
C Septa cored to prevent vacuum formation

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Agilent Technologies

Agilent 7696A Sample Prep WorkBench: How to Automate Preparation of a Sample Set by Serial Dilution for Measurement of Flame Ionization Detector Performance

Application Note

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Introduction

A challenge that arises more often than the analyst might like, is the need to prepare a set of samples by serial dilution. Serial dilution starts with a single sample of known concentration. It is then used to prepare a set of dilutions, each usually differing from the previous one, by a constant factor. Each sample is made from the previous one in the series. This task may be driven by the need to calibrate an instrument with specific analytes or measure such things as detector performance: linearity, sensitivity and minimum detectable level (MDL). If the samples are not stable over time, they may need to be prepared weekly or even daily. To minimize errors in manual preparations or reduce the frequency of tiresome dilutions, the user will often prepare larger volumes of sample than needed, which leads to unnecessary waste and expense.

The Agilent 7696A Sample Prep WorkBench provides a solution to this problem by automating the serial dilution process precisely so that small volumes of sample can be routinely prepared when needed over as large a concentration range as desired. The preparative method for serial dilution starts with a measured volume of solvent in an empty vial followed by a measured volume of sample. After mixing, this step is repeated using a new vial of solvent and an aliquot from the last dilution. For example, measuring the performance of a flame ionization detector (FID) requires a set of samples, each diluted by a factor of ten from the previous sample. The starting sample is a normal hydrocarbon such as n-tridecane (C_{13}). Each dilution consists of 90% solvent and 10% previous sample (v:v). A set of seven or eight samples, as prepared in this application, are required to demonstrate the normal seven orders of magnitude of FID linearity. As described below, eight sets of test samples were prepared over a two week period. Three were prepared manually and five with the Agilent 7696 Sample Prep Workbench at a total volume per sample of either 1 mL or 0.5 mL. Repeatability over all sets was excellent whether measured by sample weight in each set or by FID performance.

Experimental

The Agilent 7696A Sample Prep WorkBench was used to prepare a set of eight samples, each diluted by a factor of ten from the previous sample. Two sequences were used so that samples could be weighed after each addition. The first used a method that added a fixed amount of solvent to each vial. The second started with a manually-prepared 10% solution of C_{13} in solvent, then added enough solution to the next vial to make a tenfold less concentrated solution. After mixing, an aliquot of the freshly made sample was used to make the next dilution in the series until the eight sample set was complete. The empty vials were tared, and then weighed after each sequence to measure reproducibility of transfers across the series. The same preparations were also done manually for comparison.

Hardware Configuration

The Agilent 7696A Sample Prep WorkBench was equipped with two Agilent 7693A Automated Liquid Samplers. The back injector contained an enhanced syringe carriage containing a 500-µL syringe (p/n G4513-60561). The front injector used a standard syringe carriage containing a 100-µL syringe (p/n 5183-2042). The back injector was used for solvent delivery to each of the empty vials (first sequence) and the front injector was used for sample transfer from one sample to the next (second sequence).

Sample Preparation

Two protocols were used that differed only in the volume of the prepared dilution. The first used 900 µL solvent + 100 µL sample and the second used half these amounts: 450 µL solvent + 50 µL sample.

A single Agilent 7696A Sample Prep WorkBench resource layout was used for both sequences:

Resource Layout:

Vial Range	Name	Type	Usage
2-9	MT vial	Empty container	1 use/vial
12-19	Solvent	Chemical resource	1 use/vial

The single sample required was a solution of 10% C_{13} in isooctane. It was prepared by adding 100 µL C_{13} to a 1 mL volumetric and diluting to mark.[*]

The first sequence prepared the 1 mL sample (900 µL + 100 µL) by adding 900 µL solvent to an empty vial (see Appendix for syringe parameters). The sequence specified vials 2 through 9.

The second sequence specified sample dilutions according to the following steps. (see Appendix for syringe parameters):

Step	Function
1	Add 100 µL of Sample (Front) to vial #2
2	Mix vial #2 at 1500 RPM for 0 min 5 sec
3	Add 100 µL of vial #2 to vial #3
4	Mix vial #3 at 1500 RPM for 0 min 5 sec
5	Add 100 µL of vial #3 to vial #4
6	Mix vial #4 at 1500 RPM for 0 min 5 sec
7	Add 100 µL of vial #4 to vial #5
8	Mix vial #5 at 1500 RPM for 0 min 5 sec
9	Add 100 µL of vial #5 to vial #6
10	Mix vial #6 at 1500 RPM for 0 min 5 sec
11	Add 100 µL of vial #6 to vial #7
12	Mix vial #7 at 1500 RPM for 0 min 5 sec
13	Add 100 µL of vial #7 to vial #8
14	Mix vial #8 at 1500 RPM for 0 min 5 sec
15	Add 100 µL of vial #8 to vial #9
16	Mix vial #9 at 1500 RPM for 0 min 5 sec

Results

Over a period of two weeks, eight serial dilution runs were made: Three manual (two at 1 mL and one at 0.5 mL); five with the Agilent 7696A Sample Prep WorkBench (three at 1 mL and two at 0.5 mL).

Table 1. Reproducibility for Solvent Delivery (Average of Eight Samples)

Type	Manual	Manual	Manual	7696A	7696A	7696A	7696A	7696A
Volume (mL)	0.5	1.0	1.0	0.5	1.0	1.0	1.0	0.5
Average weight (g)	*	0.6165	0.6151	0.3089	0.6176	0.6195	0.6180	0.3088
%SD	*	0.17	0.26	0.11	0.16	0.09	0.06	0.17

[*] Not measured.

Reproducibility for the second step was ±1 µL, for all but the last sample. Each sample except the last was used to prepare the next. The weight should not change because the same volume is added to and then removed from each sample. The average weight change regardless of whether a 1 mL or 0.5 mL preparation was involved was equivalent to ±1 µL. The volume increase of the last sample was 100 µL or 50 µL for the 1 mL and 0.5 mL volumes, respectively.

The total Agilent 7696A Sample Prep WorkBench runtime was 49 min for the 1 mL set of samples and 41 min for the 0.5 mL set. The time for the manual preparations was not measured.

---

[*] I started with the 10% C_{13} instead of 100% C_{13} to avoid any volume shrinkage that might occur when mixing two neat compounds by volume.

Reproducibility of FID performance

The protocol used for FID linearity, sensitivity and MDL followed the ASTM protocol closely [1]. The major difference was the use of liquid samples rather than gas samples as specified by ASTM. All preparations were tested on the same FID. The linearity results (Figure 1) are essentially indistinguishable whether the samples were prepared by the Agilent 7696A Sample Prep WorkBench or manually. The average sensitivity and % SD were 26.3 and 2.4, respectively. This is very good performance for repeat runs on a single FID. The large spread in the MDL (Table 2) is caused by day-to-day variability in average detector noise in the region where C_{13} elutes. MDL is a sensitive function of noise. Table 2 and Figure 1 summarizes the results.

Table 2. FID MDL

Prep Type	**Manual**	**Manual**	**Manual**	**7696**	**7696**	**7696**	**7696**	**7696**
Volume (mL)	0.5	1.0	1.0	0.5	1.0	1.0	1.0	0.5
Sensitivity (ma-s/gC)	27.2	25.7	25.8	26.8	26.8	25.5	26.6	25.5
MDL (pgC/s)	0.96	1.14	1.66	0.92	0.68	1.31	1.23	1.15

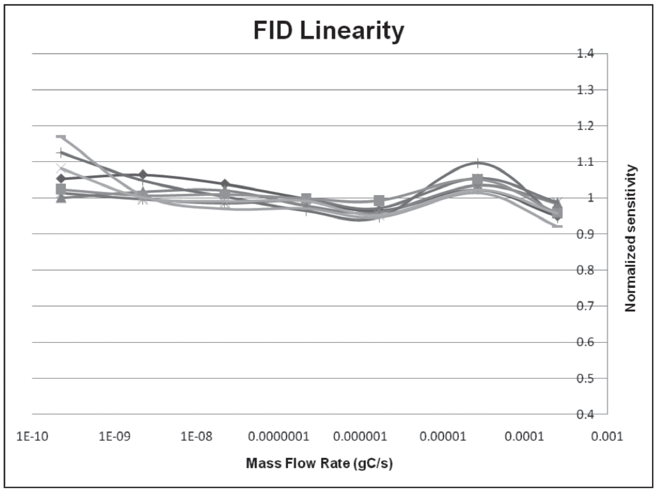

Figure 1. Linearity Plots for all eight runs overlaid.

Conclusion

The Agilent 7696A Sample Prep WorkBench simplifies the preparation of a set of samples by serial dilution. The user can prepare fresh samples only when needed at volumes no larger than necessary to satisfy the analytical requirements. The result is less boredom, less chance for operator error, less consumption of reagents, less waste disposal expense and better repeatability.

Appendix

500 µL syringe parameters:

	Tower Back	Solvent Prewash1	Solvent Prewash 2	Dispense wash	Dispense pumps	Dispense settings	Solvent postwash1	Solvent postwash2
Number pumps or washes					3			
Wash volume (µL)					50			
Draw speed (µL/min)					1250	1250		
Dispense speed (µL/min)					3000	3000		
Needle depth offset (mm)					0	0		
Viscosity delay(s)					2	2		
Turret solvent								
Air gap (% syr.vol.)						0		

100 µL syringe parameters:

	Tower Back	Solvent Prewash1	Solvent Prewash 2	Dispense wash	Dispense pumps	Dispense settings	Solvent postwash1	Solvent postwash2
Number pumps or washes		1		1	2			
Wash volume (µL)		10		20	10			
Draw speed (µL/min)		300		300	300	300		
Dispense speed (µL/min)		6000		6000	6000	6000		
Needle depth offset (mm)		0		0	0	0		
Viscosity delay(s)		2		2	2	2		
Turret solvent		A						
Air gap (% syr.vol.)						0		

Reference

1. ASTM E594-96 (2006) Standard Practice for Testing Flame Ionization Detectors used in Gas or supercritical Fluid Chromatography

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Agilent Technologies

Improved Data Quality Through Automated Sample Preparation

Application Note

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Abstract

Sample preparation tasks can be extremely time-consuming and are often prone to errors, leading to poor reproducibility and accuracy. Many of these tasks, such as calibration curve generation, sample dilution, internal standard addition, or sample derivatization are performed daily, requiring significant resources as well. The Agilent 7696 Sample Prep WorkBench can perform many common sample prep tasks with better accuracy and precision than most manual methods, while using significantly fewer reagents and requiring less time from the operator. To demonstrate this, three sample preparation tasks were adapted for use on the Agilent 7696 Sample Prep WorkBench and yielded the same, if not better, results than the manual methods for accuracy and precision.

Agilent Technologies

Introduction

The Agilent 7696 Sample Prep WorkBench can perform many sample preparation tasks for either gas chromatographic (GC) or liquid chromatographic (LC) analyses. The Agilent 7696 Sample Prep WorkBench consists of two liquid dispensing modules, a single vial heater capable of reaching 80 °C, a single vial mixer, and barcode reader (Figure 1). This enables dilutions/aliquoting, liquid addition, heating for derivatization or digestion, liquid/liquid extractions, and sample mixing. Individual racks can also be heated and/or cooled. This sample preparation instrument can perform tasks with the same accuracy and precision as the Agilent 7693A Automatic Liquid Sampler only in an offline setting instead of on top of a GC [1]. Many sample preparation tasks such as sample dilution, calibration curve standard generation, and sample derivatization within both fields can be time consuming and resource intensive. Automating these procedures with the Agilent 7696 Sample Prep WorkBench therefore is beneficial in many ways.

Figure 1. The Agilent 7696 Sample Prep WorkBench.

A side-by-side comparison of manual and automated methods was performed for three common sample prep applications to demonstrate the improved data quality achieved through automated sample preparation. Sample dilution, calibration curve standard generation, and derivatizations were performed with success on the Agilent 7696 Sample Prep WorkBench.

Experimental

Three common sample preparation tasks were performed with the Agilent 7696 Sample Prep WorkBench. First, sample dilutions and internal standard additions were performed for analysis by both GC and LC. For the GC samples, 50 µL each of isooctane and a standard solution containing four analytes were added to an empty 2-mL autosampler vial. Additionally 0.5 µL of an internal standard solution (ISTD) containing three analytes was added to the vial. The solution was mixed using the onboard mixer before transferring the vials to a GC for analysis. The samples for LC followed a similar procedure. To an empty 2-mL autosampler vial, 187.5 µL of acetonitrile, 62.5 µL of a pesticide standard, and 125 µL of an ISTD were added. The sample was mixed before being transferred to an LC for analysis. For both of these sample dilutions, n=10.

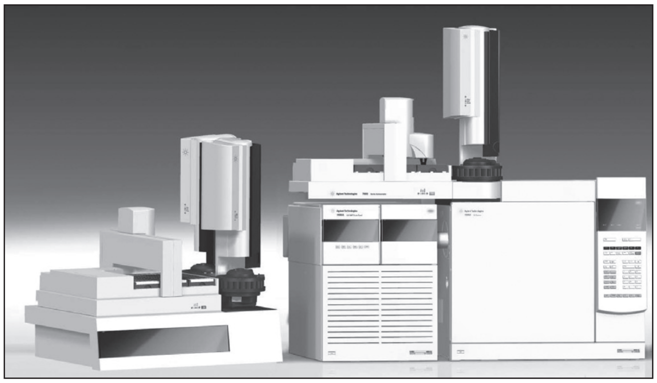

Figure 2. The Agilent 7696 Sample Prep WorkBench with a gas chromatograph and mass spectrometer.

Second, generic calibration curves for the GC were made in triplicate via linear dilution both manually in 10-mL volumetric flasks and with the Agilent 7696 Sample Prep WorkBench. To make the standards manually, small amounts of hexane was added to six clean, dry 10-mL volumetric flasks. Varying amounts of a stock solution containing five analytes at 5 mg/mL, ranging from 0.1 to 1 mL, were added using serological pipets. The flasks were diluted to the mark with hexane to yield concentrations of 50, 100, 200, 300, 400, and 500 ppm. For the automated method, 100 µL of hexane was added to six empty 2-mL autosampler vials. Again, varying amounts of the stock solution, ranging from 1 to 10 µL, was added to the vials yielding approximately the same concentrations.

Figure 3. The Agilent 7696 Sample Prep WorkBench with a liquid chromatograph.

Third, derivatization of fatty acids via silylation reaction was performed. For the manual prep, 100 µL of a silylating reagent was added to approximately 0.5 mL of a free fatty acid solution using an automatic pipettor. The solutions were heated to 70 °C using a heated block. The same derivatization was performed with the Agilent 7696 Sample Prep WorkBench using the single vial heater.

Results and Discussion

GC and LC Sample Dilution

For the 10 samples diluted for GC and LC analysis, the dispensed solvent, standard solution, and ISTD, was measured gravimetrically to determine the reproducibility of the dispensing action. Dispensing 50 µL with a 250 µL syringe results in a 0.5% relative standard deviation (RSD) for the 10 samples measured by weight. The samples were diluted within 1% accuracy, determined from the peak areas. The ISTD exhibited a slightly higher RSD. Dispensing 0.5 µL with a 25 µL syringe resulted in an RSD of 2% for the 10 samples. If a smaller syringe had been used to dispense the ISTD, a lower RSD, closer to that obtained when dispensing the solvent and standard, would have resulted. The added ISTD did not affect the accuracy of the diluted sample (Figure 4).

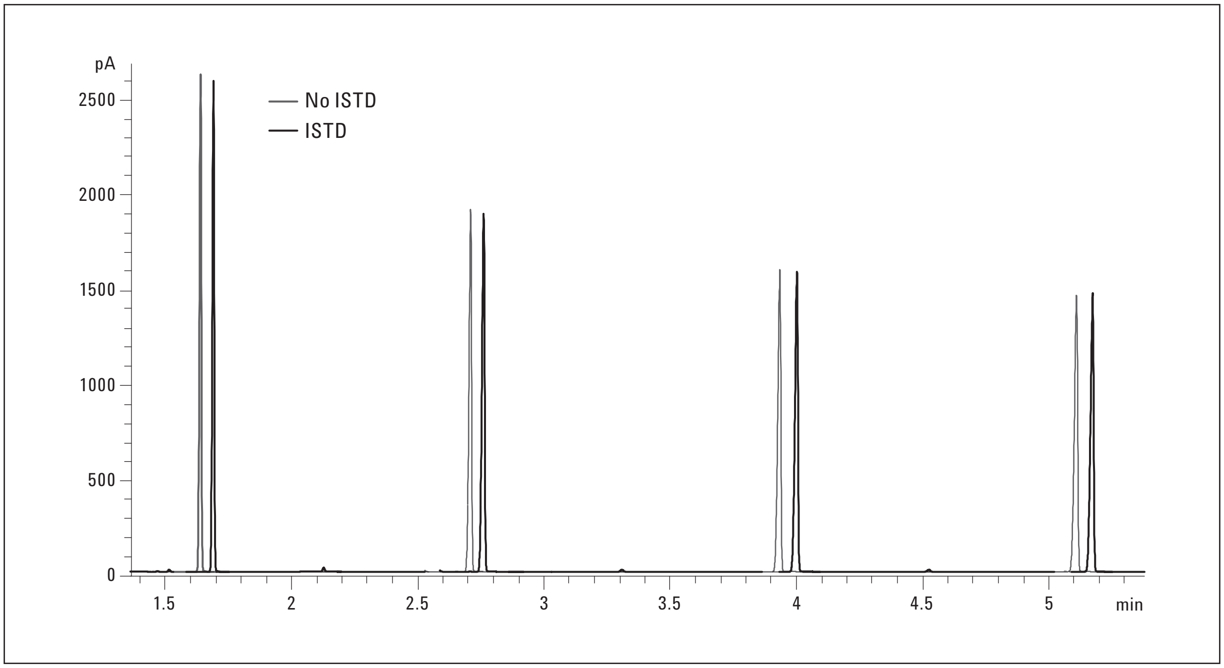

Figure 4. GC chromatograms (slightly offset) are shown for a standard solution dispensed and diluted with and without an ISTD added. No difference in peak areas are observed.

For the 10 samples diluted for LC analysis, similar results were obtained. Dispensing all three volumes with a 250 µL syringe resulted in a RSD of <0.5%, determined gravimetrically. By examining the peak areas after analysis, the dilutions were found to be accurate within 2% (Figure 5).

Calibration Curve Standard Preparation

Three sets of standards were made both manually and with the Agilent 7696 Sample Prep WorkBench. Comparing the three standard sets on the same plot highlighted the increased reproducibility of the Agilent 7696 Sample Prep WorkBench (Figure 6). While each individual curve yielded R^2 values of 0.999, when plotted together the R^2 value was reduced to 0.934 for the manually prepared standards. In contrast, the three curves prepared by the Agilent 7696 Sample prep WorkBench also yielded R^2 values of 0.999 for the individual curves, but when plotted together, the R^2 value was only reduced to 0.997.

Additionally, the relative response factor (RRF) was calculated for each set of standards. Calculating the RSD of the RRFs provides a measure of linearity and reproducibility. The individual calibration curves yielded good RSDs (<5%), demonstrating linear relationships. However, when comparing the three calibration curves together the superiority of the 7696 Sample Prep WorkBench made standards is evident. The average RSD of the RRFs for the three curves made manually was 16%; the three calibration curves made with the 7696 Sample Prep WorkBench gave an average RRF RSD of 4%.

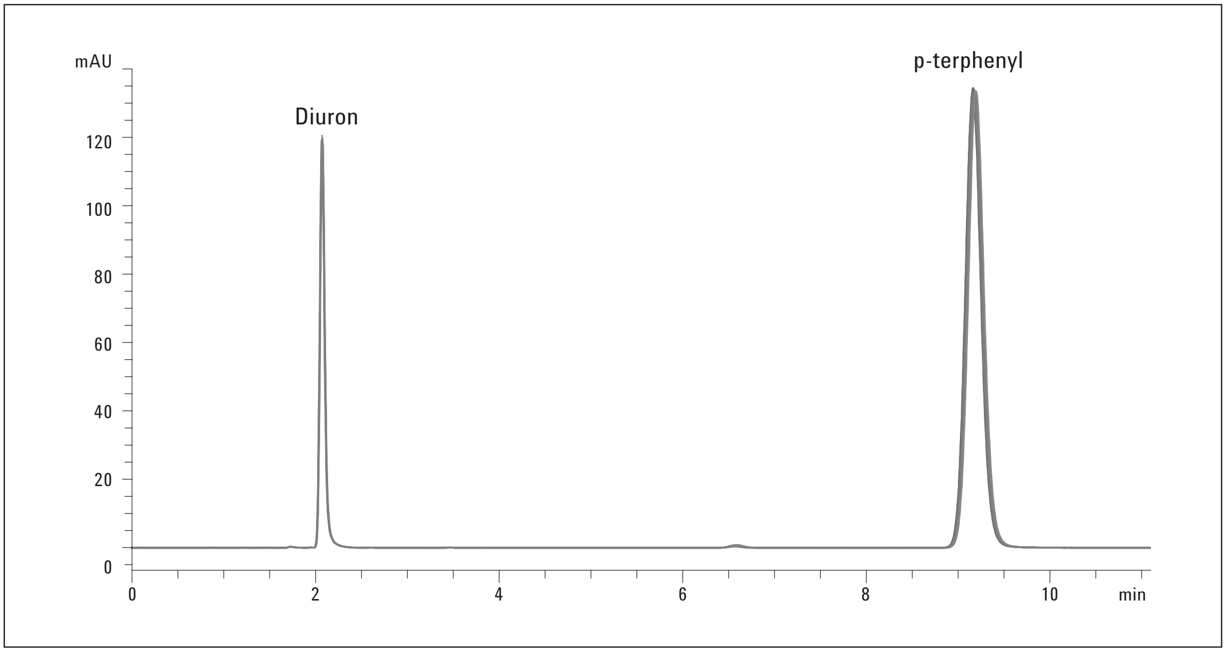

Figure 5. LC Chromatograms are shown for a diluted pesticide standard with an ISTD added. Excellent reproducibility was observed for the five samples shown.

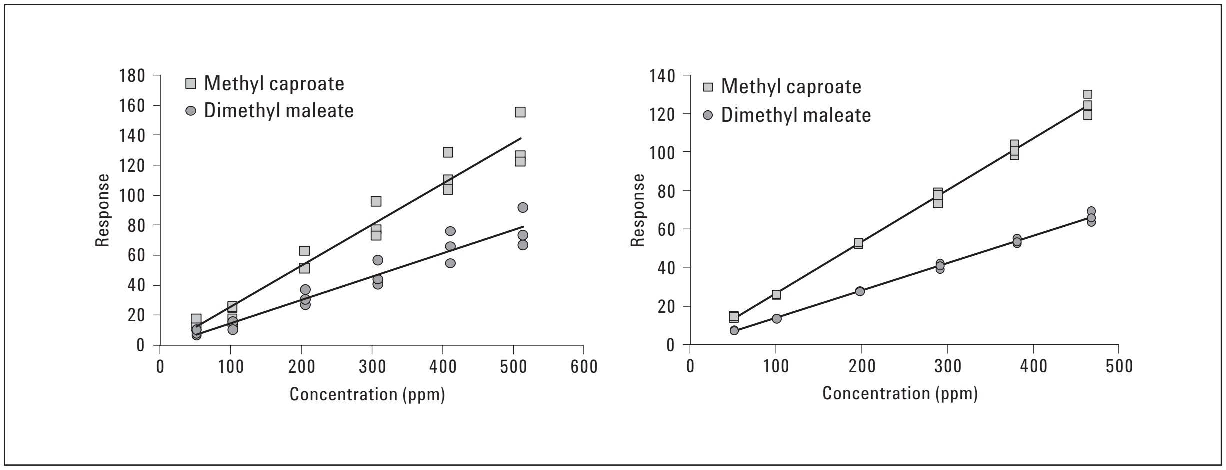

Figure 6. *Two calibration curves are shown for two representative analytes. The curves on the right, prepared with the Agilent 7696 Sample Prep WorkBench, are visibly more reproducible than the curves made manually on the left.*

Fatty Acid Derivatization

For sample derivatization, identical results were obtained whether the sample was derivatized manually or with the Agilent 7696 Sample Prep WorkBench. For a set of four fatty acids, no discrimination was observed in either method when derivatizing with a silylating reagent (Table 1). However, as seen with other sample preparation tasks, the Agilent 7696 Sample Prep WorkBench is more reproducible in its liquid delivery. The RSD from the peak areas for the three samples prepared manually 0.9%. The RSD for the three samples prepared with the Agilent 7696 Sample Prep WorkBench was 0.7%.

Table 1. *After normalizing the fatty acid peak areas to myristic acid, no discrimination was observed from automating the derivatization*

Analyte	Ratio-manual	Ratio-automated
Capric acid	0.92	0.92
Capric acid	1.2	1.2
Myristic acid	1.0	1.0
Palmitic acid	1.1	1.1

Conclusions

The three sample preparation tasks presented in this application note highlight the increased reproducibility achieved by automation with the Agilent 7696 Sample Prep WorkBench. Sample dilutions are accurate and reproducible, calibration curve standards are more linear with fewer errors, and sample derivatizations can be performed without analyte discrimination. However, additional benefits can be reaped through sample prep automation with the Agilent 7696 Sample Prep WorkBench.

By automating calibration curve standard preparation, solvent and reagent usage is significantly reduced. Instead of using >60 mL of solvent to make up standards in 10-mL flasks, only 600 µL of solvent was used, excluding the wash vials. This can result in substantial cost savings for laboratories. Additionally, calibrations curve standards required approximately half the time to complete with the Agilent 7696 Sample Prep WorkBench, compared to making up the standards manually. While the other automated sample prep tasks require the same amount of time to complete as the manual methods, the Agilent 7696 Sample Prep WorkBench frees the operator to perform other tasks, such as experiment design or data analysis.

Overall there are many benefits to sample prep automation with the Agilent 7696 Sample Prep WorkBench. While freeing personnel to perform other tasks and reduced solvent usage are important, the largest benefit comes from the reproducibility and accuracy achieved with this system. The automated methods showed better reproducibility and accuracy with fewer errors, thereby improving the quality of the data.

Reference

1. Susanne Moyer, Dale Synder, Rebecca Veeneman, and Bill Wilson, “Typical Injection Performance for the Agilent 7693A Autoinjector,” Agilent Technologies Publication 5990-4606EN.

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Agilent Technologies

GC Analysis of Sulfur Components in Propylene using a Sulfur Chemiluminescence Detector

Application Note

Hydrocarbon Processing

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Abstract

The Agilent J&W Select Low Sulfur column measures trace levels of target components in C3 hydrocarbon streams without any matrix interference.

Introduction

Hydrogen sulfide (H_2S), carbonyl sulfide (COS), and methyl mercaptan (CH_3SH) are common components in light hydrocarbon streams. They have corrosive and toxic properties, causing damage to pipes and equipment. The emission of undesired odors caused by volatile sulfur compounds in intermediates and final products have serious economic and environmental impact. In addition, the presence of sulfur can affect the performance of industrial processes, causing undesired chemical reactions, loss of catalyst activity (catalyst poisoning), and ultimately lower yield.

These sulfur components must be quantified at low ppb levels. They can be measured with sulfur specific detection devices such as the Sulfur Chemiluminescence Detector (SCD) but large sample volumes are needed to reach the desired low parts per billion (ppb) detection limits. This creates matrix overload and quenching effects (decreased signal/sensitivity due to background interferences) on most sulfur specific detectors, limiting the detector's sensitivity and linearity and raising quantification limits. The capillary PLOT column, Agilent J&W Select Low Sulfur column, with a novel stationary phase was developed for the analysis of sulfur species such as H_2S, COS and CH_3SH in light hydrocarbon C3 matrices, with high loadability properties and unique selectivity giving baseline resolution for sulfur components and matrix components.

Experimental

Technique:	GC-SCD
Column:	Agilent J&W Select Low Sulfur, 60 m × 0.32 mm (p/n CP8575)
Oven:	65 °C for 4 minutes, 30 °C/min to 120 °C for 5 minutes
Carrier gas:	Helium, constant flow, 2.0 mL/min
Injector:	200 °C, split 1:10
Detector:	SCD, 200 °C
Sample:	Propylene matrix containing ~300 ppb H_2S and CH_3SH, ~500 ppb COS
Injection volume:	1 mL
Injection:	Gas sampling valve

Results and Discussion

The stationary phase shows good selectivity between H_2S, COS and low mercaptans in various C3 hydrocarbon matrices. Therefore co-elution of the sulfur components and the matrix, which causes “quenching”, is avoided.

The system was equipped with a gas sampling valve. The gas sampling valve event table is shown in Table 1. The detector settings are shown in Table 2.

Table 1. Gas Sampling Valve Event Table

Time (min)	Gas sampling valve
Initial	Fill
0.01	Inject
1.00	Fill

Table 2. Detector SCD Settings

SCD settings	
Burner temperature	800 °C
Vacuum of burner	370 torr
Reactor hydrogen flow	40 mL/min
Reactor air flow	65 mL/min
Attenuation	1
Ozone air pressure	5 psig

Figure 1 shows a chromatogram of sulfur compounds H_2S, COS and CH_3SH in a propylene matrix. Methyl mercaptan shows peak broadening from column overloading by the large amount of propylene matrix. The propylene matrix elutes between COS and methyl mercaptan.

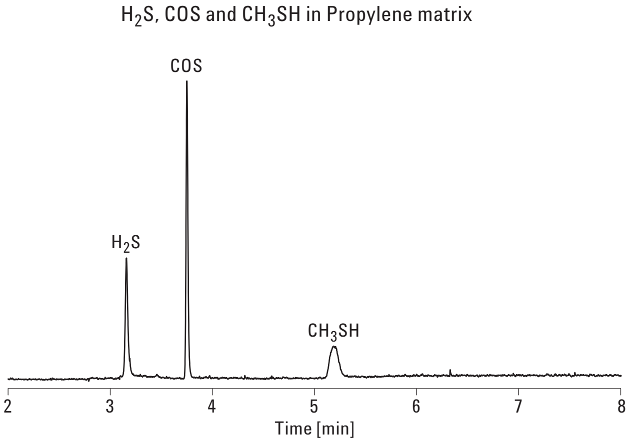

Figure 1. Chromatogram of H_2S, COS and CH_3SH in Propylene matrix, using the Agilent J&W Select Low Sulfur with GC-SCD.

Conclusion

The Agilent J&W Select Low Sulfur used in a GC with a sulfur specific detector, such as an SCD, can detect H_2S, COS and CH_3SH at trace level in a propylene matrix as a result of excellent separation of the sulfur compounds and the matrix. Separating the matrix from the sulfur components eliminates the “quenching” effects caused by the matrix. This provides a better response for the sulfur compounds. The column provides a good response for reactive sulfur compounds, such as H_2S making detections of 20 ppb possible.

Although this is a PLOT column, no spikes will be observed because the column does not shed particles. It can therefore be used safely in combination with switching valves.

References

1. W. Wardencki (1998) Review “Problems with the determination of environmental sulphur compounds by gas chromatography.” J. Chromatog. A. 793: 1-19.
2. Roger L. Firor and Bruce D. Quimby, “Comparison of Sulfur Selective Detectors for Low-Level Analysis in Gaseous Streams,” Agilent Technologies publication 5988-2426EN.

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Agilent Technologies

GC Analysis of Sulfur Components in Propylene using a Pulsed Flame Photometric Detector

Application Note

Hydrocarbon Processing

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Abstract

The Agilent J&W Select Low Sulfur column measures trace levels of target components in C3 hydrocarbon streams without any matrix interference.

Introduction

Hydrogen sulfide (H_2S), carbonyl sulfide (COS) and methyl mercaptan (CH_3SH) are common components in light hydrocarbon streams. They have corrosive and toxic properties, causing damage to pipes and equipment. The emission of undesired odors caused by volatile sulfur compounds in intermediates and final products have serious economic and environmental impact. In addition, the presence of sulfur can affect the performance of industrial processes, causing chemical reactions, loss of catalyst activity (catalyst poisoning), and ultimately lower yield.

These sulfur components must be quantified at low ppb levels. They can be measured with sulfur specific detection devices like the Pulsed Flame Photometric Detector (PFPD) but large sample volumes are needed to reach the desired low parts per billion (ppb) detection limits. This creates matrix overload and quenching effects (decreased signal/sensitivity due to background interferences) on most sulfur specific detectors, limiting the detector's sensitivity and linearity and raising quantification limits. The capillary PLOT column, Agilent J&W Select Low Sulfur column, with a novel stationary phase was developed for the analysis of sulfur species such as H_2S, COS and CH_3SH in light hydrocarbon C3 matrices, with high loadability properties and unique selectivity giving baseline resolution for sulfur components and matrix components.

Experimental

Technique:	GC-PFPD
Column:	Agilent J&W Select Low Sulfur, 60 m × 0.32 mm (p/n CP8575)
Oven:	65 °C isotherm
Carrier gas:	Helium, constant flow, 2.0 mL/min
Injector:	200 °C, split 1:20
Detector:	PFPD, 200 °C
Sample:	Propylene matrix containing ~500 ppb H_2S, COS, and CH_3SH
Injection volume:	1 mL
Injection:	Gas sampling valve

Results and Discussion

The stationary phase shows good selectivity between H_2S, COS and low mercaptans in various C3 hydrocarbon matrices. Therefore, co-elution of the sulfur components and the matrix, which causes “quenching”, is avoided.

The system was equipped with a gas sampling valve. The gas sampling valve event table is shown in Table 1. The detector settings are shown in Table 2.

Table 1. Gas Sampling Valve Event Table

Time (min)	Gas sampling valve
Initial	Fill
0.01	Inject
1.00	Fill

Table 2. Detector PFPD Settings

Combustion gases	
Air (1)	17 mL/min
H_2	13 mL/min
Air (2)	10 mL/min
Trigger level	250 mV
Tube voltage	550 V
Sampling delay	6 ms
Sampling width	20 ms

Figure 1 shows the chromatogram of sulfur compounds H_2S, COS, and CH_3SH in a propylene matrix. Methyl mercaptan shows peak broadening from column overloading by the large amount of propylene. The propylene matrix elutes between COS and methyl mercaptan.

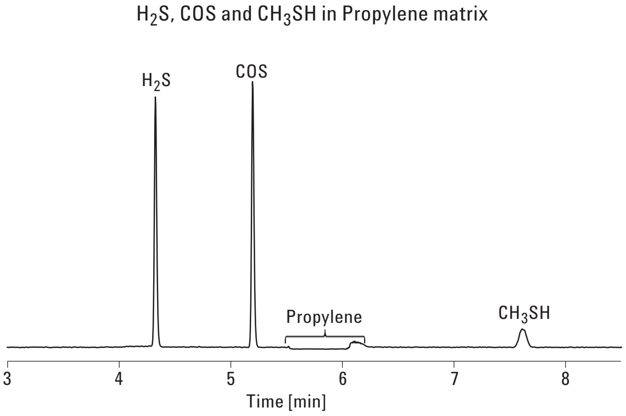

Figure 1. Chromatogram of sulfur compounds H_2S, COS and CH_3SH in a propylene matrix, using the Agilent J&W Select Low Sulfur with GC-PFPD.

Conclusion

The Agilent J&W Select Low Sulfur used in a GC with a sulfur specific detector, such as a PFPD, can detect H_2S, COS and CH_3SH at trace levels in a propylene matrix as a result of excellent separation of the sulfur compounds and the matrix. Separating the matrix from the sulfur components eliminates the “quenching” effects caused by the matrix. This provides a better response for the sulfur compounds. The column provides a good response for reactive sulfur compounds, such as H_2S, which makes detections of 20 ppb possible.

Although this is a PLOT column, no spikes will be observed because this column does not shed particles. It can therefore be used safely in combination with valves.

References

1. W. Wardencki (1998) Review “Problems with the determination of environmental sulphur compounds by gas chromatography.” J. Chromatog. A. 793: 1-19.
2. Roger L. Firor and Bruce D. Quimby, “Comparison of Sulfur Selective Detectors for Low-Level Analysis in Gaseous Streams,” Agilent Technologies publication 5988-2426EN.

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Agilent Technologies

Onsite additive depletion monitoring in turbine oils by FTIR spectroscopy

Fast, easy antioxidant measurement

Application Note

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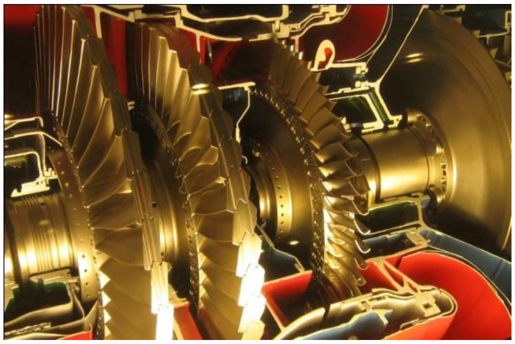


Abstract

Agilent 5500t FTIR spectrometers can independently measure phenolic and aminic antioxidants in turbine oil and provide the time sensitive results necessary to assist in preventing a non-scheduled shutdown by ensuring reliable operation of the turbine equipment. The 5500t FTIR system alerts, at pre-set warning levels, when the phenolic and aminic antioxidants are at or approaching minimal concentration milestones, and thus helps prevent turbine oils from reaching the critical point in the oxidation cycle of oil. Measurement is quick, easy and can be performed at-site. It requires no sample preparation, calibration, or electrode maintenance involved with voltammetric systems.

Introduction

The Agilent 5500t FTIR (Fourier transform infrared) spectrometer, a compact, easy-to-use and affordable system, provides the ability to perform real-time, onsite analysis of high value assets such as turbines. With 5500t FTIR spectrometers, the lubrication specialist has the ability to simultaneously monitor key parameters such as oxidation, additive concentrations and levels of water in lubricants. This application note will demonstrate the ability to monitor the depletion of key additives using the 5500t FTIR spectrometer.

Antioxidants in turbine oil

The phenolic and aminic antioxidants in turbine oils function as preservatives, which prevent the oil from oxidizing and forming harmful varnish deposits. Oxidation causes turbine oils to quickly lose viscosity and wetting characteristics, which protect metal contact surfaces and prevent wear. Oxidation arises from a combination of sources including elevated temperatures, extreme pressures, high shear conditions, the presence of water and metal particles, and is accelerated by electrostatic sparking, particularly in certain gas turbine systems. Antioxidants inhibit the formation of these decomposition products, however once the antioxidants are consumed, the process accelerates exponentially and at a certain critical point, corrective action has negligible benefit. The 5500t FTIR system measures both the antioxidant levels and the amount of oxidation present, to ensure that corrective action is taken before this critical point is reached.

Measuring antioxidants in turbine oil with the Agilent 5500t FTIR

The primary and most abundant antioxidant is the phenolic antioxidant, which works synergistically with the aminic antioxidant. It is postulated that the phenolic antioxidant protects the workhorse aminic antioxidant, which has the ability to recharge itself over and over during the cycles of oxidation. This is consistent with data we have obtained, as will be demonstrated later in this application note.

The phenolic and aminic antioxidants in turbine oil have prominent absorbance bands in select regions of the infrared spectrum, thus enabling FTIR spectroscopy to be an ASTM preferred means of measurement. Figure 1 shows one of the major infrared bands of the phenolic antioxidant in turbine oil and the change in the band, as a function of time, as the antioxidant is depleted. Similarly, Figure 2 illustrates the incremental diminishment of the aminic antioxidant as the turbine oil ages. These bands are so characteristic of these two species that they are often called 'fingerprint bands' and they are the functional groups that are automatically tracked by the 5500t FTIR spectrometer software.

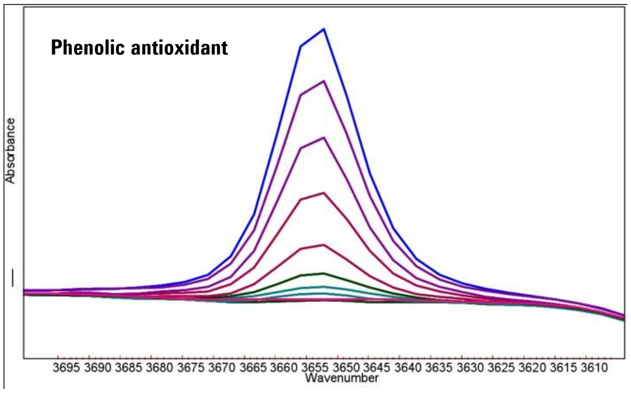


Figure 1. FTIR spectral overlay of the phenolic antioxidant functional group bands depleting as a function of time. The strongest band (light blue) is that of new ISO 32 turbine oil and the weakest absorbance (light green) is from turbine oil that has started to show some oxidation.

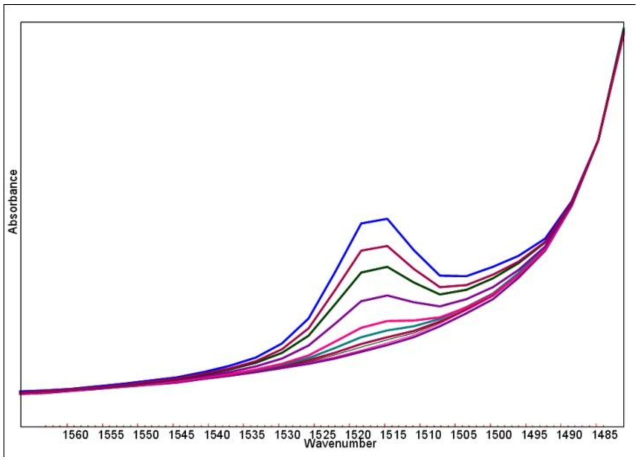
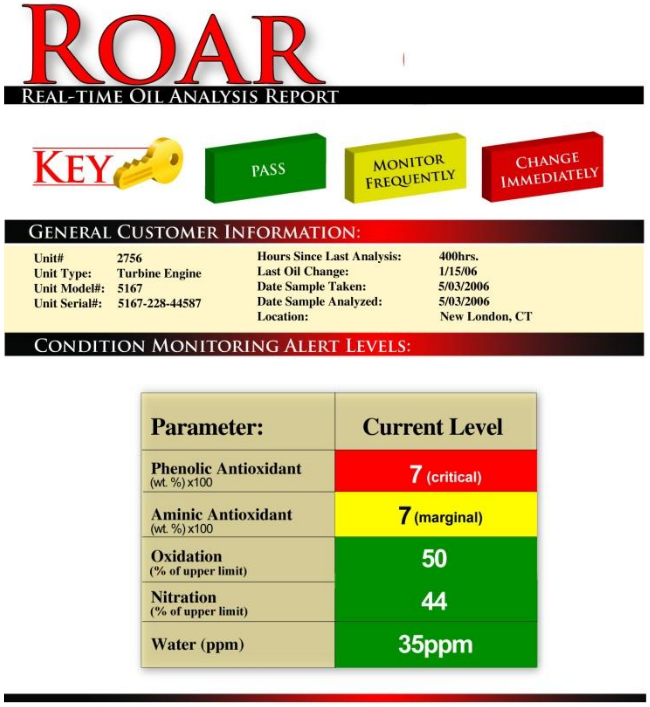


Figure 2. FTIR spectral overlay of the aminic antioxidant functional group depleting as a function of time. The strongest absorbance (red) is aminic antioxidant in new ISO 32 turbine oil and the weakest bands (blue and green) are from turbine oil with spent antioxidant.

The 5500t FTIR software (Figure 3) stores the FTIR spectrum of the initial new or reference oil. When in service used oil is measured, its spectrum is overlaid and compared to the reference oil. The user is provided a weight % for each phenolic and aminic antioxidant as well as a visual overlay of the spectral regions associated with each additive. The turbine oil methods also provide oxidation and nitration as a percentage of an upper limit, which is set from oxidation tests. The 5500t FTIR software is also programmed to inform the user via a yellow ‘Monitor Frequently’ warning when each additive is nearing the critical depletion points. Likewise, a red ‘Change Immediately’ warning is displayed on any additive, or other component such as water or oxidation, which has reached a critical threshold. Therefore, if both the phenolic and aminic antioxidants are in the red zone the critical saturation point for oxidation is imminent. The oxidation and ppm water are also provided with visual comparisons to the reference oil.



Unit# 2756
Unit Type: Turbine Engine
Unit Model#: 5167
Unit Serial#: 5167-228-44587
Hours Since Last Analysis: 400hrs.
Last Oil Change: 1/15/06
Date Sample Taken: 5/03/2006
Date Sample Analyzed: 5/03/2006
Location: New London, CT

Parameter:	Current Level
Phenolic Antioxidant (wt. %) x100	7 (critical)
Aminic Antioxidant (wt. %) x100	7 (marginal)
Oxidation (% of upper limit)	50
Nitration (% of upper limit)	44
Water (ppm)	35ppm

Figure 3. Agilent 5500t FTIR software presents the user with the specific concentration of phenolic and aminic antioxidants as well as crucial information about oxidation by-products and level of water contamination

The relationship between antioxidant depletion and oxidation

We will demonstrate the relationship of antioxidants and oxidation formation as well as the ability of the 5500t FTIR system to both predict and detect oxidation formation before the critical point is reached. Metallic iron and copper, known oxidation catalysts were added to used Chevron ISO 32 turbine oil that was in service 4 months in a steam turbine system. The iron and copper catalysts accelerate the inherent thermal oxidation mechanism, and are used in most oxidation potential tests such as RPVOT (D2272), Universal Oxidation Test (D6514 and D5846), and TOST (D943).

This mixture was heated at 135 °C for 26 days at atmospheric pressure in air, and small samples of the oil were removed every 2 to 3 days. The samples were analyzed using a 5500t FTIR spectrometer and the peak area measurements for phenolic antioxidant, aminic antioxidant, and oxidation products were recorded and plotted as a function of time as shown in Figure 4. As shown, the phenolic antioxidant diminishes to about 40% of the original amount in a relatively short time, however, the aminic antioxidant is observed to stay above 80% for almost the whole life span of the oil. Some of the initial drop in the phenolic antioxidant is due to evaporation which is a known problem with certain more simple phenolic antioxidants. The aminic antioxidant is observed to have three stages:

- Stage 1: The aminic antioxidant level is fairly constant and remains at this level approximately halfway thru the useful life of the oil. The initial slight increase in aminic may be due to volatiles in the oil, which can evaporate from the new oil during high temperature operation, thus slightly increasing the concentration of the aminic antioxidant.
- Stage 2: The aminic antioxidant depletes rapidly by about 25% at the mid-way point in the useful life of the oil.
- Stage 3: After the phenolic drops below 30% of the original concentration (70% depletion) the aminic begins a rapid descent from 80 to 40%. At this

critical point, the oxidation process accelerates exponentially. Corrective action would need to be taken prior to this stage in order to extend the useful lifespan of the oil.

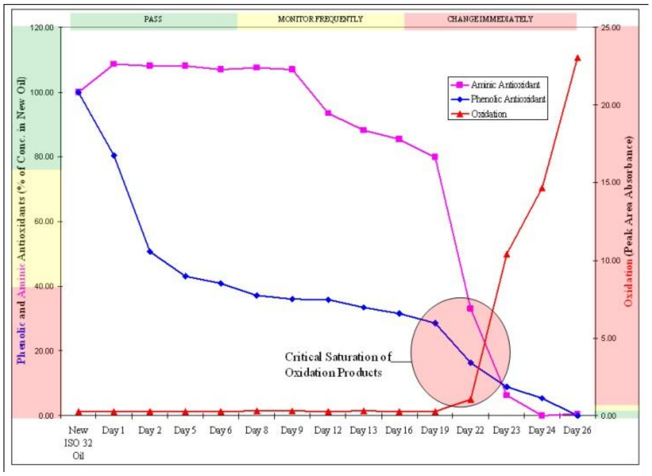


Figure 4. The additive depletion (% relative to new oil concentrations, left scale) and oxidation formation (right scale) trend analysis in thermally stressed ISO 32 turbine oil generated using the Agilent 5500t FTIR spectrometers

Lube 'useful life' measurements – Agilent 5500t FTIR versus voltammetric methods

As we have demonstrated in this application note, the 5500t FTIR system measures each antioxidant species individually, as well as providing a direct measurement of the degree of oxidation in the oil.

Cyclic voltammetric methods rely on mixing an exact amount of an oil sample with exact amounts of an electrolyte solution, the solution is shaken, at which point the antioxidants are extracted into the electrolyte solution. The results require a sample of the new oil for comparison and the used oil results are given in % depletion instead of exact concentrations such as weight %. This also causes inaccurate results if the used oil has been mixed with slightly different brands of oils. Another potential drawback to this technique is the antioxidant extraction from oil is never 100% efficient (typical extraction efficiencies are 75 to 95%), so not all of the active antioxidants are being measured. The pipetting required for voltammetric methods is not as accurate for higher viscosity oils, especially with gear oils or greases. Separate electrolyte solutions are needed for measuring oxidation and additional different solutions are needed to analyze crankcase or polyol ester based oils. The voltammetric method doesn't measure water or nitration, and contaminants in the oil such as EHC hydraulic fluid may cause inaccurate results. However, the 5500t FTIR spectrometer can detect the presence of contaminants such as EHC hydraulic fluid in turbine oils or gear oil in turbine oil.

The 5500t FTIR system requires only a drop of neat oil for its measurements and no sample preparation, whereas, voltammetric systems require careful pipetting techniques and an extraction step using an electrolyte solution. The FTIR system comes fully calibrated for weight % antioxidant functional groups in turbine, gear, hydraulic, and crankcase oils. Metal particles, water, or organic salts (that is, ionized carboxyls such as copper carboxylates) will not interfere with the antioxidant measurements using the 5500t FTIR system. The 5500t FTIR system has virtually no learning curve, requires no maintenance nor special chemicals or reagents for antioxidant measurement. Since the antioxidants can be monitored independently using the 5500t FTIR, re-additization can be carefully controlled and monitored. The effectiveness of top-offs, bleed and feed, filtration, and dehydration can be monitored as well. Mixing oil brands is not recommended, but the weight % phenolic and aminic antioxidants are still accurate measurements no matter what mineral oil basestocks are mixed together.

Conclusions

Agilent 5500t FTIR spectrometers are capable of independently measuring phenolic and aminic antioxidants in turbine oil and provide the time sensitive results necessary to assist personnel in preventing a non-scheduled shutdown by ensuring reliable operation of the turbine equipment. The 5500t FTIR system is designed to alert, at pre-set warning levels, when the phenolic and aminic antioxidants are at or approaching minimal concentration milestones, and thus help prevent turbine oils from reaching the critical point in the oxidation cycle of oil.

The capability of measuring additives in turbine oil by FTIR spectroscopy eliminates the issues associated with other measurements, including the need for sample preparation, calibrating, and maintaining electrodes based on voltammetric systems. The measurements are more rapid than electrode based antioxidant monitoring equipment, and minimize the dependency on the skill of the operator and the operating condition of the equipment. As importantly, the ability to measure antioxidant levels at-site via FTIR means that the results will be more convenient, more frequent, and obtained far more rapidly than samples that are sent for offsite analysis to a traditional oil analysis lab.

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Agilent Technologies

Low level detection of biodiesel in diesel fuel using the Agilent 5500t FTIR spectrometer

Application Note

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Background

Recent increases in production of biodiesel along with the high cost of crude oil have encouraged some producers to mix biodiesel with regular diesel fuel. Although biodiesel provides some environmental advantages, problems have been reported in the use of mixed fuels in engines designed for petroleum based diesel. Additionally, biodiesel can promote biological growth in the diesel fuel when stored for a period of time. In response to these issues there is a need to determine if biodiesel is present in regular diesel fuel, especially for industries which store large amounts of diesel fuel. The European Union has recently released regulations requiring the measurement of biodiesel in diesel and has issued an analytical test method, EN 14078, for testing.

In the United States, a recent ASTM ruling (D-975) allows shipments of up to 5% biodiesel in fuel without notification to the customer. This notification requirement does not meet the needs of all industries. As an example, the U.S. Nuclear Regulatory Commission (NRC) suggests lower limits for biodiesel in fuel blend for stationary standby diesel engines at nuclear plants because of the potential for instability of the higher percent biodiesel blends resulting from the buildup of oxidation products. These conflicting rulings make it incumbent on the user to verify the level of biodiesel before being placed in long-term storage.

The Agilent 5500t FTIR spectrometer provides an easy to use means of measuring biodiesel in diesel. The EN 14078 method comes pre-programmed on the 5500t FTIR spectrometer; this method can determine the amount of biodiesel in the range between 1 % and 10 %. The design is easy to use and provides nearly instant answers. In some cases, however, even lower levels of detection are required. To meet these needs, Agilent Technologies has modified the EN 14078 method to provide detection down to 0.025 % biodiesel in diesel. The Low Level Biodiesel in Diesel method can quantitatively determine the amount of biodiesel in the range from 0.025 % to 5 % with the same easy to use system.

Experiment

Six standards of biodiesel in diesel were made by successive dilution in the range from 0.0 to 1.5 %. Each concentration was measured using an Agilent 5500t FTIR spectrometer with a 100 μm path length Tumbler transmission cell; 32 scans were collected at 4 cm^{-1} resolution yielding a 15 second sample measurement time. Measurements were made in triplicate on two separate instruments. A calibration curve was made using the 1745 cm^{-1} carbonyl band specified in the EN 14078 method. The EN method specifies peak height but to achieve lower limits of detection the peak area was used in this method.

Results

Figure 1 shows the carbonyl region of the spectrum of the 6 samples tested plus a blank. The lowest concentration of 0.025 % is clearly visible with an absorbance which can be discerned over the blank. The absorbance increases linearly all the way to the highest concentration at 1.5 % biodiesel.

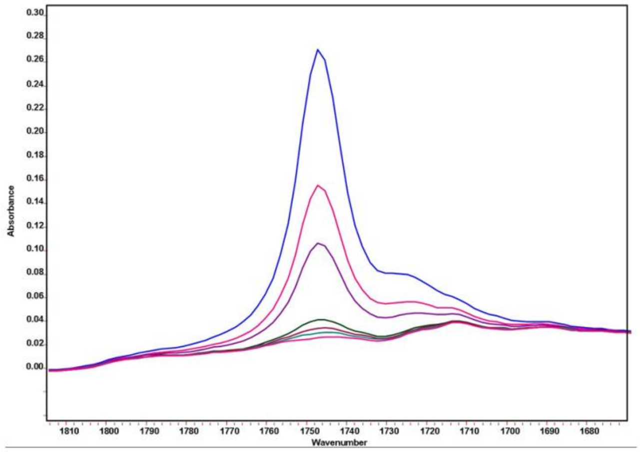


Figure 1. Absorbance at 1745 cm-1 of biodiesel in diesel fuel at 0.0, 0.025, 0.05, 0.1, 0.5, 0.8 and 1.5 % (v/v)

The calibration plot of the peak area of the 1745 cm^{-1} band is shown in figure 2. The plot shows an excellent correlation of $R^2 = 0.9998$.

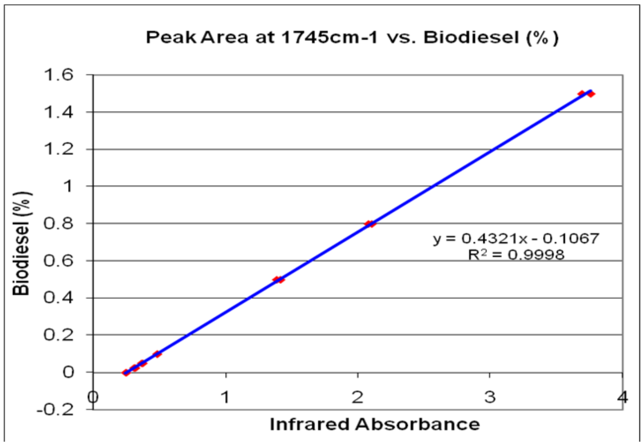
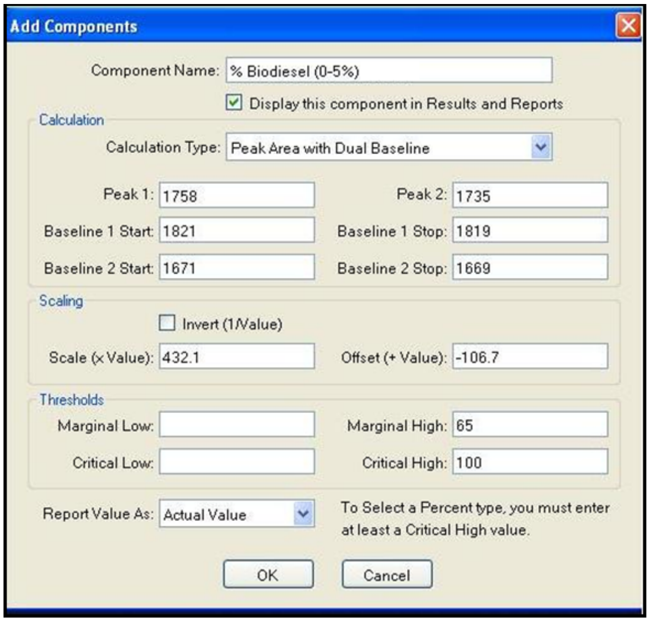


Figure 2. Calibration plot of biodiesel in diesel fuel showing linear fit of absorbance from 0 to 1.5 % (v/v)

The data from the calibration was used to generate a method in the MicroLab software. The method is shown in Figure 3.



Add Components

Component Name: % Biodiesel (0-5%)

☑ Display this component in Results and Reports

Calculation

Calculation Type: Peak Area with Dual Baseline

Peak 1: 1758 Peak 2: 1735

Baseline 1 Start: 1821 Baseline 1 Stop: 1819

Baseline 2 Start: 1671 Baseline 2 Stop: 1669

Scaling

☐ Invert (1/Value)

Scale (x Value): 432.1 Offset (+ Value): -106.7

Thresholds

Marginal Low: Marginal High: 65

Critical Low: Critical High: 100

Report Value As: Actual Value

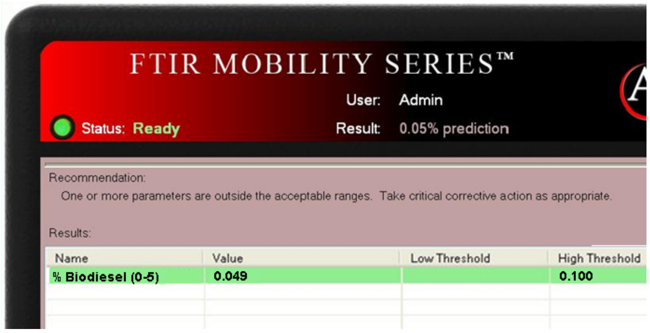
To Select a Percent type, you must enter at least a Critical High value.

Figure 3. Biodiesel method in MicroLab software

This method was used in the MicroLab software to predict the concentration of a separate validation set. The validation set ranged from 0 to 5% biodiesel in diesel. The average relative error was 1% with a maximum relative error of 2%. These results indicate that the same method can be used to predict concentrations at least as high as 5%. The results are shown in Table 1, and an example of the MicroLab software results screen is shown in Figure 4.

Table 1. Results from samples measured with the biodiesel method in the MicroLab software

Actual %	Peak Area Abs at 1745	Predicted %	Error (%)
0	0.245	0	0.0
0.025	0.307	0.025	0.0
0.050	0.365	0.049	2.0
0.100	0.482	0.101	1.0
0.5	1.382	0.491	1.8
0.8	2.078	0.790	1.3
1.5	3.691	1.488	0.8
3.0	7.122	2.971	1.0
5.0	11.674	4.938	1.2
		Average error:	1.0
		Maximum error:	2.0



FTIR MOBILITY SERIES™

Status: Ready

User: Admin

Result: 0.05% prediction

Recommendation:
One or more parameters are outside the acceptable ranges. Take critical corrective action as appropriate.

Results:

Name	Value	Low Threshold	High Threshold
% Biodiesel (0-5)	0.049		0.100

Figure 4. MicroLab results screen for a 0.05 % sample of biodiesel in diesel

www.agilent.com/chem

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Agilent Technologies

Test method for low level detection of biodiesel in diesel using the Agilent 5500t FTIR spectrometer

Application Note

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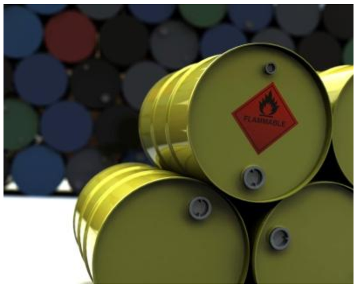

Introduction

Agilent Technologies 4500t and 5500t FTIR spectrometers are gaining rapid acceptance for measuring biodiesel (%FAME) in diesel fuel for applications where low level contamination of diesel fuel by FAME is problematic. Diesel fuel containing up to 5 % biodiesel meets the ASTM D975 standard, which does not require disclosure of the biodiesel level, and this can be a significant issue for certain diesel fuel users. Agilent has now developed an enhanced method for determining contamination levels of FAME in diesel. This method combines the more sensitive transmission IR sampling interface specified in EN 14078 with the universal algorithm and sample set specified in ASTM D7371 to produce the most sensitive and accurate method available. This enables the 5500t FTIR systems to quickly and accurately predict the percentage of biodiesel in diesel fuel in the range from 0.025 % to 20 %. In round robin testing, the accuracy of this method has been found to be superior to the other methods, especially for measuring low levels of biodiesel.

Instrumentation

The Agilent biodiesel test method was designed around the 5500t FTIR series of portable spectrometers, equipped with the innovative, patented sampling interface. This sampling system has been engineered to provide a highly reproducible 100 micron transmission pathlength, as called for in the EN 14078 method. The sample interface is one area where the ASTM method differs from the EN method. The ASTM method specifies an attenuated total reflectance (ATR) sample interface; the EN method specifies a transmission sample interface. The ASTM ATR method is easy to use, but does not provide the level of detection required for measuring biodiesel contamination; the EN transmission cell method provides the sensitivity required, but traditional IR transmission cells are not easy to use with respect to both filling and cleaning, particularly for viscous liquids like diesel fuel.

Agilent FTIR transmission sampling interface is unique in that it provides the sensitivity and limit of detection as required in EN14078, but at the same time is as easy to use as the ATR cell employed in ASTM D7371. In the sampling system, the upper window of the transmission cell is mounted in a precision rotating assembly. This opens by rotating this window into the upward position. Then, a single drop of fuel is placed on the bottom transmission window, the upper window is then rotated back into the closed position creating a path length of 100 micrometers. Clean-up is equally straightforward, since the sample is simply wiped from the windows when the FTIR instrument is in the open position. This patented sample interface gives the ease of use of the ATR measurement with the path length and sensitivity of a transmission measurement. Furthermore, the design provides a path length reproducibility of better than 0.2 micrometers. Representative spectra measured on the 5500t FTIR spectrometer of biodiesel in diesel are shown in Figure 1.

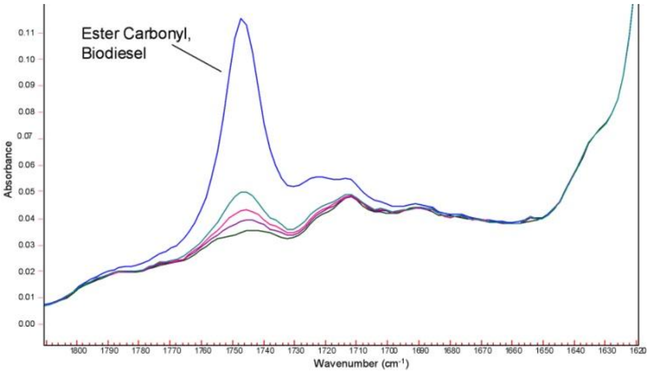

Figure 1. The overlaid IR spectra of diesel fuels with various ultra low concentrations of biodiesel, at 0.50 % (Blue), 0.10 % (Lt. Green), 0.05 % (Red), 0.025 % (Maroon), and 0.00 % (Dk. Green)

Calibration

In order to produce a quantitative measurement, the spectra generated from an infrared spectrometer must be calibrated with quantitative samples. The ASTM and EN methods specify different methods of quantitation. Both methods measure the carbonyl absorbance of the fatty acid methyl ester molecule; the EN method uses a simple linear fit to the band height while the ASTM method uses a multivariate, partial least squared (PLS) method. The univariate method specified in the EN method directly follows a Beers law calibration. As specified in the method, the absorbance of the carbonyl stretching frequency at 1745 cm^{-1} is measured with local baseline points at 1820 cm^{-1} and 1770 cm^{-1}. The absorbance intensity is then plotted against the concentration of 10 standards. A linear fit is used for the calibration curve.

ASTM D7371 specifies a more complicated multivariate PLS method. The method is still based on Beers Law; however, the full spectrum technique better accounts for baseline effects and interferents. In addition to the different algorithm, the ASTM method specifies a large collection of samples. The samples cover the entire calibration range and are made in three different diesel formulations: low, high, and ultra high Diesel Cetane Check Fuel (DCCF-Low, DCCF-High, and DCCF-Ultra High). The DCCF basestock fuels and biodiesel B100 used to create the biodiesel calibration and qualification standards are in compliance with specifications described in Annex 2 (A2.1, A2.2.1, A2.2.2, and A2.2.3). Varying the aromatic content of the diesel fuel used in the calibration and qualification sets creates a more robust and accurate PLS model.

Agilent's transmission IR based method incorporates 3 calibration models similar to the ASTM 7371 method; the Microlab software automatically selects the result from the correct calibration to display without any user input. The calibration ranges are 0.025-1 %, 1-10 %, 10-25 % biodiesel in petroleum diesel. The PLS model for the low biodiesel range (0.025-1 %) consisted of 70 spectra preprocessed with mean centering, baseline correction, and thickness correction and uses a portion of ester carbonyl region of the mid IR spectrum (1950-1720 cm^{-1}) similar to the ASTM 7371 method.

The calibration for the second range (1-10% biodiesel) consists of 46 spectra preprocessed with mean centering and baseline correction. The model uses a portion of ester carbonyl region of the mid IR spectrum (1800-1720 cm^{-1}) similar to the ASTM 7371 method. The third calibration (10-25 % biodiesel) uses 40 spectra preprocessed with mean centering and baseline correction preprocessing. Three spectral regions are used : the ester carbonyl at 1846-1758 cm^{-1} and 1738-1719 cm^{-1}, and the ester C-O stretch at 1327-1119 cm^{-1}

Method Performance

Each calibration model was tested with both a cross validation (leave one out) and a separate validation set. The cross validation data was used to calculate the standard error of cross validation (SECV) and to prepare an actual versus predicted plot. The correlation of the actual versus predicted plot was also calculated. The results of each model are listed in Table 2. All models produced a correlation greater than R_2= 0.999 and an average relative error for the separate validation set of less than 1.5%.

The Agilent method was compared to the ASTM 7371 method by two other analytical labs in a blind round robin experiment initiated and conducted by a third party. Twenty samples were received with no identification of their composition and run with the 5500t FTIR. The Agilent method performed the best of all six biodiesel methods, including the ASTM 7371 methods. The total average relative error was only 2.1% (all samples, 2-20% range), the low level accuracy was much better than any other method at only 1.1% relative error.

Range	SECV	R^2	#Validation Samples	Avg. Relative Error
0.025 - 1 %	0.0016 %	0.9999	29	1.37 %
1% - 10 %	0.0164 %	0.9999	12	0.06 %
10% - 20%	0.04 %	0.9999	8	0.57 %

Conclusion

Two established standard techniques exist for measurement of biodiesel in fuel by infrared spectroscopy: ASTM D7371 and EN 14078. Unfortunately, both of those methods are focused on measurement of levels consistent with blended fuels; they do not address the needs of users who need to minimize the amount of biodiesel in their fuel supply. Agilent Technologies, employing its 5500t FTIR system, combines the transmission sample interface specified in the EN 14078 method with the algorithm and standards specified in ASTM E7371, yielding a method that accurately predicts the percentage of biodiesel in diesel fuel in the range from 0.025 % to 20 %. The accuracy of this method has been tested and found to be superior to other methods, especially for low levels of biodiesel. Thus, users who must quickly and accurately detect low level biodiesel contamination in their diesel fuel supply will find this new technology and methodology of great value.

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Agilent Technologies

Rapid measurement of gasoline (petrol) in diesel fuel using portable FTIR spectroscopy

Application Note

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Introduction

Gasoline contamination in diesel fuel is a growing problem as diesel and alternative biodiesel blends are becoming more popular for commercial and personal fuel consumption. Gasoline can contaminate diesel fuel stocks in transit from the refinery to the final destination via tanker trucks, railcars, pipelines, or cargo ship. Gasoline contamination of diesel fuel can also occur in underground storage tanks at distribution facilities or end user filling stations. Some South American countries are experiencing problems with gasoline dilution of diesel to increase profits due to the lower cost of gasoline relative to diesel in certain markets. Some individual diesel owners mix gasoline into diesel to prevent gel formation in very cold winter locations.

Gasoline consists of light distillates with hydrocarbons in the C7-C11 range. Most hydrocarbons in gasoline are straight or branched chained aliphatics; although, 25-30 % of the hydrocarbons are aromatics consisting of hexagonal rings. Aromatics are more volatile and have lower flashpoints than their aliphatic counterparts, and high octane gasoline contains more aromatics. Additionally, gasoline in North America also contains 7-10 % ethanol (oxygenate), which lowers the smog emissions of gasoline engines.

Diesel fuels are middle distillates from the refining process and consist of hydrocarbon chains greater than C12. These longer hydrocarbon chains result in more energy per unit of volume; furthermore, the diesel combustion process is about 20 % more efficient than a spark ignition combustion engine. Both these properties make turbo diesel powered vehicles travel ~40 % further than an equal sized gasoline powered vehicle on the same volume of fuel. A gasoline contaminant in diesel fuel creates a mixture with less energy content, lower cetane value, and lower lubricity compared to straight diesel. This can cause coke formation (carbonization) on diesel fuel injectors and can also cause excessive wear on injectors, pistons, and other fuel contact engine parts. This is especially problematic for ultra low sulfur diesel (ULSD) due to its lower lubricity compared to agricultural diesel. Furthermore, gasoline can cause varnish deposits on diesel fuel filters to be washed off the filter and into the engine, which could clog injectors and contaminate other critical engine parts.

The chemical differences between gasoline and diesel can be seen in the infrared spectrum of each. Figure 1 shows a comparison between the infrared spectra of gasoline and diesel highlighting the ethanol and aromatics in gasoline. Neither ethanol or light aromatics present in gasoline are observed in the diesel fuel spectrum; in fact, the spectrum of diesel fuel is similar to mineral oil.

Diesel fuel does contain heavy aromatics, such as naphthalenes and other condensed ring compounds, but their infrared bands do not overlap the aromatics present in gasoline. The intensity of an infrared absorbance band is proportional to the concentration of that component in a mixture, as stated in Beer’s Law. This relationship allows the Agilent 5500t FTIR spectrometer to accurately measure gasoline in diesel fuels. The sensitivity of the 5500t FTIR allows gasoline to be measured down to 0.025 % in diesel. To demonstrate this, several concentrations of gasoline (87 octane) are carefully prepared in ultra low sulfur diesel (US, Danbury CT). The samples were prepared with 0 %, 0.0269 %, 0.2669 %, and 1.0586 % gasoline in diesel. The FTIR spectra were measured on the 5500t spectrometer and the gasoline absorbance results are plotted against their concentrations in Figure 2. This gasoline absorbance plot indicates a very good linear correlation with concentration. This linear correlation is common in spectroscopy and can be easily added to 5500 FTIR methods. Multiple components can be reported from a single 3 minute analysis, such as gasoline in diesel, biodiesel in diesel, oxidation, and water.

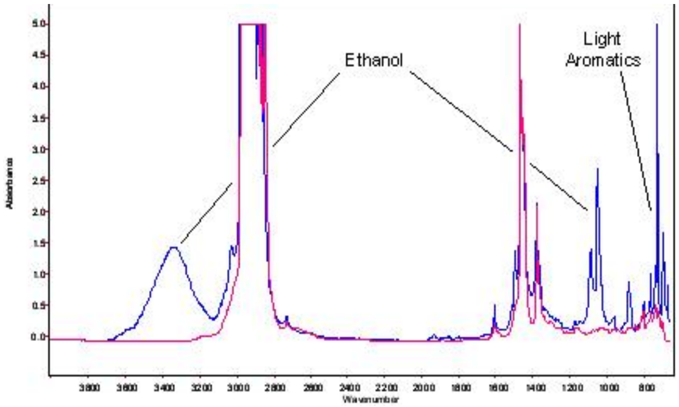

Figure 1. The IR spectral overlay of gasoline (Blue) and diesel fuel (Red) using the Agilent 5500t FTIR spectrometer, 100 µm pathlength

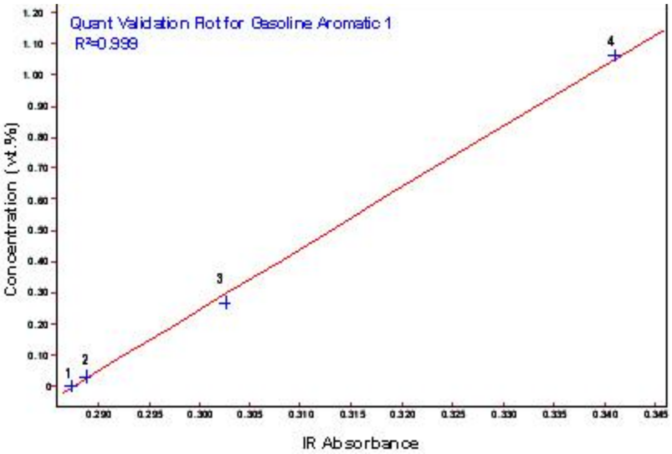

Figure 2. The IR absorbance vs. concentration plot for gasoline in diesel, Agilent 5500t FTIR 100 um pathlength

Conculsion

Fuel analysis using the Agilent 5500t FTIR spectrometer has been shown to accurately measure gasoline in diesel fuel from 0.025-100 % gasoline. This ability coupled with the 5500t FTIR's industry established measurement of biodiesel in diesel, provides highly sensitive on-site and field portable diesel contamination analysis. Oxidation and water contamination are also accurately measured using the same 5500t instrument.

The instrument can be operated from a laptop (5500t) or the Agilent 4500t FTIR which is a fully field portable version with an onboard battery and operated from a hand held computer (PDA). The instrument software is simple to use with little to no sample preparation. The instrument is not harmed by humidity or other outdoor conditions, weighs 8lbs, and takes up less bench space than a laptop computer.

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Agilent Technologies

Onsite quantitative FTIR analysis of water in turbine oil

Application Note

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Introduction

The availability of the Agilent 5500t FTIR spectrometers, which are compact, easy-to-use and affordable systems, provides new capabilities for real-time, on-site analysis of high value assets such as turbines. With the 5500t FTIR spectrometers, the lubrication specialist now has the ability to monitor key parameters such as oxidation, additive depletion and levels of water in lubricants. In this application brief, we will demonstrate that the Agilent 5500t FTIR spectrometer has the sensitivity, accuracy and reproducibility to determine the level of water in turbine oils without the difficulties associated with the conventional Karl Fischer technique.

Water in turbine oil

An important parameter to measure

The amount of water in turbine oil is critical to the performance and longevity of the equipment. Excessive amounts of entrained water in the turbine oil can cause premature failure of the turbine unit, typically due to changes in the physical properties induced by the presence of water. Physical properties of oil affected by the presence of water include viscosity (measure of the oil's resistance to flow), specific gravity (density of the oil relative to that of water), and the surface tension (a measure of the stickiness between surface molecules of a liquid). All of these properties are important for the ability of the oil to coat, lubricate, and protect the critical mechanical clearances. In addition, water in turbine oil can accelerate additive depletion and contribute to chemical degradation mechanisms such as oxidation, nitration, and varnish formation.

On-site analysis is highly desirable

The ability to measure water on-site, as soon as possible after drawing the sample, is a substantial benefit in obtaining accurate water level results. Off-site analysis for trace water in oil may be compromised due to variability of water concentration introduced by storage, transportation, or shipment of a sample. Furthermore, turbine oils contain demulsifying additives that cause microscopic water droplets to separate from the oil and concentrate in layers at the bottom and sides of containers. This demulsifying action takes time to occur, and can cause large variations in analytical measurements. Also, oil samples can sometimes pick up or lose water simply depending on the type of sample container used.

Measuring water in turbine oil

Karl Fischer (KF) coulometric titration is typically used to determine the amount of water in turbine oils. Karl Fischer has some practical draw backs for on-site analysis including complicated sample preparation, the use of hazardous and expensive chemical reagents, and length of time required to perform the analysis. However, KF analysis is considered the "gold standard" method for analyzing water in oil because it provides accurate and precise answers.

FTIR spectroscopic analysis eliminates many of the concerns associated with measuring water via Karl Fischer titration. The spectroscopic method, can be performed in far less time than KF measurement, does not require reagents and when a rugged and easy-to-use FTIR system such as the 5500t instrument is used, FTIR is ideal for on-site analysis. Karl Fischer titrations require about 10-15 minutes to perform, with the instrument properly conditioned and equilibrated overnight. For KF analysis the oil must be carefully weighed on a high precision balance before and after injecting into the titration vessel. Following each analysis the KF instrument takes another 5-10 minutes to re-equilibrate. The FTIR analysis takes about 2 minutes to perform and is immediately ready for the next sample analysis after a simple cleaning with a tissue.

This application brief will demonstrate that FTIR spectroscopic analysis using the 5500t FTIR is as accurate and precise as the Karl Fischer method within the analytical range necessary for measuring water in turbine oil. Using the 5500t, we have developed two FTIR methods for water in turbine oil and have calibrated and evaluated them against the Gold Standard Karl Fischer procedure.

Water in turbine oil - the FTIR method

Used turbine oil (C&C Oil Co.) was homogenized with water and aged overnight at 70 °C to make a very high water standard. This standard was then diluted with various amounts of a used turbine oil mix, which contains oil in-service four months and another more degraded oil with a dark amber color. These dilutions had various amounts of water based on how much "as is" oil was added. The samples were mixed well and allowed to equilibrate for about an hour before they were analyzed by coulometric Karl Fischer titration (Metrohm 756 KF Coulometer) to determine the concentration of water. The samples were run in duplicate by KF before the infrared spectra were acquired using the 5500t FTIR spectrometer. The water concentrations for the prepared standards ranged from 22-3720 ppm (parts per million). The water IR absorbance measurement for each standard sample was plotted versus the corresponding KF water data to obtain a residual least squares linear regression. The IR spectra were also analyzed using a partial least squares method to develop a regression model for the quantitative predictions of water in oil.

Calibration results

The IR analysis and calibration models indicate a very good correlation between the 5500t FTIR measurements and the Karl Fischer water data. Two different methods were developed for the quantitative measurement of water in oil using the 5500t spectrometer. The first is a relatively simple conventional IR absorbance model following Beer's Law that uses the region of the IR spectrum in which water strongly absorbs, known as the O-H stretch region. The second method uses multiple regions of the IR spectrum with partial least squares (PLS) chemometric modeling to reduce the effects of noise, baseline variance, and other interfering factors.

Beer's law model

In the first method, a peak area absorbance measurement provides a detection limit of about 30 ppm water in oil (Figure 1). The IR spectra of 15 samples with KF water values ranging from 7-270 ppm were used to build a linear calibration curve that follows Beer's Law (Figure 2). The weakest water absorbance in Figure 1 is new turbine oil with 30 ppm of water (Red) and the strongest water absorbance is shown in blue with a KF water value of 1460 ppm. The calibration plot is shown in Figure 2 with a correlation coefficient of R2=0.977 and a standard error of validation (SEV) of ~40 ppm (20-270 ppm range). The addition of higher water concentration standards to the calibration improves the correlation coefficient to R2=0.996.

Therefore, this calibration is optimized for the low levels of water (<500 ppm), but is still quite accurate for predications of higher water levels above 500 ppm if necessary.

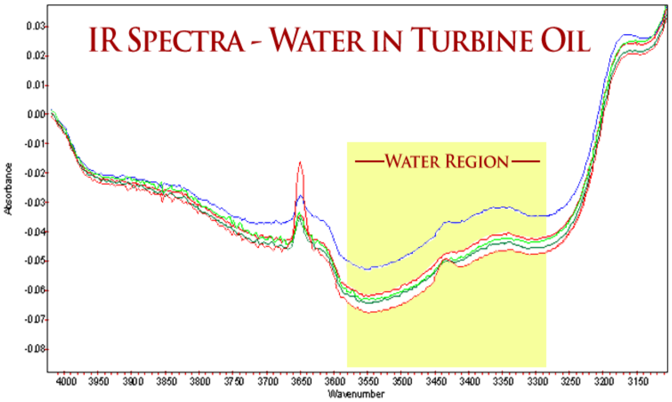

Figure 1. The overlaid IR spectra of turbine oil with the water absorbance region expanded, water values from bottom to top are 30 ppm (red), 80 ppm (dark green), 217 ppm (light green), 533 ppm (red), and 1460 ppm (blue)

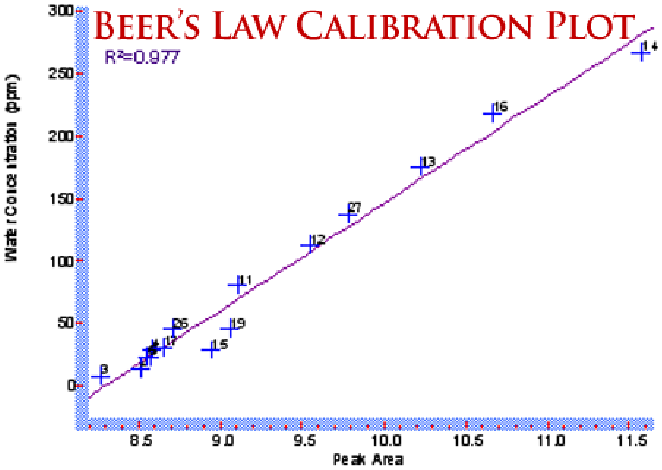

Figure 2. The calibration plot of KF water values (ppm) versus peak absorbance area for water in turbine oil using a Beer's Law peak area method

Pls model

The PLS chemometric model uses more sophisticated mathmatics to develop models that are typically more robust and accurate than the conventional Beer's Law IR absorbance method demonstrated above. Whereas both the PLS and the Beer's law quantitative methods for water in oil are sufficient for classification into 100 ppm ranges (i.e. <100 ppm, 100-200 ppm, 200-300 ppm, etc.), the PLS method provides the most accurate

KF water prediction values over the whole range of 30-1500 ppm.

In order to develop the PLS method for water in oil, we used 23 standards covering a range from 7-1460 ppm water. We then recorded the IR spectrum and measured the water level by the KF method. The two sets of results were correlated with partial least squares and the predicted versus actual KF values are plotted in Figure 3 and indicate a correlation coefficient of R^2=0.990.

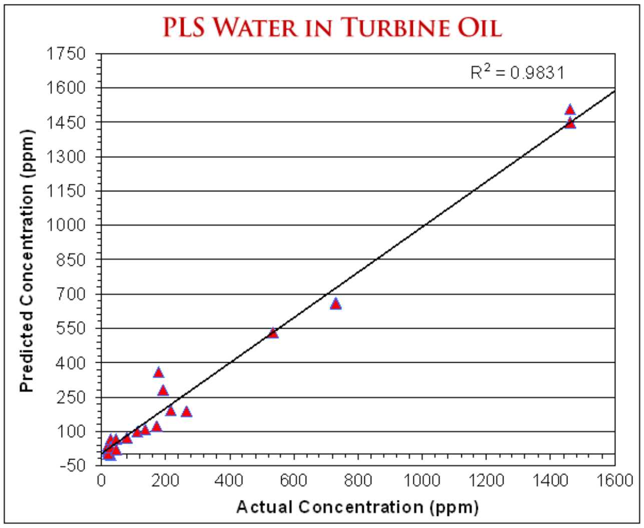

Figure 3. The PLS predicted versus actual plot of KF values using Agilent 4500 Series FTIR spectrometer

Predictions

To validate each FTIR method, 15 unknown mixtures were made by mixing used turbine oils with hydrated turbine oils, and running them by KF (in duplicate) and by FTIR (in triplicate). The coulometric KF performance was verified using 100 ppm and 1000 ppm NIST reference standards. It was found that thorough mixing was important to obtain quality data, due to the heterogeneous nature of water in turbine oil. Environmental and experimental factors caused the KF duplicate measurements to typically vary by 30-60 ppm, measured consecutively in the 100-1000 ppm range. The FTIR water predictions indicated similar variations in replicate measurements of the same sample. The averages of the replicate measurements by KF and FTIR are compared in Table 1. Good agreement with the KF measurements is observed for both FTIR methods, however, the PLS predictions are statistically better in the 100-1500 ppm range. The standard deviation between the averaged PLS predictions and the averaged KF data (0-700 ppm range) are all below 30 ppm, except for one sample (#11). The Beer's Law method predictions are better in the 0-100 ppm range, and are sufficient to classify the water concentrations into ranges as follows: <100 ppm, 100-200 ppm, 200-500 ppm, and 500+ ppm.

Validation Sample	Beer's Law (ppm water)	PLS (ppm water*)	KF (ppm water)
Turbine Oil 1	26.5	-	27.5
Turbine Oil 2	160	194.6	199.7
Turbine Oil 3	125.2	139	145.1
Turbine Oil 4	15.1	-	12.4
Turbine Oil 5	21	-	19.8
Turbine Oil 6	63	64.5	40.8
Turbine Oil 7	251.8	219.3	215.3
Turbine Oil 8	117.9	70.3	111.1
Turbine Oil 9	539.3	685.4	663.3
Turbine Oil 10	350	300	246
Turbine Oil 11	340.7	367.3	285.7
Turbine Oil 12	251.8	244.4	206.5
Turbine Oil 13	2979.3	3780.5	367.4
Turbine Oil 14	1100.3	1375	1027.5
Turbine Oil 15	1219.2	1541.9	1362.4

Conclusions

We have shown that the Agilent 5500t FTIR Spectrometer is capable of measuring water in oil at the levels that are critical to the reliable operation of the turbine equipment. The capability of measuring water in turbine oil by FTIR spectroscopy eliminates the issues associated with Karl Fischer measurements including the need for expensive and hazardous consumables, the time required for the KF measurement as well as the dependency on the skill of the operator and the operating condition of the KF equipment.

As importantly, the ability to measure water levels at-site via FTIR means that the results will be more accurate, more reproducible and obtained far more rapidly than samples that are sent for off-site analysis to a traditional oil analysis lab. We have observed that low ppm levels of water are observed to change on an hourly basis if left open to air - a sample that initially was 200 ppm can have less than 100 ppm if left in an open sample container overnight. This is also true if the sample container is not filled to the top, and water can evaporate into the head space (air) of the jar. One can only imagine the level of error that is introduced when half filled jars are sent to off site labs.

The Agilent 5500t FTIR spectrometer can detect water at the necessary warning levels. The system can alert when water reaches 100 ppm and then issue a critical warning if the water reaches 200 ppm. In addition to the analysis of water, Agilent's Mobility spectrometers can measure the depletion of additives and determine the levels of oxidation and nitration by-products in turbine oils.

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Agilent Technologies

Portable measurement of biodiesel in diesel fuels by ASTM D7371-07 (FTIR-ATR-PLS method) with the Agilent 5500t FTIR spectrometer

Application Note

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Background

Biodiesel blending with current ultra low sulfur diesel (ULSD) fuels is increasing in popularity for both large scale fleet use and individual small scale consumers. The test method detailed in this application brief can be used for quality control purposes in the production and distribution of diesel fuel and biodiesel blends. The ASTM D7371 method is applicable to 1-100 volume % biodiesel (FAME) concentrations in diesel fuel oils; it applies to all common 5 % (B5), 10 % (B10), and 20 % (B20) biodiesel blends. The ASTM D7371 method coupled with the Agilent 5500t FTIR spectrometer provides an easy, accurate, and portable means for measuring the biodiesel content of a blended fuel with petroleum diesel fuel.

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Experiment

Following the ASTM D7371 procedures, three different diesel fuels are used to create the calibration standards. The cetane index in diesel fuels is varied by changing the relative percentage of aromatic to aliphatic hydrocarbons; higher cetane index fuels have less aromatic compounds. Cetane index is typically lower during cold months. The ASTM D7371 is designed to account for these seasonal differences in the diesel fuels. The ASTM certified B100 Biodiesel was mixed with diesel fuel blended at three different cetane indexes, referred to in the D7371 as diesel cetane check fuel low, high and ultra high. As specified in the method, a total of 70 standards were produced with biodiesel concentrations ranging from 0-100%. In addition to the calibration standards, 21 qualification standards were created with different concentrations than the calibration standards. The qualification standards were used to determine the method's accuracy and robustness.

All standards were measured using the Agilent 5500 Series FTIR spectrometers with an integrated 9 reflection diamond attenuated total reflectance (ATR) sample interface. The spectra were collected using 64 scans at 4cm-1 resolution yielding a 30 second sample measurement time. A partial least squares (PLS) model was developed using Thermo Galactic PLS/IQ software. The model concentrates on the ester carbonyl and other absorbance bands specific to fatty acid methyl esters (FAME). The PLS models were incorporated into Microlab software for an easy end-user biodiesel in diesel fuel application.

Results

A series of spectra from the calibration set are shown in Figure 1. Bands due to biodiesel can be seen both at 1741cm^{-1} and between 1170-1245cm^{-1}; these areas are correlated to the concentration of biodiesel in the D7371 method. The absorbance increases linearly with the concentration throughout the whole range from 0-100 %. This provides a very accurate and precise measurement using the 5500 Series FTIR spectrometers.

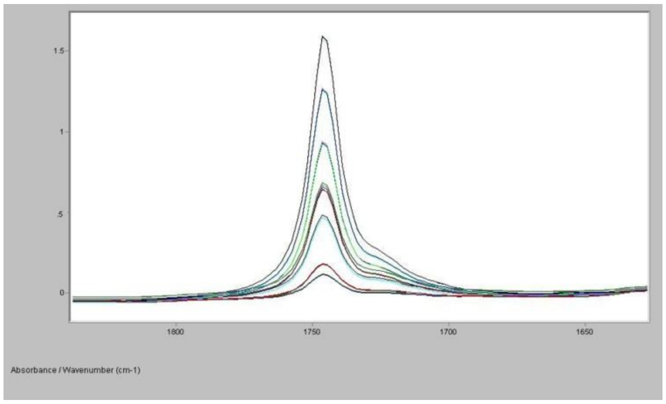


Figure 1. FTIR spectra overlaid of ASTM D7371 standards with biodiesel in diesel at 0, 2.5, 5, 10, 15, 20, 30, 50, 70, and 100 % biodiesel (v/v)

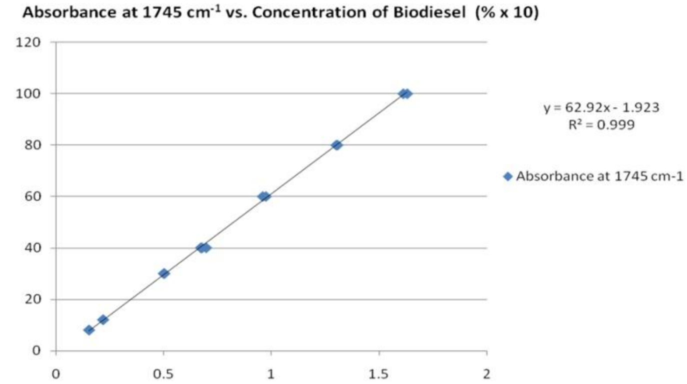


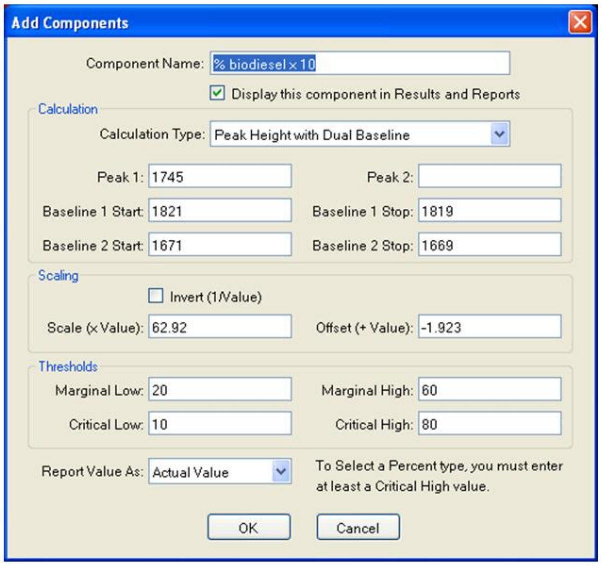
Figure 2. The PLS model's actual vs. predicted plot of biodiesel in diesel, low calibration set (0-10 % biodiesel)

ASTM D7371 specifies individual calibration models for the concentration ranges 0 -10 %, 10 - 30 % and 30 -100 %; each calibration model contains standards from each of the three cetane index diesel fuel stocks (ultra high, high and low). The 0-10 % calibration model results are plotted in Figure 2 as the actual (x-axis) vs. predicted (y-axis) biodiesel concentrations. The correlation coefficient for this model is R_2= 0.999. Results for the 10 - 30 % and 30 - 100 % models were similar. Each model uses 3 - 4 factors on mean centered data.

The three models based on the ASTM D7371 method were incorporated into a single method within the Microlab software. A screen shot showing one of the calibration definitions definition is shown in Figure 3.

The Microlab software also contains logic to report only the result from the correct model.

Using the "Component Reporting" feature, shown in Figure 4, which result will be shown to the user based on the predicted result. Using this feature, a single, correct result is present to the user even though results from three methods are calculated. This reduces confusion and allows samples to be measured by untrained users.



Add Components

Component Name: % biodiesel x 10

☑ Display this component in Results and Reports

Calculation

Calculation Type: Peak Height with Dual Baseline

Peak 1: 1745

Peak 2:

Baseline 1 Start: 1821

Baseline 1 Stop: 1819

Baseline 2 Start: 1671

Baseline 2 Stop: 1669

Scaling

☐ Invert (1/Value)

Scale (x Value): 62.92

Offset (+ Value): -1.923

Thresholds

Marginal Low: 20

Marginal High: 60

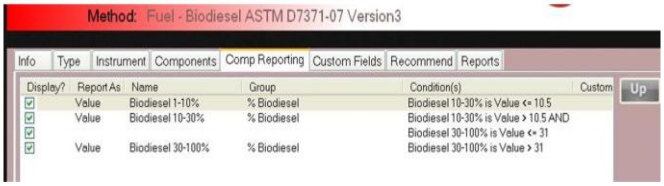
Critical Low: 10

Critical High: 80

Report Value As: Actual Value

To Select a Percent type, you must enter at least a Critical High value.

Figure 3. The Microlab methods editing feature where the 1-10 % biodiesel model is assigned



Method: Fuel - Biodiesel ASTM D7371-07 Version3

Display?	Report As	Name	Group	Condition(s)	Custom
☑	Value	Biodiesel 1-10%	% Biodiesel	Biodiesel 10-30% is Value <= 10.5	
☑	Value	Biodiesel 10-30%	% Biodiesel	Biodiesel 10-30% is Value > 10.5 AND	
☑				Biodiesel 30-100% is Value <= 31	
☑	Value	Biodiesel 30-100%	% Biodiesel	Biodiesel 30-100% is Value > 31	

Figure 4. The conditional reporting setup window from the Microlab PC software, which determines the model results to be displayed when running a sample

The Microlab ASTM D7371 method was used to predict the concentrations of a separate qualification set. The qualification set covers the entire 0-100 % range of biodiesel in diesel, and the different cetane index diesel fuels were also used to make the qualification samples. The average relative error (1-100 % range) is 0.47 % and the maximum relative error is 1.56 %. The results of the separate validation are shown in Table 1. It should be noted that the standard error of qualification calculated for these tests is less than half the acceptable standard error of qualification listed in the ASTM method. A screen shot showing the software display for a 2.5 % biodiesel validation sample is shown in Figure 5.

FTIR MOBILITY SERIES™

User: Admin

Status: Ready

Result: 2.5% 3_2009-04-28T16-26-14

Recommendation:
The biodiesel concentration is within acceptable levels.

Results:

Name	Value	Low Threshold	High Threshold
% Biodiesel	2.49		

Figure 5. Microlab results screen for a 2.50 vol % sample of biodiesel in diesel

Table 1. The results from the qualification set samples measured with the ASTM 7371 method in the Microlab software

Qualification Sample	Predicted Biodiesel (Vol %)	Actual Biodiesel (Vol %)	Error (%)
Q1	0.77	0.71	8.61
Q2	5.98	5.95	0.55
Q3	13.14	13.14	0.01
Q4	26.50	26.44	0.24
Q5	59.05	58.73	0.54
Q6	92.12	92.07	0.05
Q7	97.73	97.77	0.04
Q8	0.36	0.36	0.77
Q9	1.64	1.66	1.56
Q10	5.91	5.94	0.49
Q11	38.51	38.69	0.47
Q12	84.16	84.39	0.27
Q13	95.74	95.88	0.14
Q14	99.11	99.30	0.20
Q15	0.35	0.36	1.09
Q16	3.60	3.55	1.28
Q17	8.35	8.31	0.43
Q18	13.15	13.10	0.39
Q19	21.17	21.49	1.50
Q20	73.70	73.65	0.06
Q21	95.66	95.49	0.18
		Average Error Total (%)*:	0.47
		Maximum error (%*):	1.56
		Standard Error of Qualification (SEQ):**	0.08
		ASTM D7371 SEQ Limit (PSEQ):	0.21

Conclusions

This set of experiments show the ability of Agilent 5500 Series FTIR spectrometers with 9 reflection diamond ATR sample interface to meet the ASTM D7371 method. The method file which calculates the concentration in all ranges from 1 % to 100 % biodiesel and selectively reports the correct concentration is standard with all 5500 FTIR and 4500 FTIR systems. The results from a separate validation show that the instrument and method are very accurate while being very simple to use.

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Agilent Technologies

Returning to Fixed Pathlength Infrared Spectroscopy: Gaining Detail and Removing the Obstacles

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Introduction

This article discusses the benefits of making infrared (IR) transmission measurements from liquids with a fixed pathlength. The pros and cons, mainly cons, of traditional fixed pathlength cells are reviewed first, with the main "cons" being difficulties with filling and cleaning, and the need to protect the IR windows from moisture. ATR has become a practical alternative method for a liquid, however, the technique, by nature, is a surface-based measurement and there are significant limitations in regard to physical pathlength, which is very short.

A new system that provides a fixed pathlength IR transmission measurement for liquid sample handling and analysis is reviewed. The system features and integrated FTIR and provides three user-selectable pathlengths that are factory fixed at the time of purchase; nominally set to 30, 50 and 100/150 microns that can be used without the customary drawbacks of a fixed pathlength cell. A special sampling point, called a DialPath head (Figure 1A/B), is used to locate the sample between a pair of specially designed zinc selenide (ZnSe) windows. These are constructed not to generate any optical interference pattern in the recorded spectrum. The sampling point is easily accessible and sample preparation is reduced to applying a drop of liquid on the lower "window" and after the measurement the window is cleaned by a wipe with a tissue, Q-tip or paper towel.

Fixed pathlength measurements have the ability to provide fine detail in the measured spectrum. This is an important fact for quality-based measurements where subtleties or small variations differentiate "good" from "bad" materials. Some example applications are reviewed that illustrate the benefits of fixed path measurements. Comparisons are made with a standard laboratory-based FTIR equipped with fixed pathlength transmission cells to confirm equivalency. The featured applications include measurements of dilute solutions, alternative fuels and food products (dairy products and edible oils).

Background and the use of fixed pathlength cells

Originally, infrared spectroscopy was developed as a quantitative technique for liquid petroleum products (fuels and lubes) and polymers. It was later that it became the universal tool for material identification, as we know of today. The combination of material identification and quantitative response has made infrared spectroscopy unquestionably the most versatile instrumental method for chemical and physical analysis, covering a wide range of applications. As with any measurement, maintaining quantitative integrity by reproducible and accurate sampling is essential. In the infrared, maintaining a measureable pathlength, which is not trivial, is required for the accurate analysis of liquids. There are at least five critical factors to be considered and addressed:

- The need for a pathlength compatible with the absorption characteristics of the liquid in the mid-infrared (5000 cm^{-1} to 400 cm^{-1}/2.0 µm to 25 µm)
- Mechanical design issues of an accurate and reproducible short pathlength
- The filling, emptying and cleaning of the cells and the influence of the sample
- Window material selection based on the properties of the sample, and the optical characteristics of the window
- Alternative methods of sampling that reduce or overcome the difficulties associated with the sample...are they good substitutes?

It is obvious that there are important issues related to making infrared spectral measurements that become practical challenges. The first is the high infrared absorption cross section of most materials. Unlike other spectral regions, where cells or cuvettes are used with pathlengths measured in millimeters or centimeters, infrared measurements require pathlengths measured in microns. Generating a reproducible film of a sample this thin is a challenge. For years practical infrared spectral analysis has been performed with different methods of handling of liquid samples whereby the pathlength is controlled to the accuracy required for the analysis.

The standard, for 40 years, is the fixed pathlength cell, where the optical pathlength is generated by the use of thin spacers sandwiched between a pair of infrared transmitting windows. Two versions of these cells are used; demountable cells and sealed cells. Demountable cells are dismantled to simplify “filling”, “emptying” and cleaning. The windows are separated, and the sample is dropped into the void in the spacer, and then the top window is carefully replaced to form a sandwich with the liquid; taking care not to trap air. The problem with this approach is that assembly can be difficult and there is uncertainty in the pathlength formed. At best, it is a semi-quantitative approach to sample handling.

Sealed cells are required for accurate sampling. In a sealed cell the sample holder, the windows and the spacers have to be permanently fixed together. Such a cell is filled via special sample ports where the liquid is injected from a syringe into the cell. While this sounds simple, in practice it has significant practical drawbacks. Filling, where the liquid is “squeezed” into the confined space, which is at most 100 microns thick, is the first challenge. This can require the application of pressure from a syringe. This step requires extreme caution because the hydraulic pressure generated can damage the cell and can cause leaks. Originally, cells were sealed with special lead spacers treated with mercury to form an amalgam seal. Today, the use of these materials are not permitted, and non-toxic alternatives such as tin, steel or aluminum foils are used, sometimes in combination with an adhesive. Teflon sheet spacers are used in demountable cells and occasionally in sealed cells. However, the sealing integrity of Teflon-based spacers is questionable.

The next practical issue is emptying and cleaning the cell. As indicated above, a sealed, fixed pathlength cell is filled via filling ports. These are implemented by the use of a special drilled window, which is sealed against the metal front plate of the cell. This front plate has input tubes with female Luer fittings that couple to the male Luer tip of a syringe. The entire assembly, mounting plates, seals, windows and the selected spacer form the sealed, fixed pathlength infrared cell. This is a fragile, complex component that requires skilled assembly, and careful use, maintenance and storage.

These cells have been the mainstay of liquid sample handling of liquids for nearly fifty years. They are not ideal, they are expensive, and they are difficult to fill, empty and clean. If handled correctly, they are usually filled and emptied by a pair of syringes connected to the filling ports of the cell. This action takes skill and dexterity, and if not carried out carefully it will lead to the formation of bubbles; a serious interference in the measurement. Incorrect use can lead to cell damage, with resultant leakage of fluid. Also, short pathlengths (less than 50 µm thick) are especially difficult to use with samples of medium to high viscosity. Emptying and cleaning are equally difficult, and again a syringe is used to draw out the sample, and then to flush solvent through the cell until the cell is clean. Careful selection of the solvent is important to ensure dissolution of the sample, ease of removal and to ensure inertness towards the windows.

The best windows for good infrared transparency are sodium chloride and potassium bromide. While these are good optically speaking, they are water soluble and are readily attacked (etched) by moisture in the sample or by humidity in ambient air. Calcium fluoride and barium fluoride are water insoluble and moisture resistant they have a restricted range of infrared transparency (optical cut-offs at 1100 cm^{-1} for CaF_2 and 870 cm^{-1} for BaF_2). A practical alternative is to use windows made from zinc selenide (ZnSe). This material provides transparency similar to NaCl, and can be used to 650 cm^{-1}. The material is very durable and is not attacked by water. Unfortunately, it is not in common use as a cell window because ZnSe has a high index of refraction (Index = 2.4) and it introduces an interference pattern (sine wave) into the spectrum of most liquids. This interference is above an acceptable level and in most cases is impossible to remove from a final spectrum.

In summary, practical issues interfere with the ability to obtain fixed pathlength infrared measurements of liquids in traditional cells:

- The pathlength is required to be between a few micrometers (µm) and a few hundred micrometers (<200 µm, <0.2 mm)
- The pathlength must be accurately defined and reproducible
- Fixed pathlength cells are difficult to fill, empty and clean
- Window materials need to be carefully selected; materials such as ZnSe, which appear to be ideal, are unsuitable because of optical interference caused by a high index of refraction

Practical alternatives for fixed pathlength infrared measurements

In the 1980s the application of ATR was extended to include liquids. Commercial accessories based on cylindrical internal reflectance elements (IREs) or horizontally mounted IREs provided a practical solution. Zinc selenide turns out to be a good match for this application because of its optical range, hardness, high index and water insolubility. Consequently, ATR has become a de facto standard for the handling of liquids. ATR is a surface phenomenon and the physical optical pathlength is only a few microns deep. The effective pathlength can be extended by multiple internal reflections, where the liquid sample has multiple interactions with the internal reflections. Optical geometries with nine or ten reflections produce an "effective pathlength" in the range of 10 µm to 25 µm, dependent on the analytical wavelength.

There are downsides to the ATR measurement linked to the mechanism of the internal reflection. First, the physical pathlength, per reflection is short and is wavelength and index dependent. Consequently, the actual, physical pathlength is not absolute and is effectively unknown and variable.

Also, zinc selenide, a popular IRE substrate, is ionic and its surface is chemically reactive. Practical alternatives to zinc selenide exist, with diamond being a candidate. Commercial accessories exist based on diamond with configurations that provide from single to nine reflections for liquid handling. Diamond is an ideal substrate; it is very hard and is chemically inert. Optically it is limited in size and optical transmission with a loss in throughput performance for configurations with multiple reflections (3x and 9x).

The success of horizontal ATR accessories and diamond tipped ATR sampling systems must not be underestimated. Most laboratories have implemented these systems for liquid sample measurements. However, the approach is a compromise for many measurements. Non-reproducibility is an issue, but this can be improved by integration of the ATR into a dedicated instrument with rigid, permanent mounting. Although some non-reproducibility (linked to the index of refraction) may still exist, the permanent mounting of the IRE provides a fixed sampling point and is a popular method for routine sample handling.

The benefits offered by an integrated ATR measurement can be improved by the combination of the ATR with an optimized FTIR spectral engine. In such systems the sample can be applied to the sampling point from a dropping pipette, and the analysis completed in a few seconds. Cleaning is reduced to simply wiping material off the ATR sampling surface with a soft tissue, possibly followed by the use of a small amount of solvent. Moving forward, a similar easy-to-use interface would provide the ideal scenario for a fixed pathlength measurement. Such a system would offer the benefits of real extended pathlength, with the simplicity of a “drop-it-on”/”wipe it off” sampling point, and a measurement that is not compromised by the sample.

An integrated measurement system from Agilent Technologies, the 5500 Series FTIR and sample handling system, has been developed and introduced, fulfills this “idealized” concept for fixed pathlength sample handling. The implementation covered in this article uses a three-position version of the company’s 5500 DialPath FTIR rotary head, providing pathlengths of 30, 50 and 100 μm for the fixed path transmission measurements. This head, shown in Figure 1, is equipped with a slightly curved (bowed) zinc selenide window, which rotates to form a rigidly defined pathlength with the sample. Figure 1B shows the head located at position 1, which provides a nominal 30 μm optical path; the other two locations provide nominal 50 μm and 100 μm paths, respectively.

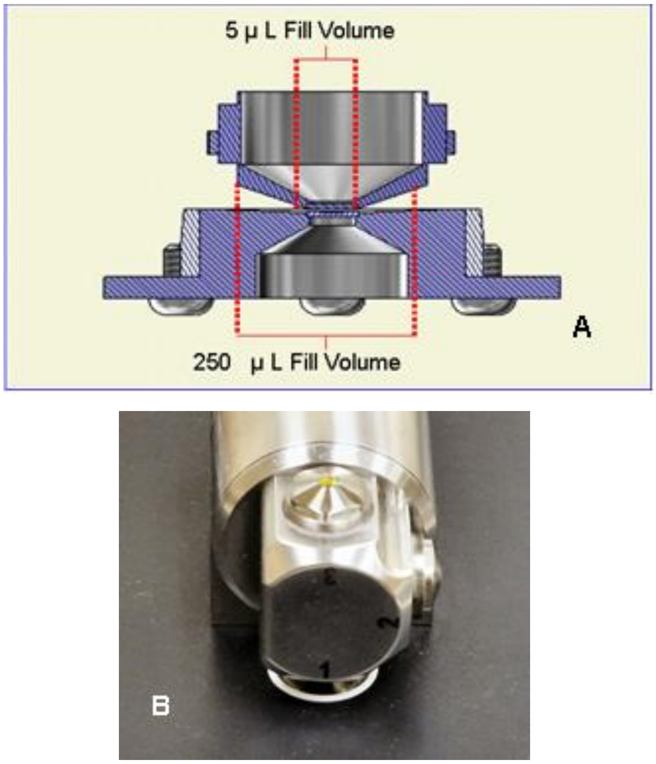


Figure 1. The 5500 DialPath FTIR sampling point concept (A); provides a user selectable pathlength, with one of three fixed/calibrated optical paths, designated 1, 2 and 3 (B)

This configuration provides the simplicity of the ATR sampling concept where the sample is dropped on to the small circular window, the sampling head is rotated in place, and the measurement made, in a few seconds. The liquid forms a uniform capillary film between the lower window and the window in the rotary head. The sweeping action of the rotary head produces a uniform film without any bubble interference. The slight curvature of the optical surface eliminates the opportunity to form an optical interference situation between the two zinc selenide windows. The optical, mechanical and water insolubility benefits of the zinc selenide windows are realized without the negative impact of optical interference. The lack of optical interference can be appreciated by Figure 2, where the three baselines (100% lines) for the empty window cavities are presented. These spectra, recorded in approximately 13 seconds have a nominal 8000:1 SNR across the analytical range of 2100 cm^{-1} to 1100 cm^{-1}.

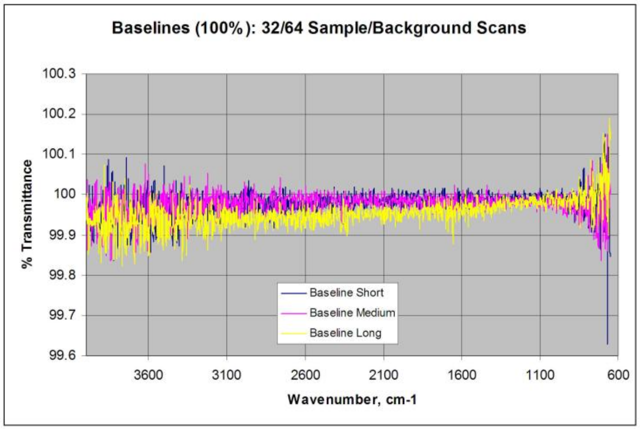


Figure 2. 100% Baseline performance; spectra from long, medium and short pathlengths presented with an average SNR of 8000:1 (2100 cm^{-1} to 1100 cm^{-1})

The SNR represented in Figure 2 is a significant result because it shows a flat 100% line without any artifacts caused by optical interference. The spectrum from a fixed pathlength cell constructed from zinc selenide windows would be dominated by a large sinusoidal pattern. This occurs with or without the sample in place. The lack of any interference pattern is further substantiated by the adherence to the square root law, where the SNR of the system is proportional to the square root of the number of scans (Figure 3). An excellent linear correlation is observed for the practical measurement timeframes; the presence of interference would result in significant deviation and curvature to this line.

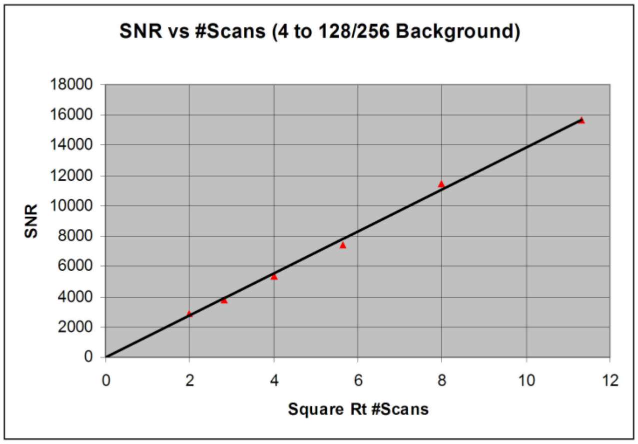


Figure 3. The adherence of the measurement system to the square root law of measured SNR

It is appropriate to compare the spectral data from a standard diamond ATR system with the fixed pathlength (5500 DialPath) measurement (Figure 4).

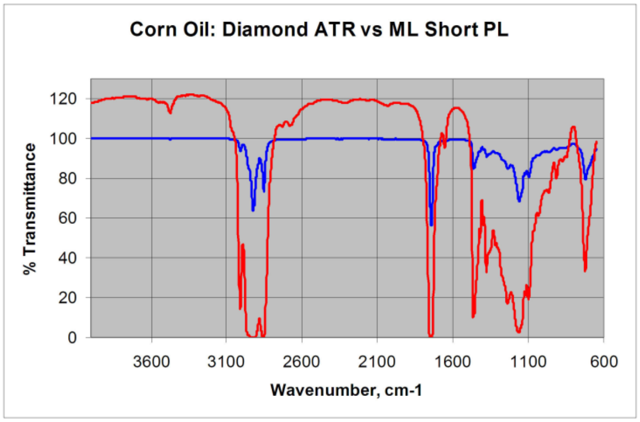
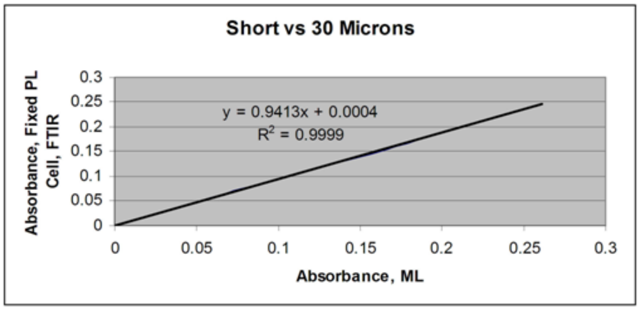


Figure 4. Comparison of the effective pathlength of a diamond ATR integrated system with the short fixed pathlength (~30 µm) transmission spectrum for corn oil

Both systems provide good quality spectral data, however, if one is looking for characteristic details in the spectrum for property measurements, such as the degree and type of unsaturation of an edible oil, then a long, fixed path measurement is required. One minor optical issue is that the high index of the ZnSe windows can be detected by the shift in the baseline of the corn oil above 100%. This result is the difference between the low index of the air (used for background), versus the higher index of the corn oil.

Analytically this is not a problem because the shift can be compensated from the absorbance form of the spectrum.

The reproducibility of the pathlength and the ability to dial in a longer pathlength are important attributes. The pathlength is defined by the height of the head from the measurement surface; a mechanical adjustment fixed at manufacture. The actual pathlength can be calibrated from the spectral response of fixed calibrated pathlengths in a standard lab instrument. The unit used for the data here was not pre-calibrated to exact values. The data shown in Figure 5 is taken from a series of standard xylene solutions prepared in carbon tetrachloride and recorded on the 5500a FTIR system. A parallel set of spectra were obtained on a commercial FTIR (PerkinElmer Spectrum 100) with a set of calibrated fixed pathlength, KBr cells (30μm, 50μm and 100μm). The results (Figure 5) indicate a high level of correlation between the two different sets of fixed pathlength spectra, providing calibration equations for the three 5500a system pathlengths; short = 31.9 μm, medium = 52.6 μm, and long = 114.7 μm.



	ML Pathlengths	PL Equation	Correlation
Short	31.9	y = 0.9413x + 0.0004	R2 = 0.9999
Medium	52.6	y = 0.9497x - 0.0013	R2 = 0.9998
Long	114.7	y = 0.8721x + 0.0018	R2 = 0.9992

Figure 5. Example calibration for the short pathlength (No 1) of the Agilent 5500 DialPath FTIR system based on comparisons with a calibrated fixed pathlength cell for a series of xylene solutions

These experiments have demonstrated that the fixed pathlengths of the 5500 DialPath system are highly reproducible, and once calibrated provide an accurate duplication of the fixed pathlength performance of the standard, calibrated fixed pathlength cells.

Practical applications of a fixed pathlength measurement system

The ability to measure with known fixed pathlengths is important for a wide range of applications. An obvious application is for the analysis of very dilute solutions where a pathlength of 100 μm or more is required. The application shown in Figure 6, are spectra of dilute solutions (<1% solute) of methanol are measured in a non-polar solvent (carbon tetrachloride).

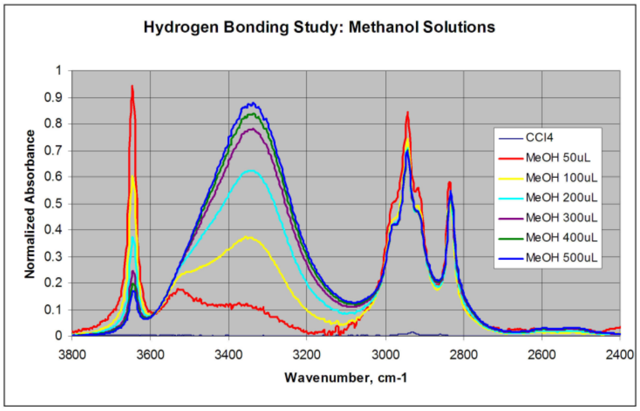


Figure 6: Dilute solutions of methanol in carbon tetrachloride; a study of the effects of hydrogen bonding in non-polar solvents

This is a classical measurement where changes in intermolecular hydrogen bonding are demonstrated. The normal condensed phase spectrum of methanol exhibits a broad absorption centered at 3450 cm^{-1} assigned to polymeric hydrogen bonding. Upon dilution with the non-polar solvent, this hydrogen bond profile changes as indicated in the red and yellow band profiles of Figure 6. These spectra correspond to the transition, through oligomeric forms to the non-bonded form with the narrow absorption at 3630 cm^{-1}. This experiment is only practical with a long path measurement (100+ μm in this case). The ATR method is impractical for this type of application.

The largest benefit of the open architecture of the 5500 DialPath system is the ability to handle medium to high viscosity liquids. Typical applications that are constrained by viscosity are measurements on vegetable oils (including cooking and edible oils), dairy products (such as milk, cream and butter products) and automotive products, including fuels, lubricating oils and greases. While an ATR liquid measurement system might be used for some of these applications, the increased spectral detail of a longer pathlength is preferred for product quality and performance-related measurements. Figure 7 is important for both edible and cooking oils and products derived from these materials, such as biodiesel fuels. Recent regulations on food quality and safety have focused on the need to eliminate trans unsaturated fats from food preparation. The total level of unsaturates and the type of unsaturates, including the trans configuration can be determined from the spectral region from 1000 cm^{-1} to 650 cm^{-1}. In the case of biodiesel, many quality parameters are linked to components formed in the esterification process. These components, such as free acid, free glycerol and glyceride fragments can be determined from the spectrum. These include the OH stretching region featured in Figure 7A where residual water (from esterification) and free glyceride components can be detected and measured. These measurements require the extended pathlengths used in the spectra shown in Figure 7A/B (100+ µm pathlength).

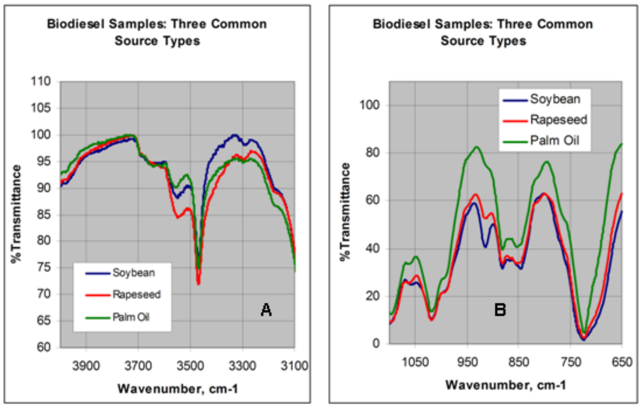


Figure 7. Detailed information from the base ester components used in the production of biodiesel methyl esters; hydroxyl (A) and unsaturation (B) functionalities

Another important issue for biodiesel is the level and type of unsaturation; a parameter linked to the chemical reactivity of unburned fuel residues in the engine oil.

Three common types of biodiesel are illustrated in Figure 7B, ranging from the rapeseed derivatives (common in Europe), the soy based product (USA), and the palm oil based product often used in Latin America and the Caribbean. These differences correlate with unsaturation and chain length. These considerations equally apply to edible oils, where unsaturation, molecular weight and reactivity are relevant to use at high temperatures.

Another important application of fixed path infrared measurements to biodiesel fuel is in the qualification of biodiesel blends. While biodiesel may be used as 100% of the methyl ester fuel, it is seldom used or distributed in that form. 100% biodiesel has a negative impact on vehicle emissions and it can attack materials used in the fuel system of a vehicle (tubing, seals and gaskets) Many vehicle/engine manufacturers, do not recommend its use; its use may violate and even void the vehicle powertrain warranty. Typically the fuel is used diluted with hydrocarbon diesel fuel to give 5 % to 20 % in blends designated B5 to B20. Figure 8 illustrates the measurement of biodiesel blends covering the full range from B0 to B100. Good calibrations for this series are obtained as indicated in Figure 9.

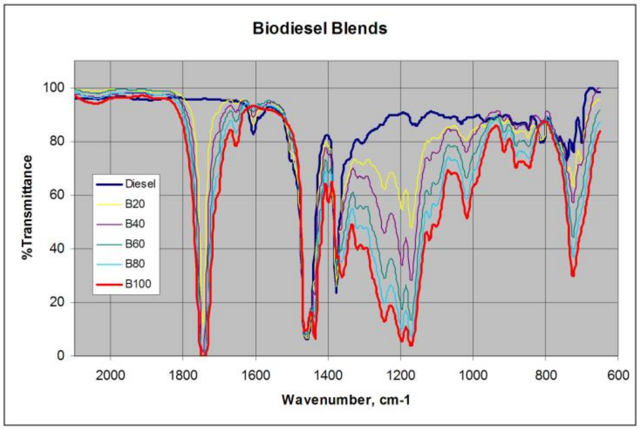


Figure 8. Measurement of biodiesel blends, experimental data from B0 (diesel fuel) to B100 (biodiesel) and intermediate biodiesel/diesel blends

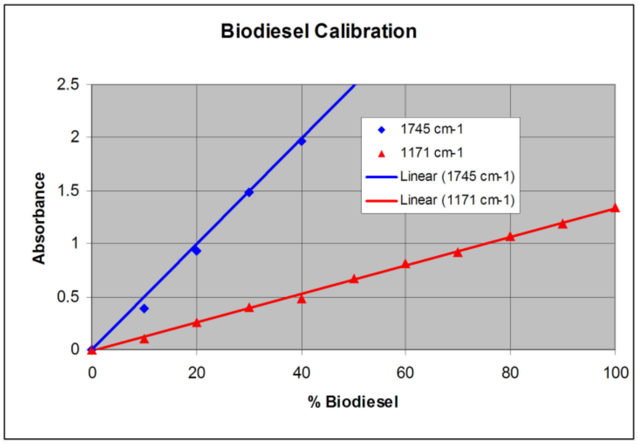


Figure 9. Quantitative measurement of biodiesel blends, B0, B10 to B90 and B10

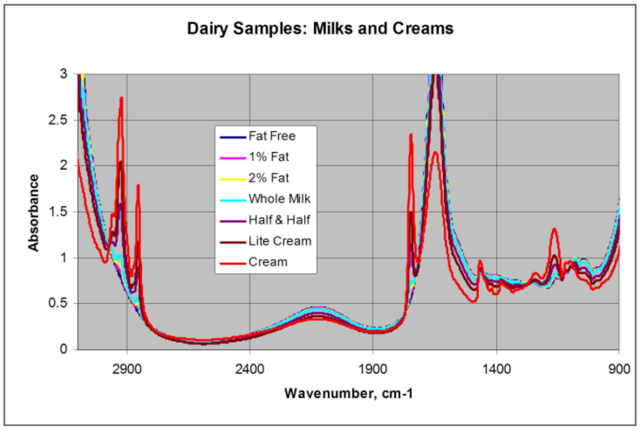


Figure 10. Dairy product spectra; short fixed pathlength (~30 mm), from fat free skim milk to standard heavy cream

The role of mid-infrared in the commercial analysis of milk and dairy products is well established. The measurement of raw milk in a fixed pathlength cell is used by regulatory agencies to control and standardize milk and dairy products. Standard methods exist for fat and protein content, which is used for the payment of the farmer. The performance and health of the dairy herd is also controlled, in pseudo real-time by monitoring fat/protein content. The results are used to control diet and medications. All of the relevant components in dairy products are derived from measurements of the infrared spectral data between 1800 cm^{-1} and 1000 cm^{-1}, a region that includes fat (ester), protein (amide bands) and sugars/lactose
(C-O-C, ether bands). Attempts to make these measurements in a standard sealed cell are fraught with difficulties. The accuracy of a fixed pathlength measurement is required, and the ease of handling high fat content materials, such as cream products, with the ease of cleaning, make the 5500a FTIR approach ideal for dairy product analysis.

Summary of the role and benefits of a “fixed” dial-a-pathlength system

This article has reintroduced the concept of making fixed pathlength mid-infrared transmission measurements without the complexity or the difficulties of the traditional sample handling method. A two-step approach summarized as “drop it on” and “wipe it off” is proposed, where the sample is put in place from a dropping pipette and is removed with the wipe of a paper towel. Anyone who has faced the challenges of working with the traditional fixed pathlength sealed cells can appreciate the ease of use and the simplicity of the system described. Traditional short path cells are impossible to fill with most liquids with average viscosity, and once filled, the cell can take five minutes or more to clean. The system described dramatically improves productivity and provides a platform for rapid, accurate quantitative analysis for all types of liquids.

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Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer

Application note

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Abstract

The OneNeb nebulizer for inductively coupled plasma optical emission spectrometry (ICP-OES) features unique Flow Blurring technology. Compared to previous nebulizers, this universal nebulizer provides improved sensitivity, greater tolerance to dissolved salts and strong acids such as HF, resistance to most common organic solvents and efficient operation over a much wider flow rate range.

This application note demonstrates the superior performance of the OneNeb nebulizer compared to commercially available glass concentric nebulizers usually provided with ICP-OES instruments. Detection limits and reproducibility were better in a range of analytes and liquids.

Introduction

The OneNeb nebulizer for use with an inductively coupled plasma optical emission spectrometer (ICP-OES) is a novel nebulizer that uses Flow Blurring technology. It is designed as a universal nebulizer offering a unique alternative to a variety of nebulizers by providing improved sensitivity, greater tolerance to dissolved salts and strong acids such as HF, resistance to most common organic solvents and efficient operation over a much wider flow rate range than existing nebulizers.

In this application note we will compare the performance of the OneNeb nebulizer to the commercially available glass concentric nebulizer normally fitted, using a range of performance criteria such as limits of detection and reproducibility using a range of analytes and liquids.

Description

The OneNeb nebulizer (Agilent part number 2010126900, Figure 1) is made completely from inert polymeric materials. It is physically robust and can withstand physical shocks that usually damage a glass concentric nebulizer.

Figure 1. OneNeb nebulizer

The capillary tubing extends nearly to the tip. The geometry at the tip, is carefully dimensioned to allow the carrier gas (in this case, argon) to mix with the sample liquid.

The OneNeb nebulizer uses Flow Blurring technology to mix argon with the sample to efficiently create an aerosol of smaller droplets with a narrower size distribution than conventional concentric nebulizers. Smaller droplets with narrow size distribution are more efficiently desolvated and excited in the plasma, ensuring better analytical precision and improved sensitivity.

By using Flow Blurring principles instead of the venturi effect for nebulization, the OneNeb is ideal for samples with high dissolved salts.

Other nebulizer designs

Concentric glass nebulizers (Figure 2) are the most common nebulizer type used in ICP-OES. The design features two concentric glass tubes with liquid pumped through the narrow inner capillary and argon forced through the gap between the inner sample capillary and outer quartz tube. A venturi effect creates an aerosol of relatively narrow droplet distribution, resulting in a nebulizer that provides good analytical RSD and detection limits. However, the narrow sample capillary is prone to blockages and precipitates forming on the end of the capillary that can affect nebulizer efficiency over time. Nebulizers using the venturi effect are not well suited for use with high dissolved salts because of this tendency to block.

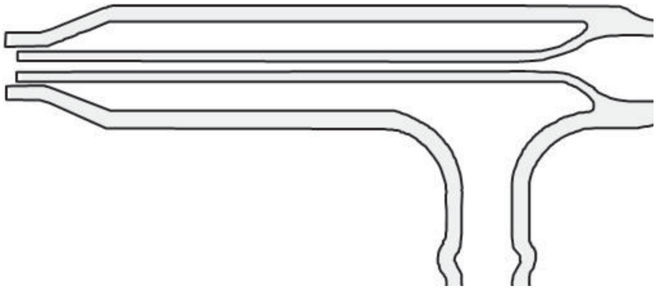

Figure 2. Concentric glass nebulizer

Nebulizers designed for samples with high total dissolved solids (TDS) such as the V-Groove nebulizer and cross-flow nebulizer do not rely on the venturi effect of the concentric glass nebulizer and are therefore more tolerant to dissolved salts. However, typically these nebulizers generate an aerosol with a wide range of droplet sizes resulting in higher analytical relative standard deviation and poorer detection limits.

Experimental

Instrumentation

An Agilent 725 ICP-OES with radially-viewed plasma and SPS 3 Sample Preparation System was used for this work.

The 725 ICP-OES features a custom-designed CCD detector, which provides true simultaneous measurement and full wavelength coverage from 167 to 785 nm. The CCD detector contains continuous angled arrays that are matched exactly to the two-dimensional image from the echelle optics. The thermally-stabilized optical system contains no moving parts, ensuring excellent long-term stability.

Operating parameters

- RF power: 1.3 kW
- Plasma gas flow: 15 L/min
- Auxiliary gas flow: 2.25 L/min
- Spray chamber: Single-pass and double-pass glass cyclonic
- Torch: Standard demountable with 0.38 mm quartz injection tube.
- Nebulizer flow: 0.7 L/min
- Replicate read time (for determining limits of detection): 30 s
- Number of replicates (for limits of detection): 10
- Stabilization time (for limits of detection): 30 s
- Replicate read time (for stability): 10 s
- Number of replicates (for stability): 6

Pump tubing

Two cases of pump tubing were used:

- Instrument: Orange-green (0.38 mm ID), of materials matched to the solvent being studied.
- Waste: Orange-orange (0.89 mm ID) Marprene for organic solutions.
- Instrument: Black-black (0.76 mm ID) for aqueous only.
- Waste: Blue-blue (1.65 mm ID) for aqueous only.

Results and discussion

The transport efficiency of the OneNeb at conventional flows is equivalent to a high-efficiency concentric glass nebulizer (Table1). As shown in Table 2, the OneNeb is capable of operating with even higher transport efficiency at very low sample flow rates, which a conventional concentric glass nebulizer is not capable of. Typically, for operation with low sample uptake rates, a specialized low flow nebulizer is required. The very high transport efficiency of the OneNeb at low flow rates makes it an ideal nebulizer for precious samples or samples with limited volumes, such as biological fluids.

Table 1. Transport efficiency at conventional ICP-OES uptake rates

Nebulizer	Solvent	Spray chamber	TE (%)
Glass concentric	Water	Double-pass	6.1
OneNeb	Water	Double-pass	6.6
OneNeb	Water	Single-pass	3.8–12.8

Table 2. Transport efficiency of OneNeb at very low uptake rates

Solvent	Spray chamber	TE (%)
Water (2–6% HNO_3)	Double-pass	12.5–18.79
Water (2–6% HNO_3)	Single-pass	17.7–31.4
ShellSol	Single-pass	44.0–48.7
Diisobutyl ketone	Single-pass	49.0

With organic solvents commonly used in ICP-OES analysis such as diisobutyl ketone and ShellSol, the OneNeb nebulizer provided excellent stability (Figures 3 and 4) over long-term runs, demonstrating excellent chemical resistance.

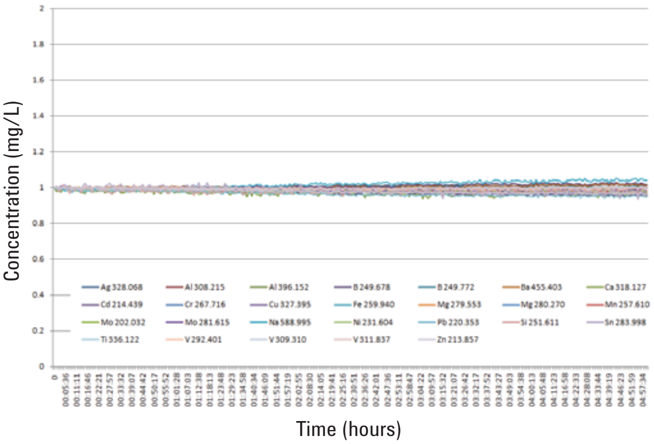

Figure 3. Long-term stability of the OneNeb nebulizer with diisobutyl ketone

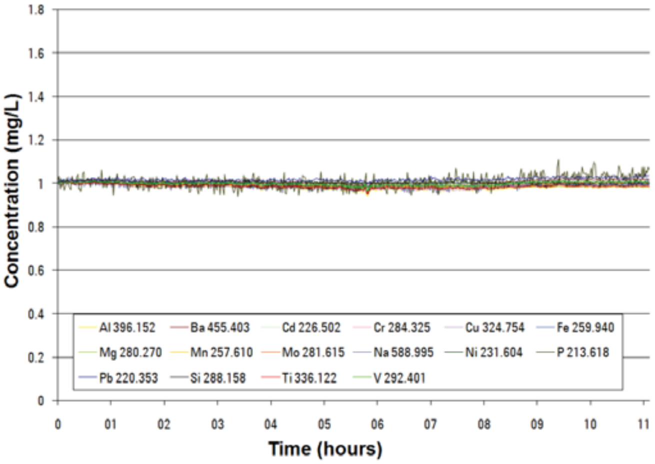

Figure 4. Long-term stability of the OneNeb nebulizer with ShellSol

The OneNeb nebulizer provided superior (>100% ratio) detection limits compared to the high performance concentric glass nebulizer for all elements analyzed, except for silver and zinc, which exhibited equivalent detection limits (Table 3).

Table 3. Comparison of 30 second detection limits (DLs) between concentric glass nebulizer (CGN) and OneNeb nebulizer

Element	CGN DL	OneNeb DL	DL ratio (%)
Ag 328.068	0.61	0.61	100
Al 167.019	1.94	1.53	127
As 188.980	12	9.84	122
Ba 455.403	0.07	0.05	162
Be 313.042	0.01	0.01	193
Ca 396.847	0.09	0.07	121
Cd 214.439	1.27	0.91	139
Co 238.892	1.9	1.7	110
Cr 267.716	0.86	0.70	123
Cu 327.395	1.76	0.96	183
Fe 238.204	0.90	0.68	132
K 766.491	59	38	154
Mg 279.553	0.05	0.05	107
Mn 257.610	0.19	0.15	131
Na 589.592	2	1.04	197
Ni 231.604	5	5	108
Pb 220.353	12	10	113
Se 196.026	17	13	133
Tl 190.794	15	12	129
V 292.401	1.24	0.96	129
Zn 213.857	0.50	0.49	101

Conclusion

The OneNeb nebulizer with Flow Blurring technology demonstrated excellent tolerance to samples with high TDS. Over weeks of extended testing of these high TDS samples, the OneNeb nebulizer proved virtually unblockable. This was in stark contrast to the regular failure of the glass concentric nebulizer due to blocking.

In terms of detection limits and tolerance to organic solvents, the OneNeb nebulizer proved superior to a high performance concentric glass nebulizer. Its resistance to strong acids such as HF proved similar to inert polymeric nebulizers. Tolerance to high TDS samples by the OneNeb nebulizer ranked it equal to nebulizers dedicated to handling high TDS such as V-groove nebulizers, without the deterioration in precision or detection limits in aqueous solutions.

The OneNeb nebulizer proved to be a genuinely universal nebulizer that is mechanically rugged and durable. It is competitive in price with a high performance concentric glass nebulizer. The OneNeb is capable of replacing many different types of nebulizers typically required to analyze the range of samples an ICP-OES is called upon to measure, without compromising performance. A universal nebulizer also simplifies method development and day-to-day operation by eliminating the need to decide which nebulizer is best for which sample, and reducing the need for many different nebulizers. It operates with very high nebulization efficiency at sample uptake rates from 40 µL/min, potentially allowing the analysis of volume limited samples.

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Using a Dual LTM Series II System with Flow Modulated Comprehensive GCxGC

Application Note

Application Area Identifier

Author

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Abstract

A comprehensive GCxGC system based on differential flow modulation is described that uses three independent programmable ovens. The first dimension separation occurs in the 7890A air bath oven while two simultaneous second dimension separations occur on 5 inch LTM Series II modules. All columns operate in constant flow mode. Oven temperature programs can be customized independently for each column. Typically the two LTM columns will be of different polarities and phase ratios to maximize the information that can be gathered from the sample. A typical column configuration consists of a 20 m x 0.18 mm x 0.25 µm DB5ms for the first dimension, a 7 m × 0.25 mm × 0.2 µm HP-INNOWax for LTM module 1 and a 5 m × 0.25 mm × 0.15 µm DB17HT for LTM module 2. Many other column combinations are possible.

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Introduction

Conventional flow modulated GCxGC usually consists of one first dimension column and one second dimension column where both are subjected to the same temperature program. The basic one-oven system has been described previously [1,2]. Flow modulation also has the distinct advantage of not requiring cryo fluids for operation, rather it relies on a high flow differential between 1st and 2nd dimensions for operation.

Careful matching of the retention factors (k) between the first and second column is necessary in a one-oven system in order to produce meaningful 2D data and avoid the wrap around effect. The wrap around effect occurs when analytes injected onto the second column do not elute in one modulation cycle. However, the single oven system is in widespread use for a variety of applications and works well if k's are matched appropriately.

Flow modulated GCxGC works best when all columns are operated in constant flow mode. The Low Thermal Mass (LTM) Series II system is fully integrated into the GC and MSD ChemStations and Agilent 7890A firmware allowing control of all parameters. Since this integration enables LTM to operate in constant flow, the system can be easily interfaced to a flow modulated GCxGC 7890 system.

Experimental

A diagram of the system is shown in Figure 1. A Capillary Flow Technology (CFT) splitter is used to direct the out flow from the CTF modulator to two LTM column modules for a simultaneous dual channel GCxGC analysis. Each column operates with its own independent temperature program.

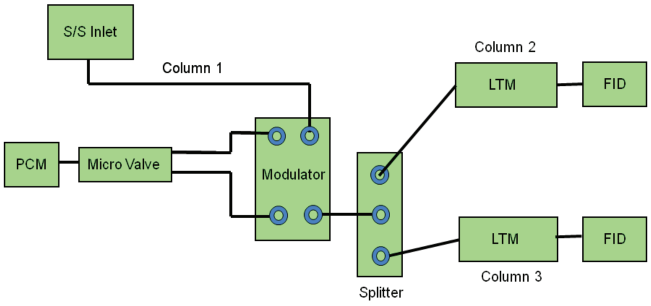


Figure 1. Diagram of the dual LTM GCxGC system.

The operation scheme of the flow modulator showing both the load and inject states is shown in Figure 2. Effluent for the first column fills the collection channel, and before significant diffusion or overfill occurs the three way valve is switched and a high flow (21 mL/min) controlled by the PCM injects the channel contents into the two second dimension columns. The modulation cycle then repeats based on the user set collect and inject times.

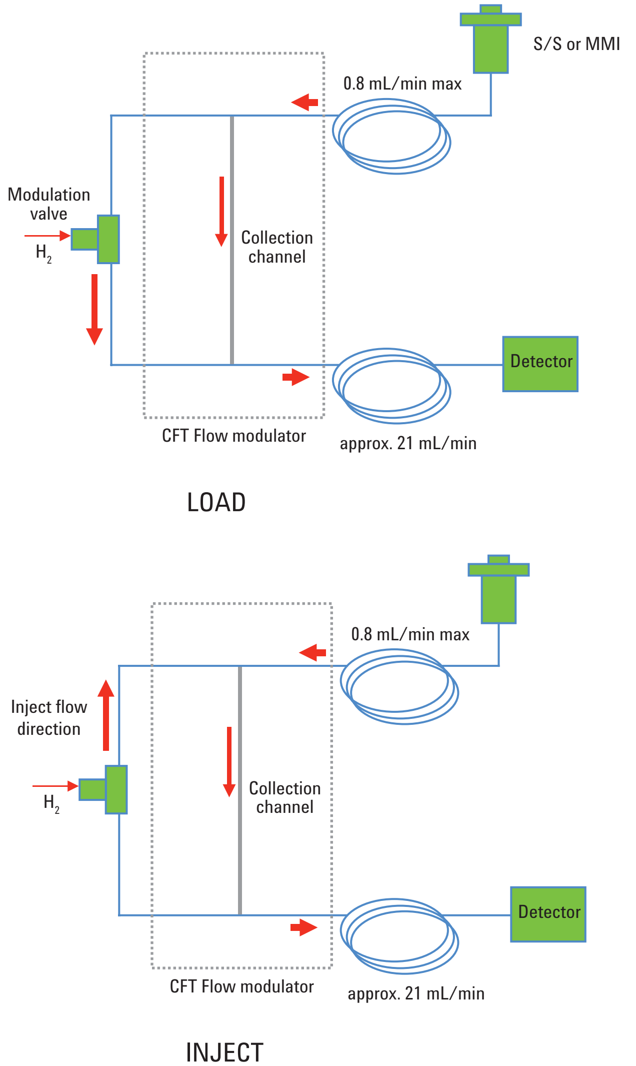


Figure 2. Operational detail of the flow modulator showing load and inject states.

Column 1 flow rate depends on column dimensions, but cannot exceed 0.8 mL/min. Figure 3 shows the relationship between modulation period and Column 1 flow rate.

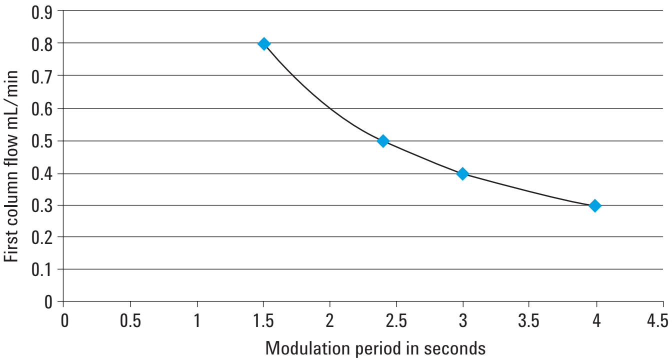
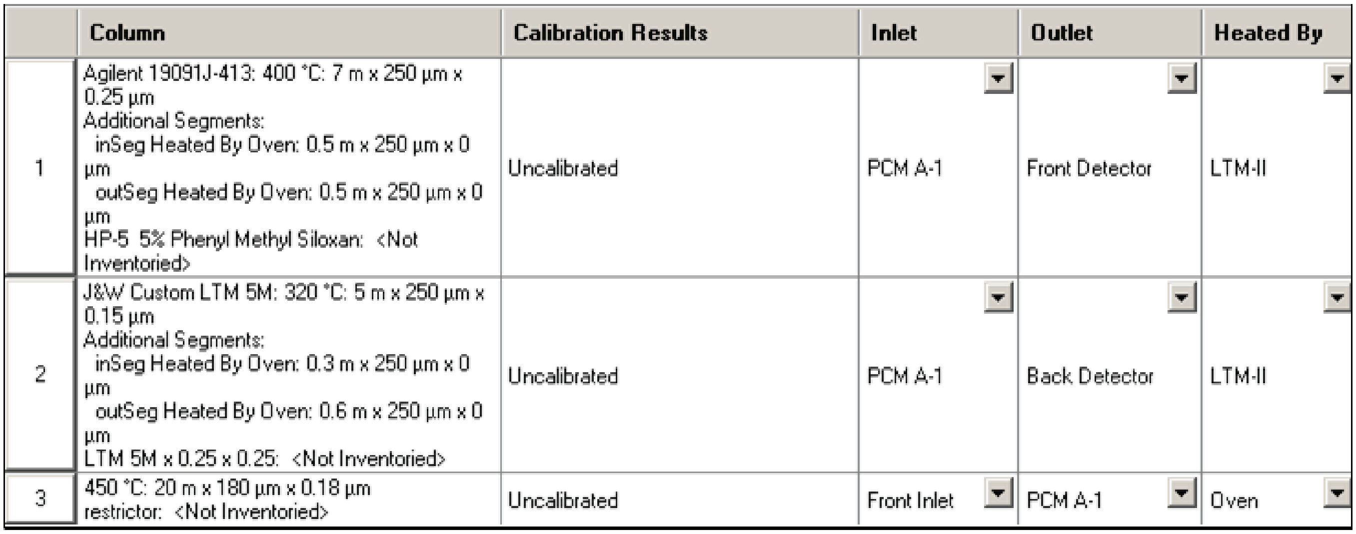


Figure 3. Relationship between modulation period and first dimension column flow rate.

Referring again to Figure 1, since LTM column flow rate is controlled by a single PCM, column flow will be the same in both modules provided they are of the same dimension. If this is not the case, the column configuration (in Chemstation) should set the PCM to control the longer or more restrictive column at 21 mL/min or greater. The second LTM column will then operate at a higher flow. Therefore, it is advisable that the two LTM columns do not differ greatly in length. Also, it is best to keep the second dimension columns at 0.25 mm ID. For this work, LTM column pairs were either both 5 meter or 5 and 7 meter. An example column configuration Chemstation pane for the system is shown in Figure 4.



	Column	Calibration Results	Inlet	Outlet	Heated By
1	Agilent 19091J-413: 400 °C: 7 m x 250 µm x 0.25 µm Additional Segments: inSeg Heated By Oven: 0.5 m x 250 µm x 0 µm outSeg Heated By Oven: 0.5 m x 250 µm x 0 µm HP-5 5% Phenyl Methyl Siloxan: <Not Inventoried>	Uncalibrated	PCM A-1 ▼	Front Detector ▼	LTM-II ▼
2	J&W Custom LTM 5M: 320 °C: 5 m x 250 µm x 0.15 µm Additional Segments: inSeg Heated By Oven: 0.3 m x 250 µm x 0 µm outSeg Heated By Oven: 0.6 m x 250 µm x 0 µm LTM 5M x 0.25 x 0.25: <Not Inventoried>	Uncalibrated	PCM A-1 ▼	Back Detector ▼	LTM-II ▼
3	450 °C: 20 m x 180 µm x 0.18 µm restrictor: <Not Inventoried>	Uncalibrated	Front Inlet ▼	PCM A-1 ▼	Oven ▼

Figure 4. Column configuration pane from the GC Chemstation showing set up of all three columns.

Hardware

Agilent 7890A GC with S/S inlet and dual FID's

Flow modulator	G3440A option887, and G3487A
If adding to existing GC	G3486A
CFT un-purged splitter	Kit: G3181-64010
LTM Series II	G6680A, 2-channel, 5-inch system, two power supplies

Firmware and Chemstation

Agilent 7890A firmware	A.01.12.1 or greater
ChemStation	B.04.03 DSP1, includes LTM II software

Typical Parameters

Carrier gas	Hydrogen
Primary column	20 m × 0.18 mm × 0.18 µm HP-1
LTM Module 1	7m × 0.25 mm × 0.25 µm HP- INNOWax, or 5 m × 0.25 mm × 0.15 µm HP- INNOWax
LTM Module 2	5 m × 0.25 mm × 0.15 µm DB17HT
Primary column flow	0.35 mL/min, 27.6 psi starting pressure
LTM 1	20 mL/min, 25.6 psi starting pressure (7 m column)
LTM 2	29 mL/min
Inlet	Split/splitless, 280 °C, 200-600 to 1 split
Primary oven program	35 °C (2 min) to 280 °C @ 3 °C/min
LTM 1 program	55 °C (3 min) to 270 °C @ 5 °C/min
LTM 2 program	60 °C (5 min) to 300 °C @ 3 °C/min
LTM InSeq retention gaps	0.5 m × 0.25 mm
LTM OutSeq retention gaps	0.5 m × 0.25 mm
Detectors	dual FID's at 300 °C

GCxGC Parameters

Load time	2.700 sec
Inject time	0.090 sec
Modulation period	2.799 sec

GCxGC Data Processing Software

GC Image, Version 2.1b4

Results and Discussion

In flow modulated GCxGC, greater flexibility in optimizing methods may be achieved by use of independent ovens for the first and second dimension columns. Correct matching of the retention factors between the 1st and 2nd dimension columns is critical for achieving the best performance with flow modulated GCxGC. If retention on the 2nd D column is too high, analytes injected during one modulation cycle may not elute completely before the next modulation begins.

When a second independent oven is available for the 2nd dimension column, more column choices are available in terms of phase ratio and length. Using a temperature offset, (2nd column starts at higher temp compared to 1st) may allow more retentive columns to be used. Then fine tuning the temperature ramp rate becomes an additional tool to help achieve a difficult separation throughout a 2D chromatographic run or in a particular section of a run. Employing an LTM module for the second dimension makes this possible.

The system can be further enhanced by inserting a CFT unpurged splitter between the modulator and the 2nd dimension. This allows two completely independent 2nd dimension LTM modules (with different stationary phase polarities) to be used which will yield two sets of 2D data for each run.

In figure 5a, a lower phase ratio 7 m INNOWax column is used for the analysis of a jet fuel. When both 1st and 2nd dimension columns are in the air bath oven, the standard 5 m × 0.25 mm × 0.15 µm column must be used to avoid wrap around at low oven ramp rates. With the second column configured as an LTM, longer, thicker film columns can be used to achieve better group separation while ensuring that all compounds will elute from the 2nd column in one modulation cycle. Figure 5b shows the same jet fuel analyzed simultaneously on a less polar 5 m × 0.25 mm × 0.15 µm DB17HT. Both offer useful information and allow different levels of compound group determination when using GC Image.

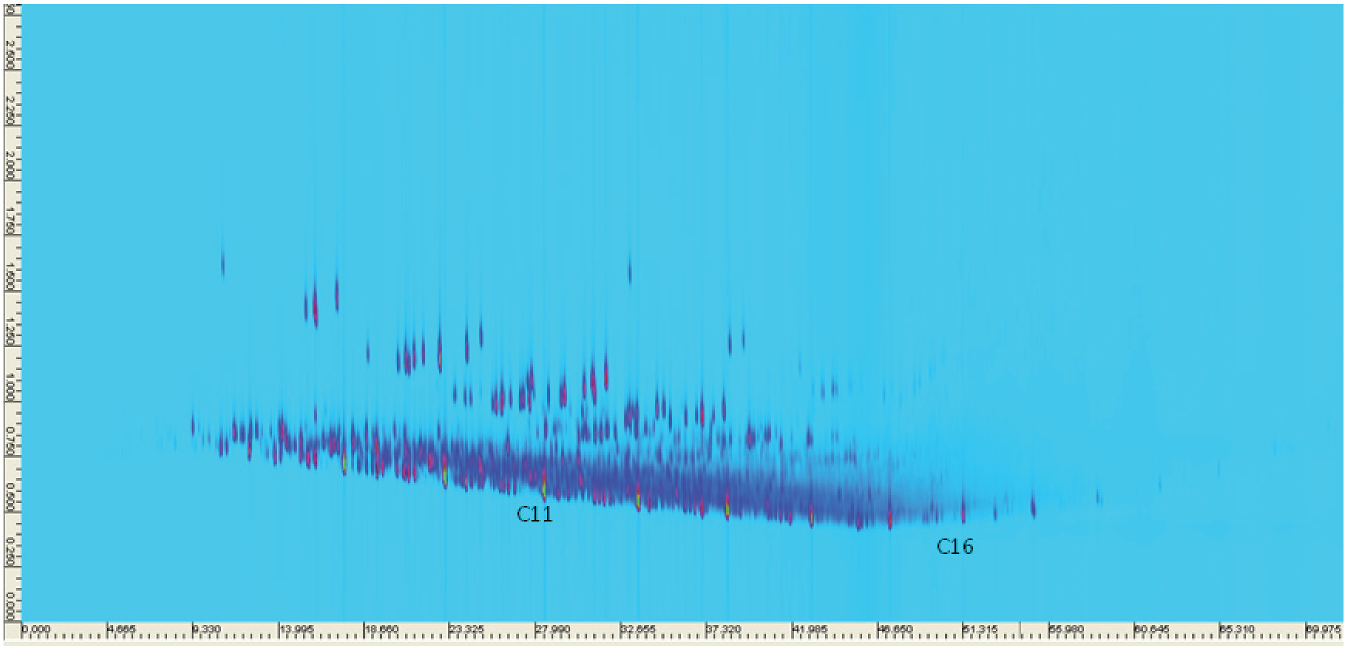


Figure 5a. Jet fuel 2D image. 7 m × 0.25 mm × 0.24 µm HP-INNOWax, LTM program: 55 °C (3 min) to 270 °C @ 5 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min.

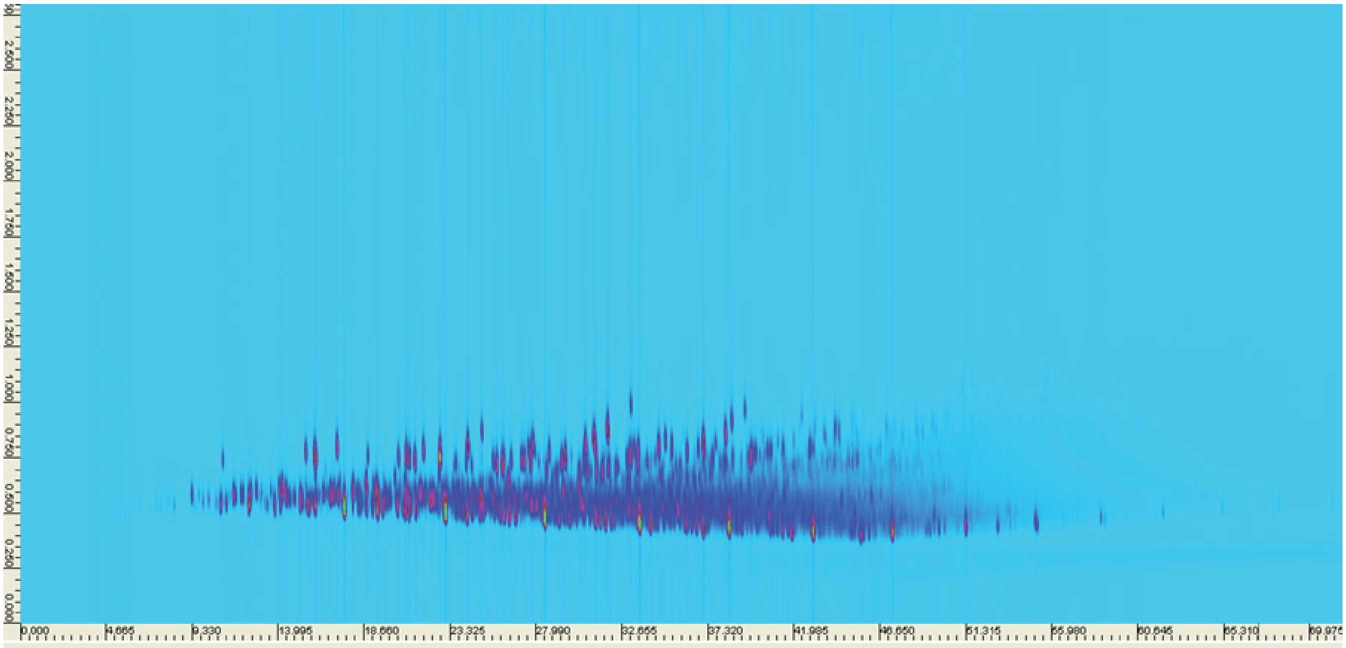


Figure 5b. Jet fuel on 5 m × 0.25 mm × 0.15 µm DB17HT, LTM program: 60 °C (5 min) to 300 °C @ 3 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min.

2D images of a fragrance additive used in detergents is shown in figures 6a and 6b, on the 7 m INNOWax and DB17HT LTM columns, respectively. Peak 3, 4-tert-butyl-cyuclohexyl acetate, shown on the wax column eluted on a second modulation cycle. However, it remains well separated from other components and does not complicate interpretation of the 2D image. Labeled compounds determined by a GC × GC - 5975C MSD system.

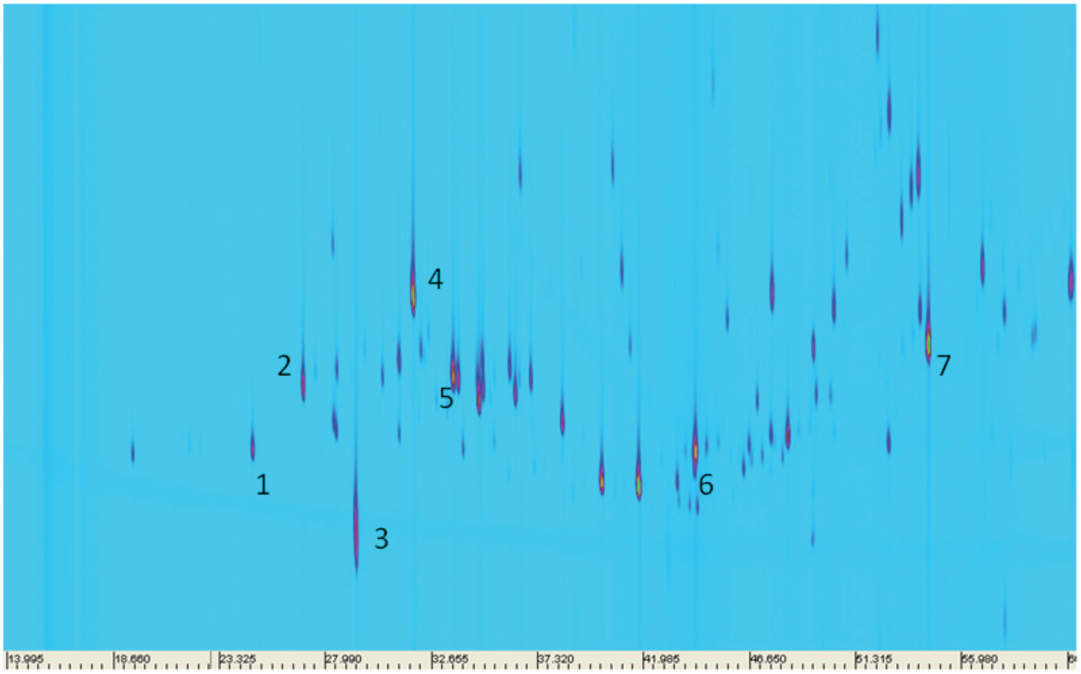


Figure 6a. Fragrance additive using 7 m INNOWax for 2nd dimension, LTM program: 55 °C (3 min) to 270 °C @ 5 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min. 1. Alpha Pinene, 2. Limonene, 3. 2,6 dimethyl 7-octen-2-ol, 4. Phenethyl acetate, 5. Terpenol, 6. Bicyclopentadiene, 7. 4-tert-butylcyclohexyl acetate.

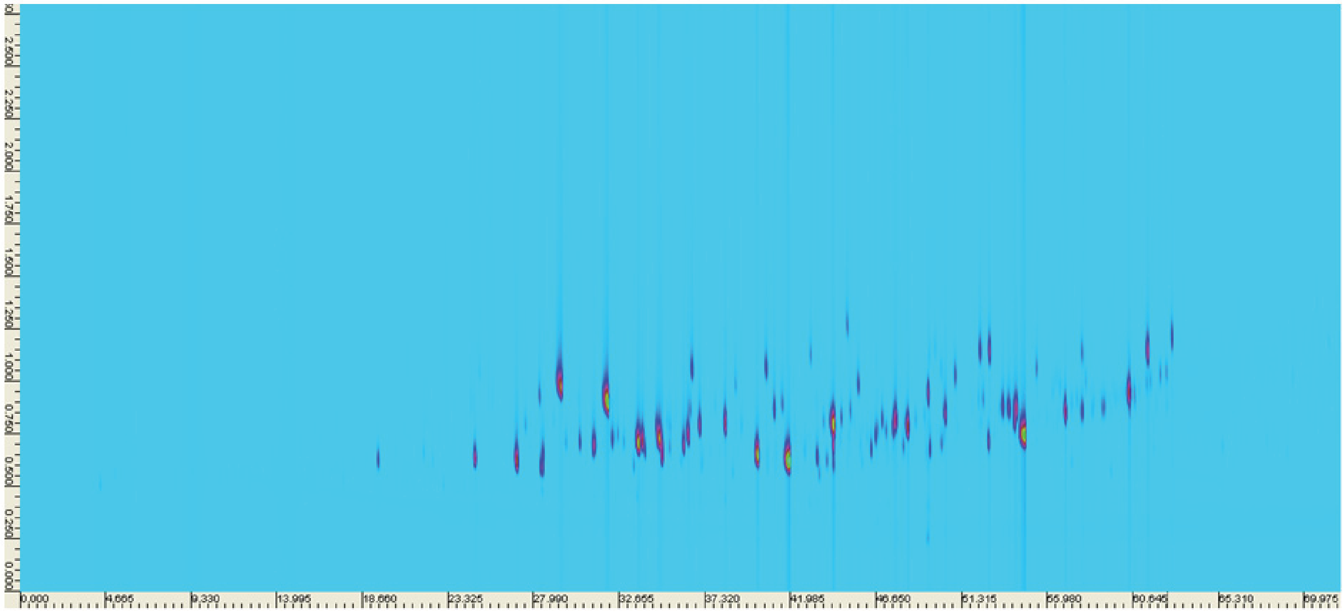


Figure 6b. Fragrance additive using 5m DB17HT for 2nd dimension separation. LTM program: 60 °C (5 min) to 300 °C @ 3 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min.

Lime oil images are shown in figures 7a and 7b. Only the regions around limonene are shown to highlight the separation differences on INNOWax and DB17HT. The 7M thicker film wax column separates minor components from dominate limonene. Compounds identified using a GC × GC - 5975C MSD system.

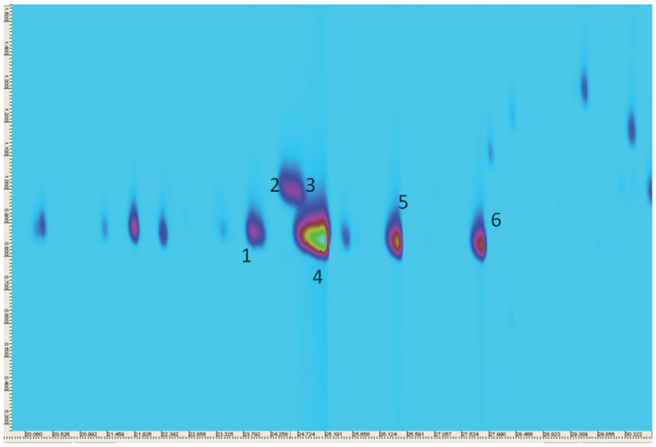


Figure 7a. Lime oil on the 7 m INNOWax. LTM program: 55 °C (3 min) to 270 °C @ 5 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min. 1. Alpha Pinene, 2. Limonene, 3. 2,6 dimethyl 7-octen-2-ol, 4. Phenethyl acetate, 5. Terpenol, 6. Bicyclopentadiene, 7. 4-tert-butylcyclohexyl acetate 1.beta pinene, 2. 1,4 Cineol, 3. m-cymene, 4. Limonene, 5. Terpinen, 6. Terpinolen

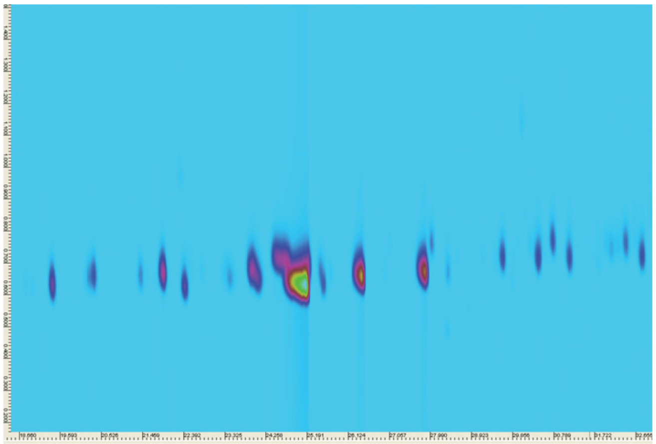


Figure 7b. Lime oil on the 5 m DB17HT. LTM program: 60 °C (5 min) to 300 °C @ 3 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min.

Finally, a 2D analysis of B20 (20% soy) biodiesel is shown in figure 8 using a 5 m × 0.25 mm × 0.15 µm INNOWax. Here, the LTM module and 7890 air oven are programmed at 3 °C/min. However the starting temperature of LTM is offset by minus 5 °C.

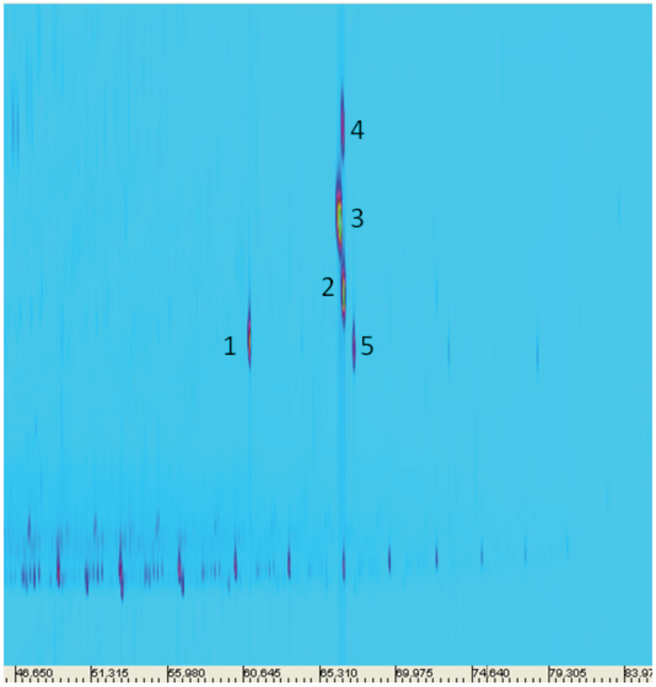


Figure 8. Separation of C16 and C18 fatty acid methyl esters in B20 biodiesel on a 5 m × 0.25 mm × 0.15 µm LTM INNOWax column in the 2nd dimension. LTM program: 30 °C (0 min) to 270 °C (5 min) @ 3 °C/min. 1. C16:0, 2. C18:1, 3. C18:3, 4. C18:3, 5. C18:0.

Conclusions

Comprehensive GCxGC is normally used when faced with a very difficult separation in a complex sample, perhaps a specific analyte determination. It is also a powerful tool for group determination, especially in fuels, and as a classification tool when used with chemometrics. The LTM series II system gives the analyst additional separation power and is easily interfaced to a flow modulated GCxGC system. Depending on how the system is configured, two or three independent temperatures programs can be used. This allows a wider range of column retention in the second dimension to be used.

This work is intended to illustrate some of the possibilities where comprehensive GC and LTM technology can be put to work. Only one combination of column stationary phases was tested (DB5ms-INNOWax-DB17HT). Many other combinations are possible. For example, some useful combinations to consider with the dual LTM system where different polarities are used include (INNOWax-DB1-DC200), and (DB1-DB200-DB35). Reversing polarities (most polar as 1st dimension) can be useful, i.e. (DB210-DB1-DB17) for problems where a few polar compounds must be separated from a complex non-polar matrix. When using LTM with GCxGC, appropriate matching of the retention factors of the 1st to 2nd dimension columns is still important; however LTM offers some additional flexibility to use lower phase ratio columns through temperature offsets and temperature ramps.

References

1. Comprehensive Flow Modulated Two-Dimensional Gas Chromatography, Roger L. Firor, Application Note 5989-6078EN, 2008

2. Comprehensive GC System Based on Flow Modulation for the 7890 GC, Roger L. Firor, Application Note 5989-8060EN, 2009

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Agilent Technologies

Asphalt Analysis with Agilent PLgel Columns and Gel Permeation Chromatography

Application Note

Materials Testing and Research, Polymers

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Introduction

Asphalt is the residual left when practically everything that can be recovered from crude oil by high vacuum, high temperature distillation has been vaporized. The result is a sticky, near solid material containing a vast array of compounds varying from paraffins to highly condensed aromatics. The choice of solvent for use as eluent in gel permeation chromatography (GPC) is very important. Polar materials in asphalt tend to associate and be adsorbed on the packing material. In addition, GPC results are affected by interactions with the solvent, which affect the apparent hydrodynamic volume.

Analysis of Asphalt

Many asphalt applications can be successfully carried out using tetrahydrofuran (THF) as eluent. Figure 1 shows such a comparison of two batches of asphalt, indicating differences in molecular weight distribution. Agilent PLgel GPC columns are compatible with solvents covering a wide range of polarity.

Conditions for Figure 1

Columns	2 × Agilent PLgel 5 µm MIXED-D, 7.5 × 300 mm (p/n PL1110-6504)
Eluent	THF (stabilized)
Flow rate	1.0 mL/min
Detector	RI
System	Agilent PL-GPC 50

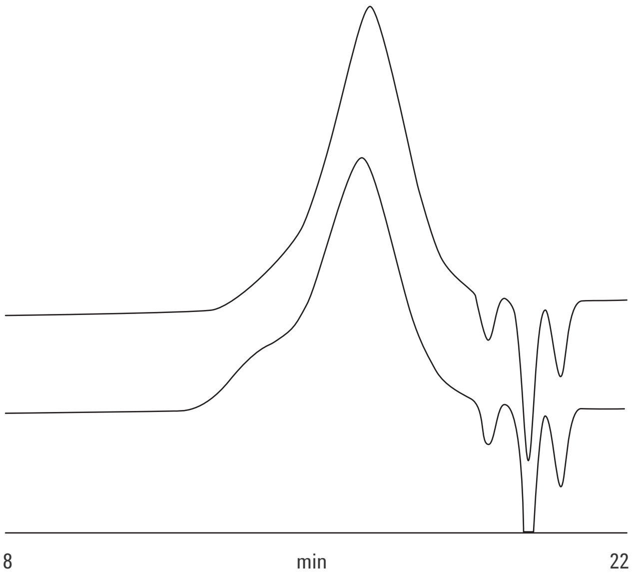

Figure 1. Comparing two batches of asphalt using an Agilent PLgel 5 µm MIXED-D two-column set with tetrahydrofuran as eluent.

Figure 2 shows another comparison of two polydisperse asphalt samples, this time analyzed using xylene as eluent. The higher viscosity of this solvent requires either a reduction in flow rate or elevation of temperature to reduce column operating pressure. The polystyrene standards separation for this application is illustrated in Figure 3. Other suitable solvents include benzene, toluene, and chloroform, all of which are compatible with PLgel columns.

Conditions for Figures 2 and 3

Columns	2 × Agilent PLgel 3 µm MIXED-E, 7.5 × 300 mm (p/n PL1110-6300)
Eluent	o-Xylene
Flow rate	0.5 mL/min
Detector	RI
System	Agilent PL-GPC 50

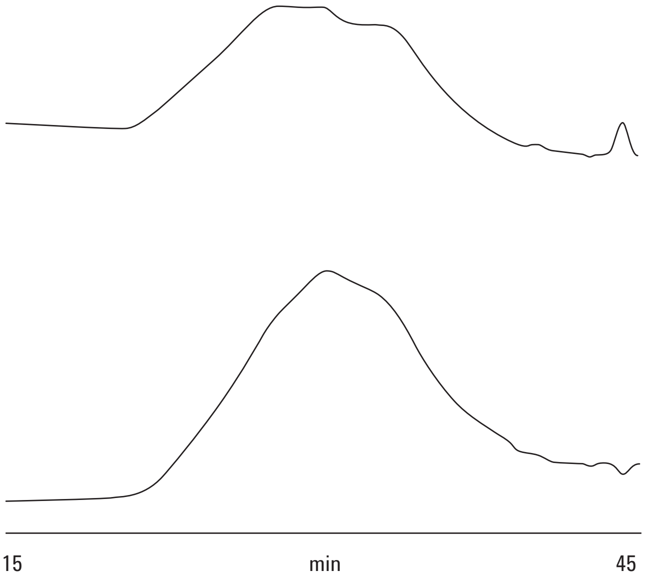

Figure 2. Comparing two batches of asphalt using an Agilent PLgel 5 µm MIXED-E two-column set with o-xylene as eluent.

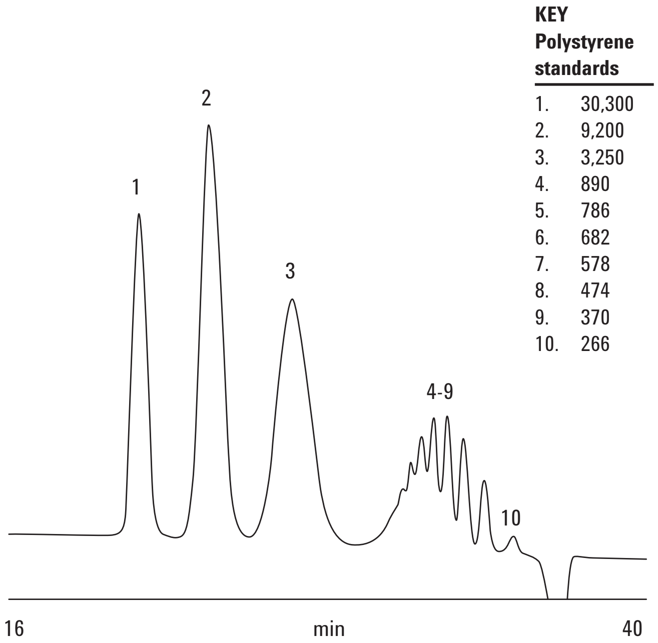

Figure 3. Separation of low molecular weight polystyrene standards on Agilent PLgel 3 µm MIXED-E columns.

Conclusions

Agilent PLgel columns can be used in a variety of solvents to investigate the composition of complex materials such as asphalt by gel permeation chromatography.

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Petroleum Analysis with Agilent PLgel Columns and Gel Permeation Chromatography

Application Note

Materials Testing and Research, Polymers

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Introduction

Crude oil, or petroleum, is the main source of organic chemicals for industry. The major chemicals are derived from two constituents of oil, xylene, and naphtha. These raw materials are then broken down into more basic products, such as polyethylene, polypropylene, elastomers, asphalts, and liquid hydrocarbons. Characterization of such products is commonly achieved using gel permeation chromatography (GPC). This involves a liquid chromatographic separation from which a molecular weight distribution calculation can be made following calibration of the system with suitable polymer standards. The diversity of petroleum products demands a variety of Agilent PLgel GPC columns for optimized analysis.

Analysis of Asphalt

Low molecular weight liquid hydrocarbons require high resolution of individual components. This is illustrated in Figure 1, where three linear hydrocarbons are resolved easily to base line in a reasonably short analysis time.

Conditions for Figure 1

Columns	2 × Agilent PLgel 5 µm 100Å, 7.5 × 300 mm (p/n PL1110-6520)
Eluent	1,2,4-Trichlorobenzene
Flow rate	1.0 mL/min
Temp	100 °C
Detector	RI
System	Agilent PL-GPC 220

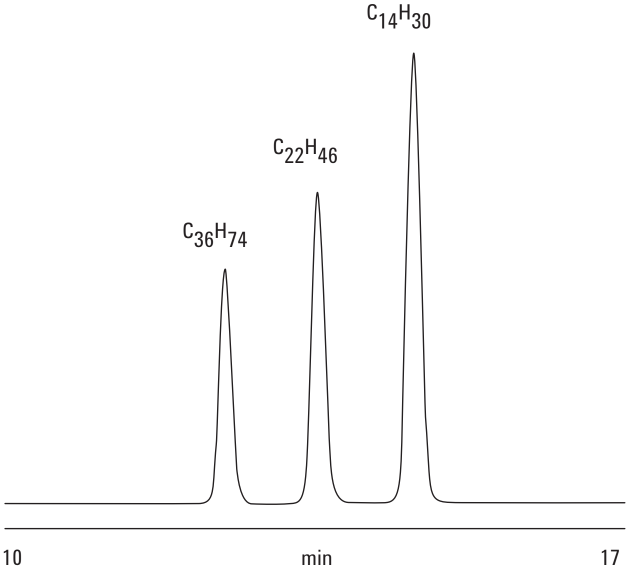

Figure 1. Low molecular weight linear hydrocarbons resolved to base line using an Agilent PLgel 5 µm two-column set.

The Agilent PLgel 5 µm 100Å columns have a GPC exclusion limit of 5,000 molecular weight (polystyrene equivalent), and efficiency is typically > 60,000 plates/m. Intermediate products can be analyzed using the Agilent PLgel 5 µm MIXED-D column, which has a linear molecular weight resolving range up to an exclusion limit of around 500,000 molecular weight. The 5-µm particle size maintains high column efficiency, therefore, fewer columns are required, and analysis time is relatively short.

Figure 2 shows the analysis of asphalt used in road surfacing. Subsequent information regarding the molecular weight distribution of such materials is invaluable in determining processibility and final properties.

Conditions for Figure 2

Columns	2 × Agilent PLgel 5 µm MIXED-D, 7.5 × 300 mm (p/n PL1110-6504)
Eluent	THF
Flow rate	1.0 mL/min
Temp	50 °C
Detector	RI
System	Agilent PL-GPC 50

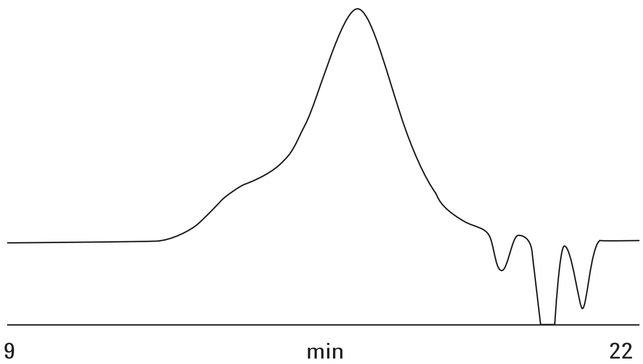

Figure 2. Asphalt separation on an Agilent PLgel 5 µm MIXED-D two-column set.

High molecular weight polyolefin polymers tend to exhibit very broad molecular weight distribution. In these applications, small particle size packings are not desirable since the incidence of polymer shear degradation is apparent. The Agilent PLgel 20 µm MIXED-A column is ideally suited, with a high exclusion limit (40,000,000 g/mol polystyrene equivalent). Its larger particle size, with subsequent lower efficiency, means that three or four columns are required in series. Figure 3 shows typical polyethylene and polypropylene analyses on Agilent PLgel 20 µm MIXED-A columns.

Conditions for Figure 3

Columns	3 × Agilent PLgel 20 µm MIXED-A, 300 × 7.5 mm (p/n PL1110-6200)
Eluent	1,2,4-Trichlorobenzene
Flow rate	1.0 mL/min
Temp	160 °C
Detector	RI
System	PL-GPC 220

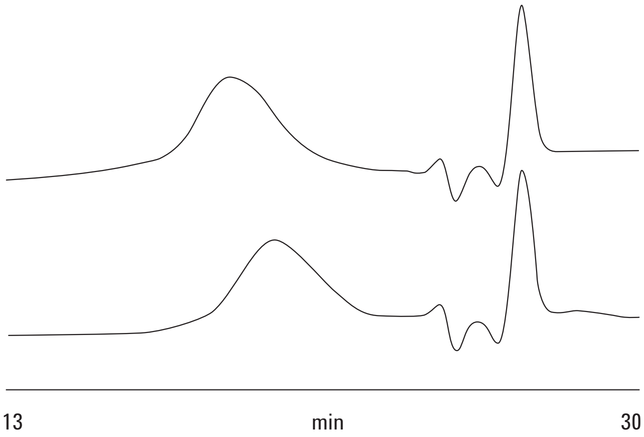

Figure 3. *Polyethylene and polypropylene separated on an Agilent PLgel 20 µm MIXED-A three-column set.*

Conclusions

For many polyolefin-based products, solubility is limited to solvents such as trichlorobenzene at temperatures in excess of the crystalline melting point. This implies that the GPC system must be carefully temperature-controlled throughout. In these examples, temperatures between 50 and 160 °C were used. As there is no UV chromophore, RI is the most common detection technique. However, RI detection is well known for its temperature instability, and in general, dedicated integrated high temperature GPC systems are preferred. The Agilent PL-GPC 220 system is ideal for these applications. Agilent PLgel 20 µm MIXED-A columns operate successfully at the elevated temperatures required for polyolefin analysis. However, for highly crystalline polyolefins of very high molecular weight (100,000,000 g/mol polystyrene equivalent), Agilent PLgel Olexis column are preferred.

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Agilent Technologies

Analysis of wear metals and contaminants in engine oils using the 4100 MP-AES

Application note

Energy and fuels

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Introduction

The regular tracking of the metals present in oils used to lubricate machinery is a vital preventive maintenance task used to gauge the condition of the lubricant and machine over time. Analysts are particularly interested in the elements found in engines, such as Cu, Fe and Al, which are present in the oil as a result of wear and tear, and elements like Na and Si, which are present as a result of contamination from water or road dust. The trend analysis of these metals is performed on the oils so that any action required to keep the engine in service can be taken and costly repairs and downtime can be avoided.

With engines and machinery being central to most transport and manufacturing industries, many laboratories are required to analyze a high volume and variety of oil samples a day, for multiple elements. While flame atomic absorption spectrometry (FAAS) has been used extensively to study trace wear metals in used oils, the sheer number of samples has forced many laboratories to consider a faster, multi-element technique that is capable of high sample throughput.

This can now be effectively achieved using fast sequential atomic emission spectroscopy in the form of the Agilent 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES). The 4100 MP-AES uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. Both aqueous and organic samples can be introduced into the MP-AES, which has good tolerance to the organic solvent load.

Experimental

Instrumentation

An Agilent 4100 MP-AES was used with an External Gas Control Module (EGCM) allowing air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and to reduce background emissions. The instrument was set up with the Organics kit comprising the EGCM, the inert OneNeb nebulizer [1] and solvent resistant tubing, along with a double pass spray chamber. The OneNeb nebulizer offers superior performance for this application over other comparable nebulizers as it offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity. An Agilent SPS 3 Sample Preparation System was used for automatic sample delivery.

The instrument is controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b. Viewing position and nebulizer pressure settings were optimized using the auto-optimization routines in MP Expert. Rational fit is a non-linear curve fit and allows an extended working range so that sample analysis can be carried out using a single wavelength without further dilutions being required.

Samples and sample preparation

Standards were prepared at concentrations of 5 ppm, 10 ppm, 25 ppm and 50 ppm from a 500 ppm oil-based metal calibration standard S21+K (Conostan). Shellsol 2046 (Shell) was used as the diluent. All standards were matrix-matched with 10% Blank Oil (Conostan).

NIST SRM 1085b Wear Metals in Lubricating Oil was prepared by performing a 1:10 dilution in Shellsol.

A sample consisting of a mix of used gear oils was diluted 1:10 with Shellsol and spiked with S21+K, giving a final spike concentration of 10.2 ppm.

Table 1a. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double-pass glass cyclonic
Sample tubing	Orange/green solvent-resistant
Waste tubing	Blue/blue solvent-resistant
Read time	3 s
Number of replicates	3
Stabilization time	15 s
Rinse time	45 s
Fast pump (80 rpm) during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte nebulizer pressures and calibration cuves

Element & wavelength (nm)	Nebulizer pressure (kPa)	Calibration curve
Cd 228.802	140	Rational
Mn 259.372	120	Rational
Fe 259.940	100	Rational
Cr 276.653	140	Rational
Pb 283.305	220	Rational
Sn 303.411	240	Rational
Ni 305.081	180	Linear
V 310.229	220	Rational
Mo 319.398	240	Rational
Ti 323.452	220	Rational
Cu 327.395	200	Linear
Ag 328.068	200	Linear
Al 396.152	240	Rational
Na 589.592	240	Linear
Si 251.611	140	Linear

Results and discussion

Analysis of standard reference materials

To test the validity of the method, NIST SRM 1085b was analyzed. The results presented in Table 2 show excellent agreement (accuracy) between the MP-AES measured results and the certified values.

Table 2. Measured results versus certified values

Element & wavelength (nm)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)
Fe 259.940	314.7 ± 0.3	301.2 ± 5.0	104
Mn 259.372	289.9 ± 0.2	300.7 ± 2.0	96
Cd 226.502	290.9 ± 2.9	302.9 ± 5.1	96
Cr 276.653	305.2 ± 0.1	302.9 ± 3.9	101
Si 251.611	295.7 ± 1.9	300.2 ± 5.0	99
Ni 305.081	291.6 ± 0.1	295.9 ± 7.4	99
Cu 327.395	300.9 ± 0.1	295.6 ± 8.5	102
Ag 328.068	308 ± 0.2	304.6 ± 8.9	101
Pb 283.305	296.1 ± 0.1	297.7 ± 6.8	99
V 310.229	287.6 ± 0.1	297.8 ± 4.6	97
Ti 323.452	293.9 ± 0.1	301.1 ± 2.9	98
Sn 303.411	295.3 ± 0.3	299.4 ± 4.8	99
Mo 319.398	296.9 ± 0.1	300.6 ± 3.2	99
Al 396.152	291.7 ± 0.2	300.4 ± 9.3	97
Na 589.592	297.4 ± 0.1	305.2 ± 7.0	97

Spike recoveries

The recoveries obtained for the spiked mixed gear oil sample are presented in Table 3. Excellent recoveries were obtained for all elements analyzed, demonstrating the validity of the analytical method. The signal graph and calibration curve for Cu are shown in Figures 1 and 2 respectively.

Table 3. Accurate recovery for all analytes of 10 ppm spikes in a mixed gear oils sample

Element	Wavelength (nm)	Unspiked gear oil (ppm)	Spiked gear oil (ppm)	Spike recovery (%)
Ag	328.068 nm	0.27	11.01	105
Al	396.152 nm	0.32	10.31	98
Cd	228.802 nm	0.14	9.85	95
Cr	276.653 nm	0.25	9.92	95
Cu	327.395 nm	2.68	13.14	103
Fe	259.940 nm	10.41	20.09	95
Mn	259.372 nm	0.80	11.54	105
Mo	319.398 nm	9.02	19.34	101
Na	589.592 nm	0.46	10.70	100
Ni	305.081 nm	0.07	10.13	99
Pb	283.305 nm	0.25	11.36	109
Si	251.611 nm	2.23	11.60	92
Sn	303.411 nm	0.16	10.62	103
Ti	323.452 nm	0.01	10.87	106
V	310.229 nm	0.15	10.71	104

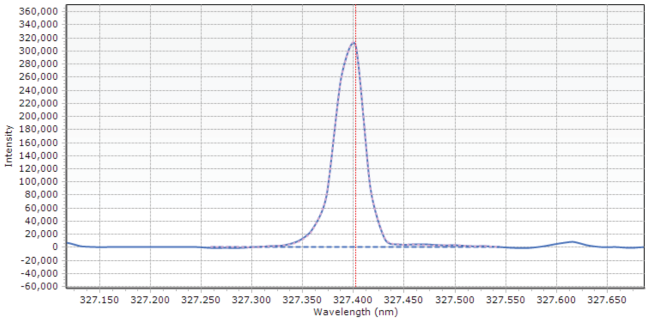

Figure 1. The signal from Cu 327.395 nm at 5 ppm shows the excellent sensitivity of the Agilent 4100 MP-AES

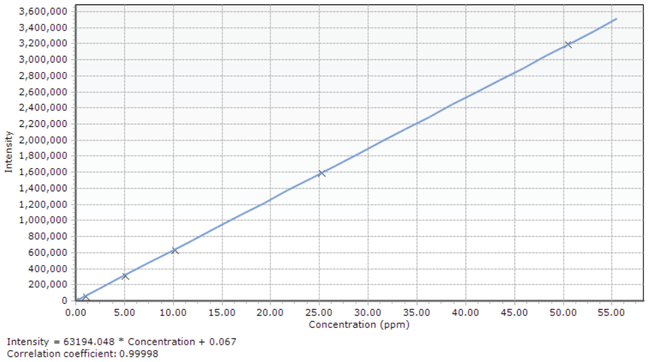

Figure 2. The calibration curve for Cu 327.395 nm up to 50 ppm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99998

Using the Agilent SPS 3 Sample Preparation System, the sample throughput time for the analysis was under 5 minutes per sample, or about 13 samples per hour. With the ability to run unattended, the 4100 MP-AES is capable of greater sample throughput than FAAS.

Long-term stability

Long-term stability of the MP-AES was investigated by continuously aspirating a 10 ppm S21+K solution over an 8 hour period. The resulting stability plot is shown in Figure 3, and the %RSDs for each element are listed in Table 4.

The sample handling capability of the vertically-oriented plasma in the 4100 MP-AES, combined with the air injection from the EGCM and the solids handling of the inert OneNeb nebulizer [1] means that excellent long-term stability (< 1% RSD) can be achieved, even when analyzing challenging organic samples.

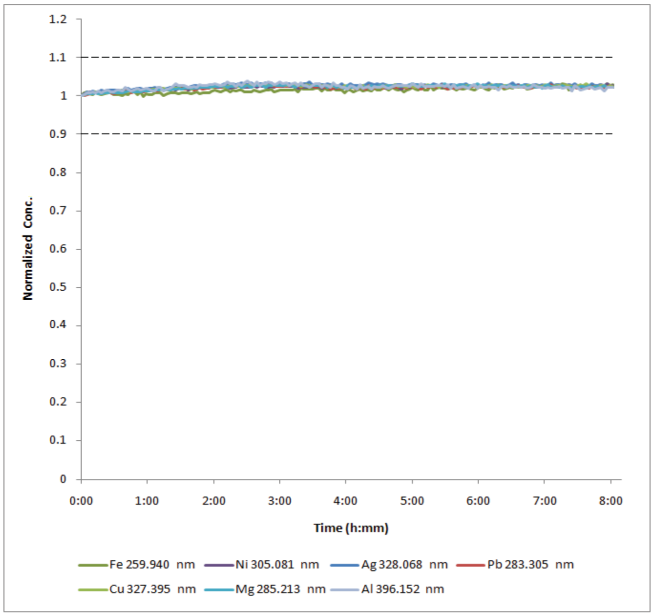

Figure 3. Normalized stability plot for 10 ppm S21+K solution run repeatedly over an 8 hour period

Table 4. %RSDs for each element spiked at 10 ppm level over an 8 hour sampling period

Element	Wavelength (nm)	%RSD
Fe	259.940	0.7
Ni	305.081	0.5
Ag	328.068	0.5
Pb	283.305	0.6
Cu	327.395	0.6
Al	396.152	0.6

Conclusions

The Agilent 4100 MP-AES equipped with a OneNeb nebulizer and fitted with the EGCM is an ideal solution for the routine multi-element analysis of wear metals in oils. Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent recoveries were achieved for SRM samples and on spiked solutions at the 10 ppm level. Excellent long-term stability was also achieved.

Reference

1. J. Moffett and G. Russell, “Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer”, Agilent Application Note 5990-8340EN

www.agilent.com/chem

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Agilent Technologies

Measurement of additives in lubricating oils using the Agilent 4100 MP-AES

Application note

Energy and fuels

Authors

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Introduction

The regular tracking of the additives present in oils used to lubricate machinery is a vital preventive maintenance task used to gauge the condition of the lubricant and machine over time. Several compounds such as Zn, P, Ca, Ba and Mg are typically added to lubricating oils. These metal-containing additives act as detergents, oxidation and corrosion inhibitors, dispersants, anti-wear agents, viscosity index improvers, emulsifiers and anti-foaming agents etc.

With engines and machinery being central to most transport and manufacturing industries, many laboratories are required to analyze a high volume and variety of oil samples per day, for multiple elements. While flame atomic absorption spectrometry (FAAS) has been used extensively to study additives used in oils, the sheer number of samples has forced many laboratories to consider a faster, multi-element technique that is capable of high sample throughput.

This can now be effectively achieved using fast sequential atomic emission spectroscopy in the form of the Agilent 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES). The 4100 uses magnetically coupled microwave energy to generate a robust and stable plasma using nitrogen gas. Both aqueous and organic samples can be introduced into the MP-AES with a good tolerance to organic solvent load.

Experimental

Instrumentation

An Agilent 4100 MP-AES was used with an External Gas Control Module (EGCM) for air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and to reduce background emissions. The instrument was set up with the Organics kit comprising the EGCM, the inert OneNeb nebulizer [1] and solvent resistant tubing, along with a double pass spray chamber. The OneNeb nebulizer offers superior performance for this application over other comparable nebulizers as it offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity. An Agilent SPS 3 Sample Preparation System was used for automatic sample delivery.

The instrument is controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b. Viewing position and nebulizer pressure settings were optimized using the auto-optimization routines in MP Expert.

Samples and sample preparation

Standards were prepared at concentrations of 5 ppm, 10 ppm, 25 ppm and 50 ppm from a 500 ppm oil-based metal calibration standard S21+K (Conostan). Shellsol 2046 (Shell) was used as the diluent. All standards were matrix matched with 10% Blank Oil (Conostan).

NIST SRM 1085b Wear Metals in Lubricating Oil was prepared by performing a 1:10 dilution in Shellsol.

A sample of mixed gear oils were diluted 1:100 with Shellsol and a spiked with S21+K giving a final spike concentration of 10.1 mg/kg.

Table 1a. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double-pass glass concentric
Sample tubing	Orange/green solvent-resistant
Waste tubing	Blue/blue solvent-resistant
Read time	3 s
Number of replicates	3
Stabilization time	15 s
Rinse time	45 s
Fast pump during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte nebulizer pressures and EGCM settings

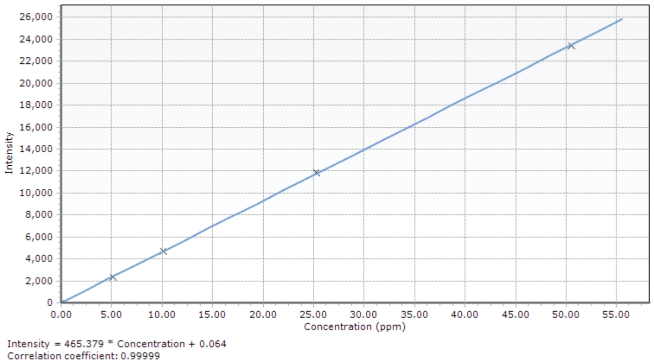
Element & wavelength (nm)	Nebulizer pressure (kPa)	EGCM setting
Mg 285.213	180	High
Ca 422.673	240	High
Zn 481.053	120	High
Ba 614.171	240	High
P 213.618	120	Medium

Calibration parameters

The calibration fit and correlation coefficients for the elements analyzed are shown in Table 2. Rational fit is a non-linear curve fit and allows an extended working range so that sample analysis can be carried out using a single wavelength without further dilutions being required. The excellent correlation coefficients demonstrate the capability of the MP-AES to cover the range of concentrations expected in this analysis. The calibration curve for Zn is shown in Figure 1.

Table 2. Analyte calibration fits and correlation coefficients

Element & wavelength (nm)	Calibration fit	Correlation coefficient
Ba 614.171	Rational	0.99908
Ca 422.673	Linear	0.99958
Mg 285.213	Rational	0.99933
Zn 481.053	Linear	0.99999
P 213.618	Rational	0.99998



Intensity = 465.379 * Concentration + 0.064
Correlation coefficient: 0.99999

Figure 1. Calibration curve for Zn 481.0.53 nm showing excellent linearity up to 50 ppm with a correlation coefficient of 0.99999

Results and discussion

Analysis of standard reference materials

To test the validity of the method, NIST SRM 1085b was analyzed. The results given in Table 3 show excellent agreement (accuracy) between the MP-AES measured results and the certified values.

Table 3. Measured results versus certified values

Element & wavelength (nm)	Measured concentration (mg/kg)	Certified (mg/kg)	Recovery (%)
P 213.618	301.5 ± 0.1	299.9 ± 7.2	101
Zn 481.053	314.9 ± 0.3	296.8 ± 6.8	106
Mg 285.213	300.6 ± 0.2	297.3 ± 4.1	101
Ca 422.673	279.6 ± 0.1	(298)	94
Ba 614.171	281.2 ± 0.1	300.1 ± 2.4	94

Spike recoveries

The recoveries obtained for the spiked mixed gear oil sample are given in Table 4. Excellent recoveries were obtained for all elements analyzed, demonstrating the validity of the analytical method. The spectrum for Zn is shown in Figure 2.

Table 4. Accurate recovery for all analytes of 10 ppm spikes in a mixed gear oils sample

Element & wavelength (nm)	Unspiked gear oil (ppm)	Spiked gear oil (ppm)	Spike recovery (%)
P 213.618	17.16	26.71	95
Zn 481.053	6.99	17.17	101
Mg 285.213	1.53	11.32	97
Ca 422.673	8.89	19.69	107
Ba 614.171	0.00	9.16	91

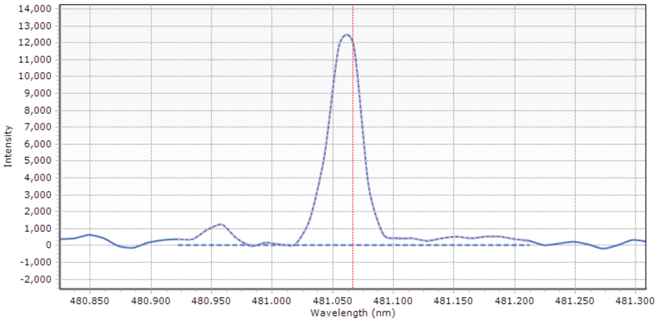


Figure 2. The spectrum for Zn 481.053 nm corrected with Auto background correction

Conclusions

The new Agilent 4100 MP-AES equipped with a OneNeb [1] nebulizer and fitted with the EGCM is an ideal solution for the routine multi-element analysis of additives in oils. The nitrogen-based plasma excitation source exhibits a high tolerance to organic solvent load. Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent recoveries were achieved on SRM samples and on spike solutions at the 10 ppm level.

Reference

1. J. Moffett and G. Russell, "Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer", Agilent Application Note 5990-8340EN

www.agilent.com/chem

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Agilent Technologies

Direct measurement of metallic impurities in petroleum fuels using the 4100 MP-AES

Application note

Energy and fuels

Authors

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Introduction

The performance of engine or turbine components can be compromised over time through exposure to certain trace elements that may be present in gasoline (petrol) and petro-diesel fuels. It is important to monitor these elements in order to ensure the quality of the fuel and to guard against corrosion and deposition on moving parts. For example, ASTM method D6751 specifies a maximum limit of 5 ppm for the combined concentration of Ca and Mg, and 5 ppm for the combined concentration of Na and K [1]. Even though the method relates to biofuels, it is equally relevant to other petroleum fuels such as gas turbine fuel oil [2].

This application note describes the determination of trace elements in gasoline, without dilution or digestion, using the innovative Agilent 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES). The 4100 is a fast sequential atomic emission spectrometer that uses magnetically-coupled microwave energy to generate a robust and stable nitrogen plasma. This stable plasma is capable of analyzing both aqueous and challenging organic matrices. By using a nitrogen plasma, the 4100 MP-AES eliminates the need for expensive and dangerous gases, such as acetylene, resulting in lower running costs, unattended operation, and improved productivity when compared with traditional elemental analysis techniques like flame atomic absorption spectrometry.

Experimental

Instrumentation

The Agilent 4100 MP-AES was fitted with an optional External Gas Control Module (EGCM) allowing air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and reduce background emissions. The instrument was set up with Organics kit comprising the EGCM, the inert OneNeb nebulizer [3], along with a double-pass glass cyclonic spray chamber. The OneNeb nebulizer offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity.

Due to the high volatility of the gasoline sample, an IsoMist cooled spray chamber from Glass Expansion was used to reduce the solvent loading on the plasma, resulting in a more stable plasma and further reducing background emissions.

The instrument was controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected.

MP Expert also provides Standard Addition Calibration to allow the analysis of samples where finding a matrix matched set of standards is difficult. A further feature of the software, which simplifies analysis and method development, is the easy-to-use off-peak background correction markers that can be directly modified on the spectra in real time.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b.

Table 1a. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double-pass glass cyclonic
Sample tubing	Orange/green solvent-resistant
Waste tubing	Blue/blue solvent-resistant
Read time	3 s
Number of replicates	3
Stabilization time	45 s
Fast pump during sample uptake	On
Background correction	Off-peak
Pump speed	5 rpm
Calibration	Standard additions
Cooled spray chamber temperature	-10 °C

Table 1b. Analyte viewing positions, nebulizer pressures and EGCM settings

Element & wavelength (nm)	Nebulizer pressure (kPa)
Mg 285.213	240
Ca 422.673	240
Na 588.995	240
K 766.491	240

Samples and sample preparation

Gasoline fuel standards were prepared by spiking a sample with an oil-based metal calibration standard, S21+K (Conostan), giving final concentrations of 0.89 ppm, 1.92 ppm and 3.94 ppm.

The gasoline samples were directly analyzed, without any sample preparation.

For the spike recovery test, gasoline samples were spiked with S21+K to give spike concentrations of 1.1 ppm.

Results and discussion

Detection limits

Method detection limits were calculated as the concentration equivalent to 3 standard deviations of 10 blank gasoline measurements. The detection limits for gasoline are sufficiently low for the requirements of the analysis. These detection limits demonstrate the ability of the Agilent 4100 MP-AES to handle tough organic samples when coupled with the EGCM, the OneNeb nebulizer and the cooled spray chamber.

Table 2. Method detection limits (ppb) for Mg, Ca, Na and K in gasoline

Element	Wavelength (nm)	Gasoline MDL (ppb)
Mg	285.213	2.7
Ca	422.673	4.3
Na	588.995	5.3
K	766.491	29.4

Calibration

When measuring gasoline samples, the high volatility of the samples makes finding matching standards difficult, even if samples have been diluted with kerosene. For this reason, standard additions calibration was used for this analysis.

Standard addition also means that the gasoline samples can be directly analyzed, without the need for further sample preparation. The stable nitrogen plasma of the MP-AES can easily handle these volatile samples and, as shown in Table 3, excellent correlation coefficients were found for the elements measured in this analysis. A typical spectrum for Mg 285.213 with off-peak background positions, and a calibration curve for Mg 285.213 are shown in Figures 1 and 2.

Table 3. Calibration correlation coefficients for Mg, Ca, Na and K

Element	Wavelength (nm)	Correlation coefficient
Mg	285.213	0.99993
Ca	422.673	0.99934
Na	588.995	0.99939
K	766.491	0.99975

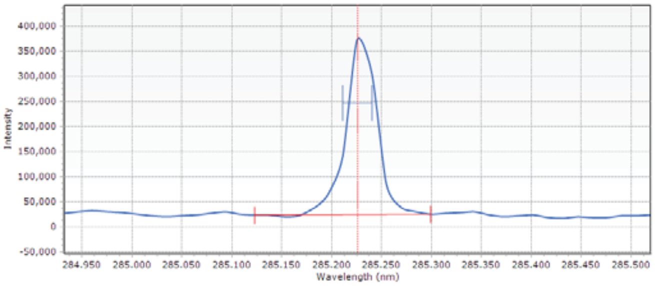

Figure 1. Representative spectrum for Mg 285.213 in the spiked sample

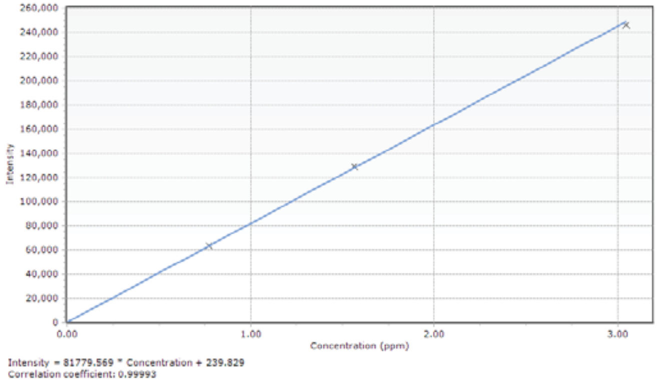

Figure 2. Calibration curve for Mg 285.213

Spike recoveries

The spike recovery results for the gasoline samples are shown in Table 4. The spike concentration was 1.1 ppm and all recoveries were within ±10% of the target value. The excellent recoveries demonstrate the ability of the 4100 MP-AES to accurately determine Mg, Ca, Na and K at the levels required in the gasoline samples.

Table 4. Spike recovery results for Mg, Ca, Na and K in gasoline

Element & wavelength (nm)	Sample (ppm)	Spiked sample (ppm)	Recovery (%)
Mg 285.213	< MDL	1.11	100
Ca 422.673	< MDL	1.06	95
Na 588.995	< MDL	1.11	100
K 766.491	0.05	1.12	96

Conclusions

The Agilent 4100 MP-AES equipped with a OneNeb nebulizer, the EGCM and the IsoMist cooled spray chamber provides an ideal solution for the routine and direct analysis of highly volatile gasoline. The nitrogen-based plasma excitation source exhibits a high tolerance level to organic solvent loading, and the powerful features of the MP Expert software such as standard addition enables analysis of tough samples. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent calibrations, detection limits, and recoveries were achieved in spiked gasoline samples at levels likely to be encountered in this analysis (low ppm).

Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. The Agilent 4100 MP-AES also improves sample throughput and removes the need for hollow cathode lamps.

References

1. ASTM D6751 – 11b, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International.

2. ASTM D2880 – 03, Standard Specification for Gas Turbine Fuel Oils, ASTM International.

3. J. Moffett and G. Russell, “Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer”, Agilent Application Note 5990-8340EN

www.agilent.com/chem

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Publication number: 5990-8973EN

Analysis of diesel using the 4100 MP-AES

Application note

Energy and fuels

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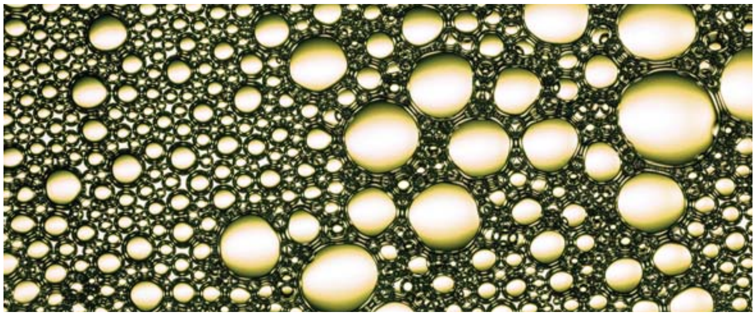

Introduction

The presence of certain trace elements in petro-diesel and biodiesel fuels can cause corrosion and deposition on engine or turbine components, especially at elevated temperatures. Some diesel fuels therefore specify the maximum levels of these elements to guard against the occurrence of engine deposits. For instance ASTM method D6751 specifies a limit of 5 ppm for the combined concentration of Ca and Mg, and 5 ppm for the combined concentration of Na and K [1]. Trace elemental analysis is used to determine the level of contamination of diesel fuels.

The Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. This stable plasma is capable of analyzing not only aqueous solutions, but also challenging organic matrices. When compared to conventional flame AA, the 4100 MP-AES eliminates expensive and dangerous gases such as acetylene, resulting in lower running costs, unattended operation, and improved productivity.

This application note describes the determination of trace elements in diesel fuels using the Agilent 4100 MP-AES.

Experimental

Instrumentation

The Agilent 4100 MP-AES was fitted with an External Gas Control Module (EGCM) allowing air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and reduce background emissions. The instrument was set up with the Organics kit comprising of the EGCM, the inert OneNeb nebulizer [2] and solvent resistant tubing, along with a double pass spray chamber. The OneNeb nebulizer offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, whilst maintaining excellent sensitivity.

The instrument was controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected. Also, the powerful Auto background correction mode easily and accurately corrects for the emission background arising from the organic matrix.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b.

Table 1a. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double-pass glass cyclonic
Sample tubing	Orange/green solvent-resistant
Waste tubing	Blue/blue solvent-resistant
Read time	3 s
Number of replicates	3
Sample uptake delay	15 s
Stabilization time	30 s
Fast pump during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte viewing positions, nebulizer pressures and EGCM settings

Element & wavelength (nm)	Nebulizer pressure (kPa)	EGCM setting
Mg 285.213	240	High
Ca 422.673	240	High
Na 588.995	240	High
K 766.491	240	High

Samples and sample preparation

Method EN 14538 [3] was followed for the analysis of the diesel samples. Calibration standards were prepared at concentrations of 0.5 ppm, 1 ppm, 5 ppm and 10 ppm by diluting a 500 ppm S21+K solution (Conostan) with Shellsol (Shell). All standards were matrix matched with Blank Oil 75 (Conostan).

A commercial diesel sample was spiked with S21+K at the 0.5 ppm level and the spikes were measured to validate the method.

Results and discussion

Detection limits

Method detection limits were calculated as the concentration equivalent to 3 standard deviations of 10 blank diesel measurements. The detection limits reported in Table 2 are in solution, and are sufficiently low for the requirements of the analysis. These detection limits demonstrate the ability of the 4100 MP-AES to handle tough organic samples, provide excellent detection limits at low sample flow rates, and handle the challenging background from carbon emissions using the power and simplicity of auto background correction.

Table 2. Method detection limits (ppb) for Mg, Ca, K, and Na

Element	Wavelength (nm)	MDL (ppb)
Mg	285.213	2.7
Ca	422.673	8.2
Na	588.995	18.7
K	766.491	2.7

Spike recoveries

The spike recoveries in diesel fuel are shown in Table 3. The spike concentration was 0.55 ppm and all recoveries were within ±10% of the target value. The excellent recoveries demonstrate the ability of the 4100 MP-AES to accurately determine Mg, Ca, Na and K at the levels required in the diesel fuel samples. A typical spectrum and calibration graph for K are shown in Figures 1 and 2 respectively.

Table 3. Results of spike recovery test

Element and wavelength (nm)	Sample (ppm)	Spike (ppm)	Recovery (%)
Mg 285.213	< MDL	0.53	97
Ca 422.673	< MDL	0.51	93
Na 588.995	< MDL	0.51	93
K 766.491	< MDL	0.51	93

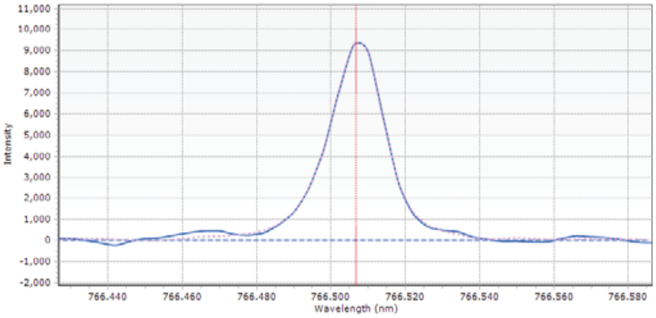

Figure 1. Signal for K 766.491 at 0.5 ppm showing the excellent sensitivity of the 4100 MP-AES when analyzing fuel samples

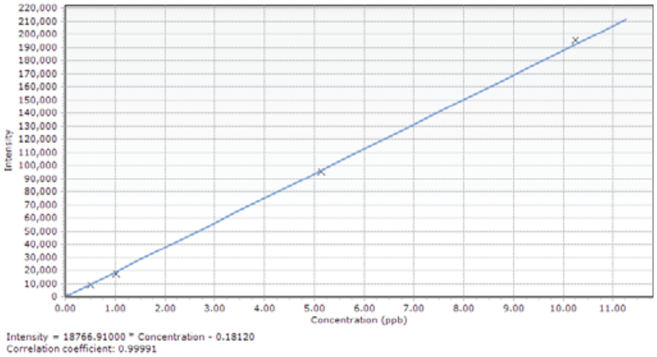

Figure 2. Calibration curve for K 766.491 showing excellent linearity across the calibrated range and a correlation coefficient of 0.99991

Conclusions

The Agilent 4100 MP-AES equipped with the OneNeb nebulizer and the EGCM provides an ideal solution for the routine analysis of semi-volatile organic samples such as diesel. The nitrogen-based plasma excitation source exhibits a high tolerance to the organic solvent load and the easy-to-use yet powerful features of the MP Expert software, such as the auto background correction mode, ensure excellent detection limits. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent calibrations, detection limits, and recoveries were achieved in spiked diesel fuel samples at levels likely to be encountered in this analysis (low ppm).

Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. The 4100 MP-AES also improves sample throughput and removes the need for consumables like hollow cathode lamps.

Reference

1. ASTM D6751 – 11b, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, www.astm.org

2. J. Moffett and G. Russell, "Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer", Agilent Application Note 5990-8340EN

3. EN 14538:2006, Fat and oil derivatives – Fatty acid methyl ester (FAME) – Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES), European Committee for Standardization, www.cen.eu

www.agilent.com/chem

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Agilent Technologies

C1 – C3 Hydrocarbon Analysis Using the Agilent 490 Micro GC – Separation Characteristics for PoraPLOT U and PoraPLOT Q Column Channels

Application Note

Micro Gas Chromatography, Hydrocarbon analysis

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The Netherlands

Introduction

This application note shows the possibilities and limitations in fast analysis of saturated and unsaturated C1 to C3 hydrocarbons using an Agilent 490 Micro GC. The chromatograms and results outline the similarities and differences when using a PoraPLOT U and a PoraPLOT Q column channels. Both the PoraPLOT U and the PoraPLOT Q are capable of resolving methane from the composite air peak and separate CO_2 from methane and the C2 hydrocarbons.

The PoraPLOT U column channel will have the following separation characteristics:

- Baseline separation for ethane, ethylene and acetylene
- Coelution of propane and propylene

The separation characteristics for the PoraPLOT Q column channel are:

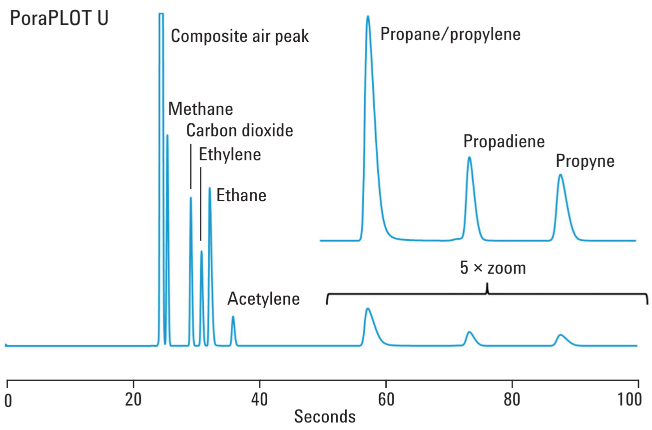
- Coelution of ethylene and acetylene
- Baseline separation for propane and propylene

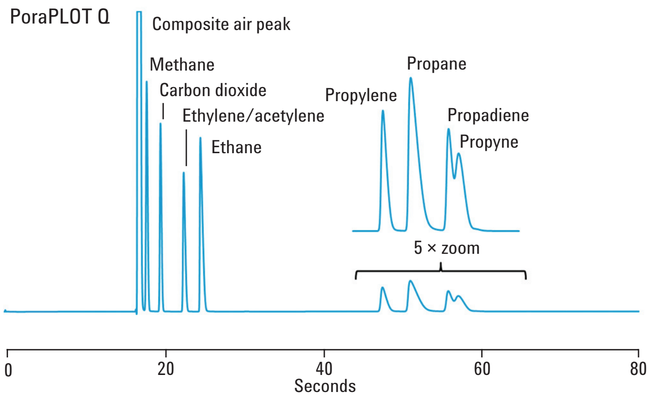
If you want to the ability to measure anywhere and get the results you need in seconds, the Agilent 490 Micro GC is the ideal solution. With its rugged, compact, laboratory quality gas analysis platform, the 490 Micro GC generates more data in less time for faster, and better, business decisions.

Instrumentation

For this application an Agilent 490 Micro GC (G3581A) equipped with a PoraPLOT U and a PoraPLOT Q was used. The setup parameters for the column is found in the table below.

	PoraPLOT U, 10 m	**PoraPLOT Q, 10 m**
Column temperature	80 °C	80 °C
Carrier gas	Helium, 200 kpa	Helium, 200 kpa
Injector temperature	110 °C	110 °C
Injection time	20 ms	20 ms





Sample information

Nitrogen	Balance
Methane	5.0 %
Carbon dioxide	3.0 %
Etylene	2.0 %
Ethane	4.0 %
Acetylene	1.0 %
Propylene	1.0 %
Propane	2.0 %
1,2-Propadiene	0.97 %
Propyne	0.99 %

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Agilent Technologies

The Determination of Lead in Unleaded Gasoline Using the Agilent 55 AA Atomic Absorption Spectrophotometer

Application Note

Atomic Absorption

Author

John Sanders

Introduction

The reduction of lead levels in gasoline has been a priority of environmental agencies around the world since the early eighties.

In this paper we describe the use of Agilent's 55B AA atomic absorption spectrophotometer when applied to the analysis of unleaded gasoline for trace lead levels.

The methodology used in sample preparation was taken from the ASTM D3237-79 [1], with a change in the sample solvent from methyl isobutyl ketone (MIBK) to di-isobutyl ketone (DIBK).

A National Institute of Standards and Technology (NIST, Gaithersburg, MD, U.S.A.) Standard Reference Material (SRM) 2712 Pb in Reference Fuel was used to establish the accuracy and precision of the method.

Experimental

Instrumentation

An Agilent 55B AA atomic absorption spectrometer, air/acetylene burner, organics solvent "O" ring kit for the spray chamber, and a serial printer.

This system was also operated with a simulated LIMS connection through Hyperterminal under Windows®95.

A series of analyses was also conducted using the Agilent 55 AA software.

The instrument operating conditions are shown in Table 1.

Table 1. Instrument operating conditions

Element	Pb
Instrument mode	Absorbance
Active current mA	10.0
Standby current mA	0.0
D_2 background correction	Yes
Flame type	Air acetylene
Wavelength nm	217.0
Slit nm	1.0
Measurement parameters	
Measurement mode	Integration
Read time sec	5.0
Replicates sec	3
Pre-read delay sec	3.0
Calibration parameters **Standard concentrations**	
Cal 0	0.000
Std 1	20 mg/USgal
Std 2	50 mg/USgal
Std 3	100 mg/USgal
Nebulizer uptake rate	5 mL/min

Reagents and Solutions

All reagents were Analytical Reagent grade.

- Di-isobutyl ketone, DIBK (818831, Merck, Schuchardt, Germany)
- Lead free gasoline: Retail grade (containing less than 0.005 g/USgal)
- Aliquat 336 (tricaprylylmethylammonium chloride, Aldrich, Milwaukee, WI, U.S.A.)
- 10% (v/v) Aliquat 336/DIBK solution Dissolve Aliquat 336 (88 g) in DIBK and dilute to 1000 mL
- 1% (v/v) Aliquat 336/DIBK solution: Dissolve Aliquat 336 (8.8 g) in DIBK and dilute to 1000 mL
- Iodine Solution: Dissolve iodine crystals (3.0 g) in toluene and dilute to 100 mL
- 5g/USgal lead standard solution: Dissolve anhydrous lead chloride ($PbCl_2$, 0.4433 g), previously dried at 105 °C for 3 hours, in about 200 mL of 10% Aliquat 336/DIBK solution in a 250-mL volumetric flask. Dilute to the mark with 10% Aliquat 336/DIBK. This solution contains 1321 ig Pb/mL and is equivalent to 5.0 g Pb/USgal
- 1g/USgal lead standard solution: Accurately pipette 50.0 mL of the 5.0 g Pb/USgal solution to a 250-mL volumetric flask and dilute to the mark with 1% (v/v) Aliquat 336/DIBK
- Lead standard solutions: (0.02, 0.05, and 0.1 g Pb/USgal.) Accurately pipette 2.0, 5.0, and 10.0 mL of the 1 g/USgal Lead Standard solution to 100-mL volumetric flasks respectively and add 5.0 mL of 1% (v/v) Aliquat 336 solution to each flask. Dilute to the mark with DIBK.

Calibration Solutions

Prepare working standards and a blank using the 0.02, 0.05 and 0.10 g Pb/USgal standard lead solution.

1. Add 30 mL DIBK and 5.0 mL of lead free gasoline to each of four 50-mL volumetric flasks. add 5.0 mL of standard solution respectively to three flasks. The last flask represents a blank.
2. Add immediately 0.1 mL of iodine/toluene solution by means of a 100 µL Eppendorf pipet, mix well and allow to stand for 5 minutes.
3. Add 5 mL of 1% (v/v) Aliquat 336/DIBK solution and mix well.
4. Dilute to volume with DIBK and mix well.

Sample Preparation

1. To each of four 50 mL volumetric flasks containing 30 mL DIBK add 5.0 mL the gasoline sample.
2. Add immediately 0.1 mL of iodine/toluene solution using a 100 µL digital (Eppendorf or similar) pipette, mix well and allow to stand for 5 minutes.
3. Add 5 mL of 1% (v/v) Aliquat 336/DIBK solution and mix well.
4. Dilute to volume with DIBK and mix well.

Instrument Optimization

Set up the spectrophotometer and adjust the nebulizer uptake to approximately 5 mL/min.

On the optimize page, maximize the lamp signal intensity and the background lamp intensity.

Then adjust the signal intensity, by adjusting the burner rotation, lateral controls, and the gas flows while continuously aspirating the 0.1 g Pb/USgal standard.

Instrument Measurement

Set the instrument zero while aspirating the blank. Read the calibration solutions from Cal 0 to Standard 3 respectively. Read the samples relative to the calibration.

Results and Discussion

The Agilent 55 AA provides a simple and accurate means of determining lead in unleaded gasoline. Output can be fed either to a LIMS system or to a printer. By using computer control sample identification and data manipulation can be accomplished.

The use of the Agilent 55 AA v2 software and computer control provides access to result storage and archival retrieval.

Table 2 shows the results obtained from this study for the certified reference fuel. The experimental results compare well with the certified values.

Table 2. SRM 2712 Result Summary

SRM 2712	**g/USgal**
Measured value	0.0302 ± 0.0001
Certified value	0.0297 ± 0.0010

Samples of regular unleaded gasoline and premium grade unleaded gasoline were also analyzed. The results in Table 3 show the lead level in the regular grade was close to the detection limit, while the level in the premium unleaded gasoline was easily measured.

Table 3 expresses the results in mg/USgal. In using these units the Agilent 55B AA provides an increased number of significant figures to enable the results to be expressed to the full capability of the instruments performance.

Table 3. Analytical Results Agilent 55 AA 217.0nm

	mg/USgal	**mg/L**	**Mean Abs**
Unleaded regular gasoline	1.0	0.10	0.006
Premium unleaded gasoline	3.0	0.80	0.012
SRM 2712	30.2	8.00	0.071
SRM 2712 certified value	29.7 ± 0.10	7.9 ± 0.3	
Instrument detection limit 3δ	0.28	0.07	

Tables 4 and 5 illustrate the results obtained using the Agilent 55 AA Windows®95 software, using the two common wavelengths for lead. Both wavelengths gave the same result for the analysis.

Table 4. Agilent 55 AA Results Using the 283.3 nm Line

	g/USgal	**g/L**	**Mean Abs**
Cal zero	0	0	0.0001
Standard 1	0.0200	0.0053	0.0228
Standard 2	0.0500	0.0132	0.0542
Standard 3	0.1000	0.0265	0.1013
Regular unleaded	0.0002	0.0001	0.0002
Premium unleaded	0.0024	0.0006	0.0027
SRM-2712	0.0303	0.0080	0.0338
SRM-2712 certified value	0.0297 ± 0.0010	0.0079 ± 0.0003	
Instrument detection limit 3δ	0.0007	0.0002	

Table 5. Agilent 55 AA Results Using the 217.0 nm Line

	g/USgal	**g/L**	**Mean Abs**
Cal zero	0	0	-0.0019
Standard 1	0.0200	0.0053	0.0508
Standard 2	0.0500	0.0132	0.1217
Standard 3	0.1000	0.0265	0.2262
Regular unleaded	0.0011	0.0003	0.0028
Premium unleaded	0.0028	0.0007	0.0073
SRM-2712	0.0302	0.0080	0.0757
SRM-2712 certified value	0.0297 ± 0.0010	0.0079 ± 0.0003	
Instrument detection limit 3δ	0.0006	0.0002	

No significant difference was found between the values measured at the 217.0 nm and 283.3 nm wavelengths.

The 283.3 nm line is preferred due to the higher signal intensity and lower non-specific background absorbance at the higher wavelength.

Conclusion

The Agilent 55B AA is able to measure lead in unleaded gasoline with precision of better than 0.0001 g/USgal using the ASTM method D3237. Accuracy is excellent and is shown to be better than 0.0005 g/USgal.

Both the 217.0 nm and 283.3 nm lines can be used.

Safety Notice

Solvents used in this methodology present a hazard risk to users; all operators should consult the relevant Material Safety Data Sheet, and local hazardous substances precautions, before carrying out this procedure.

Use of flame atomic absorption systems with gasoline samples requires complete observation of all relevant safety practices for the presence of flammable materials in the presence of flames.

References

1. ASTM D3237-79 (Re-approved 1984); current version D3237-97

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Agilent Technologies

Obtaining Optimum Performance When Using the SIPS Accessory

Application Note

Atomic Absorption

Introduction

The SIPS accessory, which was introduced in December 1994, was the first practical dilution system for flame AA to provide calibration from a single standard and fast, on-line dilution of over range samples. A few simple procedures, outlined in this information sheet, ensure reliable and productive operation of this accessory.

The Agilent SIPS pump tubing is manufactured from a composite material known as Santoprene. The pump tubing commonly used on VGA and ICP pumps is a single-mix polymer. All types of pump tubing, but especially composite tube materials, can sometimes show signs of "spalling" under normal operation. This is a variable effect in which very small particles of the tubing material break away. If severe spalling occurs, these particles can stick together and cause blockage of the nebulizer.

Spalling occurs in various degrees with all peristaltic pump tubing manufactured from composite materials. It is not unique to SIPS.

The Effect of Spalling

The symptom of severe spalling is an initial increase in the absorbance followed by a decrease as the nebulizer capillary becomes increasingly blocked. A totally blocked nebulizer will cause the sample to be pumped into the diluent bottle thus contaminating the diluent. Sometimes the blockage may clear without intervention.

The extent of the blockage can depend on the nature of the solutions being pumped. It has been found that very dilute solutions are more likely to induce spalling and block the nebulizer than are concentrated solutions.

Why Use Composite Materials?

Composite materials produce long-wearing tubes that have consistent performance. Spalling usually has no noticeable effect. Some formulations, however, display a higher level of spalling. Naturally these are not recommended for use with SIPS.

Achieving Reliable SIPS Operation

There are four easy steps required to minimize spalling effects and to achieve reliable operation. These are:

1. Use only Agilent-supplied SIPS pump tubing
2. Determine, and use the correct arm pressure for each unit
3. Condition new pump tubes, and re-condition (used) tubes before a run
4. Add a detergent to the diluent

A brief summary of these procedures follow. The complete procedures are outlined in publication no. 85-101710-00, which is supplied with all batches of pump tubes.

Use Only Agilent-Supplied SIPS Pump Tubing

It is recommended that SIPS users obtain their pump tubing from Agilent only. Agilent supplied pump tubing is guaranteed to achieve our specified performance and this minimizes batch to batch variations. As with graphite tubes, individual batches of pump tubes are tested to ensure satisfactory operation. Only those batches passing our tests are accepted. Stretching and other problems have been noted with tube batches sampled from a range of vendors.

Determine the Correct Arm Pressure

When the SIPS is first installed, the user must determine the optimum arm pressure setting for that particular unit. This setting does vary from one SIPS unit to another. By optimizing the arm pressure setting, tube life is maximized and the optimum pumping efficiency is achieved.

In practice, this calibration does not have to be repeated when new tubes are installed as there is little variation from one batch of tubes to another.

The procedure need only be repeated if the SIPS unit is repaired or changed (for example, if a SIPS-10 is upgraded to a dual pump SIPS-20).

Condition the Pump Tubing

Before each use of a new pump tube, the pump tubing should be cleaned and conditioned, using the following procedure. Briefly, a dilute detergent solution (such as a 1% solution (mass/volume) of Triton X-100) is pumped through the tube for 15 minutes. Then distilled water is pumped for 30 minutes to rinse it. Once this time has elapsed, the SIPS unit is ready for regular operation.

If the pump tubing has been used previously, it is recommended that before use of the SIPS, the pump tubing is re-conditioned. This is achieved by pumping a solution of 0.01 % Triton X-100 (mass/volume) through the tube for 15 minutes. This procedure can be completed while waiting for the hollow cathode lamp and the burner to warm-up and stabilize. Once this time has elapsed, the SIPS unit is ready for regular operation.

Add a Detergent

To minimize nebulizer blockage from spalling, it is recommended that all SIPS users add Triton X-100 (a readily available laboratory detergent) at a concentration of 0.01% (mass/volume) to the Rinse and Make-up (Diluent) solutions. The Triton X-100 evidently alters the surface of the particles so that the particles do not stick together, but pass through the nebulizer and disappear in the flame.

Summary

The SIPS accessory offers real time-saving and cost-saving benefits to users. Completing the simple procedures described above ensures users can achieve the best performance and the maximum benefit from their SIPS.

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Agilent Technologies

Routine Maintenance for Atomic Absorption Spectrophotometers

Application Note

Atomic Absorption

Author

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Introduction

Instruments in good operating condition are a necessity in any analytical laboratory. This level of integrity can be achieved by a regular maintenance schedule with minimal work. The four main areas of such a program for atomic absorption spectrophotometers include:

- General instrument maintenance
- Gas supply maintenance
- Flame component maintenance
- Furnace component maintenance

The benefits of routine maintenance include:

- Increased instrument lifetime
- Reduced downtime
- Overall improvement in instrument performance; giving the operator greater confidence in the validity of his analytical results

General Instrument Maintenance

Dust and condensed vapors can accumulate on the instrument case, and corrosive liquids can be spilled on the instrument. To minimize damage, wipe off the instrument with a damp, soft cloth using water or a mild detergent solution. DO NOT USE ORGANIC SOLVENTS. The sample compartment windows and the lamp windows can accumulate dust or fingerprints. In such cases, clean the windows with a soft tissue moistened with a methanol or ethanol and water solution. If the windows are not clean, the operator will observe noisy lamp signals and non-reproducible analytical results.

The remaining optical components are sealed, but they should not be exposed to corrosive vapors or a dusty atmosphere. In laboratories where high concentrations of dust or vapors are unavoidable, schedule a yearly check by a service engineer to maintain the efficiency of optical light transmission in the instrument. There is no need for an operator to clean the sealed optical components.

Gas Supply Maintenance

Three gases are suitable for flame M. Air and nitrous oxide are used as combustion support gases (oxidants). Acetylene is used as the fuel gas. Each gas is supplied to the instrument through piped supply systems and rubber hoses. Copper or copper alloy tubing may be used for the oxidant gases. Acetylene should only be supplied through stainless steel or black iron pipe. Check connections regularly between the supply and instrument for leaks, especially when tanks are changed using a soap solution or commercial leak detector. Check the rubber hoses connected to the instrument for fraying and cracking. In addition, each time a tank is changed, check the regulators and valves for proper operation.

Because potentially toxic gases are used or produced in the flame, it is necessary to use a suitable exhaust system with a minimum capacity of 6 m^3/min (200 cfm). A simple smoke test will indicate if it is functioning properly.

Compressed Air Supply

Air may be supplied to the instrument from cylinders, a house air system, or small compressor. Cylinders are the most expensive source of air, particularly where large amounts are consumed and cylinders must be changed frequently. If compressed air from an in-house supply is used, a filter/regulator assembly must be installed in the input line to the instrument. An acceptable “Air Service Unit” (Part No. 01 102093 00) may be ordered from any Agilent sales office.

Whatever source is used, the supply must be continuous and have a delivery pressure of 420 kPa (60 psi). The air must be clean, dry and oil free. Approximately 50% of all gas unit failures are caused by moisture or other impurities inthe air supply.

Excessive noise in the readout has also been attributed to contaminated air. An air filter assembly is therefore an essential component of the atomic absorption spectrophotometer, and its inclusion in the air supply installation is mandatory. Weekly, check the air filter for particle and moisture accumulation. When necessary, dismantle the air filter assembly and clean the filter element, bowl, and drain valve components. Use the following procedure for dismantling and cleaning the air filters supplied with the instrument.

1. Shut off the air supply and allow the system pressure to bleed off.
2. Unscrew the filter bowl, complete with automatic drain valve.
3. Unscrew the retaining ring and push the drain valve back into the bowl.
4. Unscrew the baffle carefully, and remove the filter and filter shield.
5. Clean the filter bowl, drain valve components, baffle, and filter shield by washing in a solution of soap and water. DO NOT USE ORGANIC SOLVENTS AS THEY WILL DESTROY THE BOWL AND VALVE COMPONENTS. Rinse thoroughly in fresh water.
6. Clean the filter element by washing in ethyl alcohol or similar solvent.
7. Ensure that all components are properly dried before reassembly.

Nitrous Oxide Supply

The nitrous oxide used for atomic absorption spectrophotometry must be oil free. If a heated regulator is not used, loss of regulation can occur due to the expansion cooling effect encountered when nitrous oxide is drawn from a cylinder. This can lead to erratic results and create a potential flashback situation with manual gas control units: An acceptable heated regulator may be ordered from any Agilent sales office. The consumption rate is dependent on the application, but is usually 10–20 liters per minute.

Acetylene Supply

Acetylene is the only combustible gas which is normally used in MS. The gas must be supplied packed in acetone. Some companies supply acetylene packed in proprietary solvents, but unfortunately the disadvantages outweigh the advantages. The major disadvantage is that the solvent may be carried over into the instrument and corrode the internal tubing, causing a potential explosion hazard. Ensure that the acetylene is at least 99.6% pure “M Grade” and packed in acetone.

The delivery pressure must be regulated and never exceed 105 kPa (15 psi). Check the instrument operation manual for the correct delivery pressure for the particular instrument being used. In addition, check the acetylene cylinder pressure daily, and maintain in excess of 700 kPa (100 psi) to prevent acetone from entering the gas line and degrading analytical results or causing damage to the instrument.

Flame Component Maintenance

The flame component section of the instrument can be divided into three areas; the nebulizer, spray chamber and burner. Each requires routine maintenance to assure optimum performance.

Nebulizer

The nebulizer area of the flame component consists of the capillary tubing and the nebulizer body. Always ensure that the plastic capillary tubing used for aspirating solutions is correctly fitted to the nebulizer capillary. Any leakage of air, tight bends, or kinks will cause unsteady, non-reproducible readings.

At times the plastic capillary tubing can become clogged and it will be necessary to cut off the clogged section or fit a new piece of capillary tubing (about 15 cm long). in any event, make sure the plastic capillary tubing fits tightly on the nebulizer capillary. The nebulizer capillary can also become clogged. If this occurs, proceed as follows:

1. TURN THE FLAME OFF.
2. Remove the plastic capillary tubing from the nebulizer.
3. Remove the nebulizer from the bung.
4. Dismantle the nebulizer as described in the instrument operation manual or the instruction manual supplied with the nebulizer.
5. Place the nebulizer in an ultrasonic cleaner containing 0.5% liquid soap solution such as Triton X-100 for 5 to 10 minutes. If the ultrasonic bath fails to clear the blockage, pass a burr-free nebulizer wire CAREFULLY through the nebulizer and then repeat the ultrasonic cleaning procedure.
6. Re-assemble the nebulizer in accordance with the instructions.
7. Install the cleaned nebulizer.

   Replace the plastic capillary tubing.

   If blockages are allowed to build up and are not removed, the analytical signal will steadily drop until no absorbance is observed.
8. Check the nebulizer body, capillary, and venturi occasionally for corrosion. Nebulizer problems can be minimized by taking care to always aspirate 50–500 mL of distilled water at the end of each working day.

Spray Chamber

As the sample leaves the nebulizer it strikes the glass bead and breaks into an aerosol of fine droplets. The efficiency of the glass bead can be degraded by surface cracks, pitting and the accumulation of solid material. The reduction in bead efficiency can cause lower absorbance readings and noisy signals. When removing the nebulizer for inspection, always check the glass bead. Look for pitting, cracks, breakage, ensure that the adjusting mechanism operates properly and that the bead is correctly positioned over the nebulizer outlet (venturi).

While the nebulizer and glass bead are removed from the instrument for inspection, the spray chamber and liquid trap should be removed, dismantled, and cleaned. Discard the liquid in the liquid trap and wash both the spray chamber and liquid trap thoroughly with laboratory detergent and warm water. Rinse completely with distilled water and dry all components. Refill the liquid trap and reassemble the spray chamber, checking for any distortion of O-rings or blockages in the gas inlets. Reconnect the drain hose. If a bottle or jug is used to collect the waste solutions, check that the hose is not below the level of the waste. If the hose is below that level, absorbance readings will steadily decrease with occasional abrupt increases as intermittent drainage of the spray chamber occurs. Therefore, it is necessary to daily check the level of the waste and to dispose of it frequently. This is imperative when using organic solvents because of the potential hazards introduced by flammable liquids. Only wide necked, plastic containers can safely be used to collect the waste solutions.

Burner

The final area of concern in the flame component is the burner. During aspiration of certain solutions, carbon and/or salt deposits can build up on the burner causing changes in the fuel/oxidant ratio and flame profile, potential clipping of the optical beam, and degradation of the analytical signal. To minimize the accumulation of salts, a dilute solution of acid (HNO_3) may be aspirated between samples. However, if salts continue to build up, turn off the flame and use the brass cleaning strip supplied with the instrument. Insert the strip in the burner slot and move it back and forth through the slot. This should dislodge any particles which will then be carried away once the flame is lit and water aspirated.

DO NOT USE SHARP OBJECTS such as razors to clean the burner as they can nick the slot and form areas where salt and carbon can accumulate at an accelerated rate.

If this type of cleaning is inadequate, remove the burner, invert, and soak it in warm soapy water. A scrub brush will facilitate cleaning. Soaking may also be done in dilute acid (0.5% HNO_3). Ultrasonic cleaners containing dilute non-ionic detergent only are another alternative for cleaning. After cleaning, thoroughly rinse the burner with distilled water and dry before installing in the instrument. NEVER DISASSEMBLE THE BURNER FOR CLEANING. IMPROPERLY RE-ASSEMBLED BURNERS WILL LEAK COMBUSTIBLE GAS MIXTURES, POTENTIALLY CAUSING EXPLOSIONS.

Each day after all analyses are completed, 50–100 mL of distilled water should be aspirated to clean the nebulizer, spray chamber, and burner. This is even more important after aspirating solutions containing high concentrations of Cu, Ag, and Hg, since these elements can form explosive acetylides. The entire burner/nebulizer assembly should be disassembled and thoroughly cleaned after analyzing these types of solutions. The burner should be removed weekly, scrubbed with a laboratory detergent, and rinsed with distilled water.

Furnace Component Maintenance

The graphite furnace accessory maintenance can be divided into three major areas; the gas and water supplies, the workhead, and the autosampler. Each plays an important role in obtaining valid analytical results. The following general maintenance program refers to the GTA-95.

Gas and Water Supplies

Normally the gases used in FAAS are inert gases such as N_2 and Ar. Either one may be used, but must be clean, dry, and of high purity. The regulated pressure should be 100–340 kPa (15–50 psi). At times the incorporation of air may be useful to fully ash a sample. However, air should not be used at ash temperatures higher than 500 °C because of the accelerated rate of graphite component deterioration at elevated temperatures.

The water supply, used to cool the furnace, may be supplied either from a laboratory tap or a cooling-recirculating pump. If a recirculating pump is used the water must be kept below 40 °C. The water used must be clean and free of corrosive contamination. The flow should be 1.5–2 liters/minute. Maximum permissible pressure is 200 kPa (30 psi).

Workhead

The workhead is a closed assembly with quartz windows on either end. Before starting an analysis, check the windows for dust or fingerprints. If needed, clean both sides of the quartz windows with a soft tissue moistened with an alcohol/water solution. Never use coarse cloths or abrasive cleaning agents. While the windows are removed, inspect the gas inlets on the window mountings. If the graphite components have deteriorated extensively, graphite particulates may have dropped into the gas inlets, blocking the proper flow of gas. This will cause further graphite deterioration at an accelerated rate and lead to poor analytical performance. To clean, carefully blow out the particulates with a supply of air. Inspect the inside of the window mountings and clean off any sample residue which may have deposited over time.

In the center of the workhead are the graphite components. At frequent, regular intervals, remove the graphite tube atomizer and inspect the inside of the graphite shield. Ensure that the bore and the injector hole area are free of loose carbon or sample residue. Check the electrodes on either end of the graphite shield for proper tapering. If the tapering is worn or burnt, the electrodes will not make the correct contact with the graphite tubing, causing fluctuations in applied power resulting in irreproducibility. The electrodes also have a series of gas inlets which must be free of loose carbon or sample residue.

Above the graphite shield is the titanium chimney. Injected sample or sample residue from the ash/atomize cycles may deposit in this area. A cotton swab soaked with alcohol can be used to clean both the inside and outside of the chimney. Alternatively, the titanium chimney may be soaked in dilute acid to remove deposits.

Autosampler

The components of the autosampler requiring routine maintenance are the rinse bottle, syringe, and capillary tubing, the proper care of which will minimize contamination and improve reproducibility of analytical results.

Regularly remove the rinse bottle for cleaning. This involves soaking the bottle in 20% HNO_3 followed by rinsing with distilled-deionized water. Refill the bottle with a solution of 0.01–0.05% HNO_3 in distilled-deionized water. The solution may also include 0.005% v/v Triton X-100 R. The Triton helps maintain the sample capillary in clean condition and assists in obtaining good precision.

At times, graphite particulates may accumulate on the capillary tip and should be carefully removed with a tissue. If these particulates are not removed, the dispensing characteristics of the capillary may change. Contamination of the capillary may become a problem when using some matrix modifiers. In such cases, direct the capillary to a vial containing 20% HNO_3, draw up 70 µL, and stop the autosampler while the capillary is in the vial. After a period of a few minutes, the autosampler RESET should be utilized to rinse out the acid solution. This will clean the internal and external areas of the capillary. Similarly, organic residues can be removed by directing the capillary to a vial of acetone and repeating the above procedure. The PTFE capillary should be treated carefully during cleaning and operation. If bends or kinks appear, it can take time to reshape, and while doing so the repeatability of injection may be degraded. If the capillary tip is damaged, the damaged portion should be cut off at a 90° angle with a sharp scalpel or razor blade.

The final area of the autosampler maintenance schedule is the syringe. Daily, check for bubbles in both the capillary and syringe. Any bubbles in the system can cause dispensing errors and lead to erroneous results. Follow the instructions in the operating manual to free the system of bubbles. If the bubbles continue to cling to the syringe, it may need cleaning. The syringe can be washed with a mild detergent solution and thoroughly rinsed with deionized water. Ensure that contamination is not introduced through the syringe. Be particularly careful not to bend the plunger while washing the syringe.

Conclusion

Attached is a routine maintenance schedule for atomic absorption spectrophotometers (Figure 1). By adhering to this program, the overall integrity of the atomic absorption spectrophotometer can be maintained and the laboratory analyst will reap the benefits of increased instrument lifetime, reduced downtime, and gain greater confidence in the analytical results.

Maintenance Schedule (Flame AA)	
Daily	**Completed**
1. Check Gas	
2. Check Exhaust system with smoke test	
3. Empty the drain receptacle	
4. Clean lamp and sample compartment windows	
5. Rinse spray chamber with 50-100 mL of distilled water	
Weekly	
1. Disassemble spray chamber	
(a) Check glassbead	
(b) Check nebulizer components	
(c) Wash the spray chamber and liquid trap	
(d) Scrub the burner	
(e) Change the liquid in the liquid trap	
(f) Check the O-rings	
2. Check air filter assembly	
3. Wipe off instrument	
4. At Time of Gas Tank Change	
5. Check for leaks	
6. Check for operation of the regulators	
7. Check for operation of the shut off valves	
8. Check the gas supply hoses	
Yearly	
1. Schedule an Agilent service engineer to perform Preventive Maintenance	

Figure 1. Routine maintenance schedule for atomic absorption spectrophotometers.

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Guidelines for Using Non-Aqueous Solvents in Atomic Absorption Spectrometry

Application Note

Atomic Absorption

Author

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Introduction

Much of our environment consists of water. Therefore the bulk of AA methodology deals with water as a solvent. The use of water also has advantages:

- Restricted density range
- Relatively constant viscosity
- Constant specific heat
- Nonflammable
- Transparent in UV and visible region

The relatively constant physical properties allow optimized design of nebulizers, spray-chamber and burner. Background correction is not necessary for many applications.

Some disadvantages of water as a solvent include:

- Potentially corrosive action towards metal
- Dissolved solids levels can be very high
- Flame characteristics affected by cooling

The first can be controlled by careful selection of instrument construction materials. Correct instrument setup (such as glass bead adjustment) can substantially minimize flame perturbation caused by the last two.

The use of non-aqueous (mainly organic) solvents for AA is necessary for certain applications. These include:

- Solvent extraction of metal chelates
- Direct analysis of petroleum products like oil
- Direct analysis of edible oil products
- Direct analysis of pharmaceuticals

The use of organic solvents introduces many complicating aspects including:

- Wide range of densities
- Differing viscosities
- Flammability
- Major effect on flame stoichiometry
- Relatively low flashpoints
- Effect on plastics
- Irritating and noxious fumes
- Increased care required for safe disposal

This wide range of physical and chemical properties (Table 1) makes it difficult to anticipate all the requirements of a particular application. An instrument used with organic solvents must be more flexible than one used for aqueous solvents. The operator also requires more training, especially with the safety aspects. Materials used to protect an instrument from corrosive aqueous solutions are often attacked by organic solvents. Sometimes expensive alternative materials must be used in instrument construction.

Safety Aspects

Organic solvents generally used in AA include the following:

- Hydrocarbon (kerosene, white spirit, xylene)
- Ketone (MIBK, DIBK)
- Alcohol (butanol)
- Ester (isobutylacetate)

The most widely used solvents are usually either a hydrocarbon or a ketone. Further information may be found in Table 1.

Table 1. Physical Properties of Some Organic Solvents

Solvent	**Flash point °C**	**Boiling point °C**	**Specific gravity**
4-Methylpentan-2-one (MIBK)	22	118	0.79
2-Methylpropan-2-ol	23	148	0.83
m-Xylene	29	139	0.86
Cyclohexanone	34	155	0.95
Kerosene (Jet-A1)	39-74	175-325	0.78
3-Heptanone	46	148	0.82
Shellsol T	50	186-214	0.75
White spirit (Pegasol)	55	179-194	0.76
2,6-Dimethylheptan-4-one (DIBK)	60	166	0.81
Cyclohexanol	68	161	0.96
Tetrahydronapthalene (Tetralin)	71	207	0.76

Note: The flash point is the lowest temperature at which the liquid gives sufficient vapor to form an ignitable mixture with air and to produce a flame when an ignition source is brought near the surface of the liquid.

To varying degrees, all organic solvents are both flammable and toxic. The use of organic solvents requires great care.

Organic solvents should be kept in glass bottles. The bottles should be stored in a metal cabinet or in a separate storage area well away from flames and other ignition sources. When using solvents only a relatively small quantity (less than 2 L) should be open to the atmosphere at any one time. In addition most countries have legislation which applies to the storage and handling of flammable liquids. These legal aspects must also be considered.

Prolonged exposure to organic solvent fumes is a health risk. All work with them should be carried out in a fume cupboard which has adequate venting. Samples not being analyzed should be covered. If a sampler is used, it should be placed in an venting system which removes the vapors from the area.

There is always a risk of fire from fumes reaching the flame and adequate ventilation must be provided for the instrument itself. These vapors also absorb ultraviolet radiation and if present in the sample beam light path, can cause a significant background signal.

The plastics materials and paints used in the instrument and its accessories should be protected from direct contact with any solvents. Nearly all plastics except fluorinated plastics are affected to some degree by organic solvents and will swell and distort. Instrument parts are made to close tolerances and such changes may cause malfunctions. Generally if allowed to dry thoroughly these parts will return to their original shape.

A plastic waste container must be used for the instrument wastes. A flashback may shatter a glass waste container with potentially dangerous results. The waste container must be emptied often. All wastes including those from the instrument must be stored in approved containers. Legislation should be consulted for proper disposal of all waste liquids.

The following should never be used as solvents for AA (especially flame):

- Halogenated hydrocarbons (chloroform, Freon)
- Very low boiling point hydrocarbons (petroleum spirit)
- Ethers and acetone
- Tetramethylfuran (TMF)
- Dimethylsulphoxide (DMSO)

Halogenated hydrocarbons are toxic. If aspirated into a flame, even more dangerous gases (phosgene is the most common) are produced.

The other solvents in the list are extremely hazardous in the vicinity of a naked flame because they are volatile. Some are so flammable that they could support a spectrometer flame without acetylene.

Standards

Atomic absorption spectrometric measurement and calibration is based on comparison. Care is needed in preparing standards to obtain accurate results. The amount of care and time needed depends on how accurate the results must be.

Aqueous standard solutions are not generally suitable to calibrate an instrument for organic work. Hydrated metal cations in water have different physical and chemical properties to metallo-organic compounds in an organic solvent.

Metal compounds soluble in organic solvents are commercially available. These can either be dry powders or else dissolved in a matrix oil.

The oil-based standards are easy to use. Single element standards can be weighed out and blended together. This multi-element standard can then be weighed into a clean base matrix. If it is not known whether the base matrix is free of the analyte of interest, then the calibration should be treated as a standard additions calibration. This prepared standard is then diluted by an organic solvent to give a working standard to calibrate the instrument. This approach allows the matrix and concentration range to be adapted to specific requirements. Companies such as Conostan (Ponca City, OK USA) and National Spectrographic Laboratories (Cleveland, OH USA) offer a range of single and multi-element standards that only need dilution to the required levels. Most countries have agents who represent these companies.

The dry standards are typically the cyclobutyrate salts of most metals. The powders are stable and can be stored for long periods. Dissolving the powders can be time consuming and may require two or three liquids. Once dissolved, they may be used in the same way as the oil-based standards. Chemical companies supplying atomic absorption standards also offer the dry powder standards.

Some ways of checking standards accuracy and instrument calibration are:

- Recovery studies
- Measure reference materials
- Inter-laboratory studies

A recovery study is done by spiking a sample with a known amount of standard. The absorption of the sample and spiked sample are measured and the respective concentration calibrated. Percent recovery is calculated by the following equation (US EPA abbreviations are used):

$$\% \text{ Recovery} = (SSR - SR)/SA \times 100$$

where:
SSR = spiked sample result
SR = sample result
SA = spike added

Reference materials are check samples which have accurately known compositions. There are organizations which supply reference materials. A list of these is given in later in this document. Consult their catalogs for further information. Reference materials should be treated in the same way as the other samples. A measured result should be within experimental error of the certified result. These materials could also be used as calibration standards. This is not recommended for two reasons:

- Cost is very high
- Calibration standards and quality control (QC) samples should have different sources to reduce systematic errors

Inter-laboratory studies require the cooperation of laboratories doing the same type of analyses. A sample is divided among the laboratories and measured. The results are all collated and compared. When done as a long term project, this method can monitor a laboratory's performance and allows any necessary remedial action to be taken.

Calculations

Units

Concentration of oil standards are generally expressed as µg/g or ppm (mass).

For solutions presented to the instrument for aspiration, the range is generally in mg/L or ppm (volume).

The term ppm (parts per million) in particular must be very carefully defined. An oil standard may contain 500 µg/g of the element of interest. If diluted 1:10, the solution contains 50 mg/L. To allow direct comparison of oil samples, the concentration of the standard can be entered as 500 in the instrument software. However, when comparing absorbances with other studies, it must be remembered that the solution concentration is 50 mg/L. The unit part per million (ppm) is therefore somewhat ambiguous and will not be used in this discussion.

Dilution

Very often organic samples cannot be presented directly to an instrument's nebulizer. For example an oil sample is too viscous to be aspirated directly without dilution. A gasoline sample is too flammable to be used with a flame instrument. These must be diluted in a suitable miscible liquid. Dilution must be done to allow meaningful measurement of the analyte in question. A 1:5 or 1:10 dilution is usually appropriate for the determination of copper or iron in used oil analysis. The determination of zinc or sodium may require a greater dilution and/or selection of a suitably sensitive resonance line. Burner rotation may also be necessary to reduce sensitivity.

Remember that when the sample has been diluted, the analyte concentration must be carefully defined. It must be very clearly stated whether the concentration refers to the analyte in the original sample or in the diluted solution.

Some examples of typical dilutions are given below.

Case 1: Preparation of oil standards using an oil-soluble metallo-organic salt.

Mass (in grams) of salt to be weighed out, m, can be calculated by equation 1.

$$\text{mass salt} = \frac{MC}{10{,}000\ P}\ \text{grams} \qquad (1)$$

where M is mass of oil standard required (g)
C is concentration of analyte in oil (µg/g))
P is percent analyte in salt

Example 1: Prepare a 500 µg/g Si standard in 100 g oil. The silicon was assayed at 14.29% in the salt. Using equation 1,

$$\text{mass salt} = \frac{100 \times 500}{10{,}000 \times 14.29} = 0.3499\ \text{g}$$

Method: Weigh out 0.3499 g salt. Dissolve in xylene and organic solubilizers (refer to the instructions provided by the chemical supplier) with warming. Add 80–90 g warm base oil with stirring. Cool. Make up to 100.00 g.

Case 2: Preparation of an oil standard using an oil dissolved standard and clean base oil.

Mass of oil standard (in grams) to be weighed out, m, can be calculated by equation 2.

$$\text{mass oil standard} = \frac{M\,C}{S}\ \text{grams} \qquad (2)$$

where M = mass of standard to be prepared
C = concentration of analyte required
S = stock oil concentration

Example 2: Prepare 10 g of multi-element oil containing 120 µg/g Cu and 300 µg/g Al starting with 5000 µg/g standards.

Using equation 2,

Cu	Al
$m = \frac{10 \times 120}{5000}$	$m = \frac{10 \times 300}{5000}$
$= 0.2400$ g	$= 0.6000$ g

Method: Weigh out 0.2400 g of the copper standard and 0.6000 g of the aluminium standard. Dissolve in about 8–9 g of warm base oil. Cool. Make up to 10.000 g.

Case 3: Prepare 20 g of a standard to analyze an oil sample with less than or equal to 1.5% Zn.

In this case, there are two possible methods. One method is to make up a standard from the cyclobutyrate salt (assayed at 16.18% Zn) as shown in Case 1.

Method 1: 1.5% Zn = 1.5 × 10,000 µg/g Zn

From equation 1: $m = \frac{20 \times 1.5 \times 10\,000}{10{,}000 \times 16.18} = 1.854$ g

Dissolve the salt in xylene and organic solubilizer as recommended by the chemical supplier. Add about 18 g warmed clean base oil with stirring. Make up to 20.000 g.

To reduce the amount of diluent required, the 307.6 nm resonance line could be used in this analysis. A 1:5 or 1:10 dilution would be sufficient. Note that the signal to noise ratio for the 307.6 line is not as good as the 213.9 line, but would still give acceptable results.

Another method is to use a variation of Case 2 and make up a standard from a more easily handled oil-based standard. However the sample (15 000 µg/g) is more concentrated than the standard (usually 5 000 µg/ g). So this method uses a different dilution for the sample compared to that for the standard. If the very sensitive 213.9 nm zinc line is used, then a 1:10 000 dilution of sample is necessary to obtain about 1.5 mg/L. Such a large dilution would mean that the sample solution would have almost the same physical properties as the solvent.

If a 5000 µg/g standard is used, a 150 µg/g working standard can be made which only has to be diluted 1:100. At a 1:100 dilution the physical properties of the standard solution would also be similar to the solvent.

Method 2:

From equation 2 $$m = \frac{20 \times 150}{5000} = 0.600 \text{ g}$$

Weigh out the oil standard. Add about 12 g warm clean base oil with stirring. Cool. Make up to 20.000 g.

Dilute the sample by weighing out 1.000 g and dissolving in 100 mL solvent solution. Pipette out 1 mL of the solution and make up to 100 mL. This is the solution to be analyzed.

Dilute the standard by weighing out 1.000 g and dissolve in 100 mL solvent solution. This standard is equivalent to 1.5% Zn in the original oil sample.

Ionic Suppression

A nitrous oxide-acetylene flame is recommended for the measurement of the Group II elements (magnesium, calcium, strontium, barium). Under these conditions, the analytes are partially ionized and require the use of an ionization suppressant for their accurate measurement. An organic soluble potassium or sodium salt is added to the standards and samples to give a final concentration of 2000–5000 ppm. The salts are either napthenates, sulphonates or cyclobutyrates.

A branched capillary to aspirate an ionization suppressant and sample simultaneously has been described [1] and it has been claimed to work with organic samples. This has not yet seen wide application.

Hardware

Spraychamber: Check that the components are resistant to solvent attack and do not distort. Removable components should be checked to ensure they are not binding or tight.

O-Rings: Inspect these frequently. KALREZ O-rings are resistant to solvent attack and are available as sets.

Liquid Trap: This should be filled with the liquid being aspirated or a liquid miscible with the solvent being aspirated.

It is recommended that the spraychamber and liquid trap be dismantled and cleaned at the end of each working day. Wash with hot water and detergent or acetone and allow to dry. Reassemble while checking the O-Rings.

Nebulizer: An adjustable nebulizer which allows control of the uptake rate is necessary. The uptake can be continuously varied from zero up to about 10 mL/min.

An adjustable nebulizer does not have a thimble like the standard preset nebulizer. Instead it has a housing with an uptake control. Refer to the instructions on initial setup.

Setting the correct uptake rate should be done using an air-acetylene flame and the selected solvent:

1. Check nebulizer is set for zero uptake rate
2. Light flame and adjust gas flows to give a very lean flame
3. Place capillary in solvent
4. Slowly rotate uptake control clockwise until flame is beginning to become fuel-rich (some yellow may be seen)
5. Measure and record uptake

   Generally, MIBK, DIBK and xylene - 2 mL/min white spirit, kerosene - 4 mL/min. The nitrous oxide-acetylene flame can tolerate higher uptake rates (MIBK - 6 mL/min).

   A high uptake rate is not desirable for a number of reasons: the flame may be extinguished between samples because of insufficient fuel; the risk of background and inter-element interferences is increased; the gains in signal are usually not significant enough.

Burner: An air-acetylene burner should only require periodic cleaning. The use of organic solvents however increases the possibility of carbon buildup with the nitrous oxide-acetylene flame. More frequent cleaning of the nitrous oxide-acetylene burner may be needed.

A carefully cleaned burner gives the best performance and reduces salt blocking and carbon build-up. The use of a brass strip is no longer recommended. Studies revealed that a metal strip does not clean sufficiently well and that it does not polish the jaws [2]. For optimum performance, any burner should be cleaned as follows:

1. Use a card (for example, business card) and a brass polish (for example, "Brasso")
2. Wet card on both sides with polish
3. Slide card into slot
4. Move card up and down to polish inside of burner jaws
5. Rub card along top of slot
6. Scrub with a soft nylon brush (for example, toothbrush) using hot water and detergent
7. Use ultrasonic bath if available
8. Rinse with hot running water
9. Rinse with distilled water
10. Allow to dry or use a card to remove water from inside slot

Background correction: The organic nature of the matrix means that UV absorption is significant. Background correction is more likely to be required for most elements. Background studies are recommended to determine if correction is needed.

Programmable Gas Box: The sample uptake rate affects the flow of oxidant through the nebulizer into the spraychamber. At low sample uptake rates in the air-acetylene flame, the oxidant flow must be set somewhat higher than the default 13.0 L/min. It is suggested the flow should be about 19 L/min.

Graphite Furnace Operation

Many of the practical precautions of flame are not needed for graphite furnace operation. For example the fire potential is greatly reduced because there is no naked flame and the volumes involved are very small. However some precautions are still necessary. Guidelines for handling, storing and disposing organic solvents must still be observed.

The chemical nature of the metallo-organic compounds means that organic standards may still be required for calibration.

The solvent used for dilution should not be too volatile. A furnace run can take a long time. The solution concentrations could be affected because of evaporation. The ketones (MIBK and DIBK) are probably the most suitable general purpose solvents for furnace work. They are miscible with many organic compounds and solvents. DIBK is also immiscible with water. The organic phase is very mobile. When injected into a furnace, this mobility may cause more spreading than is desirable. To control droplet spreading in the furnace, a partition graphite tube should be used. Some analyzes of volatile elements like lead and cadmium may require the use of a platform [3]. The platform controls droplet spreading provided no more than about 20 mL is injected. For both types of atomization (wall and platform), the hot injection facility can also be used to control spreading. For example, using DIBK as a solvent the inject temperature on the sampler page can be set to 130 °C and the injection rate slowed down to 5. This facility also helps shorten the time needed to dry the injected solution and allows faster furnace cycles [4].

The solution in the rinse bottle of the sampler does not have to be organic. The rinse solution can be distilled water with 0.01% nitric acid and 0.1% Triton X-100 (a non-ionic detergent)3. If the samples are such that the dispenser tip is not being cleaned, a slightly higher concentration of Triton X-100 may be tried. A small amount (0.5 - 1%) of propan-2-ol in the rinse solution as well can assist with keeping the tip free of grease and oil.

Safety Checkpoints

Choose a Suitable Solvent Which Has the Following Properties

- Miscible with sample
- Uitably high flashpoint
- Density greater than 0.75
- No toxic by-products formed

Handling Solvents

- Use small volumes near instrument
- Keep solutions covered when not in use
- Do not inhale vapors
- Empty waste vessel often
- Use fume cupboard for solution preparation
- Dispose of all wastes carefully and responsibly
- Do not mix with nitric or perchloric acids or wastes

Instrument

- Fill liquid trap with suitable solvent before starting
- Attach tube to spraychamber vent and allow other end to vent safely away from flame
- Install an efficient exhaust system above instrument
- Keep burner clean
- Do not clean burner while flame is on
- Drain liquid trap at the end of each day
- Wash spraychamber and allow to dry overnight; check condition of O-rings often

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Company Addresses

Conostan Division Continental Oil Co. PO Drawer 1267 Ponca City OK 74601 U.S.A.

National Spectrographic Laboratories Inc. 19500 South Miles Road Cleveland OH 44128 U.S.A.

Bureau of Analyzed Samples Ltd Newham Hall Newby, Middlesbrough, TS8 9EA England

U.S. Department of Commerce National Institute of Science and Technology Gaithersburg, MD, 20899 U.S.A.

Commission of European Communities Community Bureau of Reference (BCR) 200 Rue de la Roi B-1049 Brussels Belgium

National Physical Laboratory Office of Reference Materials Teddington, Middlesex, TW1 0LW England

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Agilent Technologies

Agilent Oil Analyzer: customizing analysis methods

Application Note

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Introduction

Traditionally, the analysis of used oils has been conducted by physical and wet chemical methods. FTIR spectroscopy has become a routinely used technique to analyze used oils, providing the following major advantages[1]:

- Ability to simultaneously determine several parameters from a single experiment
- Increase in speed of analysis
- More cost effective than traditional techniques
- Mobility and portability allowing remote on-site analysis

The Agilent FTIR Oil Analyzer is designed to meet the requirements of the US Department of Defense Joint Oil Analysis Program (JOAP)[2] for use in their condition monitoring program as well as commercial applications. It is optimized for monitoring relative changes in various indicators of oil conditions (oil failure symptoms) using a standardized protocol developed by the Joint Oil Analysis Program Technical Support Center (JOAP-TSC). This protocol sets the data extraction algorithm for several types of petroleum and synthetic-based lubricants and hydraulic fluids, and eliminates the need for reference samples as spectral subtraction is no longer required.

The Agilent Oil Analyzer software allows users to readily customize existing methods as well as create new methods to measure other parameters and properties of lubricants defined by the user. The methods can be easily adjusted for performing analysis of samples where spectral subtraction is required.

This application note describes the tools available with the Agilent FTIR Oil Analyzer and procedures that a user should follow to customize analysis methods, while reinforcing the importance of reliable calibration in quantitative spectral analysis.

Analysis methods

The sampling and analyzing procedures available in the Agilent FTIR Oil Analyzer conform to the ASTM E 2412–04 "Standard practice for condition monitoring of used lubricants by trending analysis using Fourier Transform Infrared (FTIR) Spectrometry"[3]. These methods provide a generalized protocol for condition monitoring of contaminants and breakdown products in used lubricants including water, ethylene glycol, fuels, incorrect oil, soot, oxidation, nitration and sulfonation. The methods are based on calculating trends and distributions from mid-IR absorption measurements, and encompass both direct and differential (spectral subtraction) trend analysis approaches.

The Agilent Oil Analyzer software is configured to run twelve predefined analysis methods that correspond to different classes of lubricating oils or hydraulic fluids, and their applications with differing limits. The methods are:

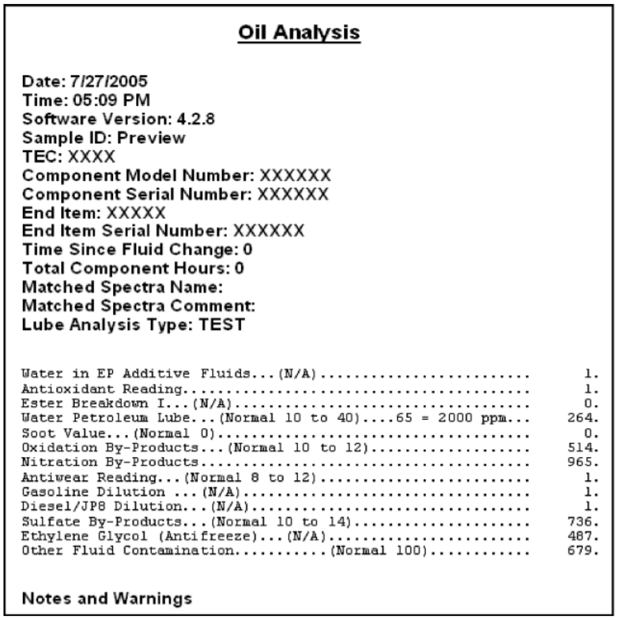
- Aircraft hydraulic (Mil-H-83282)
- Aircraft hydraulic (Mil-H-83282_350 ppm limit for water)
- Dextron transmission fluid
- Engine crankcase (Diesel_gasoline_natural gas)
- Fire retardant hydraulic (Mil-H-46170)
- Gas turbine or Helo Gbx (Mil-L-23699)
- Ground equipment hydraulic (Mil-L-2104_10W)
- Ground equipment synthetic hydraulic (Mil-H-5606)
- Marine diesel crankcase (Mil-L-9000)
- Conostan IR OTS fluid
- Steam turbine (Mil-L-17331)
- Generic or undetermined (Unknown lubricant type)

Each of the methods measures numerical indicators (parameters) that are related to the oil's condition. The software then generates a report that contains thirteen measurement parameters, as listed below:

- Water in EP fluids
- Antioxidant reading
- Ester breakdown
- Water in petroleum
- Soot value
- Oxidation by-products
- Nitration by-products
- Antiwear reading
- Gasoline dilution
- Diesel/JP8 dilution
- Sulfate by-products
- Ethylene glycol
- Other fluid contamination

Additionally, a separate procedure for predicting Total Base Number (TBN) is available and can be integrated into existing methods.

The parameters are reported in the units of spectral absorbance (peak areas or heights) rather than in physical concentrations, such as ppm, wt.% or mg of KOH. Figure 1 shows an example of a typical standard Oil Analysis report.



Oil Analysis

Date: 7/27/2005
Time: 05:09 PM
Software Version: 4.2.8
Sample ID: Preview
TEC: XXXX
Component Model Number: XXXXXX
Component Serial Number: XXXXXX
End Item: XXXXX
End Item Serial Number: XXXXXX
Time Since Fluid Change: 0
Total Component Hours: 0
Matched Spectra Name:
Matched Spectra Comment:
Lube Analysis Type: TEST

```
Water in EP Additive Fluids...(N/A)........................      1.
Antioxidant Reading........................................      1.
Ester Breakdown I...(N/A)..................................      0.
Water Petroleum Lube...(Normal 10 to 40)....65 = 2000 ppm...   264.
Soot Value...(Normal 0)....................................      0.
Oxidation By-Products...(Normal 10 to 12)..................    514.
Nitration By-Products......................................    965.
Antiwear Reading...(Normal 8 to 12)........................      1.
Gasoline Dilution ...(N/A).................................      1.
Diesel/JP8 Dilution...(N/A)................................      1.
Sulfate By-Products...(Normal 10 to 14)....................    736.
Ethylene Glycol (Antifreeze)...(N/A).......................    487.
Other Fluid Contamination...........(Normal 100)...........    679.
```

Notes and Warnings

Figure 1. Typical standard Oil Analysis report

Calibration

All analysis methods in the Agilent FTIR Oil Analyzer consist of a set of calibration models (procedures) in the form of corresponding files with an indication of the calibration model's type (univariate, or multivariate, or a combination). The analysis method may be composed of one or several calibration files.

The construction of calibration models in quantitative spectral analysis is a two-step procedure: calibration and validation. In the calibration step, indirect instrumental measurements (spectra) are obtained from standard samples in which the value of the parameter of interest has been determined by a standard reference method (an accurate direct measurement method). The set of spectra and results from the reference method, referred to as the calibration set or training set, is used to construct a model that relates parameter values to the spectra. Before the calibration model is accepted and used for prediction, it should be validated by a set of independent (not used in the calibration set) samples of known parameter concentrations (validation set). If parameters from the validation set fall within acceptable accuracy limits using the model derived from the calibration set, an acceptable model has been constructed that can be used to predict for new "unknown" samples.

To build a univariate calibration model, it is necessary to specify a single measurement from a spectrum, such as peak area or height that demonstrates the most distinctive spectral response for the parameter of interest. The univariate calibration and prediction procedures are available as a standard part of Resolutions/Resolutions Pro software and are defined as a simple quantitative analysis. The analysis is described in detail in the Resolutions online help and the corresponding system reference manuals for previous software versions (Win-IR Pro and Merlin). The user must generate a quantitative calibration document and save it as *.BSQ file using Resolutions/Resolutions Pro (Win-IR Pro or Merlin) software.

Where spectral responses attributed to different parameters overlap and the selective spectral measurements for the parameter of interest is very difficult, univariate models may not be reliable. Multivariate methods such as Principal Component Regression (PCR) and Partial Least Squares (PLS) allow multiple responses at the selected wavenumbers to be used. These methods are better suited to extracting spectral information where bands overlap and it is difficult to discern the relevant spectral regions attributable to a particular parameter. The main advantage of multivariate methods is the ability to calibrate for a parameter of interest when it correlates in a complicated (non-specific) way with multiple spectral regions, while minimizing background matrix interferences in the lubricants.

The Agilent Oil Analysis software allows multivariate calibration models created with the use of third party software to be incorporated in analysis methods. The PLSplus IQ package available as an additional application in the Galactic GRAMS/AI (GRAMS/32) software suite must be used. The "PLSplus IQ User's guide" gives step-by-step instructions on how to construct and validate a multivariate calibration model as well as theory of advanced statistical analysis in spectroscopic quantitative analysis. The user must build an accurate calibration model and save it into a *.CAL file using PLSplus IQ.

The validity of empirically-built calibration models depends heavily on how well the standard samples (calibration set) represents the unknown samples to be analyzed (prediction set). In all cases, the selection of standard samples to be used for calibration must adequately cover the expected range of measurement parameters in the prediction set. This means that the expected extreme values for each parameter of interest in unknown samples must be included in the calibration set, as extrapolation outside the calibrated value range can be unreliable. It is important to ensure that any phenomena that influence the spectral measurements (e.g., not only the total amount of soot but its particle size distribution) also vary in the calibration set over ranges that span the levels of the phenomena occurring in the prediction set. It is also very important to minimize the errors in the standard sample parameters that are used to construct the empirical calibration model, as any calibration model can only be as accurate as the reference measurements from which it was constructed.

Many conditions can affect the results obtained from FTIR lubricant monitoring such as lubricant type, engine type, operational conditions, environmental conditions, etc. When the conditions are changed significantly, new calibration models and methods may be required to ensure accurate prediction of oil properties. For instance, new calibrations may be required when a new oil type with a different base stock and additive chemistries comes for the analysis.

Care must be taken when measuring overall oil quality parameters such as Total Acid Number (TAN) and Total Base Number (TBN) using FTIR spectroscopy. The secondary formation of acidic products in lubricants is characterized by TAN or indirectly by TBN, which assesses the consumption of basic reserve additives in the oil. While the various acids or bases present in a lubricant could, in principle, be individually quantified based on their characteristic absorption bands, no unique absorption bands can be directly related to TAN or TBN. Thus, only indirect FTIR spectroscopic methods for TAN and TBN have been standardized to date. In addition, there is a large discrepancy in new lubricant TAN values, from less than 0.1 mg KOH/g for R&O type oils to 9 or higher for some synthetic oils in industrial applications. On the other hand, the incremental decrease in TBN used to indicate that a product is failing, varies in broad ranges: some oils may have a new TBN value of 12, but rapidly decrease to a value of 3, whereas other synthetic oils may have the beginning TBN of 40.

A calibration model for TBN is currently available in Agilent Oil Analyzer. The calibration is intended for prediction of the values in gasoline and diesel engine oils having typical baseline numbers not higher than 12 mg KOH/g.

Note that in many individual cases, in order to estimate TAN and TBN satisfactorily the user needs to construct a multivariate calibration model that would cover the higher range of values as well as take into account any other factors that could influence the accuracy and the reproducibility of spectral measurements.

Method editor

Once the univariate or multivariate calibration models are built, the corresponding *.BSQ or *CAL files must be moved or copied into the directory C [Local Disk]:\ Program Files\Varian\Resolutions\Oil Analyzer\Methods. This is the storage location for the available calibration and method files. Then, log in as Administrator to the Agilent Oil Analysis software and enter the Method editor. Follow the Chapter 11 “Method Editor” in “Agilent Oil Analyzer operational manual” to incorporate the calibrations to an existing method or to develop a new method.

Note that spectral subtraction is available in the Agilent Oil Analyzer but was not utilized in JOAP protocol. It is not considered to be practical in view of the deployability aspect of many JOAP laboratories and that the required sample volume would increase because of the necessity of new oil samples to act as references. In order to apply the spectral subtraction procedure, the user needs to select "Use spectral subtraction" option in the Sampling method group in the General option dialog and edit the relevant analysis method, by clearing the "Zero less than Zero" check box in all the associated calibration models. Refer to Chapter 4 "General Options–Setup" and Chapter 11 "Method Editor" of "Agilent Oil Analyzer operational manual" for more information.

Conclusion

FTIR spectroscopy has been gaining increased acceptance as a method of choice for used oil analysis. Designed and optimized as a complete system for predictive maintenance programs, according to JOAP standards, the Agilent FTIR Oil Analyzer combines specific capabilities with the flexibility to be successfully used in any oil analysis laboratory.

The Oil Analyzer software allows new and improved analysis methods to be built and ensures that new types of lubricating oils and fluids used in a variety of different machinery are timely and reliably monitored and tested.

The software allows the user to include PCR/PLS methods to measure oil parameters and convert the units of spectral absorbance into physical results (ppm, wt.%, cSt, mg KOH/g oil, etc.) applying spectral subtraction if needed.

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www.agilent.com/chem

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AA or ICP – Which Do You Choose?

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

For many analysts Atomic Absorption Spectrometry (AAS) is a well established and understood technique. However, even though Inductively Coupled Plasma Emission Spectrometry (ICP-ES) instrumentation has been commercially available for over a decade, the technique has proven to be more complex. This article discusses the main differences between the two techniques.

AAS Versus ICP

The basic difference between the two techniques is that one relies upon an atomic absorption process while the other is an atomic/ionic emission spectroscopic technique. The next essential difference is the means by which the atomic or ionic species are generated. A combustion flame or graphite furnace is typically used for AA while ICP-ES uses a plasma.

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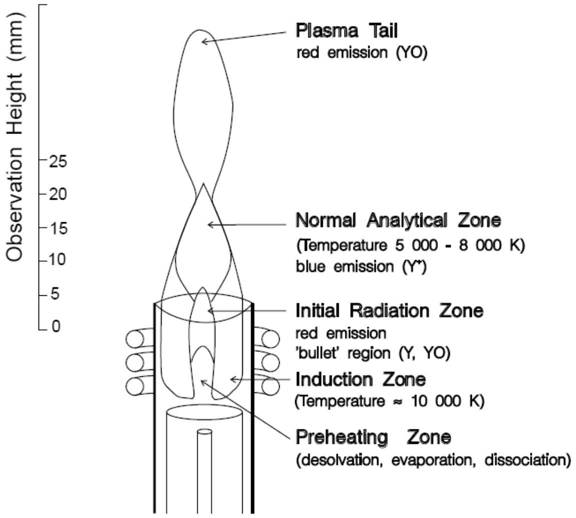

Figure 1. A plasma used for emission spectrometry. The regions refer to those seen when a Yttrium solution is introduced.

The typical maximum temperature for an air/acetylene flame is 2300 °C while for nitrous oxide acetylene, it is 2900 °C. Temperatures as high as 10,000 K can be reached in an argon plasma.

Detection Limits

The comparison of detection limits in Table 1 highlights the following differences:

- Furnace AA detection limits are generally better in all cases where the element can be atomized.
- Detection limits for Group I elements (for example, Na, K) are generally better by flame AAS than by ICP.
- Detection limits for refractory elements (for example, B, Ti, V, Al) are better by ICP than by flame AAS.
- Non metals such as sulfur, nitrogen, carbon, and the halogens (for example, I, Cl, Br) can only be determined by ICP.

While it is possible to determine phosphorous by AAS, its detection limit by ICP is more than three orders of magnitude better.

Optimum detection of non metals such as S, N and halogens by ICP-ES can only be achieved if a vacuum monochromator, with purged transfer optics, is used. The optics must be purged to exclude atmospheric oxygen and eliminating its absorption.

Sulfur can be measured at 180.73 nm by purging the monochromator. To detect the primary aluminium wavelength at 167.08 nm, the monochromator must first be evacuated, then purged with the inert plasma gas.

Note that a continuous flow vapor generation accessory can be used with either ICP-ES or AAS for improved detection limits for As, Se, Hg, Sb, Bi and Ge.

Sample Throughput

In ICP-ES, the rate at which samples may be determined depends on the type of instrument: both simultaneous and sequential ICP spectrometers are available. Most ICP spectrometers purchased are the sequential type, providing maximum flexibility of choice of element and analytical wavelength. Surveys have shown that most analysts are interested in 6–15 elements per sample and choose to pump the sample (which increases washout times) to improve precision and accuracy by minimizing viscosity effects. Simultaneous ICP spectrometers demonstrate an advantage in analytical speed over sequential ICP spectrometers when more than 6 elements/sample are measured.

If a "one off" sample is presented for a few elements, flame AAS is faster. However, with flame equilibration time, program recall and monochromator condition changes, the cross over point where sequential ICP becomes faster than AAS is approximately 6 elements/sample for routine analysis.

Unattended Operation

Flame AAS cannot be left completely unattended for safety reasons. An ICP-ES instrument or graphite furnace AA can be left to run overnight as no combustible gases are involved, effectively increasing the working day from 8 hours to 24 hours.

Linear Dynamic Range

The inductively coupled plasma is doughnut shaped (with a “hollow” center). The sample aerosol enters the base of the plasma via the injector tube. The “optical thinness” of the ICP results in little self absorption and is the main reason for the large linear dynamic range of about 10^5. For example, copper can be measured at the 324.75 nm wavelength from its detection limit of about 0.002 ppm to over 200 ppm. In ICP, extrapolation of two point calibrations can be accurately used to achieve orders of magnitude above the top standard. This compares to a linear dynamic range of typically 10^3 for AAS.

Interferences

Chemical

Chemical interferences are relatively common in AA, especially with graphite furnace AA, but may be minimized with chemical modifiers.

ICP-ES is almost free from chemical interferences. The chemical bonds that still exist at below 3000 °C are completely ruptured at above 6000 °C. The high temperatures reached in a plasma eliminate chemical interferences, which accounts (for the most part) for the better detection limits achieved for refractory elements.

Ionization

The ICP contains a large number of free electrons, so ionization interferences for most applications are virtually nonexistent. Ionization interferences can be encountered when determining elements in matrices that contain very high concentrations of Group I elements (for example, Na & K). However, these effects can be minimized by optimizing the plasma viewing height.

Ionization interferences may also be found in AAS, such as, when measuring certain Group II elements in a nitrous oxide flame. An ionization buffer such as Cs, Li or K can be added to both samples and standards to minimize this effect.

Spectral

The optical requirements of AAS are fairly simple. The monochromator only needs to distinguish a spectral line emitted from the hollow cathode lamp from other nearby lines. The lamp itself only emits a few spectral lines. Most elements require 0.5 nm resolution with only iron, nickel and cobalt of the common elements requiring 0.2 nm or better.

In ICP-ES, the rich spectra present in the plasma means that there is a greater possibility of spectral interference. Spectral resolutions of 0.010 nm or better are required to resolve nearby interfering lines from the atomic and ionic analytical emission signals of interest.

Spectral interference in sequential ICP spectrometers can, in most cases, be overcome by selecting a different elemental wavelength with similar detection limits. With simultaneous ICP spectrometers, the elements and the wavelengths which may be determined are fixed at the time of purchase, and an alternative line may not be available. In this case, inter-element correction may be used to minimize the spectral interference.

Physical

These interferences relate to the different properties of various samples and can affect sample transport and droplet formation. ICP tends to be more susceptible to such interference because of the smaller droplet size required and lower transport efficiency.

Precision

Precision can be termed short term (or within-run) and long term (over a period of one day). For AAS a precision of 0.1–1% is typical for the short term, but recalibration is required over a longer period. With ICP-ES the short term precision is typically 0.3–2%, but precisions of 2–5% are not uncommon over an 8 hour period without recalibration.

One technique used to eliminate backlash in the grating drive mechanism of ICP spectrometers is by scanning and measuring at the same time. This method of measurement can be termed as “measurement on the move” and effectively results in poor short term precision. A more recent method drives the grating to a wavelength near the analytical peak. A refractor scan is then performed over a smaller wavelength region in order to identify and locate the peak position. Finally the refractor plate is repositioned “at the peak” where the replicate measurements are then performed. This method offers better precision.

AAS v ICP – A quick guide

	ICP-OES	**Flame AAS**	**Furnace AAS**
Detection limits	Best for : Refractories Non metals P, S, B, Al V, Ba, Ti	Best for : Group I metals Na, K Volatile elements Pb, Zn Rare Earths	Best for : All elements except : B,W,U, Refractories, for example P, S Halogens
Sample throughput	Best if more than 6 elements/sample	Best if less than 6 elements/sample	Slow (typically 4 mins/element)
Linear dynamic range	10^5	10^3	10^2
Precision Short term	0.3 – 2%	0.1 – 1%	0.5 – 5%
Long term (over 8 hrs)	Less than 5%		
Interferences			
Spectral	Many	Virtually none	Minimal
Chemical	Virtually none	Some	Many
Ionization	Minimal	Some	Minimal
Operating costs	High	Low	Relatively high
Combustible gases	No	Yes	No

Table 1. Guide to ICP/AAS Analytical Values

				ICP	**Flame AA**			**Zeeman Furnace AA**			
Element		**AA λ (nm)**	**ICP λ (nm)**	**Detection limit µg/L**	**Characteristic conc µg/L**	**Detection limit µg/L**	**Flame type**	**Characteristic*** conc** µg/L**	**Mass pg**	**MSR %**	**El**
Silver	Ag	328.1	328.068	3	30	2	Air	0.035	0.7	97	Ag
Aluminium	Al	309.3	167.081	1.5	800	30	N_2O	0.25	5	100	Al
Arsenic	As	193.7	188.985	12	500	300	N_2O	0.5	10*	86	As
Gold	Au	242.8	267.595	5.5	100	10	Air	0.22	4.4	94	Au
Boron	B	249.8	249.773	1.5	8000	500	N_2O	43	855*	70	B
Barium	Ba	553.6	455.403	0.07	200	20	N_2O	0.85	17	100	Ba
Beryllium	Be	234.9	313.042	0.2	15	1	N_2O	0.025	0.5	64	Be
Bismuth	Bi	223.1	223.061	12	200	50	Air	0.45	9	88	Bi
Bromine	Br		163.340	6000							Br
Carbon	C		247.856	65						–	C
Calcium	Ca	422.7	393.366	0.03	10	1	N_2O	0.03	0.6	94	Ca
Cadmium	Cd	228.8	228.802	1.5	10	2	Air	0.01	0.2*	87	Cd
Cerium	Ce	520.0	418.660	7.5	100000	100000	N_2O			–	Ce
Chlorine	Cl		725.665	200000						–	Cl
Cobalt	Co	240.7	228.616	5	50	5	Air	0.21	4.2	98	Co
Chromium	Cr	357.9	267.716	4	50	6	N_2O	0.075	1.5	100	Cr
Cesium	Cs	852.1	455.531	3200	20	4	Air	0.55	11	58	Cs
Copper	Cu	324.7	324.754	2	30	3	Air	0.3	6	84	Cu
Dysprosium	Dy	421.2	353.170	0.3	600	30	N_2O	2.3	45	100	Dy
Erbium	Er	400.8	337.271	0.7	500	50	N_2O	5	100	100	Er
Europium	Eu	459.4	381.967	0.3	300	1.5	N_2O	1.3	25	100	Eu
Iron	Fe	248.3	259.940	1.5	50	6	Air	0.06	1.2	97	Fe
Gallium	Ga	294.4	417.206	6.5	800	100	Air	0.23	4.5*	80	Ga
Gadolinium	Gd	368.4	342.247	2.5	20000	2000	N_2O			–	Gd
Germanium	Ge	265.1	265.118	13	1000	200	N_2O	0.45	9*	100	Ge
Hafnium	Hf	307.3	264.141	4	10000	2000	N_2O			–	Hf
Mercury	Hg	253.7	184.950	8.5	1500	200	Air	7.5	150*	69	Hg

*Modifier used to obtain these results.

**20 µL injection

***The Characteristic Masses listed were determined in aqueous solution using maximum heating rate in argon with zero gas flow during atomization.

Table 1. Guide to ICP/AAS Analytical Values (continued)

				ICP	Flame AA			Zeeman Furnace AA			
Element		**AA λ (nm)**	**ICP λ (nm)**	**Detection limit µg/L**	**Characteristic conc µg/L**	**Detection limit µg/L**	**Flame type**	**Characteristic*** conc** µg/L**	**Mass pg**	**MSR %**	**El**
Holmium	Ho	410.4	345.600	0.5	700	40	N_2O			–	Ho
Iodine	I		178.276	60							I
Indium	In	303.9	325.609	18	150	40	Air	0.35	7.0*	100	In
Iridium	Ir	208.9	224.268	3.5	800	500	Air	6.8	135	97	Ir
Potassium	K	766.5	766.490	10	7	3	Air	0.02	0.4	90	K
Lanthanum	La	550.1	379.478	0.02	40000	2000	N_2O			–	La
Lithium	Li	670.8	670.784	0.6	20	2	Air	0.2	4	49	Li
Lutetium	Lu	336.0	261.542	0.05	7000	300	N_2O			–	Lu
Magnesium	Mg	285.2	279.553	0.1	3	0.3	Air	0.01	0.2	75	Mg
Manganese	Mn	279.5	257.610	0.3	20	2	Air	0.03	0.6	92	Mn
Molybdenum	Mo	313.3	202.030	4	300	20	N_2O	0.35	7	96	Mo
Nitrogen	N		174.272	50 000							N
Sodium	Na	589.0	588.995	1	3	0.2	Air	0.005	0.1	92	Na
Niobium	Nb	334.9	309.418	4	20000	2000	N_2O			–	Nb
Neodymium	Nd	492.5	401.225	2	6000	1000	N_2O			–	Nd
Nickel	Ni	232.0	231.604	5.5	70	10	Air	0.24	4.8	98	Ni
Osmium	Os	290.9	225.585	5	1000	100	N_2O			–	Os
Phosphorous	P	213.6	177.499	18	120000	40000	N_2O	110	2200*	69	P
Lead	Pb	217.0	220.353	14	100	10	Air	0.28	5.5	92	Pb
Palladium	Pd	244.8	340.458	7	50	10	Air	0.43	8.6	100	Pd
Praseodymium	Pr	495.1	417.939	0.8	20000	10000	N_2O			–	Pr
Platinum	Pt	265.9	265.945	20	1000	100	Air	3.5	70	82	Pt
Rubidium	Rb	780.0	780.023	35	50	10	Air	0.05	1	90	Rb
Rhenium	Re	346.1	227.525	11	8000	1000	N_2O			–	Re
Rhodium	Rh	343.5	343.489	5	100	5	Air	0.4	8	95	Rh
Ruthenium	Ru	349.9	267.876	5.5	400	100	Air	0.75	15	100	Ru
Sulphur	S		180.734	20						–	S
Antimony	Sb	217.6	217.581	18	300	40	Air	0.5	10	96	Sb
Scandium	Sc	391.2	361.384	0.4	300	50	N_2O			–	Sc
Selenium	Se	196.0	196.026	37	1000	500	N_2O	0.7	14*	92	Se
Silicon	Si	251.6	251.611	5	1500	300	N_2O	0.75	15	100	Si
Samarium	Sm	429.7	442.434	7	6000	1000	N_2O			–	Sm
Tin	Sn	235.5	242.949	15	700	100	N_2O	0.5	10*	93	Sn
Strontium	Sr	460.7	407.771	0.02	40	2	N_2O	0.1	2	94	Sr
Tantalum	Ta	271.5	268.517	9	10000	2000	N_2O			–	Ta
Terbium	Tb	432.7	350.917	5	7000	700	N_2O	0.18	3.5	90	Tb
Tellurium	Te	214.3	214.281	27	200	30	Air	0.45	9*	93	Te
Thorium	Th		274.716	17						–	Th
Titanium	Ti	364.3	334.941	0.6	1000	100	N_2O	2.5	50	100	Ti
Thallium	Tl	276.8	351.924	16	200	20	Air	0.75	15	63	Tl
Thulium	Tm	371.8	346.220	1.5	300	20	N_2O			–	Tm
Uranium	U	358.5	385.958	18	100000	40000	N_2O			–	U
Vanadium	V	318.5	309.311	2	700	100	N_2O	1.1	22	79	V
Tungsten	W	255.1	239.709	17	5000	1000	N_2O			–	W
Yttrium	Y	410.2	371.030	0.2	2000	200	N_2O			–	Y
Ytterbium	Yb	398.8	328.937	0.3	60	4	N_2O	0.15	3	97	Yb
Zinc	Zn	213.9	213.856	0.9	8	1.0	Air	0.0075	0.15	92	Zn
Zirconium	Zr	360.1	339.198	1.5	9000	1000	N_2O			–	Zr

*Modifier used to obtain these results.

** 20 µL injection

*** The Characteristic Masses listed were determined in aqueous solution using maximum heating rate in argon with zero gas flow during atomization.

Analytical Requirements

Before deciding which technique is appropriate, the chemist must define both present and future analytical requirements. That is:

- Number of samples/week?
- What matrices need to be analyzed? For example, steels, bronzes, effluents, soils.
- How many elements need to be determined for each sample type?
- What are the typical sample volumes?
- What elements need to be determined?
- What concentration ranges are present in the matrices?
- Would an Internal Standard be useful? For example, where the samples may change in viscosity from sample to sample, for example, battery acid analysis.
- What expertise do the operators have?
- How much money is available to purchase or lease costs/month?
- Cost of ownership and running costs. Can the user afford an automated AAS or ICP-ES, or is a simple AAS sufficient?

The answers to these questions will help you to decide which is the preferred technique. Sometimes the answer is further complicated by the fact that neither flame AAS nor ICP-ES will satisfy all requirements. You may find, as many do, that both an ICP-ES and a furnace AAS will be necessary to meet the analytical requirements.

For Deuterium Furnace systems, the equivalent Characteristic Concentration and Characteristic Mass is easily calculated using the following conversion:

CMn = CMz X MSR (%)/100 CCn = CCz X MSR (%)/100

where:

CMn = Characteristic Mass for Deuterium Furnace Systems

CMz = Characteristic Mass for Zeeman Furnace Systems (from Table 1)

MSR = Magnetic Sensitivity Ratio (as % from Table 1)

CCn = Characteristic Concentration for Deuterium Furnace Systems

CCz = Characteristic Concentration for Zeeman Furnace Systems (from Table 1).

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Improving Throughput for Oils Analysis by ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

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Introduction

Trend analysis of wear metals in lubricating oils is a proven, cost-effective predictive maintenance technique. The presence and levels of various metal elements in lubricating oils gives an indication of the type of wear occurring in an engine. For example, an increase in the level of copper may indicate increased wear of bushings. Non-metals such as silicon, boron and phosphorus elements can also be determined. Monitoring the levels of wear metals and other elements in lubricating oils provides many benefits apart from predicting engine failure. For example, machinery can be kept up and running until maintenance becomes necessary, avoiding premature maintenance. Potential problems can be associated with specific components, eliminating complete teardowns.

The inductively coupled plasma optical emission spectroscopy (ICP-OES) technique for monitoring wear metals is the method of choice for trend analysis because it is fast and accurate. For the busy laboratory, not only is accuracy and long-term stability important; sample throughput is often a vital factor. The most significant contributor to the time taken for an analysis is the sample introduction system; the actual measurement time is most often less than one tenth of the total analysis time. This work shows that the use of a novel pump tubing arrangement can improve the speed of analysis. Using an improved sample introduction system, it was possible to accurately determine key wear metals and other elements in less than 50 seconds per sample using one simple method.

Experimental

Instrumental

A Vista-PRO simultaneous ICP-OES with a radially viewed plasma was used. The radial plasma configuration is the accepted standard for the oils industry. The radial plasma orientation allows direct venting of combustion products, thereby reducing carbon build-up on the torch. The highly efficient 40 MHz free-running RF generator is easily able to cope with solvents to produce a stable, robust plasma with excellent long term stability. The instrument was fitted with a 3 channel peristaltic pump to allow a modified pump tubing configuration for faster sample uptake and washout. A glass concentric nebulizer with wide internal bore size was used to better handle particulates, and a glass double-pass spraychamber was used to prevent overloading the plasma with sample. Optimized instrument operating conditions are set out in Table 1.

Table 1. Instrument Operating Conditions

Parameter	Setting	Part number (where applicable)
Power	1.35 kW	
Plasma gas flow	15.0 L/min	
Auxilliary gas flow	2.25 L/min	
Nebulizer pressure or flow	110 kPa or 0.60 L/min	
Viewing height	10 mm	
Pump speed	12 rpm	
Sample uptake delay	15 s	
Stabilization time	5 s	
Rinse time	10 s	
Replicate read time	1 s	
Replicates	2	
Nebulizer type	Slurry glass concentric	20-100976-00
Torch type	Radial fully demountable torch kit (includes bracket and clamp)	99-101064-00
Spraychamber	Twister double pass	79-100437-00
Sample tubing to nebulizer	Grey/grey solvent flex	37-100352-00
Sample tubing to waste	Black/black solvent flex	37-100348-00
Tubing to waste from spraychamber	Solvent flex waste tubing	37-100354-00
Transfer tubing	Solvent flex transfer tubing ¼"internal diameter	37-100378-00
Drain tubing	Purple/black solvent flex	37-100470-00
Autosampler	AIM 1250*	

* Manufactured by A.I. Scientific, Scarborough, Qld, Australia

Standards and Reagents

Calibration solutions of 5, 10, 25, 50, 100, and 250 mg/L were prepared from Conostan S-21 certified standard, which contains 21 elements (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn) at 500 mg/kg in oil. These calibration solutions were viscosity matched using Conostan base oil 75. Single element standards of Ca, Fe, Pb, P, and Zn were prepared from certified 5000 mg/kg Conostan standards (Conostan Division, Conoco Specialty Products Inc., Ponca City, OK, USA). The single element standard concentrations prepared were 10, 25, 50, 100, 250, 500, 1000 and 2500 mg/L. Jet-A1 kerosene (Mobil, Melbourne, Australia) was used as diluent.

Results

Detection Limits

In general, sensitive emission line wavelengths have lower detection limits than less sensitive emission line wavelengths for any given element. This is because sensitive emission lines produce a larger signal for a given concentration than less sensitive emission lines. Thus, low concentrations can be better detected using a sensitive emission line wavelength than an insensitive one. Frequently, detection limits improve with increasing read time because readout noise is reduced. The detection limits of various elements in kerosene are shown in Table 2. All detection limits in the table are below 1 mg/L, which easily allows trace levels of wear metals to be detected and a trend to be observed, even at low levels.

Table 2. Detection Limits of Elements in Kerosene at 2, 5 and 10 Seconds Integration Time

Element and emission line wavelength	3 σ Detection limits (mg/L) 1 s	2 s	3 s
Ag 328.068	0.006	0.003	0.002
Al 308.215	0.05	0.02	0.02
Al 396.152	0.05	0.02	0.01
B 249.772	0.021	0.007	0.005
Ba 455.403	0.003	0.002	0.001
Ba 493.408	0.0010	0.0007	0.0005
Ca 317.933	0.02	0.01	0.01
Ca 396.847	0.002	0.002	0.002
Cd 226.502	0.023	0.003	0.002
Cr 284.325	0.012	0.005	0.003
Cu 327.395	0.011	0.004	0.003
Fe 259.940	0.014	0.006	0.005
Fe 274.932	0.06	0.02	0.02
Mg 280.270	0.001	0.001	0.001
Mn 257.610	0.002	0.001	0.000
Mo 202.032	0.072	0.009	0.005
Na 589.592	0.004	0.002	0.002
Ni 230.299	0.08	0.02	0.01
P 213.618	0.26	0.03	0.02
Pb 220.353	0.39	0.05	0.03
Si 251.608	0.05	0.02	0.02
Sn 283.998	0.11	0.04	0.02
Ti 336.122	0.003	0.002	0.001
V 311.837	0.012	0.004	0.003
Z n 206.200	0.063	0.007	0.005
Zn 213.857	0.017	0.002	0.002

Linear Range

In general, the maximum accurately measurable concentration of an element is obtained by using a less sensitive emission line wavelength for that element. Although sensitive emission line wavelengths have lower detection limits than insensitive ones, insensitive emission line wavelengths can measure higher maximum concentrations. Some elements, such as calcium and phosphorus, may be present at high concentrations in oils, so a high maximum measurable concentration is desirable. The wavelengths chosen for analysis reflect a compromize between best detection limits and desired concentration range.

Table 3. Maximum Measurable Concentration of Selected Elements at Specified Emission Line Wavelengths

Element and emission line wavelength	Maximum concentration (mg/L)
Ag 328.068	250+
Al 308.215	250+
Al 396.192	100
B 249.772	250+
Ba 455.403	100
Ba 493.408	250+
Ca 317.933	2500
Ca 396.847	100
Cd 226.502	250+
Cr 284.325	250+
Cu 327.395	250+
Fe 259.940	250+
Fe 274.932	1000
Mg 280.270	100
Mn 257.610	250+
Mo 202.032	250+
Na 589.592	250+
Ni 230.299	250+
P 213.618	2500
Pb 220.353	1500
Si 251.608	250+
Sn 283.998	250+
Ti 336.122	250+
V 311.837	250+
Zn 206.200	2500
Zn 213.857	250

* Note that 250+ designates an accurately measurable concentration that may surpass 250 mg/L.

Modified Pump Tubing Setup

To speed up sample delivery to the plasma, the flow rate of sample through the autosampler probe was increased based on the "rapid flow" concept conceived by Shane Elliott and investigated as applied to organic solutions by Ross Ashdown (both from Agilent). The idea is to increase the flow rate of sample from the autosampler to the peristaltic pump. To increase the sample flow rate, a wider internal diameter peristaltic pump tubing could have been used, but this would overload the nebulizer, adversely affecting nebulization. Instead, an additional sample peristaltic pump tube was introduced to the system via a T-piece inserted between the end of the autosampler line and the start of the sample peristaltic pump tubing so that sample would flow through two sample perstaltic pump tubings instead of one. One of the peristaltic pump tubes was directed to the nebulizer, and the other to waste, which avoided overloading the nebulizer with sample. By having sample flow through two pump tubings, the sample flow rate through the autosampler probe up to the point where the T-piece was inserted was increased, thus reducing sample uptake time.

To measure sample uptake time, kerosene was introduced to the autosampler probe manually after aspirating air, and the time taken for the plasma to turn bright green (which indicates that organic solution is being aspirated into the plasma) was measured by stopwatch. Table 4 shows that using the modified pump tubing setup, the sample uptake time was decreased by approximately 10 seconds. An added benefit of decreasing sample uptake time is that the time taken to achieve a fixed degree of washout is also reduced.

Table 4. Time Saved Using Modified Pump Tubing Setup

Pump tubing configuration	Acutal sample uptake time (s)	Sample uptake time in method (s)
Standard	24	25
Modified	15	15

Washout

To determine the washout achieved in an autosampler run, an analysis was performed where a blank kerosene solution was measured immediately following a solution containing 1000 mg/L of Fe. These two solutions were then measured in pairs six times each. Table 5 shows that three orders of reduction in sample concentration was achieved in an autosampler run with a rinse time of 10 seconds. If a more thorough rinse was required, then SmartRinse could have been used. The SmartRinse feature of the ICP Expert software optimizes the rinse time for each sample, ensuring that the rinse time is only as long as required to return the signal to that of a blank for each wavelength in the analysis [1]. This means that high concentration samples will take longer to analyze than low concentration samples. For this work, a washout of three orders was acceptable, so a short, fixed rinse time was used.

Table 5. Blank Results After Measuring 1000 mg/L Iron. This Demonstrates that Three Orders of Washout is Achieved with a Rinse Time of 10 Seconds.

Kerosene blank measurement number	Measured Fe conc. (mg/L)
2	0.66
4	0.77
6	0.79
8	0.79
10	0.80
12	0.64

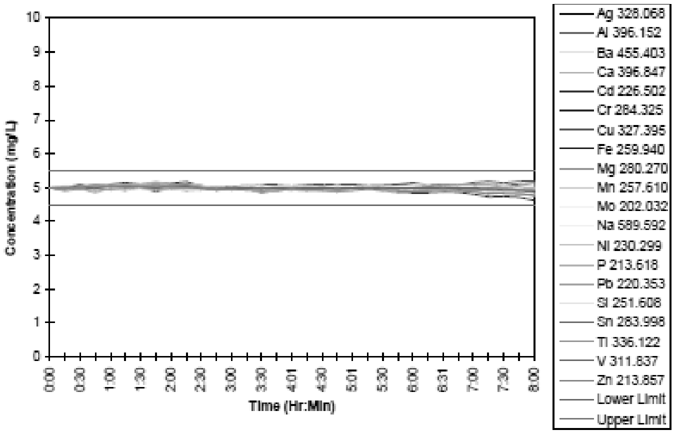

Figure 1. Stability of the Vista-PRO radial instrument over 8 hours. Results remained within ±10% for all elements in the 5 mg/L S21 kerosene solution without internal standardization or recalibration.

Long-Term Stability

A 5 mg/L solution of S21 elements in Jet-A1 kerosene was analysed continuously over an eight hour period. No recalibrations were performed, and no internal standard was used. Figure 1 shows that results remained within 10% of the true value over the entire 8 hours. Precision was typically better than 2 %RSD.

Conclusion

The Vista-PRO radial ICP-OES provides excellent throughput at 47 seconds per sample using a simple optimized sample introduction system. The detection limits and maximum measurable concentration of selected wavelengths allows typical oil samples to be analysed, while the excellent stability allows continuous running without recalibration, providing a saving on costs by reducing analysis time and the amount of standard solution used.

Acknowledgements

The author would like to thank Shane Elliott (Varian Australia) for the initial concept and his advice with alternative sample pump tubing configurations, Ross Ashdown (Varian U.K.) for his early work with fast throughput for organics, Barry Sturman, Alan Wiseman and Kate Pearson-Santiago (Varian Australia) for editing, and Glyn Russell (Varian Australia) for his input, encouragement and review of this work.

Reference

1. I. Szikla, SmartRinse - the latest advance in maximizing

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Printed in the USA
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Agilent Technologies

Analysis of Fluid Cat Cracker Feed using an Agilent J&W FactorFour VF-5ht UltiMetal Column

Application Note

Author

John Oostdijk
Agilent Technologies, Inc.

Introduction

This analysis of fluid cat cracker feed is performed using a VF-5ht UltiMetal column. The column has been developed using proprietary UltiMetal technology that provides a virtually unbreakable metal column material with excellent inertness properties similar to fused silica tubing. The UltiMetal tubing is coated with the VF-5 low bleed arylene stabilized liquid phase, resulting in a highly temperature stable and durable column perfectly suited for a variety of high temperature applications.

Conditions

Technique: GC-FID

Column: VF-5ht UltiMetal, 15 m x 0.32 mm Df = 0.1 µm + Retention Gap, 2 m x 0.53 mm (p/n CP9095)

Sample: 1 % CDU5 FCC Feed, 1 % in CS2

Carrier Gas: Hydrogen, constant flow mode 10 mL/min

Injector: On-column (1093), reversed liner, 100 °C (0 min) to 400 °C with 15 °C/min

Injection Volume: 1.0 µl

Temperature: 50 °C (1 min) to 450 °C (20 mins) with 10 °C / min

Detection: FID (HT), 400 °C

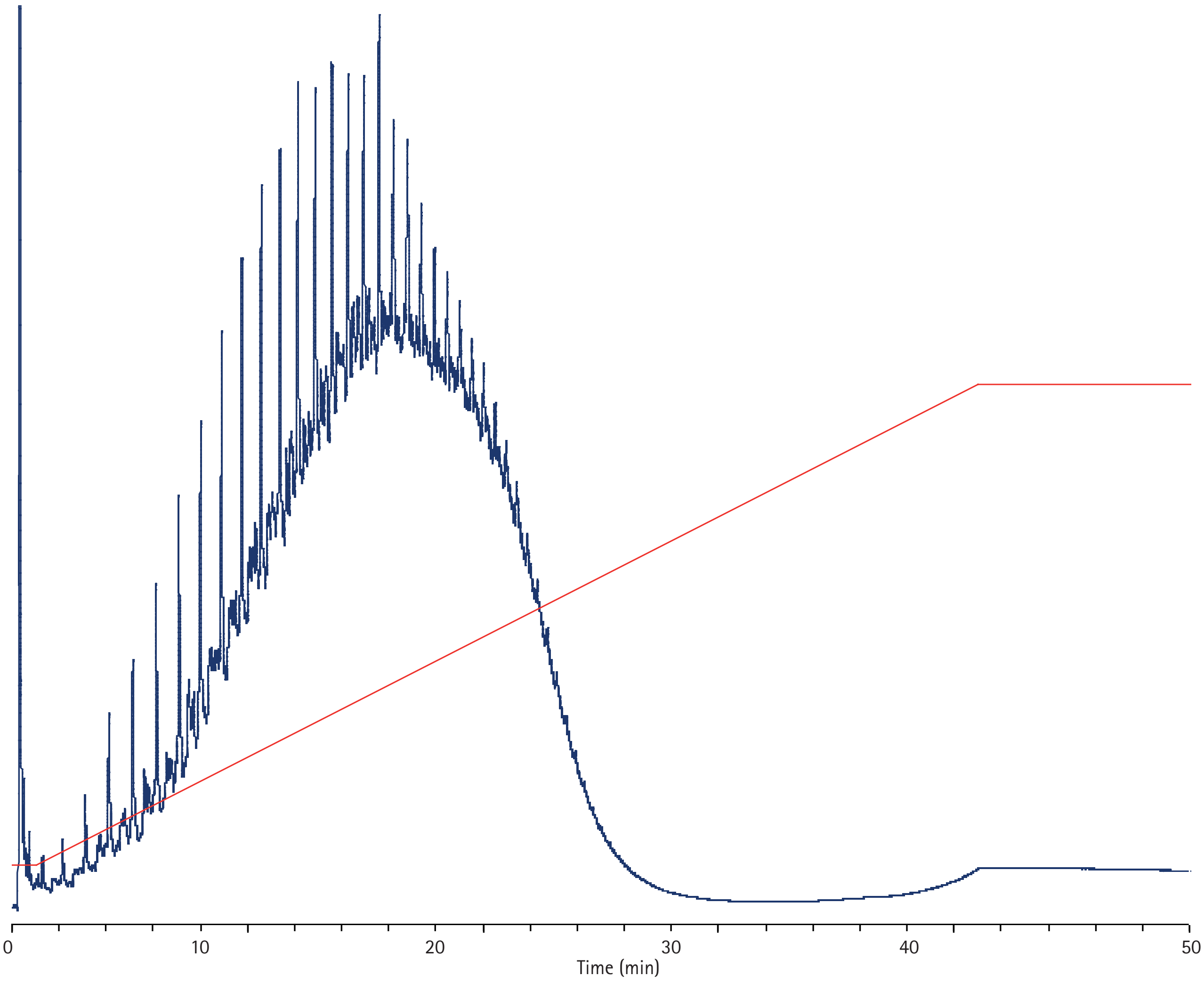

Figure 1. Analysis of fluid cat cracker feed using a VF-5ht UltiMetal column

www.agilent.com/chem

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Agilent Technologies

Analysis of Diesel using an Agilent J&W FactorFour VF-5ht UltiMetal Column

Application Note

Author

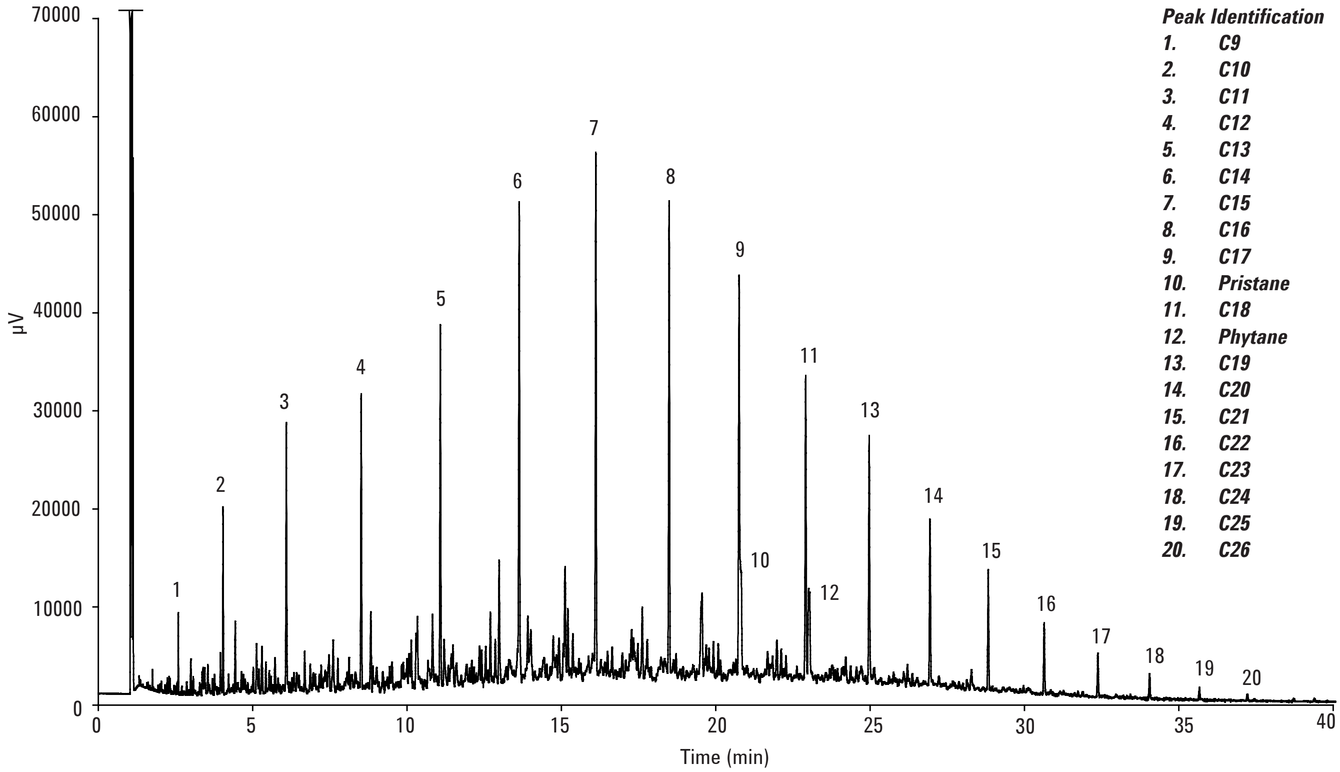
John Oostdijk
Agilent Technologies, Inc.

Introduction

This analysis of diesel is performed using a VF-5ht UltiMetal column. The column has been developed using proprietary UltiMetal technology that provides a virtually unbreakable metal column material with excellent inertness properties similar to fused silica tubing. The UltiMetal column tubing is coated with the VF-5ms low bleed arylene stabilized liquid phase, resulting in a highly temperature stable and durable column perfectly suited for a variety of high temperature applications.

Conditions

Technique:	GC	Carrier Gas:	Hydrogen, 65 kPa (9 psi)
Column:	VF-5ht UltiMetal, 30 m x 0.25 mm (part number CP9093) Df = 0.1 µm + Retention Gap, 2 m x 0.53 mm	Injector:	Split, 325 °C, split ratio 1:100
		Injection Volume:	2.0 µl
		Temperature:	50 °C to 400 °C with 5 °C/ min
Sample:	Diesel, 0.1 % (Pentane)	Detection:	FID, 340 °C



Peak Identification

1.	***C9***
2.	***C10***
3.	***C11***
4.	***C12***
5.	***C13***
6.	***C14***
7.	***C15***
8.	***C16***
9.	***C17***
10.	***Pristane***
11.	***C18***
12.	***Phytane***
13.	***C19***
14.	***C20***
15.	***C21***
16.	***C22***
17.	***C23***
18.	***C24***
19.	***C25***
20.	***C26***

Analysis of Diesel using a VF-5ht UltiMetal column

www.agilent.com/chem

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SI-01131

Agilent Technologies

Determination of Rhodium in Catalyst Oil and Aqueous Samples Using the Agilent 710 ICP-OES

Application Note

Energy and Fuels

Author

Jin-Na Chang

Introduction

A series of oil catalyst samples and an unknown aqueous sample were supplied for analysis. The rhodium content in these samples was determined using the Agilent 710 ICP-OES axially viewing ICP-OES. The oil catalyst samples were prepared using microwave digestion.

The axially viewing ICP-OES was selected for measurement as the expected rhodium content was low, and this system provides better sensitivity than that achieved by the radially viewed configuration, independent of the complexity of the sample medium [1]. The improvement in sensitivity with the axially viewed configuration is typically up to a 20 fold improvement in detection limits [1,2].

Instrumentation

All sample measurements were performed on a Agilent 710 ICP-OES axially viewing ICP-OES with simultaneous CCD detection.

The Agilent 710 ICP-OES is a simultaneous ICP-OES featuring an Echelle polychromator and a megapixel CCD detector, which provides the benefit of simultaneous measurement and continuous wavelength coverage over the range from 177 to 785 nm. The polychromator can be purged with a low flow of either argon or nitrogen for improved detection capability when measuring emission lines at low UV wavelengths.

The system is supplied as standard with a 3-channel peristaltic pump and manual pressure control of the nebulizer gas flow. The standard sample introduction system consists of a glass concentric nebulizer (Conikal) and a glass cyclonic spray chamber. Agilent ICP Expert II software was used for instrument operation. The operating parameters of the system are listed in Table 1.

Table 1. Instrument Operating Parameters

Condition	Setting
Power	1.15 kW
Plasma gas flow	16.5 L/min
Auxiliary gas flow	1.5 L/min
Spray chamber type	Glass cyclonic (single-pass)
Torch	Standard one piece axial torch
Nebulizer pressure	200 kPa
Nebulizer type	Conikal
Replicate read time	5 s
Auto-integration	On
Number of replicates	3
Stabilization time	15 s
Pump tubing	Sample: white-white (1.05 mm ID) Waste: blue-blue (1.65 mm ID) Buffer/Reference element: black-black (0.76 mm ID)
Sample uptake delay time	15 s
Pump speed	15 rpm
Rinse time	10 s
Fast pump	On
Background correction	Fitted

Sample Preparation and Instrument Conditions

All chemicals and reagents used were of high purity grade.

- HNO_3, Ultrapure, 60%, Merck.
- 40 and 100 mg/L Rh standard solutions as supplied by the client.
- Milli-Q water with resistivity less than 18 Mohm–cm^{-1}.

The oil catalyst samples were prepared using a microwave digestion system with temperature and pressure control (Shanghai EU Microwave Chemistry Technology Co. Ltd. model WX-4000).

0.3 g of sample was accurately weighed and placed into a digestion vessel. The digestion vessel was heated on a conventional hot plate at 80 °C for approximately 20 minutes. The aim of this sample pre-treatment was to remove the volatile organic components from the sample. The digestion vessel was removed from the hot plate and allowed to cool.

This solution was quantitatively transferred into a microwave digestion vessel and 4 mL of nitric acid (HNO_3) was added. The digestion vessel was sealed and placed into the microwave digestion system. The microwave digestion method used is summarized in Table 2.

Table 2. Microwave Digestion Settings

Step	Temperature (°C)	Pressure (atm.)	Time (min.)
1	130	10	5
2	160	16	5
3	180	20	5
4	200	25	5

The digestion vessels were removed from the microwave digestion system and left to cool to room temperature. The digest was transferred to a volumetric flask and diluted on a mass basis. A summary of the initial sample weights, the final weights after dilution and observations on the digest obtained are summarized in Table 3.

As the expected concentration of rhodium in the aqueous sample was around 60 mg/L, no preparation was required for analysis. The aqueous sample was measured directly.

All the prepared samples were analyzed directly for rhodium.

Table 3. Actual Sample Weights Used for Digestion Together with Observations on the Samples Before and After Microwave Digestion

No.	Sample ID	Sample type	Expected Rh concentration	Observations	Sample weight (g)	Weight of predetermined volume (g)	Digest obtained
1	Q22321 2007-08-04	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3033	23.8461	Clear
2	Q22321 2007-08-05	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3260	27.5567	Clear
3	Q22321 2007-08-06	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3442	23.2292	Clear
4	Q22321 2007-08-07	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3386	22.7784	Clear
5	Q22321 2007-08-08	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3043	24.2429	Clear
6	Q22321 2007-08-09	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3380	24.9658	Clear
7	Q22321 2007-08-10	Oil catalyst	Very low	Light yellow, transparent oil sample with pungent odor	0.3025	22.2151	Clear
8	Q21011 2007-08-06	Oil catalyst	Est. 100-200 mg/L	Yellow, transparent oil sample with pungent odor	0.3096	52.3151	Light yellow color, but basically clear
9	Rhodium acetate solution	Aqueous solution	Est. 60 mg/L	Light yellow, transparent sample	N/A	N/A	N/A

Calibration Solutions

Conventional aqueous Rh standard solutions of 40 and 100 mg/L were provided by the client together with the samples.

For the determination of the aqueous sample, which was expected to be at a concentration of 60 mg/L, these standard solutions were used directly to calibrate the instrument.

For the determination of the digested oil samples, for which the Rh content was expected to be low, these standard solutions were diluted by a factor of 10 to concentrations of 4 and 10 mg/L respectively.

Results and Discussion

The calibration graphs obtained are shown in Figures 1 and 2.

The weight/dilution corrected sample results are listed in Table 4. These results have been converted back to report the actual rhodium content contained in the original samples. This takes into account the sample weight used for digestion and the applied dilution ratio during preparation.

The measured concentrations for rhodium in a number of the samples were close to the calibration blank solution. Accordingly, these results have been reported as "Not Detected" (ND).

Signal traces for the measured solutions where the Rh content could be quantified are included in Figures 3 to 5.

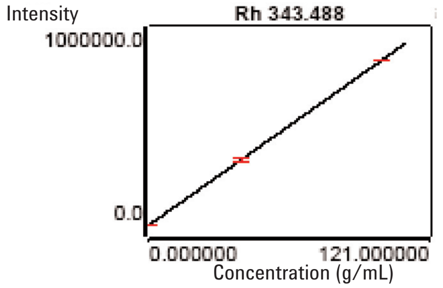

Figure 1. Calibration graph used for the determination of the aqueous sample at the Rh 343.488 nm emission line.

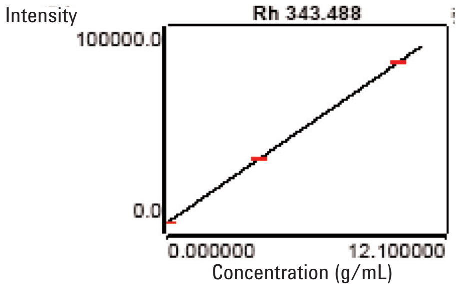

Figure 2. Calibration graph used for determination of the digested oil catalyst samples at the Rh 343.488 nm emission line.

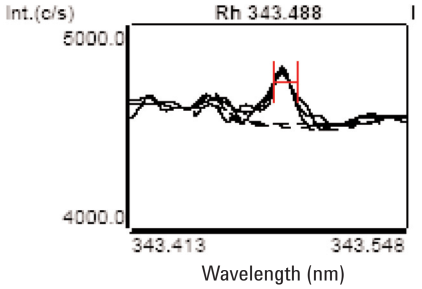

Figure 3. Signal trace for oil sample Q22321 2007-08-07.

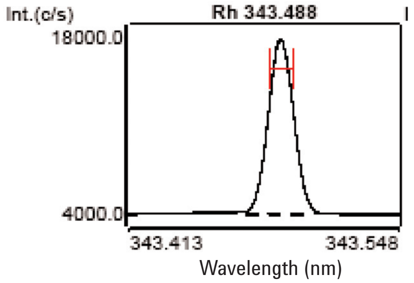

Figure 4. Signal trace for oil sample Q21011 2007-08-06.

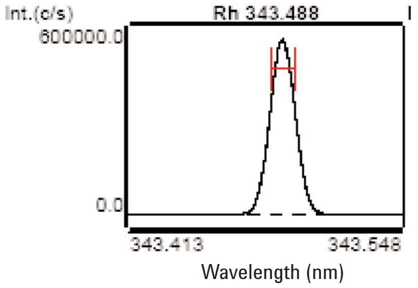

Figure 5. Signal trace for the rhodium acetate aqueous solution.

Table 4. Measured Rhodium Concentrations in Each of the Samples

Sample Type	Sample ID	Expected Rh Concentration (mg/L)	Measured Rh Concentration (mg/L)	Precision (% RSD)
Oil samples	Q22321 2007-08-04	Very low	ND	N/A
	Q22321 2007-08-05	Very low	ND	N/A
	Q22321 2007-08-06	Very low	ND	N/A
	Q22321 2007-08-07	Very low	3.08	4.15
	Q22321 2007-08-08	Very low	ND	N/A
	Q22321 2007-08-09	Very low	ND	N/A
	Q22321 2007-08-10	Very low	ND	N/A
	Q21011 2007-08-06	Est. 100–200 mg/L	216.20	0.197
Aqueous samples	Rhodium acetate	Est. 60 mg/L	55.26	0.842

Conclusion

Using the Agilent 710 ICP-OES axially viewing ICP-OES, it was possible to determine the rhodium content in both the oil catalyst and the aqueous samples without interferences. The oil catalyst samples were prepared using a microwave digestion system with temperature and pressure control. The digests obtained were clear, confirming complete digestion. The method demonstrated good results, although the Rh concentration in most samples was not detectable.

The results demonstrate this method can be readily applied to the routine determination of rhodium in oil catalyst and aqueous samples.

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1. F.V. Silva, L.C. Trevizan, C.S. Silva, A.R.A. Nogueira and J.A. Nobrega, Evaluation of inductively coupled plasma optical emissions spectrometers with axially and radially viewed configurations, Spectrochim. Acta, 2002, 57B, 1905.
2. I.B. Brenner and A.T. Zander, Axially and radially viewed inductively coupled plasmas – A critical review, Spectrochim. Acta, 2000, 55B, 1195.

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Agilent Technologies

Separation of Permanent Gases on a Liquid Phase

Separation of 5 permanent gases on a WCOT column with a liquid phase with high retention

Application Note

Authors

Rick Hamerlinck and Norbert Reuter
Agilent Technologies, Inc.

Introduction

Normally permanent gases are separated by PLOT (porous layer open tubular) columns with their high retentive phases. With WCOT (wall coated open tubular) columns sub-ambient temperatures are normally necessary. Thick films, like the 8 µm film thickness of the Agilent J&W Select CP-Sil 5CB for Formaldehyde, allow the use of high-inert liquid phases for the (pre-) separation of the standard permanent gases from carbon dioxide for possible column switching at normal ambient temperatures.

Materials and Methods

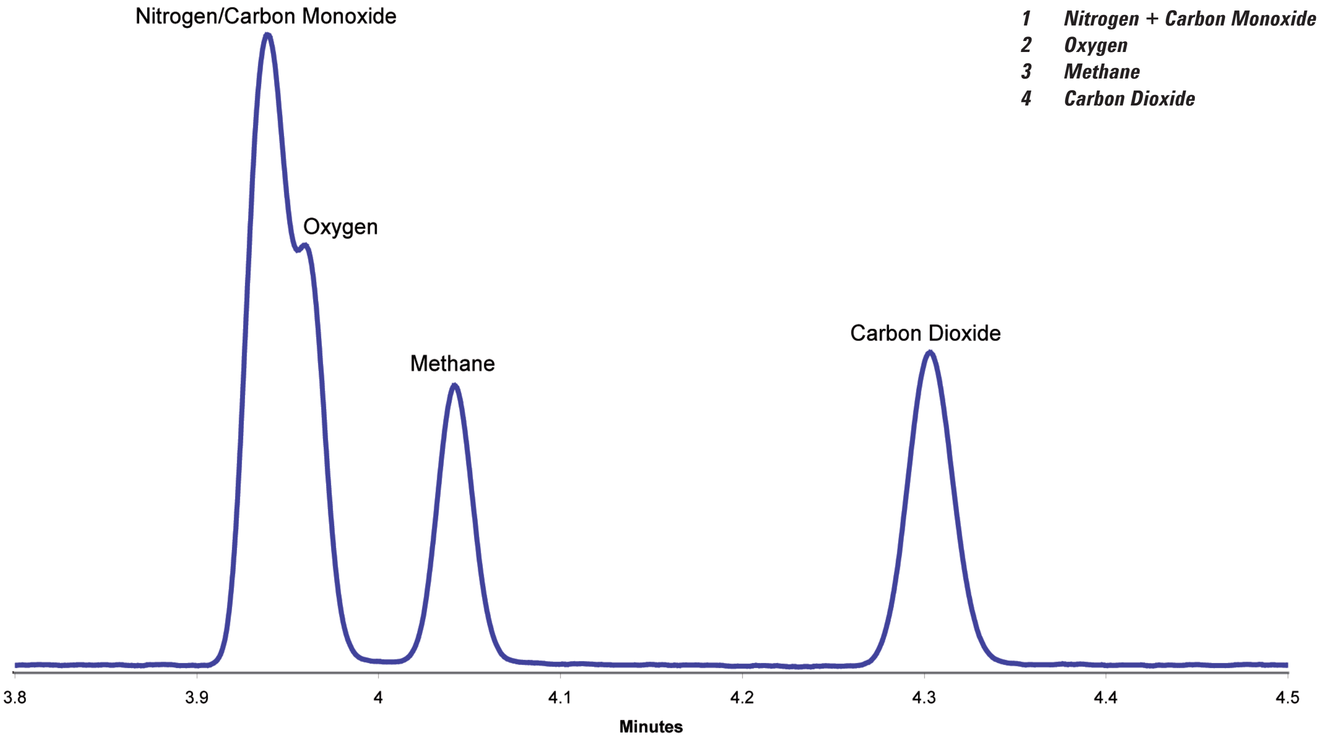
Technique: GC-Capillary Medium Bore
Instrument: GC Gas Chromatograph
Column: CP-Sil 5 CB for Formaldehyde, 0.32 mm x 60 m, df=8 µm (part number CP7475)

Carrier Gas: Helium at 25 psi (170 kPa)
Temp Program: 35 °C isothermal
Injector: Split/Splitless-Injector (1177) at 250 °C
Inj Volume: 500 µL (split ratio 1:20)

Detector: Thermal Conductivity Detector at 220 °C (Filament Temp. 280 °C)
Sample: All Gases 1% in Helium

Peak Identification

1	***Nitrogen + Carbon Monoxide***
2	***Oxygen***
3	***Methane***
4	***Carbon Dioxide***



Analysis of permanent gases at 35ºC

www.agilent.com/chem

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Agilent Technologies

Fast Refinery Gas Analysis Using the 490 Micro GC QUAD

Application Note

Authors

Coen Duvekot
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Introduction

There is a large variation in the composition and source of refinery gases. Therefore, the precise and accurate analysis of these gases is a significant challenge in today’s refineries. Typical sources include fluid coking overheads, ethylene, propylene, fuel gas, stack gas, off gas, etc. The physical stream ranges from gas to highly pressurized gas or liquid.

Very fast refinery gas analysis (RGA) is possible with the portable 490 Micro GC QUAD. This note describes the use of the 490 Micro GC for RGA, with results obtained in about two minutes.

Instrumentation

490 Micro GC QUAD

- Channel 1: Molsieve with back flush
- Channel 2: CP-PoraPlot U with back flush
- Channel 3: Aluminium oxide with back flush
- Channel 4: CP-Sil 5 CB

The Molsieve channel and the aluminium oxide channel are equipped with extra in-line filters between the manifold and the column module to ensure moisture and carbon-dioxide-free carrier gas. This enhances column lifetime and, most importantly, leads to stable retention times.

GC control and data handling software: Galaxie Chromatography Software.

Materials and Reagents

Channel 1, equipped with a Molsieve column, separates and analyzes the permanent gases except for carbon dioxide. Channel 2, with a CP-PoraPLOT U column, separates and analyzes the C2 gases and hydrogen sulfide. The C3 and C4 hydrocarbons are analyzed on the third channel with an Al2O3 column. Finally, the higher hydrocarbons are analyzed on the fourth channel, with a CP-Sil 5 CB column.

Table 1. Peak identification and composition of gas standards

Gas Standard

Peak #	Component	Amt (%)
1	Hydrogen	
3	Oxygen	
4	Nitrogen	
5	Methane	Bal
6	Carbon monoxide	

Refinery Gas standard

Peak #	Component	Amt (%)	Peak #	Component	Amt (%)
2	Helium	Bal	15	Propadiene	0.62
4	Nitrogen	5.1	16	n-Butane	1.0
5	Methane	24.9	17	tr-2-Butylene	0.5
6	Carbon monoxide	1.0	18	1-Butylene	0.5
7	Carbon dioxide	0.5	19	iso-Butylene	1.01
8	Ethylene	24.9	20	cis-2-Butylene	0.5
9	Ethane	5.0	21	iso-Pentane	0.5
10	Acetylene	1.0	22	Methyl acetylene	1.0
11	Hydrogen sulfide	1.01	23	n-Pentane	0.2
12	Propane	5.0	24	1, 3-Butadiene	1.0
13	Propylene	5.0	25	n-Hexane	0.2
14	iso-Butane	0.5			

Conditions

Table 2. Chromatographic conditions

	Channel 1	Channel 2	Channel 3	Channel 4
	10 m Molsieve	10 m CP-PoraPLOT U	10 m Al2O3/KCL	8 m CP-Sil 5 CB
Injector Temp (°C)	110	110	110	110
Column Temp (°C)	80	100	100	80
Carrier Gas	Argon	Helium	Helium	Helium
Column Head Pressure (kPa)	150	205	70	205
Injection Time (ms)	40	10	10	100
Back Flush Time (s)	11	7.1	33	N/A

Results and Discussion

Figures 1 and 2 show chromatograms of the Molsieve channel 1.

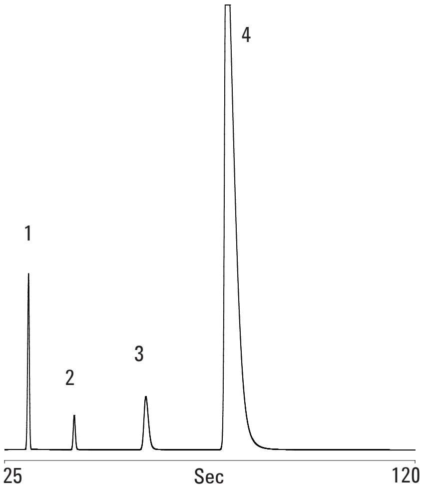

Figure 1. Standard gas on the Molsieve column, channel 1

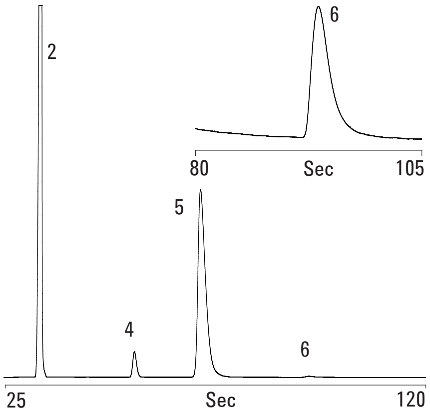

Figure 2. Refinery gas on the Molsieve column, channel 1

Hydrogen or helium, oxygen, nitrogen methane and carbon monoxide were separated and analyzed. Later eluting components were back flushed to vent.

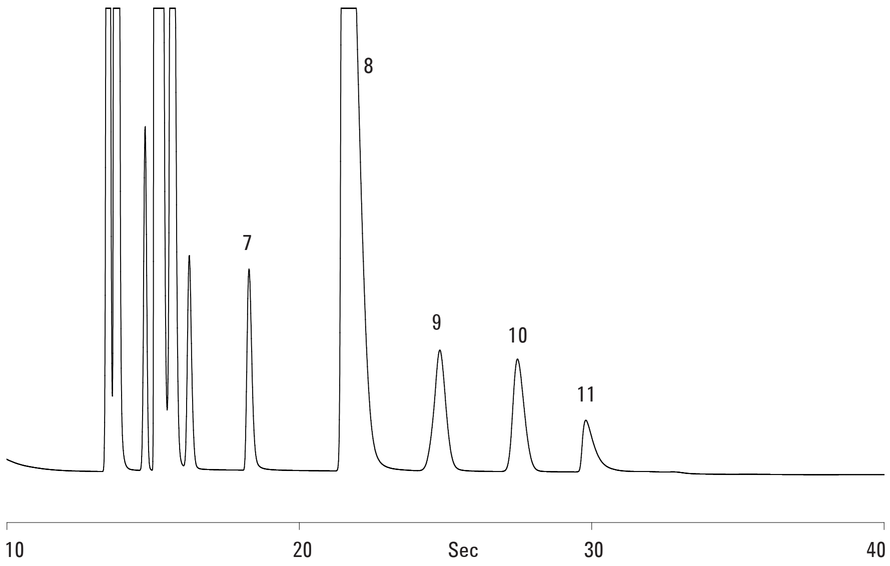

Figure 3. Refinery gas on the CP-PoraPLOT U column, channel 2

On the CP-PoraPLOT U channel (channel 2), the C2 hydrocarbons, hydrogen sulfide and carbon dioxide were separated and analyzed. The channel was equipped with a back flush later eluting components to vent.

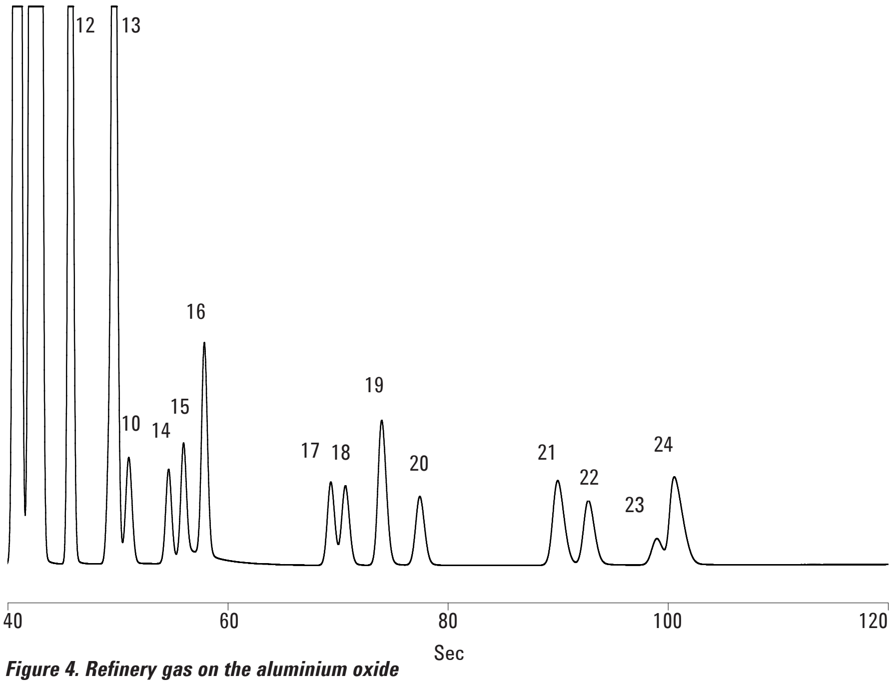

Figure 4. Refinery gas on the aluminium oxide column, channel 3

On channel 2 the C3 and C4 saturated and unsaturated hydrocarbons were separated and analyzed. This channel was also equipped with back flush in order to prevent the later eluting hydrocarbons from entering the analytical column. This prevented the later eluting components from interfering with the next analysis causing “ghost” peaks and/or baseline drift and higher noise. Furthermore, this channel was equipped with extra filters in the carrier gas lines, effectively protecting the analytical column from traces of moisture and carbon dioxide that could influence the chromatographic properties of the stationary phase in the long term.

Stable retention times are key factors for good chromatographic results. Repeatability results derived from Table 3 and Figure 5 for retention times are superb with RSDs around 0.1% and no drift.

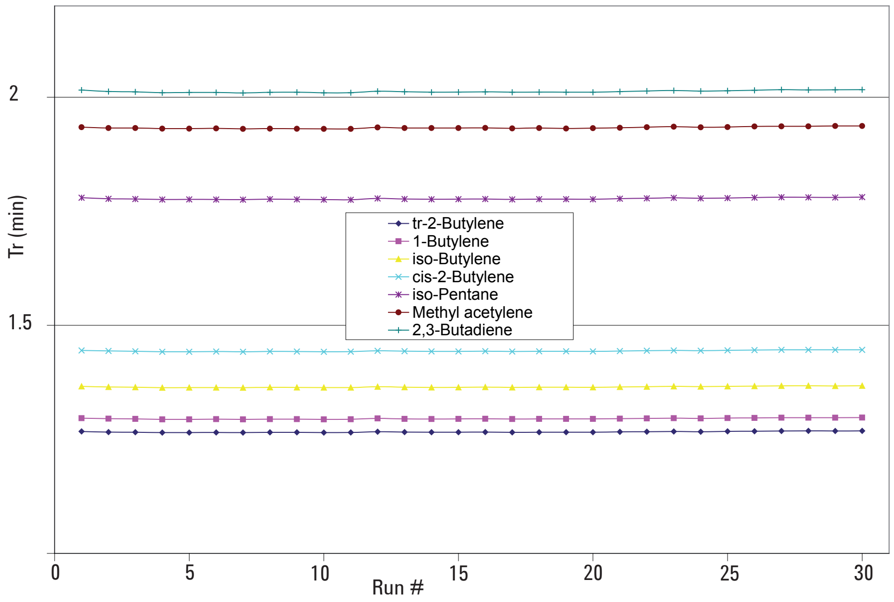

Figure 5. Repeatability figures for the aluminium oxide channel, channel 3

Table 3. Repeatability figures for the aluminium oxide channel

Run #	Tr (min) tr-2-Butylene	Tr (min) 1-Butylene	Tr (min) iso-Butylene	Tr (min) cis-2-Butylene	Tr (min) iso-Pentane	Tr (min) Methyl acetylene	Tr (min) 2, 3-Butadiene
1	1.2672	1.2963	1.366	1.4447	1.7797	1.934	2.0155
2	1.266	1.2952	1.3647	1.4437	1.7772	1.9322	2.0122
3	1.2657	1.2948	1.3643	1.443	1.7768	1.9323	2.0115
4	1.2647	1.2938	1.3632	1.442	1.7755	1.931	2.0097
5	1.2647	1.2937	1.3633	1.442	1.7758	1.931	2.0102
6	1.265	1.2942	1.3633	1.4423	1.7757	1.9315	2.0102
7	1.2648	1.2938	1.3632	1.442	1.7753	1.9303	2.0092
8	1.2653	1.2943	1.364	1.4427	1.7763	1.931	2.0105
9	1.2653	1.2943	1.3638	1.4423	1.776	1.9308	2.0108
10	1.2647	1.2938	1.3633	1.442	1.7753	1.9305	2.0095
11	1.265	1.294	1.3633	1.4422	1.7752	1.9303	2.0098
12	1.2667	1.2958	1.3653	1.444	1.778	1.9337	2.0128
13	1.2658	1.2948	1.3643	1.4432	1.7768	1.9322	2.0117
14	1.2655	1.2945	1.3638	1.4427	1.7762	1.9322	2.0108
15	1.2655	1.2947	1.364	1.4428	1.7763	1.9322	2.011
16	1.2658	1.295	1.3645	1.4432	1.7768	1.9325	2.0115
17	1.2653	1.2945	1.3638	1.4425	1.776	1.9315	2.0107
18	1.2657	1.2948	1.3642	1.443	1.7765	1.9322	2.011
19	1.2657	1.2947	1.3642	1.443	1.7765	1.9312	2.0108
20	1.2655	1.2947	1.364	1.4428	1.7762	1.932	2.0108
21	1.2663	1.2953	1.3648	1.4435	1.7775	1.9328	2.012
22	1.2667	1.2958	1.3653	1.4443	1.7782	1.934	2.0133
23	1.2672	1.2963	1.366	1.4448	1.7793	1.9353	2.0145
24	1.2667	1.2958	1.3655	1.4443	1.7782	1.9338	2.013
25	1.2675	1.2967	1.3662	1.445	1.7788	1.9343	2.0138
26	1.2678	1.2968	1.3667	1.4455	1.7798	1.9357	2.015
27	1.2683	1.2975	1.367	1.446	1.7807	1.936	2.0162
28	1.2685	1.2975	1.3673	1.4462	1.7803	1.936	2.0158
29	1.2682	1.2973	1.3668	1.446	1.7802	1.9367	2.016
30	1.2685	1.2977	1.3673	1.4462	1.781	1.9367	2.0163
Average	1.2662	1.2953	1.3648	1.4436	1.7774	1.9329	2.0122
Std Dev	0.0012	0.0012	0.0013	0.0014	0.0018	0.0020	0.0022
Rsd %	0.10%	0.09%	0.10%	0.10%	0.10%	0.10%	0.11%

Table 4. Reproducibility figures

Day	tr-2-Butylene	1-Butylene	iso-Butylene	cis-2-Butylene	iso-Pentane	Methyl acetylene	2, 3-Butadiene
1	1.2695	1.2988	1.3687	1.4481	1.7849	1.9406	2.0216
2	1.2678	1.2970	1.3668	1.4458	1.7815	1.9370	2.0173
3	1.2668	1.2958	1.3654	1.4443	1.7787	1.9339	2.0137
4	1.2665	1.2956	1.3652	1.4439	1.7781	1.9333	2.0130
8	1.2697	1.2989	1.3689	1.4483	1.7854	1.9405	2.0222
9	1.2681	1.2973	1.3671	1.4462	1.7821	1.9367	2.0180
10	1.2667	1.2957	1.3655	1.4443	1.7785	1.9345	2.0139
Average	1.2679	1.2970	1.3668	1.4458	1.7813	1.9366	2.0171
St. dev.	0.0013	0.0014	0.0015	0.0018	0.0031	0.0030	0.0037
RSD	0.10%	0.11%	0.11%	0.13%	0.17%	0.15%	0.19%

Table 4 and Figure 6 show the effects over several days. RSDs are only slightly higher when compared to the "results-per-day" which is to be expected. However, the results are very good, demonstrating the suitability of the Al2O3 channel for this type of analysis.

RSDs below 0.2% are shown in Table 4. During the ten day laboratory experiments no drift in retention times were observed, as can be seen in Figure 6.

Figure 6 shows no drift in retention time of components analyzed on the Al2O3 channel over ten days.

Figure 7 shows a chromatogram of refinery gas on the CP-Sil 5 CB channel. In this case the higher hydrocarbons C5+ were analyzed.

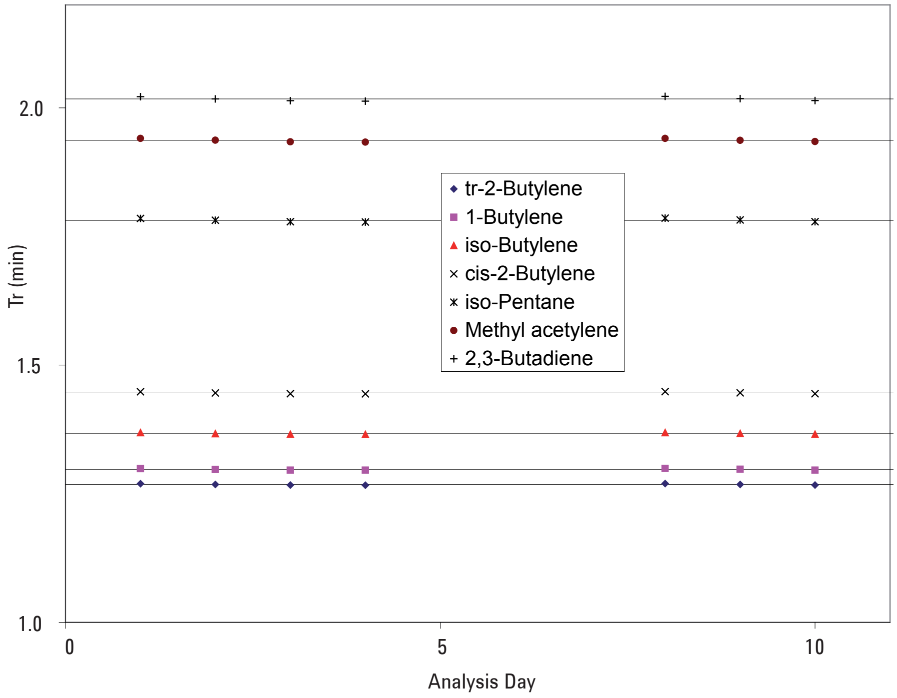

Figure 6. Reproducibility of the aluminium oxide channel, channel 3

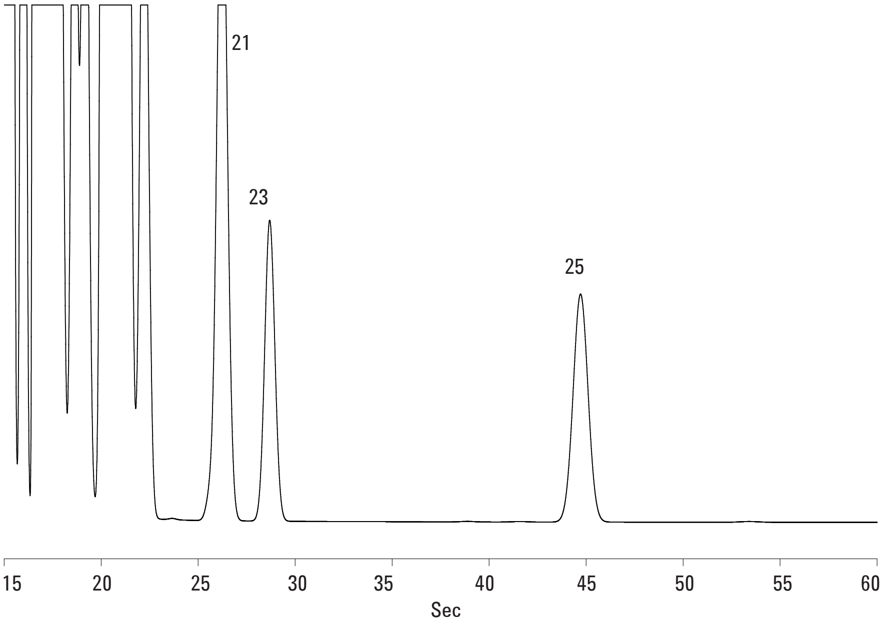

Figure 7. Refinery gas on the CP-Sil 5 CB column, channel 4

Conclusion

The 490 Micro GC QUAD was successfully used for the analysis of refinery gas. The permanent gases helium, hydrogen, oxygen, nitrogen, methane and carbon monoxide were analyzed on the Molsieve channel. The C2 hydrocarbons, carbon dioxide and hydrogen sulfide were analyzed on the second channel equipped with a CP-PoraPLOT U column. On the third channel, with an aluminium oxide column, the C3 and C4 hydrocarbons were analyzed. This channel was equipped with extra in-line filters to ensure moisture and carbon-dioxide-free carrier gas. This significantly enhanced column lifetime and ensured long-term stable retention times. Finally, the fourth channel, equipped with a CP-Sil 5 CB column, analyzed the C5+ hydrocarbons.

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Agilent Technologies

Detailed Separation of C_1-C_5 Light Hydrocarbons on CP-Al_2O_3/Na_2SO_4 PLOT GC Column

Application Note

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Introduction

Aluminum oxide PLOT columns are specifically designed for detailed C_1-C_{10} hydrocarbon analysis in chemical and petrochemical industries. Due to the high selectivity of CP-Al_2O_3 PLOT columns, it is possible to analyze ppm to percent levels of any C_1-C_5 impurities, including isomers, in main stream C_1-C_5 products. CP-Al_2O_3 PLOT columns offer a higher level of analytical selectivity and efficiency compared to super-thick film non-polar liquid stationary phase columns.

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The aluminum oxide column carries a sodium sulfate (Na_2SO_4) deactivation layer. The deactivation provides a reproducible and stable selectivity up to 200 °C. Sodium sulfate deactivation results in a more polar surface than potassium chloride (KCl)-treated alumina, retaining unsaturated compounds such as ethylene, acetylene (ethyne) and methyl acetylene (propyne) more strongly than their unsaturated peers.

The analysis of light hydrocarbons is performed in refinery gas, liquefied petroleum gas (LPG) and natural gas. Refinery gas is a mixture of gases generated during refinery processes used to process crude oil into various petroleum products as intermediate products or high grade end-products. The composition of refinery gas may vary. Common components include butanes, butenes (butylenes), methane, ethane and ethene (ethylene). The aluminum PLOT column offers added value in separating all of the components.

Natural gas consists of methane, light hydrocarbons such as ethane, propane and butane, and small quantities of derivatives such as carbon dioxide and nitrogen. The precise composition of natural gas may differ from region to region. LPG is a mixture of light hydrocarbons. It occurs naturally in crude oil and natural gas production fields and is also produced in the oil refining process. The main component gases of LPG are propane and butane.

The CP-Al_2O_3/Na_2SO_4 GC column provides separation of the main components and gives detailed quantitative data on the impurities.

This application note shows the analysis of 18 light hydrocarbons on a CP-Al_2O_3/Na_2SO_4 GC column.

Materials and Methods

Technique:	GC-FID
Column:	CP-Al_2O_3/Na_2SO_4, 50 m x 0.32 mm, df=5 µm (part number CP7565)
Temperature:	70 °C, 3 °C/min, 170 °C
Carrier Gas:	Hydrogen, constant pressure, 100 kPa (1.0 bar, 14.5 psi)
Injection:	250 °C, split 1:50
Detection:	FID, 275 °C
Sample:	Gas mixture, for concentrations see Table 1
Injection Volume:	5 µL

Results and Discussion

Figure 1 shows the chromatogram of the detailed analysis of 18 hydrocarbons within 20 minutes. The CP-Al_2O_3/Na_2SO_4 column provided very good peak shape and baseline separation. The alkynes, acetylene and propyne, show some tailing. This tailing is typical for Na_2SO_4 deactivated Al_2O_3 PLOT and is caused by the higher interaction of the polar alkynes with the polar Na_2SO_4 deactivation layer.

Table 1. Peak Identification

Peak	Compound	Concentration % (moles in He)
1	Methane	24.9
2	Ethane	5.0
3	Ethene (ethylene)	24.9
4	Propane	5.0
5	Cyclopropane	0.50
6	Propene (propylene)	5.1
7	Isobutane	0.50
8	n-Butane	1.00
9	Propadiene	0.60
10	Ethyne (acetylene)	1.01
11	*trans*-2-Butene	0.50
12	1-Butene	0.50
13	Isobutene	1.00
14	*cis*-2-Butene	0.50
15	Isopentane	0.50
16	n-Pentane	0.199
17	1,3-Butadiene	1.00
18	Propyne (methyl acetylene)	1.01

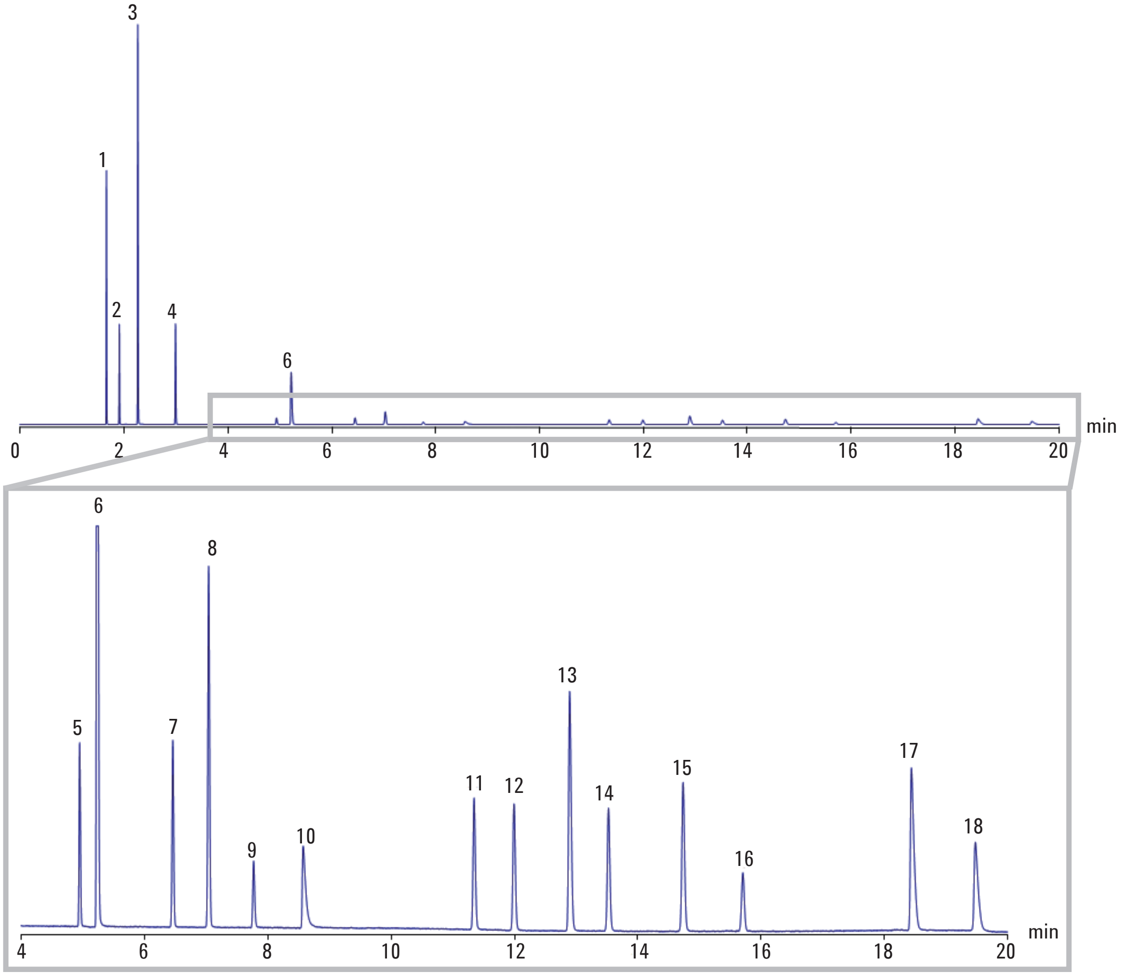

Figure 1. C_1-C_5 hydrocarbons analyzed on a CP-Al_2O_3/Na_2SO_4 column

Conclusion

The CP-Al_2O_3/Na_2SO_4 column is very suitable for the analysis of light hydrocarbons. The sodium sulfate deactivation provides additional resolution for separating all C_4 isomers.

The robustness of the column allows temperatures up to 200 °C to be used, enabling bake-out of the column at the end of the analysis without changes in selectivity.

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Agilent Technologies

Sensitivity Enhancement for Flame Atomic Absorption Spectrometry Using an Atom Concentrator Tube, the ACT 80

Application Note

Atomic Absorption

Author

Jonathan Moffett

Abstract

A simple attachment to enhance the sensitivity of flame atomic absorption spectrometry (FAAS) is described along with some performance results and practical applications. An historical review is also presented.

Introduction

In theory, atomic absorption spectrometry (AAS), is very simple: introduce ground state (metal) atoms into the appropriate instrument's optical path and measure the absorption of light at an appropriate wavelength [1]. The device that generates the atoms is called an atomizer and there are several types:

- Flame
- Vapor generation (cold and heated)
- Graphite furnace
- Cathodic discharge [2,3]

The flame atomization system offers several advantages:

- Relative freedom from interference
- Low capital cost
- Low running cost
- Rapid and simple operation

Flame atomic absorption spectrometry (FAAS) is routinely used to measure solutions at the parts per million level–equivalent to one gram of element per 1000 kg of solution–which is suitable for a wide range of analyses. The other atomizers offer such benefits as greater sensitivity or minimal sample preparation. However the initial outlay and running expenses can be higher. Much closer attention to the chemistry of the samples is also required. Consequently various schemes have been devised to enhance the sensitivity of FAAS without incurring the expense associated with the other techniques. Some of the more commonly used methods as well as some speculative ideas will be outlined.

Enhancements in FAAS

All methods to improve the sensitivity of FAAS must involve at least one of the following stages:

- Sample preparation/preconcentration
- Nebulization
- Atomization

Each of these techniques is discussed in turn.

Sample

The simplest and cheapest methods for improving sensitivity rely on increasing the concentration of the sample solution. After sample dissolution, one of the following methods of sample preconcentration may be applied:

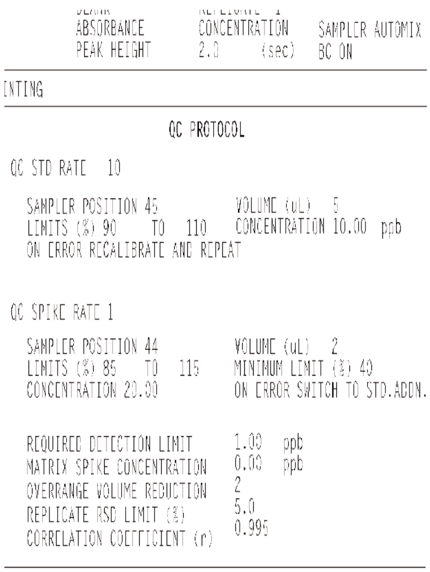
- Solvent evaporation
- Solvent extraction (for example, APDC/MIBK)
- Ion-exchange (for example, Chelex-100)
- Co-precipitation

While all are used [4], the method of solvent extraction (chelating the analyte and extracting with an organic solvent) is probably the most common. All of the methods are slow, increase the possibility of contamination and need a sample volume of at least 10 to 100 mL. The ion-exchange technique is the only one which could be developed into an automated online system and may overcome the speed and contamination problems.

Nebulization

Nebulization is the physical process of changing the bulk solution into a spray of fine droplets and mixing the droplets with the combustion gases.

The premix (laminar flow) burner assembly is invariably used in commercial FAAS instruments (Figure 1). A venturi is used to create a low pressure zone which draws up and causes nebulization of the solution. An impact bead breaks up the droplets even further. Mixing paddles or baffles may also be used to improve gas mixing and to remove larger droplets. The gas mixture is then passed into the burner and the combustion zone.



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          ABSORBANCE        CONCENTRATION      SAMPLER AUTOMIX
          PEAK HEIGHT       2.0       (sec)    BC ON
INTING

                           QC PROTOCOL

 QC STD RATE   10

   SAMPLER POSITION 45           VOLUME (uL)   5
   LIMITS (%) 90     TO   110    CONCENTRATION 10.00  ppb
   ON ERROR RECALIBRATE AND REPEAT


 QC SPIKE RATE 1

   SAMPLER POSITION 44           VOLUME (uL)   2
   LIMITS (%) 85    TO   115     MINIMUM LIMIT (%) 40
   CONCENTRATION 20.00           ON ERROR SWITCH TO STD.ADDN.


   REQUIRED DETECTION LIMIT      1.00   ppb
   MATRIX SPIKE CONCENTRATION    0.00   ppb
   OVERRANGE VOLUME REDUCTION    2
   REPLICATE RSD LIMIT (%)       5.0
   CORRELATION COEFFICIENT (r)   0.995
```

Figure 1. The Agilent Mark-VI spraychamber: (1) nebulizer, (2) ceramic face-plate, (3) adjustable glass bead, (4) drainage tube, (5) dual-head mixing paddle, (6) enhanced slope floor.

The main advantage of the premix burner assembly is its low noise and reproducibility. Agilent Technologies has introduced a new nebulizer [5], spraychamber [6], and a burner [7] to enhance further these benefits. However these improvements were not intended to improve the sensitivity significantly.

The difficulty of improving sensitivity can be demonstrated by using some typical numbers from this process. The nebulization process is only about 10% efficient so an uptake rate of 5 mL/min implies 0.5 mL/min passes through the burner. In most instruments 15–20 L/min of gas also flows through the burner. The effective dilution of the sample is therefore approximately 0.5/15000 or 1/30000.

The spraychamber would appear to be the obvious area to look for improvements in sensitivity. However even after decades of research and experimentation further significant improvements have yet to be made.

A heated spraychamber has been described which improves sensitivity for dilute, low solid solutions [8,9]. It appears likely that the premix spraychamber has been refined to its optimum performance.

Logically the next potential area for improvement would be the nebulizer. Indeed it is possible to adjust the standard Agilent nebulizer to improve substantially the sensitivity for aqueous copper solutions. However the penalty of this mode of operation is an increased uptake rate and larger droplets in the flame. This would be perfectly acceptable if all samples behaved like aqueous copper solutions. In practice, under these conditions most solutions are known to cause unacceptable problems such as inter-element interferences, signal noise and blocking of the burner or nebulizer. Therefore obtaining sensitivity by increasing uptake rate is not recommended. Other nebulization schemes have been proposed. For example, it is quite feasible to use ultrasonic vibrations for improved nebulization. A different approach is to use electrostatic precipitation of the solid solutes in the aerosol [10-12]. However both techniques have yet to find wide acceptance in FAAS.

Atomization

The physical changes occurring to the solution aerosol in a flame are summarized in Reference 1. Work has been done on trying to understand the process better [8,13,14] but knowledge is still somewhat empirical, even without considering the chemical aspects or interferences. The number of analyte atoms present should in principle depend only on the volume of liquid reaching the combustion zone and the efficiency of atom formation. The flame sensitivity is determined by the number of ground state analyte atoms present in the optical path.

If the removal rate of the atoms from the optical path could be reduced, then an improvement in sensitivity should be observed. Such an approach was pioneered by Robinson [15] on a total combustion burner. Watling [16,17] experimented using a laminar flow burner with a slotted tube above the flame and Brown *et al* [18–20] have done additional work. (It should be mentioned that the Delves cup technique [21] also uses a tube.) This scheme is discussed in more detail in the following section.

A closely related approach pioneered by Lau [22] and investigated by several others [23–31] is to trap the atoms physically on the surface of a narrow diameter water-cooled silica tube placed just above the cone of the flame. After a suitable collecting period, the atom-trap tube is allowed to heat up (by stopping the flow and removing the water) and atoms are released to give an enhanced transient signal. Enhancements of 10 to 30 times have been reported. Practical difficulties have limited the application of this technique.

Atom Concentrator Tube, ACT 80

Watling, in 1977, described a slotted quartz tube which he placed over a conventional AA-6 air-acetylene burner and observed an improvement in analytical sensitivity [16,17].

The commercially available ACT 80 is a quartz tube 150 mm long with two lengthwise cuts. The longer slot is 100 mm × 2 mm, the shorter 80 mm × 2 mm. These cuts are angled at 120 degrees to each other relative to the tube's axis. The ACT 80 is installed in a standard Agilent Vapor Generation Accessory (VGA 76) cell holder and fits on a burner as does the VGA 76 cell. The longer slot is aligned over the burner slot; the shorter faces towards the rear of the instrument away from the holder. As with the VGA 76 cell, only the air-acetylene flame can be used as a hotter flame would destroy the tube. Figure 2 shows the tube in its holder.

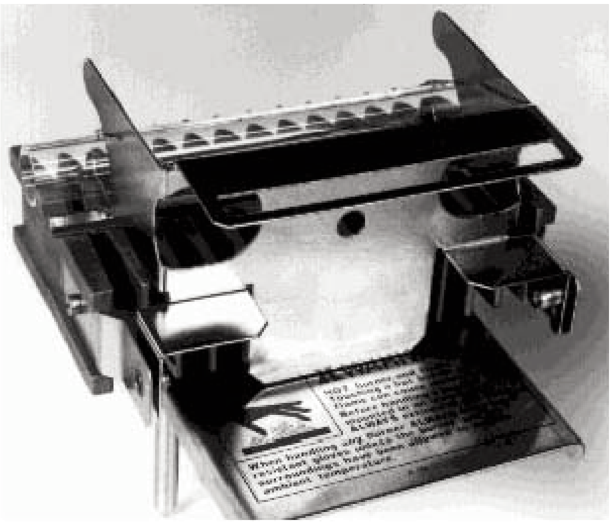


Figure 2. The ACT 80 Atom Concentrator Tube.

The ACT 80 tube must also be optically aligned so that the long axis of the tube coincides with the light beam. It was found in practice that the burner and ACT 80 needed to be lowered about 7 mm (equivalent to the radius of the tube).

Experimental

The performance of the ACT 80 was evaluated using SpectrAA-300/400 spectrometers fitted with a Mark VI spraychamber and a Mark VA or a Mark VI air-acetylene burner. A VGA cell holder clamp was attached to the burner. Instrument default conditions were used for all measured elements. Where nitrous oxide-acetylene was the default flame, air-acetylene was used instead. Oxidant flow was 13.5 L/min and acetylene flow 2.0 L/min. Delay time was 20 s and the read time period was 10 s integrated. All measurements were made after the system had been operated at least ten minutes to reach equilibrium.

Results and signal graphics were sent out to a printer. In addition, sample absorbances were sent to an ASCII file for further data manipulation.

Standard solutions were made from BDH (Poole, England) Spectrosol 1000 mg/L standards. Solutions and blanks were acidified with Analar grade concentrated nitric acid to give 0.5% v/v in final volume. Water was distilled from a Pyrex still and deionized with a Waters Milli-Q system to 18 MOhms conductivity.

Practical Points

The ACT 80 must be tilted back out of the way when lighting the flame. Otherwise for tongue-of-flame igniters a significant amount of acetylene builds up inside the ACT 80 with subsequent noisy ignition. Mechanical igniters would physically damage the ACT 80.

Flame composition is also an important factor. It was found that a lean to stoichiometric flame was needed. A rich flame causes soot formation and the signal noise becomes unacceptably high. Elements requiring a rich flame such as arsenic, chromium or molybdenum are therefore not usefully measured using the ACT 80. It was noted with arsenic that each blank signal increased and the blank and solution absorbances tended to give the same value. While this observation is not strong evidence for a memory effect, it cannot yet be eliminated. Alkali and alkaline earth (Group I and II) metals which etch heated silica [22] are also not usefully measured with this technique.

Devitrification of the tube inevitably occurs and starts initially around the inlet slot. The presence of Group I and II metals tends to accelerate this process. However it is possible to aspirate strong solutions (1000 mg/L or greater) of aluminium or lanthanum which provide a protective coating [23] and so retard the devitrification process. This should be done each time the tube is used and must be repeated on a regular basis. Tube lifetimes for samples with simple acidified matrices for example, water or dilute solutions of solids should typically be several hours of continuous operation. At a rate of approximately 200 samples/hour many samples may be determined using one tube.

Lifetime is maximized by continuous operation because cooling and reheating stresses the quartz.

Results and Discussion

Performance

As a guide to performance, improvements in characteristic concentration and detection limit were measured for selected air-acetylene elements. For both values the absorbance of a dilute solution of the analyte must be measured. The absorbance must be determined on a linear portion of the calibration graph and so concentrations were selected to be approximately equal to the characteristic to determine the characteristic concentration (determined using values previously published by Agilent). In practice ten measurements of the solution were made interspersed by measurement of the blank solution. Measurements of each series were done without the ACT-80 and repeated with the ACT-80 fitted (the burner height was reoptimized as needed).

Each element required a large number of readings and to avoid transcription errors the measurements were also printed to an ASCII file. This file was subsequently read by a BASIC program written to extract the absorbance values and perform the necessary calculations. Each solution absorbance was corrected by subtracting the mean of the two adjacent blank readings. The mean and standard deviation of the ten corrected absorbances were used to determine the characteristic concentration and detection limit values. These values were then loaded into a a LOTUS1-2-3 spreadsheet to generate Table 1.

Table 1 also lists, for reference only, Agilent data on detection limit and characteristic concentration values. The values found from this study were obtained using fixed air-acetylene flows and should not be directly compared with values obtained by optimizing conditions for each element.

The following points are drawn from Table 1:

1. All the elements listed showed some improvement in sensitivity. These tended to be consistent as indicated by duplicate runs. Copper was repeated on different systems.
2. All improvements appear to be about 2X to 3X, which reflects the findings of Watling [16,17] and Brown [18–20].
3. Generally there was a corresponding improvement in detection limit. The statistical nature of detection limit means direct comparisons should be interpreted cautiously but since the improvement factor is almost always greater than unity it is inferred that the ACT-80 does improve detection limits. Gold, cadmium and lead appear to show the best improvements.
4. Iron and platinum showed no significant improvements in characteristic concentration or detection limit.

Table 1. Comparison of Detection Limits and Characteristic Concentrations for Selected Air-Acetylene Flame Elements

	Characteristic concentration				Detection limit			
Element	**Literature FAAS**	**Standard FAAS (Ht=10)**	**Act-80 FAAS (Ht=3)**	**Act-80 improvement factor**	**Literature FAAS**	**Standard FAAS (Ht=10)**	**Act-80 FAAS (Ht=3)**	**Act-80 improvement factor**
Ag	0.030	0.0134	0.0049	2.7	0.002	0.0019	0.0020	1.0
Au	0.100	0.1226	0.0451	2.7	0.010	0.0148	0.0036	4.1
Bi	0.200	0.2647	0.0919	2.9	0.050	0.0766	0.0177	4.3
Bi		0.2498	0.0903	2.8		0.0414	0.0211	2.0
Cd	0.010	0.0123	0.0054	2.3	0.002	0.0047	0.0011	4.3
Cu	0.030	0.0422	0.0214	2.0	0.003	0.0055	0.0056	1.0
Cu		0.0496	0.0212	2.3		0.0047	0.0034	1.4
Cu *		0.0448	0.0189	2.4		0.0066	0.0065	1.0
Fe	0.050	0.0538	0.0362	1.5	0.006	0.0110	0.0102	1.1
Hg	1.500	2.4278	0.8581	2.8	0.150	0.3094	0.1121	2.8
Mn	0.029	0.0291	0.0141	2.1	0.002	0.0025	0.0019	1.3
Pb	0.100	0.1182	0.0404	2.9	0.010	0.0301	0.0090	3.3
Pt	1.000	2.0064	1.9328	1.0	0.100	0.1220	0.0967	1.3
Sb	0.300	0.3866	0.1244	3.1	0.040	0.0678	0.0462	1.5
Se	1.000	0.3356	0.1010	3.3	0.500	0.1381	0.0927	1.5
Te	0.200	0.2476	0.0903	2.7	0.030	0.0760	0.0492	1.5
Tl	0.200	0.1509	0.0588	2.6	0.020	0.0112	0.0052	2.2

Notes:

-Ten readings were taken and the mean calculated for each value.
-Uptake rate was fixed at 6 mL/min.
-All conditions constant except for burner height ("Ht").
-"Ht" is burner position as shown on the instrument's burner vertical scale.
-Concentrations are about 10 times detection limit (except for Cu which was 100 times).*
-Quoted results for Se used nitrous oxide-acetylene flame. This study used an air-acetylene flame.
-Some elements show replicate results. With Cu, results were from different burners.

The following definitions apply:

$$\text{Detection limit} = \frac{2 \times \text{Standard Deviation} \times \text{Concentration}}{\text{Mean Absorbance}}$$

(IUPAC now recommend detection limit to be 3 times standard deviation, for comparison with literature values 2 times is used here.)

$$\text{Characteristic concentration} = \frac{0.0044 \times \text{Concentration}}{\text{Mean Absorbance}}$$

As an illustration, signal graphics for a standard lead solution measured with and without the ACT-80 tube in place are shown in Figure 3.

Variation in tube dimensions were not investigated, however Brown used a tube 8 mm id (Watling did not specify dimensions). The similarity between the results of this study and the published data indicates that the enhancement is not influenced greatly by the tube dimensions.

Watling suggested the flame characteristics are being affected in a way to encourage atom residence time in the optical path. Whether the flame has less entrained air or the reducing interconal zone is broadened or the diffusion of atoms is slowed down requires more work to elucidate. However, it appears that atoms are not trapped but merely delayed.

The sensitivity of the nitrous oxide-acetylene flame would perhaps also benefit from this technique but its higher temperature (2600 °C) means that the tube would need to be very refractory. The Delves cup method has been applied to the nitrous oxide-acetylene flame [32] so a refractory atom concentrator tube may be feasible.

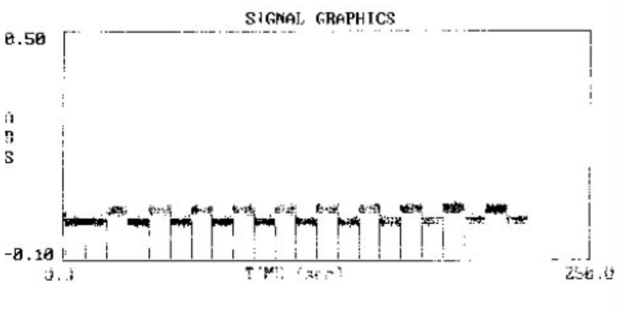


Figure 3(a). Pb signal compared to blank without ACT-80 tube.

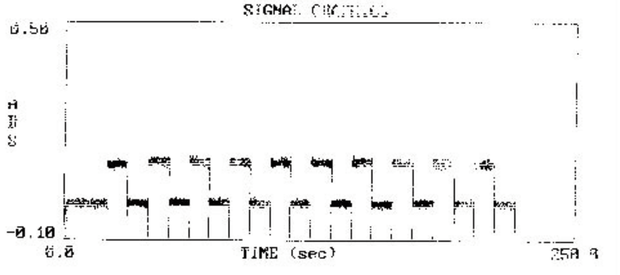


Figure 3(b). Pb signal compared to blank with ACT-80 tube.

Calibration Graphs

Calibration graphs were generated for four selected elements. The highest standard was selected to give about 0.3 Abs without the ACT-80 tube. As shown in Figure 4 the slope is clearly increased as would be anticipated from the improvements seen for the characteristic concentration. The graph for selenium shows that curvature is apparently more pronounced with the ACT-80 in place. However the same curvature is seen with higher solution concentrations without the tube in place. To corroborate this, the highest standard concentration used with the ACT-80 gave an absorbance equivalent to a standard three times the concentration without the tube.

Practical Applications

To illustrate the use of the tube in practical applications, quality control samples supplied by the United States Environmental Protection Agency (US EPA) were measured against aqueous standards. The levels of cadmium, copper and lead in EPA samples #4 and #5 are at or below the quoted detection limits for normal flame operation. A limited amount of National Bureau of Standards SRM 1643b water was also available and used for cadmium determinations.

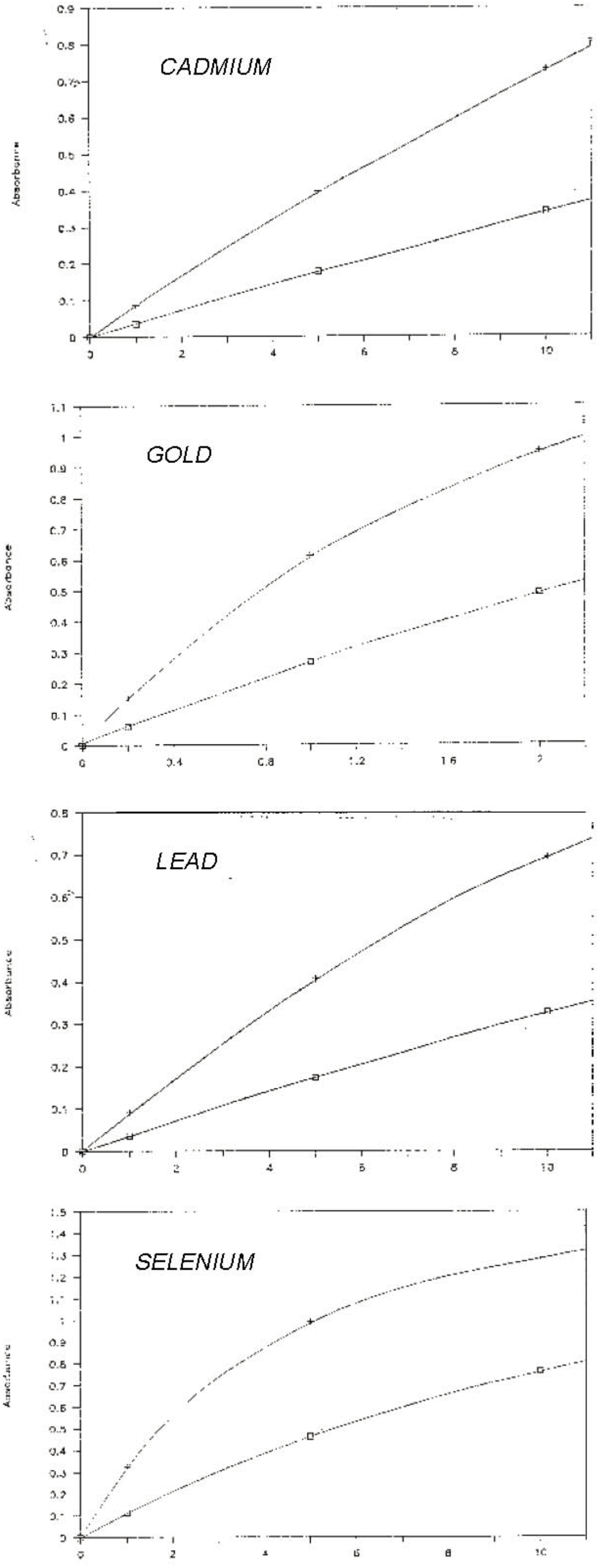
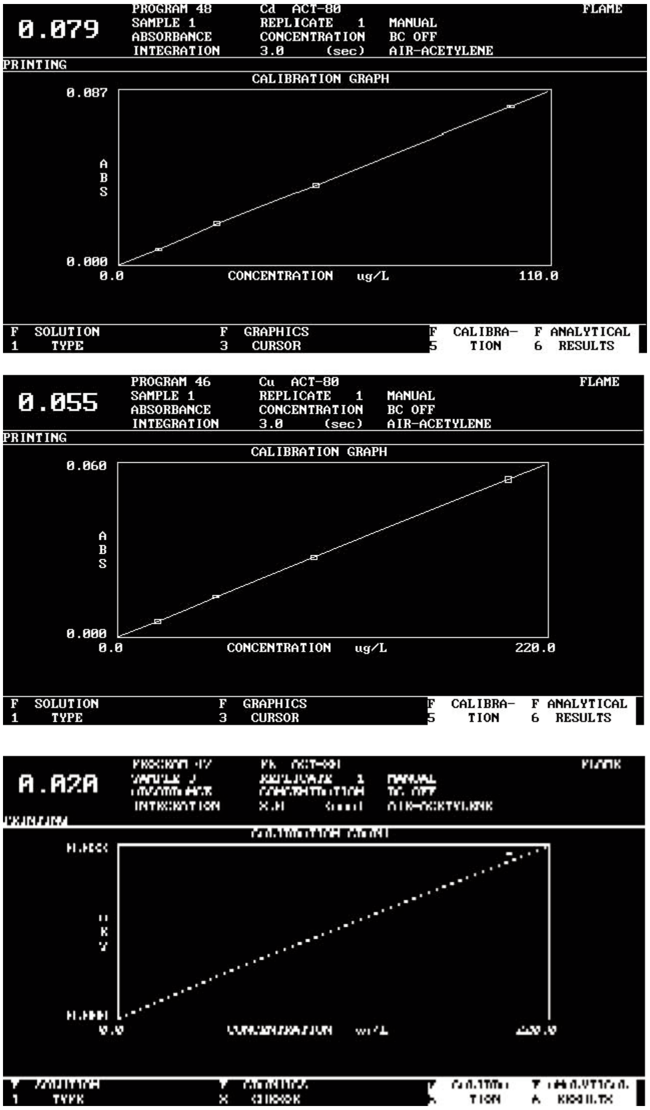


Figure 4. Calibration graphs of selected elements showing improvement in sensitivity. (+ = ACT-80, □ = normal FAAS)

The recommended instrument settings were used for each element. A delay time of five seconds and a read time of three seconds with three replicates were used. With these conditions about 200 solutions could be measured per hour. At least ten readings were taken for each sample to calculate standard deviations. The calibration graphs obtained are shown in Figure 5. A summary of the measured means and standard deviations are listed in Table 2. It can be seen that the measured results agree closely with the certified values even when working at the quoted detection limit for normal flame operation.



```
0.079   PROGRAM 48      Cd  ACT-80                    FLAME
        SAMPLE 1        REPLICATE    1   MANUAL
        ABSORBANCE      CONCENTRATION    BC OFF
        INTEGRATION     3.0      (sec)   AIR-ACETYLENE
PRINTING
```

```
0.055   PROGRAM 46      Cu  ACT-80                    FLAME
        SAMPLE 1        REPLICATE    1   MANUAL
        ABSORBANCE      CONCENTRATION    BC OFF
        INTEGRATION     3.0      (sec)   AIR-ACETYLENE
PRINTING
```

Figure 5. Calibration graphs used to measure quality control samples.

Table 2 Results for Quality Control Samples

Material	Mean ng/g	SD	Mean abs	Comments
Results for Cd using ACT-80				
US EPA sample 4	2.38	0.17		
Found	1.5	0.3	0.001	At quoted detection limit
US EPA sample 5	12.3	1.4		
Found	12.1	0.2	0.009	
NBS SRM 1643b	20	1		
Found	20.6	1.0	0.017	
Results for Cu using ACT-80				
US EPA sample 4	11.3	2.6		
Found	11.7	0.2	0.003	
US EPA sample 5	49.4	3.5		
Found	49.6	0.5	0.014	
Results for Pb using ACT-80				
US EPA sample 4	24.7	3.7		
Found	23.8	2.8	0.002	Twice quoted detection limit
US EPA sample 5	122	14.8		
Found	127.6	2.2	0.013	

Notes: Ten or more readings were taken for each solution.
SD is the standard deviation.

Conclusion

There is a measurable improvement in signal using the ACT-80. The improvements seen are comparable with those previously published. This study shows that there is an improvement in characteristic concentration between two and three times that of the normal FAAS. Detection limits generally show somewhat similar improvements. The ACT-80 is simple, cost effective and offers benefits in low level analyses.

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Sensitivity Enhancement for Flame AAS Using an Atom Concentrator Tube for Elements Dissolved in Organic Solvents

Application Note

Atomic Absorption

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Introduction

The application of a slotted tube placed on an ordinary atomic absorption burner head in order to increase the sensitivity and detection limit for a number of elements in flame-atomic absorption spectrometry (FAAS) was first demonstrated by Watling [1,2]. A very similar technique had been used before in combination with either a nickel "cup" [3] or a tantalum "boat"[4] for the same purpose. The enhancement effect using the combination of a slotted tube and an ordinary acetylene/air flame was later confirmed by several authors who demonstrated that the sensitivity and the detection limit could typically be improved by a factor of 2–5 for easily atomized elements [5–11].

Extraction of aqueous samples into a small volume of an organic solvent after addition of a complexing agent in order to enhance the detection limit is a well established method [12–14]. A concentration factor of at least 20 times can easily be achieved.

Moreover, it is also well known that atomizing organic solutions (especially those rich in oxygen, for example, ketones) can result in 3–5 times better sensitivity for many elements [15] and references therein. Thus the improvement in sensitivity for flame-AAS after extraction should be about 20 x (3–5) = 60 – 100 times.

A combination of extraction into an organic solvent and the atom concentrator tube should thus theoretically result in a total improvement in sensitivity and detection limit of (60 to 100) × (2 to 3) = 120 to 300 times.

Surprisingly, the possibility of combining these techniques has not been investigated. The present paper therefore reports results from a number of experiments using the atom concentrator tube for organic solutions of some metals. For comparison the same solutions have been analyzed without the concentrator tube.

Experimental

Apparatus

An Agilent SpectrAA-10BQ Atomic Absorption Spectrometer equipped with a Mark VI burner head was used together with an Agilent Atom Concentrator Tube (ACT 80) including a special metal holder constructed to fit the quartz tube to this particular burner–the holder being identical with that used for the quartz tube of the Agilent Vapor Generation Accessory (VGA-77). The quartz tube was 150 mm long with two lengthwise cuts 2 mm wide by 100 and 80 mm long respectively, angled at 120 degrees relative to each other. New tubes were conditioned in the flame by nebulizing a 1% lanthanum nitrate solution for 10–15 min before use in order to prolong the tube life.

The built-in instrument graphics together with an Epson RX-80 printer were used for the recording of the signals and for construction of the calibration graphs.

Gas flow-rates of acetylene for the organic and aqueous solutions were 1.2 and 1.8 L/min respectively. The air flow-rate was 12 L/min in both cases.

The instrument parameters were as follows:

Measurement time	4 sec
Delay time	4 sec
Replicates	3
Recommended SBW and wavelength for each element	Background correction was not used

Experiments

Test solutions containing mixtures of Ag, Cu, Fe Ni and Pb made by appropriate dilutions of a metallo-organic standard mixture of the elements (Conostan S-12 100 ppm (Wt)) with methyl isobutyl ketone (MIBK) were used. A corresponding series of aqueous metal standards were made by diluting a stock solution made from the appropriate amounts of the respective metal nitrates (of A.R. grade) dissolved in water.

The following concentrations were measured: 0, 2, 4, 6, 8 and 10 mg/L of each metal.

The instrument calculated and displayed the calibration graph for each element. From the four graphs: for example, water, MIBK, water + ACT and MIBK + ACT the relative enhancement factors were calculated for each element using the absorbance values for 6 mg/L. The factors are given in Table 1.

Results and Discussion

Both the aqueous and the MIBK-solutions were measured with and without the ACT tube. The No.1 value in the table should be compared with those obtained for No. 4. Both series demonstrated the enhancement factors that can be expected when the ACT is used and that the tube indeed has almost the same effect for organic solutions. Comparison of No. 2 and No. 6 confirms this.

Experiment No. 3 illustrates the total enhancement obtained using an organic solution combined with the concentrator tube relative to aqueous solutions without the tube.

No. 5 shows that atomizing MIBK-solutions without the tube is always more effective than atomizing aqueous solutions with the tube.

The results in Table 1 also confirm that the enhancement effect using the tube is best for the easily atomized elements.

Conclusion

The results show that using a quartz atom concentrator tube for metal compounds in methyl isobutyl ketone solutions will result in the same enhancement of the sensitivity as for aqueous solutions multiplied with a factor of 3–4 due to the beneficial (exothermal) atomizing conditions for organic solvents (see above). This can be utilized in the application of extraction methods for the determination of ions present in water samples thus achieving a much better detection limit relative to that obtained for aqueous samples without extraction.

It is evident that the enhancement effect is caused mostly by the prolonged residence time of the atoms in the light path and is most pronounced for the easily atomized elements. Thus for iron (and nickel) the tube does not seem to offer any advantage at all. This can be explained by the lower temperature inside the quartz tube, this being too low for an effective atomization of the more refractive elements. For such elements it is better to atomize an organic solution without tube.

In many cases, the combination of extraction of metal complexes into organic solvents using an atom concentrator tube for flame-AAS could be an alternative to the graphite furnace technique, for instance for sea-water samples. This approach can be even more attractive if using the extraction equipment recently described for a fast, non-manual extraction of large volumes which can solve the problems associated with the use of the conventional and inconvenient separatory funnels [15].

Alternatively, programmable probe height of the SPS-5 Flame Sampler may be used to advantage in the extraction procedure.

The SPS-5 probe operates through a range of 160 mm. When two immiscible liquids are in a test tube, the probe may be programmed to descend into the upper liquid layer. Thus, the extraction procedure could be as follows:

- Pipette a volume of sample into a stopped test tube, and add a known volume of extractant
- Then pipette a volume of organic solvent into the tube, stopper and shake it
- Remove the stopper, start the SPS-5 Flame Sampler
- The probe will then descend into the upper organic layer. This eliminates the use of separatory funnels.

Table 1. Enhancement Factors for Pb, Cu, Ag, Fe and Ni

	Pb	Cu	Ag	Fe	Ni
$\frac{\text{MIBK/ACT}}{\text{MIBK}}$	2.4	1.6	2.8	0.6	1.1
$\frac{\text{MIBK/ACT}}{\text{AQ/ACT}}$	3.3	4.0	3.8	2.1	n.d.
$\frac{\text{MIBK/ACT}}{\text{aq}}$	8.6	6.0	10.9	2.2	n.d.
$\frac{\text{AQ/ACT}}{\text{aq}}$	2.7	1.5	2.8	1.0	n.d.
$\frac{\text{MIBK}}{\text{aq/ACT}}$	1.3	2.5	1.3	3.5	n.d.
$\frac{\text{MIBK}}{\text{aq}}$	3.6	3.8	3.6	3.6	n.d.

n.d. = Not determined

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