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- DuraGuard Columns: GC Columns with Built-In Protection
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- Achieving fastest analyses with the Agilent 1200 Series Rapid Resolution LC system and 2.1-mm id columns
- Improving the Effectiveness of Method Translation for Fast and High Resolution Separations
- Improving Productivity and Extending Column Life with Backflush
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- Prefractionator for Reliable Analysis of the Light Ends of Crude Oil and other Petroleum Fractions
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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
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- Improved Data Quality Through Automated Sample Preparation
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- Returning to Fixed Pathlength Infrared Spectroscopy: Gaining Detail and Removing the Obstacles
- Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer
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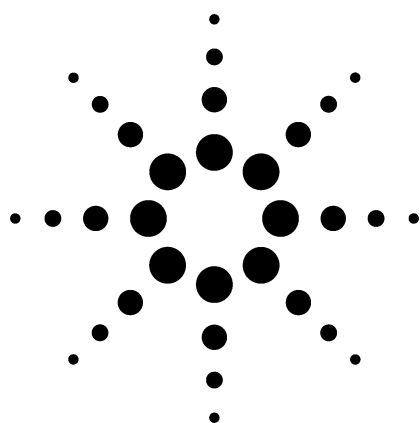


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- Fast Refinery Gas Analysis Using the 490 Micro GC QUAD
- Sensitivity Enhancement for Flame Atomic Absorption Spectrometry Using an Atom Concentrator Tube, the ACT 80
- Sensitivity Enhancement for Flame AAS Using an Atom Concentrator Tube for Elements Dissolved in Organic Solvents



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 (B) 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 μ m	1997 (28)
	75 meters	0.540 mm	3.00 μ m	1447
DB-624	75 meters	0.446 mm	2.55 μ m	1402 (22)
	75 meters	0.546 mm	3.00 μ m	1090
DB-502.2	75 meters	0.453 mm	2.55 μ m	1526 (20)
	105 meters	0.544 mm	3.00 μ m	873
DB-WAX	30 meters	0.447 mm	0.85 μ m	1656 (25)
	30 meters	0.544 mm	1.00 μ m	1357
DB-1	30 meters	0.455 mm	1.30 μ m	1477 (27)
	30 meters	0.551 mm	1.50 μ m	1357
DB-5	30 meters	0.446 mm	1.30 μ m	1895 (23)
	30 meters	0.540 mm	1.50 μ m	1454
DB-608	30 meters	0.450 mm	0.71 μ m	1477 (23)
	30 meters	0.535 mm	0.83 μ m	1134

[1] Phase ratio (B) 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-Dichloroethene
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

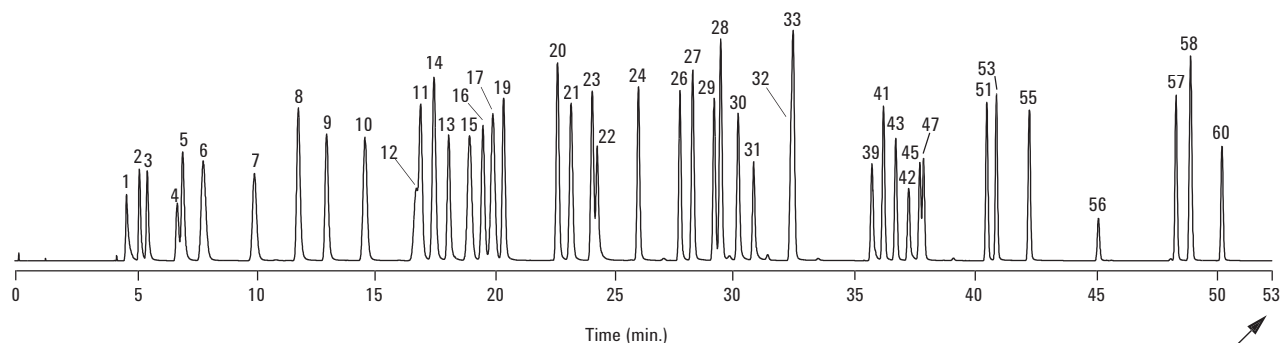
41. 1,1,2,2-Tetrachloroethane
42. Bromobenzene
43. 1,2,3-Trichloropropane
44. n-Propylbenzene
45. 2-Chlorotoluene
46. 1,2,3-Trimethylbenzene
47. 4-Chlorotoluene
48. tert-Butylbenzene
49. 1,2,4-Trimethylbenzene
50. sec-Butylbenzene
51. 1,3-Dichlorobenzene
52. para-Isopropyltoluene
53. 1,4-Dichlorobenzene
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

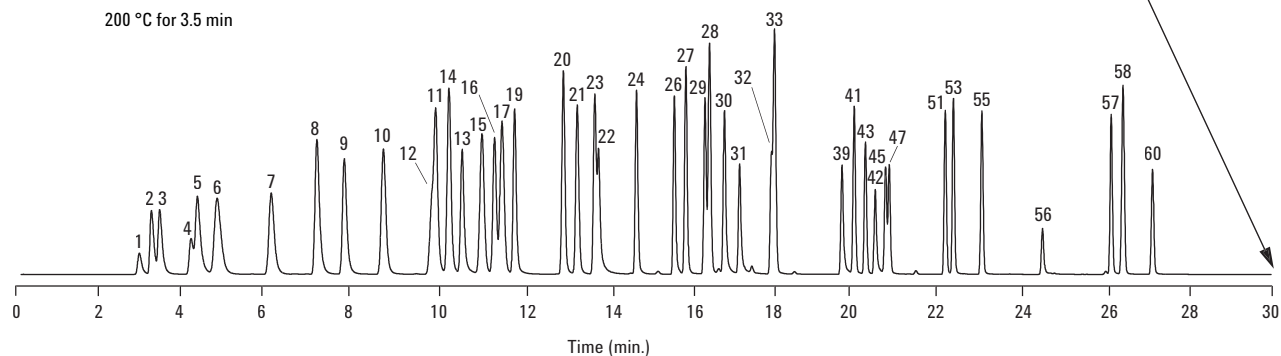


Conditions

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



High-Speed Megabore
saves 23 minutes!

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

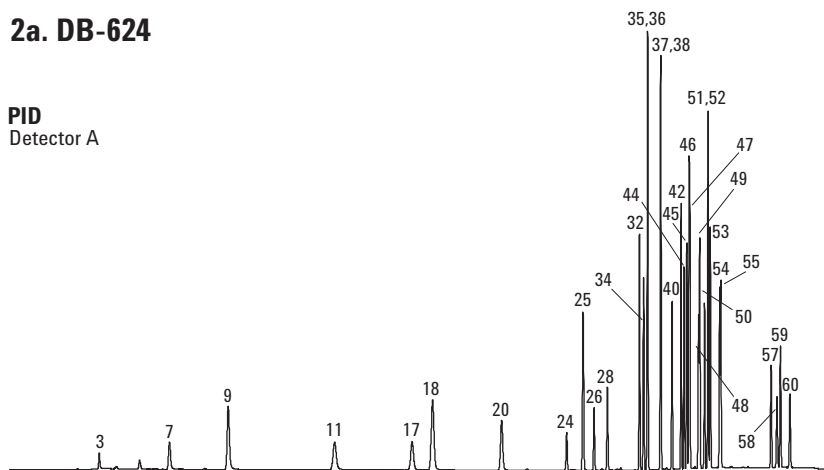
200 °C for 4 min

Injector: Purge and trap (OIA 4560)
40 ppb per component in 5 mL water

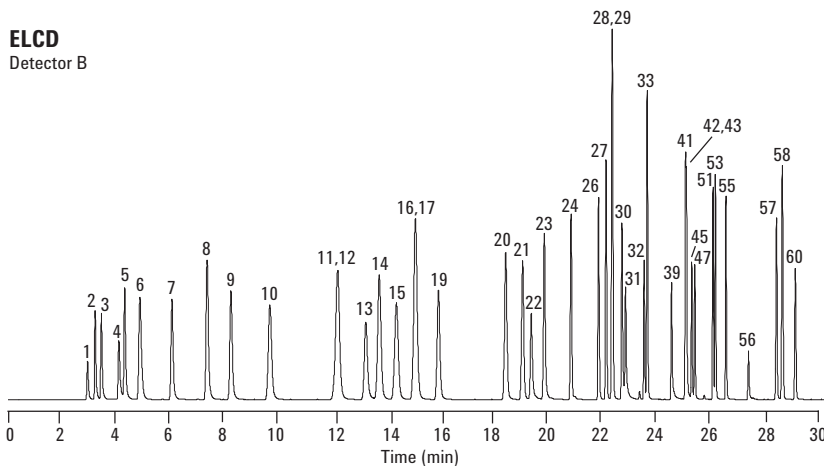
Trap: Tenax/Silica gel/Charcoal

Detector A: Photoionization detector (PID)
(OIA 4430) at 220 °CDetector B: Electrolytic conductivity detector
(ELCD) (OIA 4420) with NiCat
reaction tube in the halogen
mode**2a. DB-624****PID**

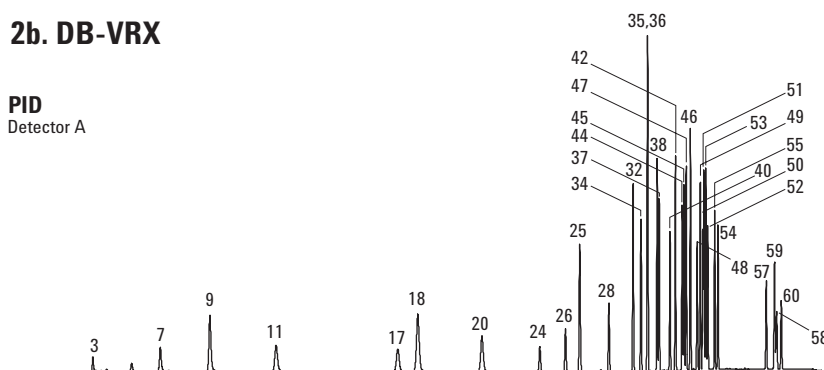
Detector A

**ELCD**

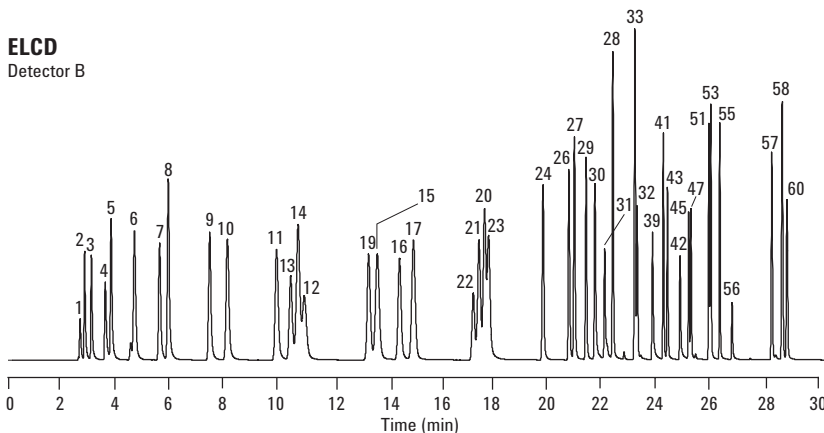
Detector B

**2b. DB-VRX****PID**

Detector A

**ELCD**

Detector B

**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

¹Additional 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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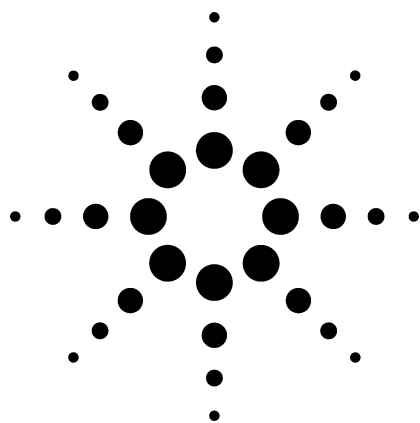
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DuraGuard Columns: GC Columns with Built-In Protection

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.

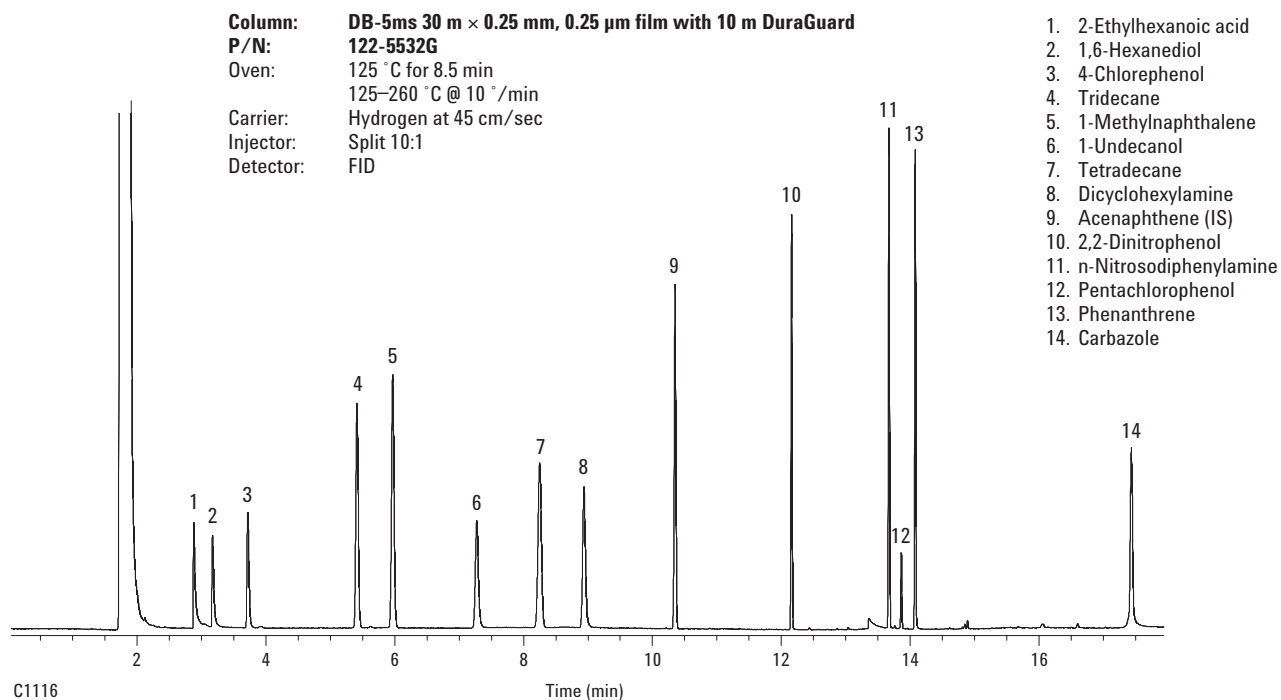


Figure 1. Chromatogram of test mixture using combination guard and analytical columns.

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.

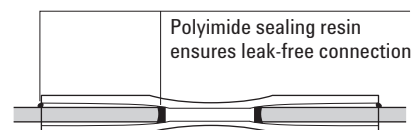


Figure 2. Detail of glass press fit union with polyimide sealing resin.

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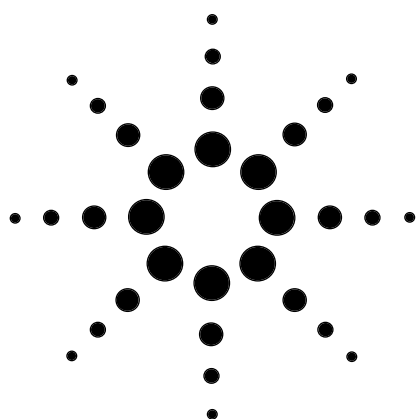
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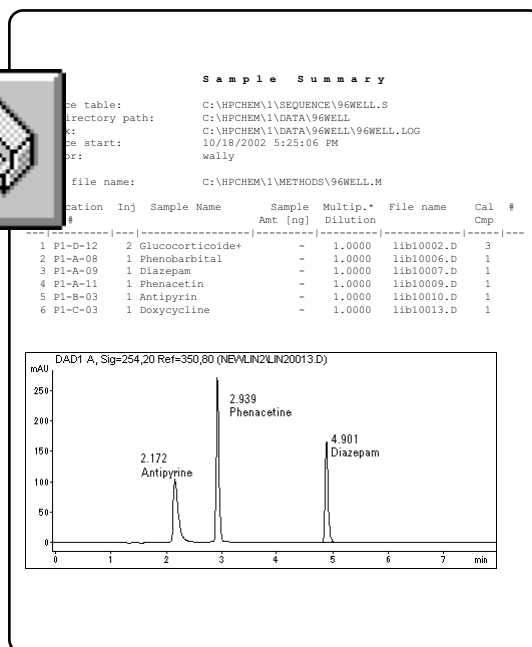
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Using Agilent ChemStation to generate summary reports for a single analysis or a sequence of analyses

Application

Angelika Gratzfeld-Huesgen



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.



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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 information 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.

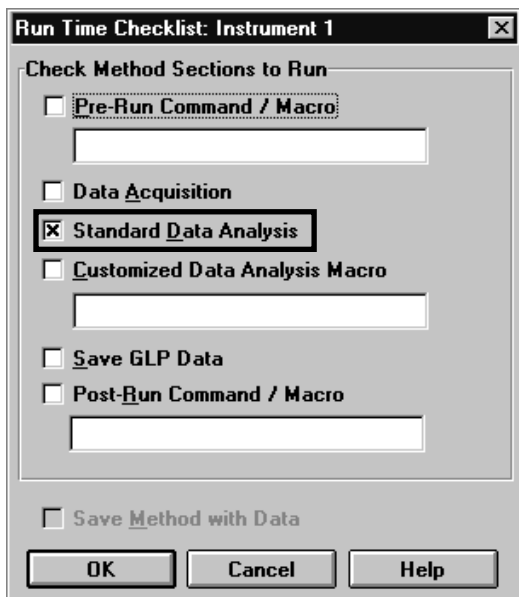


Figure 1
Activating *Standard Data Analysis*, including integration and quantification as part of the ChemStation method, is mandatory to obtain automated printouts of all report types available in the ChemStation base software

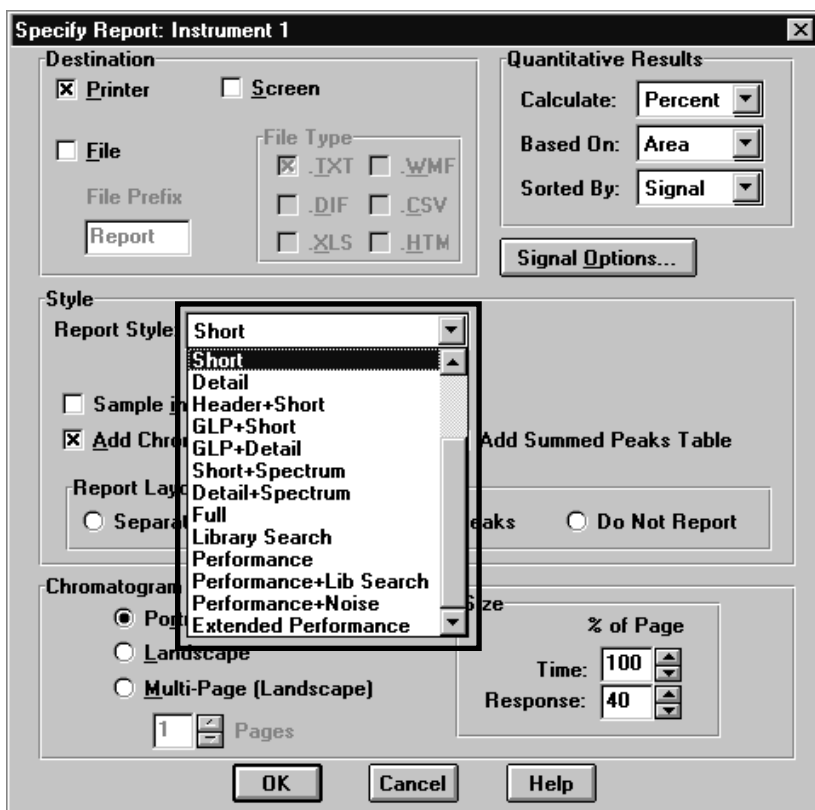


Figure 2
Specifying individual run reports

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 Search 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.

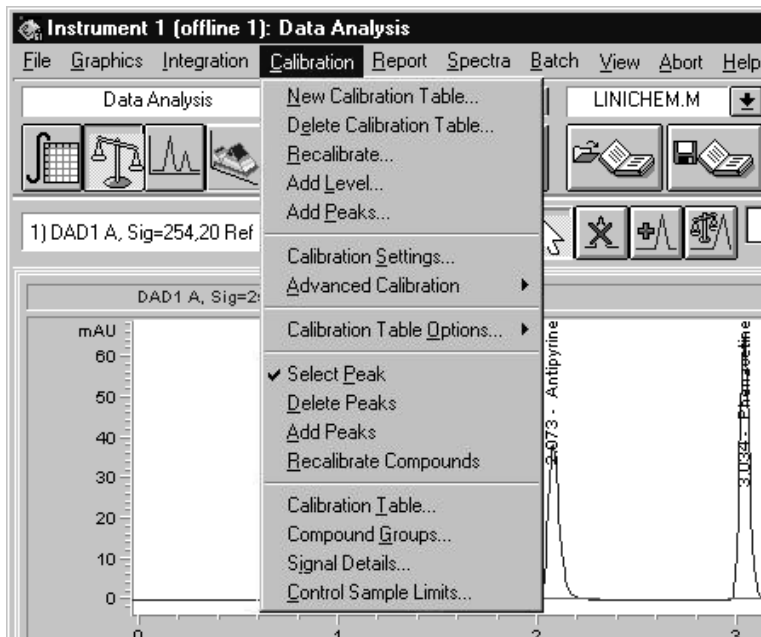


Figure 3
Calibration setup menu

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:

File Type

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

Style

Report Style:

Quantitative Results

Calculate:
Based On:
Sorted By:

☒ 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)

Pages

Size

% of Page
Time:
Response:

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 continuous 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.

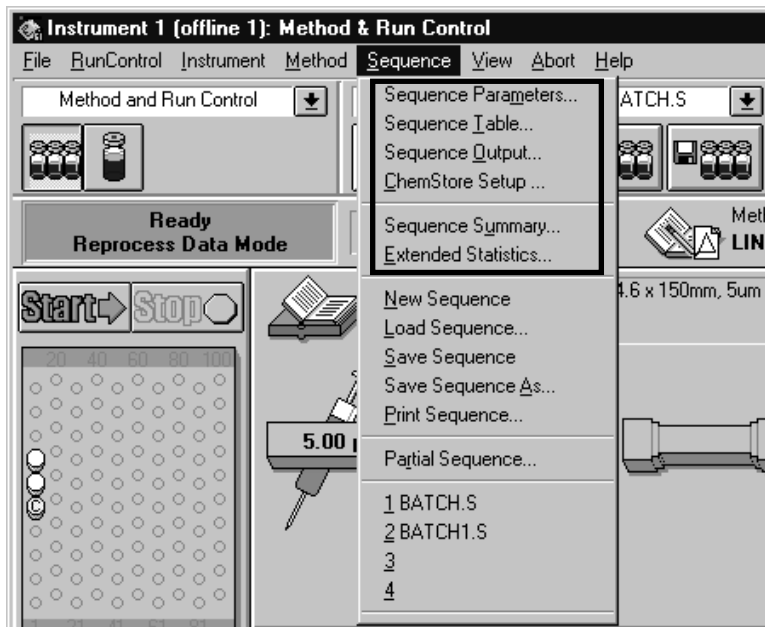


Figure 7
Entries need to be made in these sections to obtain automatically a sequence summary report at the end of a sequence

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 screen 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-

Figure 8
Sequence parameters screen

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

OK Cancel

Figure 10
Setup of statistical calculations for sequence runs

Sequence Table: Instrument 1

Currently Running

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	Triphenelamine	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

Insert Cut Copy Paste Append Line

Insert Location Range.. Run Sequence Read Bar Code

OK Cancel Help

Figure 11
The Sequence Table screen

Sample Summary

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 Amt	Multip.* [ng]	File name	Cal #	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

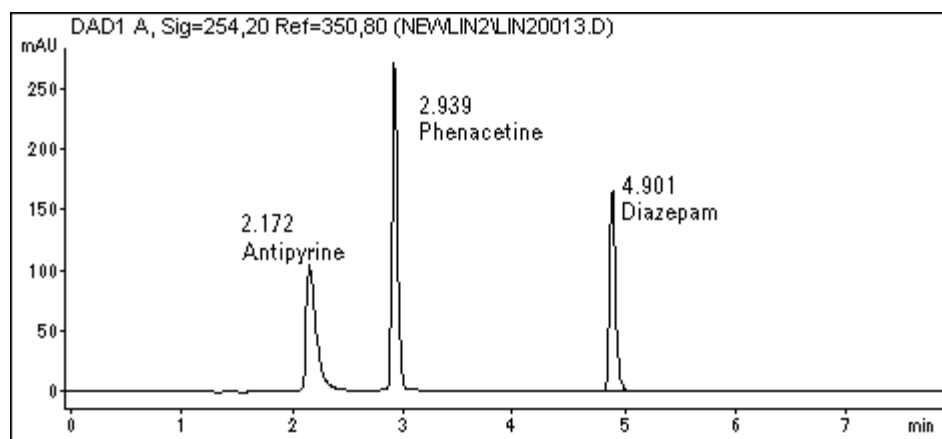
The following pages show examples of summary reports that can be generated with the ChemStation base software. The examples were generated using the print-to-file function and may have different pagination than a report printed directly from the ChemStation. Reports shown include:

- 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 [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
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		

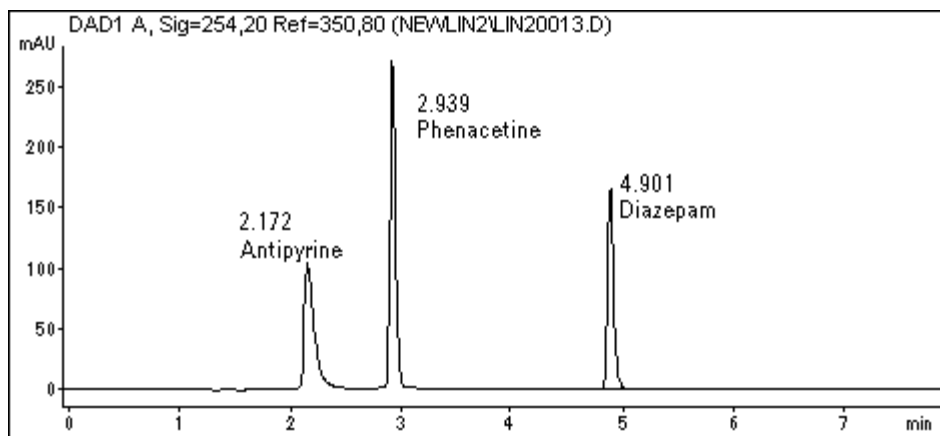
*** End of Report ***

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 [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng]	Grp	Name
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		

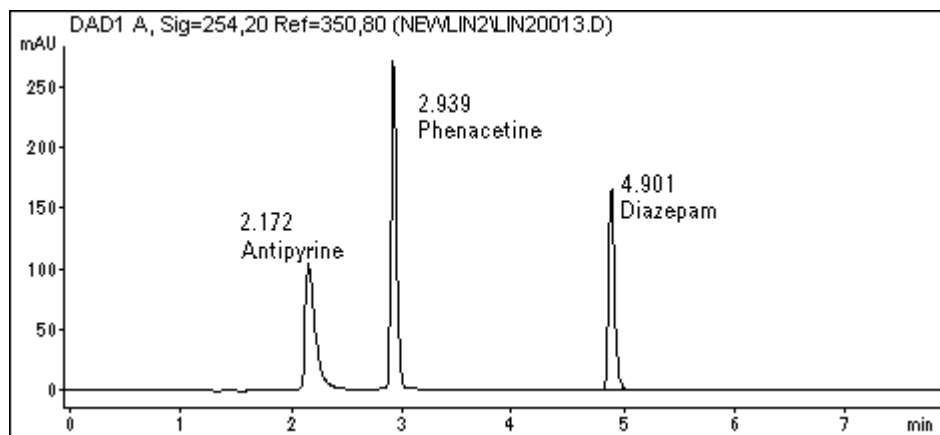
*** End of Report ***

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
```

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 ***

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

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
Column Temp. (right)  :      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   :
PMPL, Solvent A       : Water
PMPL, Solvent B       : acn
=====
```

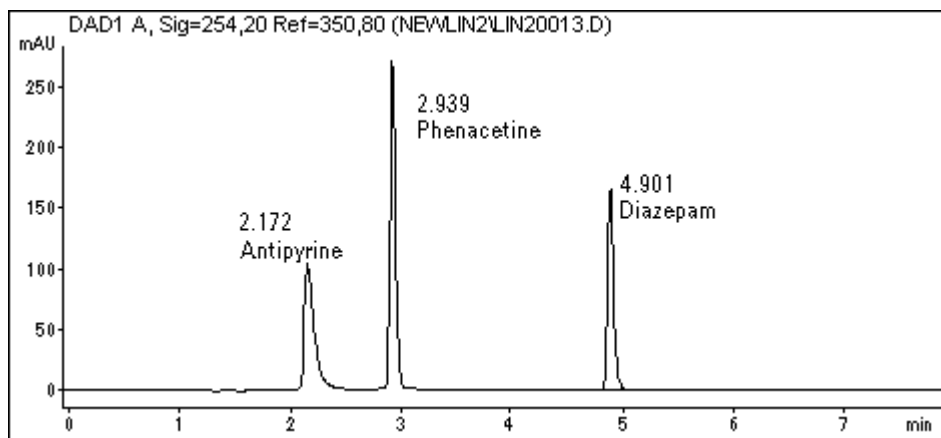
Short GLP Report (continued)

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 [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng]	Grp	Name
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 ***

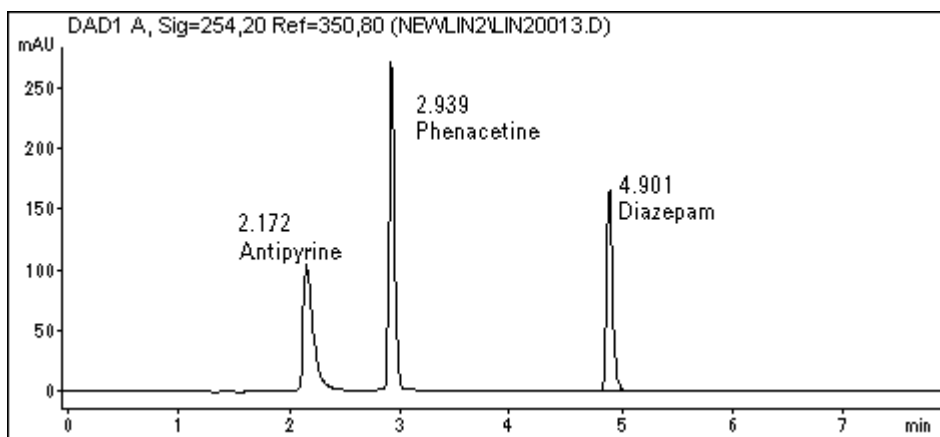
Performance report

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!

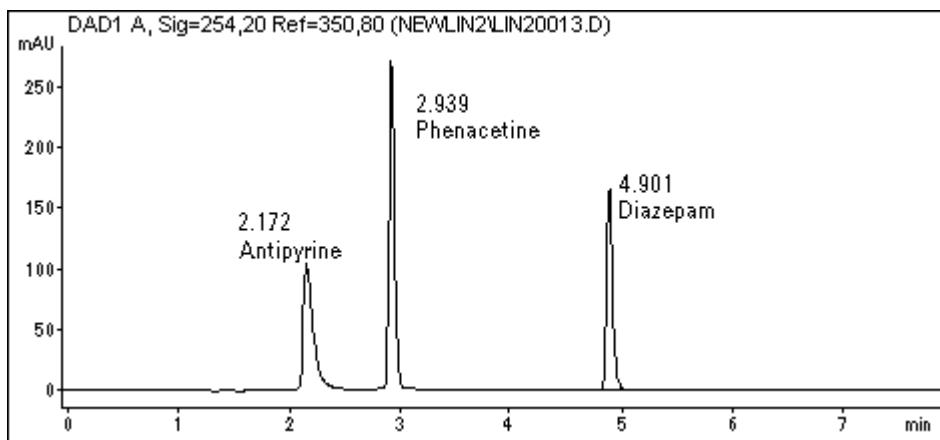
RetTime [min]	k'	Sig	Amount [ng]	Symm.	Width [min]	Plates	Resol	Name
2.172	0.81	1	438.70069	0.44	0.0883	3351	4.47	Antipyrine
2.939	1.45	1	937.28787	0.83	0.0524	17435	6.40	Phenacetine
4.901	3.08	1	599.59734	0.80	0.0550	43990	21.47	Diazepam

*** End of Report ***

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

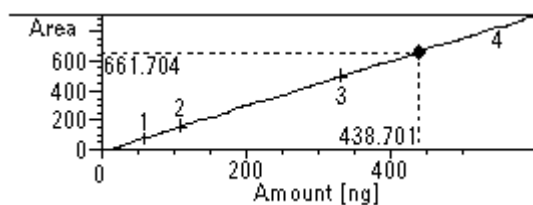
RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng]	Grp	Name
2.172	BB	661.70422	6.62986e-1	438.70069		Antipyrine
2.939	BB	934.32690	1.00317	937.28787		Phenacetine
4.901	BB	610.64050	9.81915e-1	599.59734		Diazepam
Totals :				1975.58590		

=====

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 = ax3 + bx2 + 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 ***

Extended Performance Report

Data File D:\HPCHEM\1\DATA\SYSSUI\CON00005.D

Extended Performance Report

Instrument: Instrument 1

Module	Firmware revision	Serial number
1100 Quaternary Pump	A.04.11	DE1 1116042
1100 Wellplate Autosampler	A.04.13	DE02700294
1100 Column Thermostat	A.04.11	DE53400174
1100 Diode Array Detector	A.04.11	DE00900051
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\1\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:

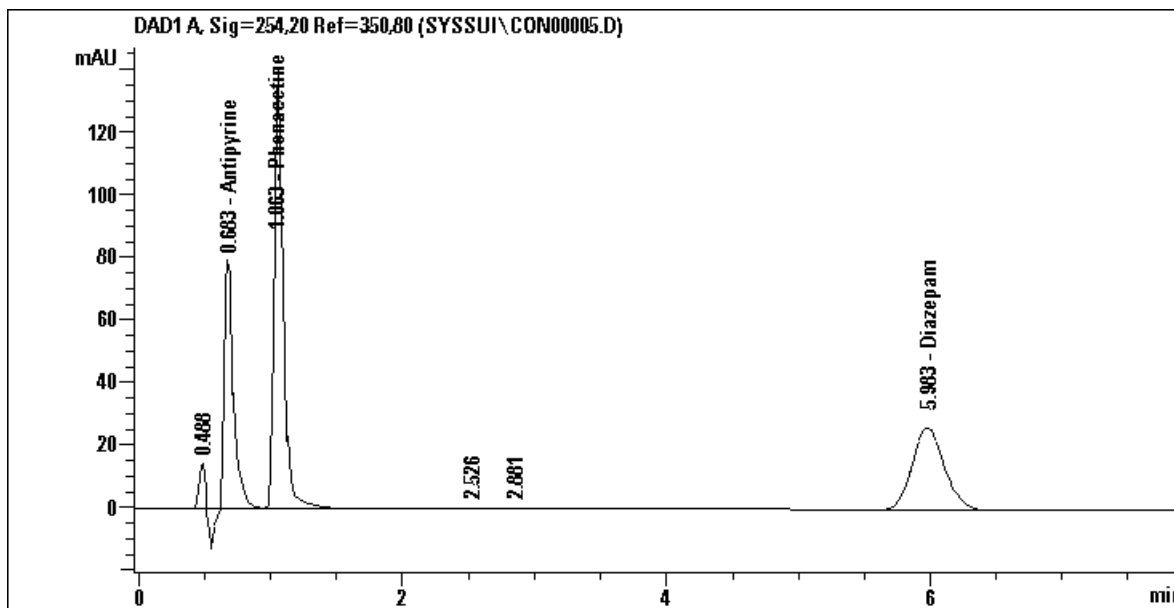
Operator:	agratz
Date/Time:	2/11/029:06:34 AM
Data file name:	D:\HPCHEM\1\DATA\SYSSUI\CON00005.D
Method file name:	D:\HPCHEM\1\METHODS\SYSSUIP.M

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

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

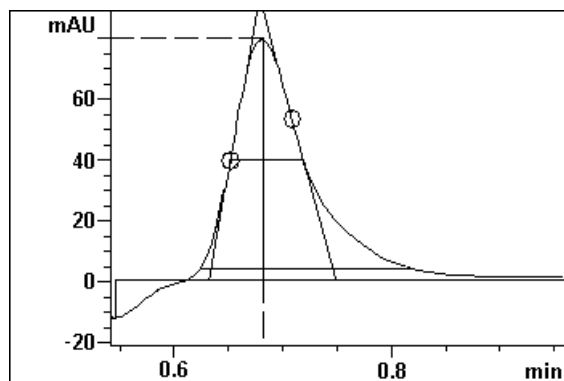
Symmetry: 0.483

USP Tailing: 1.657

Integration type: HV

Time increment [macc]: 400.0

Data points: 66



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

:
:
:

The peak description
and statistical moments
are repeated for each
compound

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

Sequence Summary Report – Compound Summary

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

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
- ☐ 8. Statistics sample runs
- ☒ 9. Summary

Standard Statistic

Standard Statistic

Compound Summary

Sample Summary

Compound Summary

OK

Cancel

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

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

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

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

Sequence Summary Report – Compound Summary (continued)

Compound Summary

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 [ng]	Multip.* Dilution	FileName .D	RetTime [min]	Amount [ng]	Compound
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

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 ***

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

☒ 8. Statistics sample runs

☒ 9. Summary

Standard Statistic

Standard Statistic

Sample Summary

Sample Summary

Compound Summary

OK Cancel

Statistic Report

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 [min]	Amount [ng]	Area [mAU*s]	Height [mAU]	Width [min]	Symm.
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

Sequence Summary Report – Standard Statistics for Sample Runs

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

Run #	Type	RetTime [min]	Amount [ng]	Area [mAU*s]	Height [mAU]	Width [min]	Symm.
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 [min]	Amount [ng]	Area [mAU*s]	Height [mAU]	Width [min]	Symm.
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

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 [ng]	Multip.* Dilution	File name	Cal #	Page	#
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 ***

*Angelika Gratzfeld-Huesgen is
application chemist at Agilent
Technologies GmbH, Waldbronn,
Germany.*

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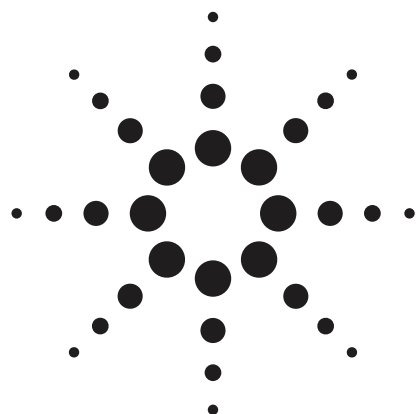
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Agilent Technologies



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 Technologies

Introduction

Particularly analytical service laboratories in the pharmaceutical industry, responsible for analyzing chemical libraries¹ or performing MS based quantifications of certain ADME-properties and drug metabolism studies of drug candidates² 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 columns³. 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

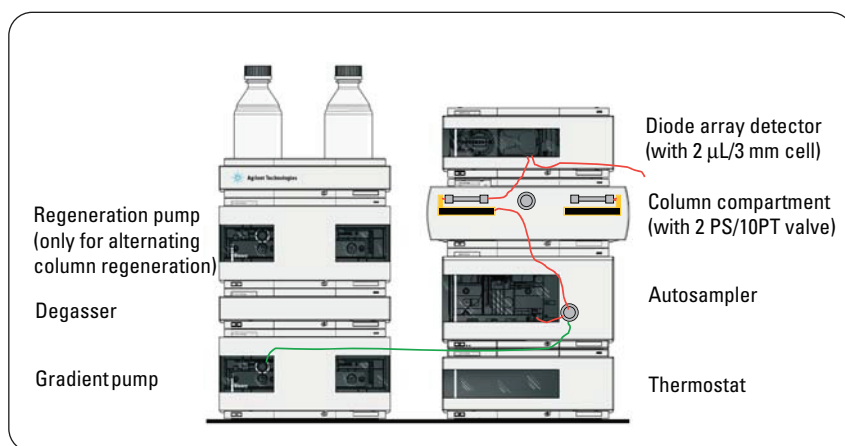


Figure 1
System setup with low delay volume for high speed applications using 2.1-mm id columns with lengths from 20 to 50 mm.

The Agilent 1200 Series binary pump SL is designed to fulfill the demands for high throughput, highest performance, optimum resolution and low-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 $\mu\text{g}/\mu\text{L}$ for each compound except butyrophenone which was 0.2 $\mu\text{g}/\mu\text{L}$. The solvent was water-acetonitrile 2:1.

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

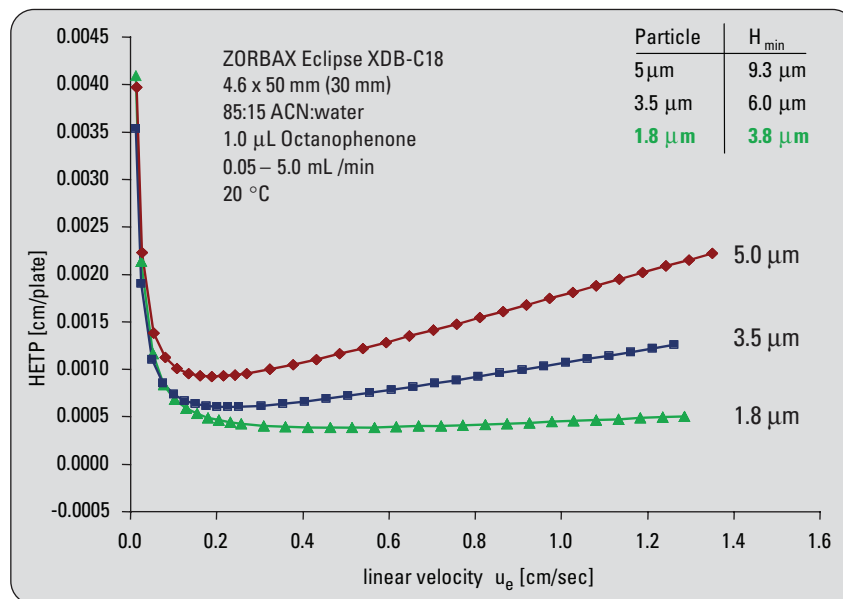


Figure 2
Van Deemter curves of columns packed with 1.8 μm , 3.5 μm and 5.0 μm particles.

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 $R_s = 2.1$ up to $R_s = 3.5$ 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:

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

(tg = gradient time, F = flow rate, V_m = column void volume, $\Delta\%B$ = 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 base-line 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).

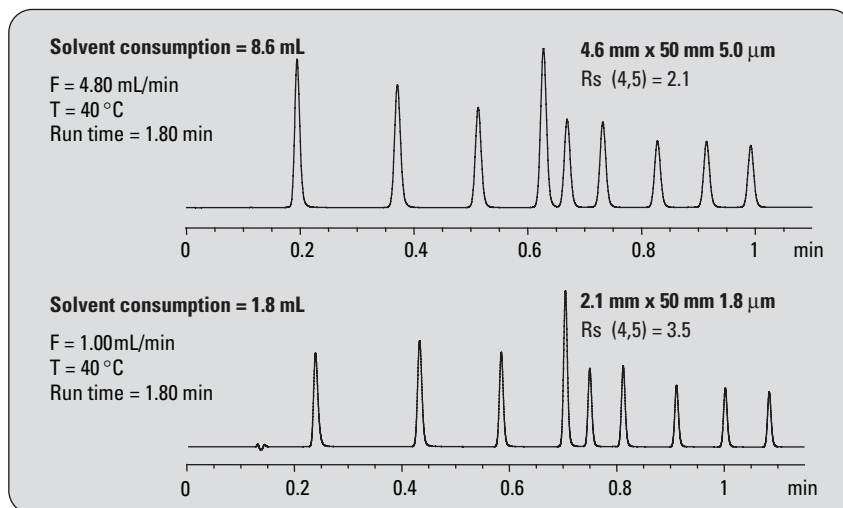


Figure 3
Analysis with 1.8-µm particle column vs. 5.0 µm particle column.

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 0.90 min 95 %B 1.10 min 95 %B 1.11 min 35 %B 1.15 min	0.00 min 35 %B 0.90 min 95 %B 1.10 min 95 %B 1.11 min 35 %B 1.15 min
Stoptime:	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
<i>Time values for F = 0.35 mL/min. For all other flow rates times are scaled so that (tg x F) = 0.90 mL</i>	
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

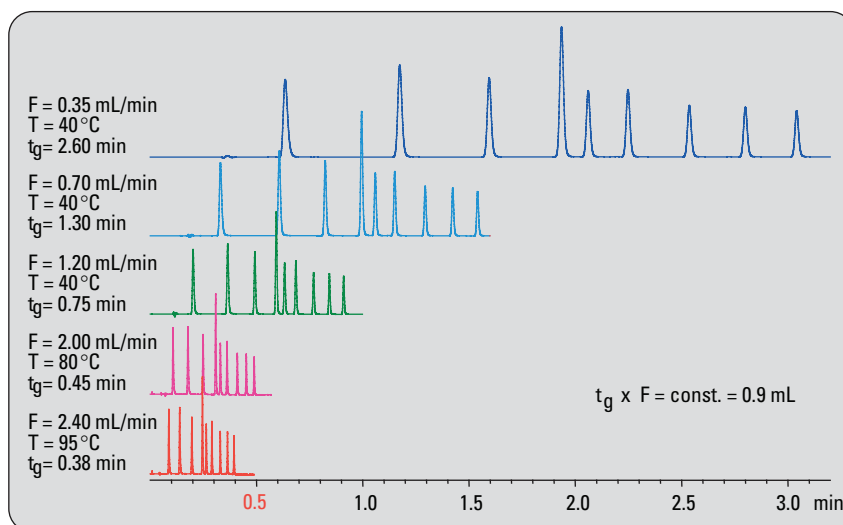


Figure 4
Increasing separation speed by increasing temperature and flow rate while decreasing gradient time.

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 isocratically 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

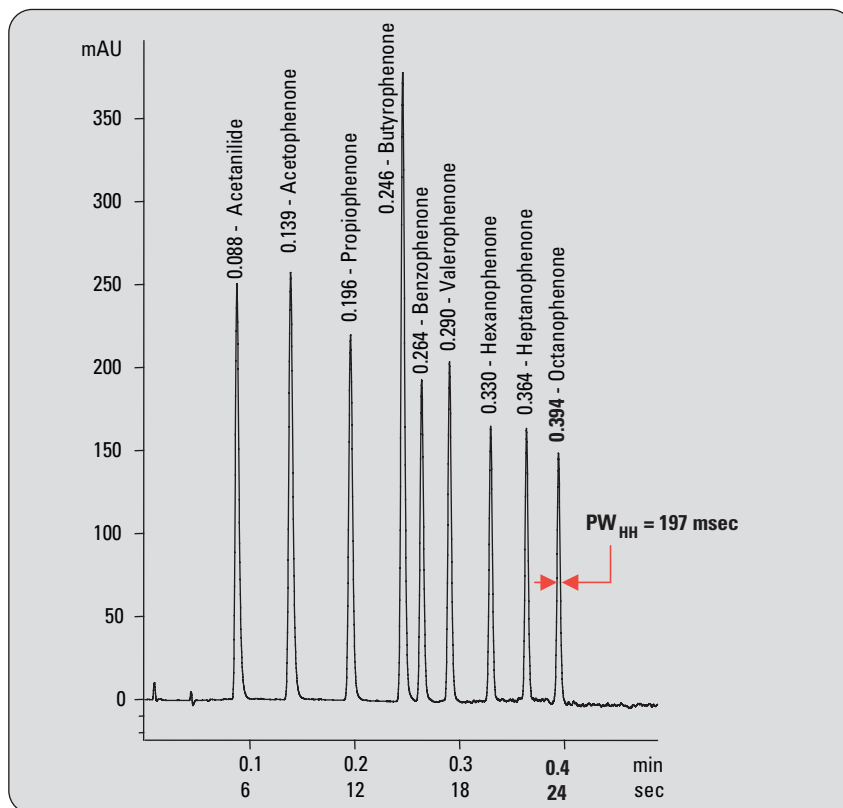


Figure 5
Separation of a nine compound mixture under ultra fast conditions.

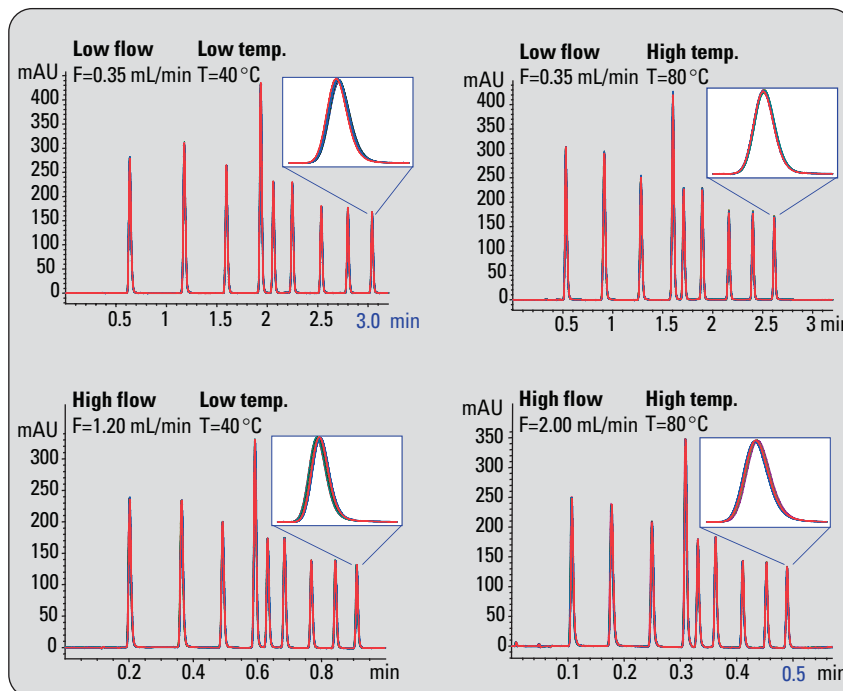


Figure 6
Overlaid chromatograms of the repeated analysis of a 9 compound mixture under various conditions.

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- μ m 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.
	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
Column compartment	no OI – Draw/Eject speed	Low speed causes increased sampling time	Low speed results in better injection precision
	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.

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

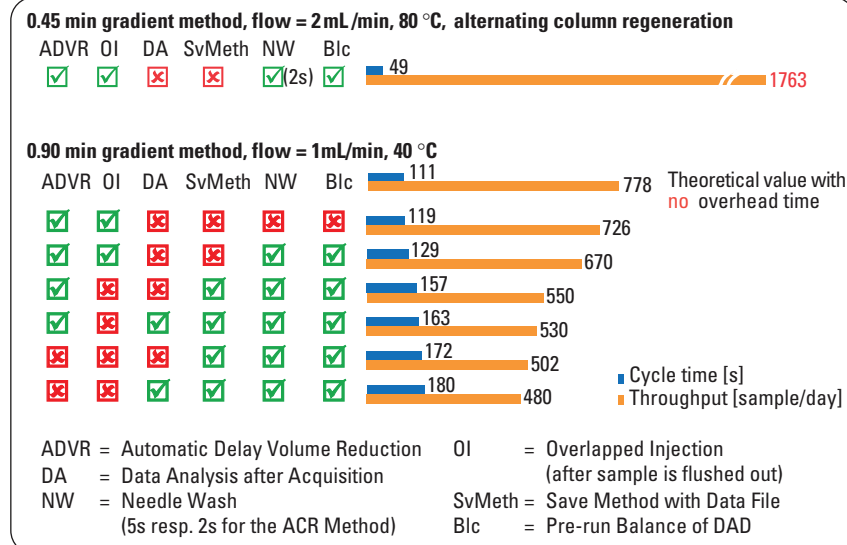


Figure 7
Cycle time and daily throughput optimization.

Chromatographic conditions:

Alternating Column Regeneration Method

Solvent: A = Water, B = ACN
 Temp.: 80 °C
 Flow: 2.0 mL/min
 ADVR: Yes
 Gradient:

Gradient-Pump

0.00 min 35 %B
 0.45 min 95 %B
 0.46 min 35 %B
 0.57 min 35 %B

Regeneration-Pump

0.00 min 35 %B
 0.01 min 95 %B
 0.11 min 95 %B
 0.12 min 35 %B

Stoptime: 0.57 min
 Posttime: 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
 Gradient:

0.00 min 35 %B
 0.90 min 95 %B
 1.10 min 95 %B
 1.11 min 35 %B
 1.15 min

No

0.00 min 35 %B
 0.90 min 95 %B
 1.10 min 95 %B
 1.11 min 35 %B

Stoptime: 1.15 min
 Posttime: 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

1.40 min (add. 300 µL extra column volume, increased retention times)
 0.70 min

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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Michael Frank is Application Chemist at Agilent Technologies, Waldbronn, Germany.

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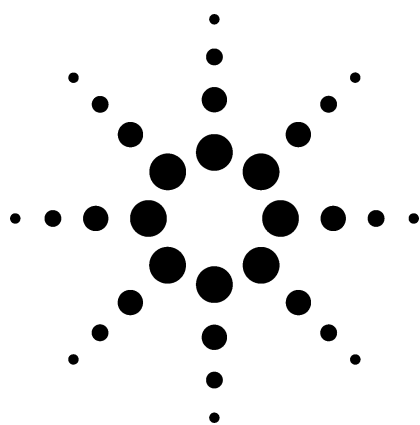
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Agilent Technologies



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

Application

Author

Michael Woodman
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

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 L_1/L_2 , 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.

$$\text{Flow}_{\text{col. 1}} \times \left[\frac{\text{Diam. column 2}}{\text{Diam. column 1}} \right]^2 = \text{Flow}_{\text{col. 2}} \quad (\text{eq. 1})$$

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 opti-

um 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

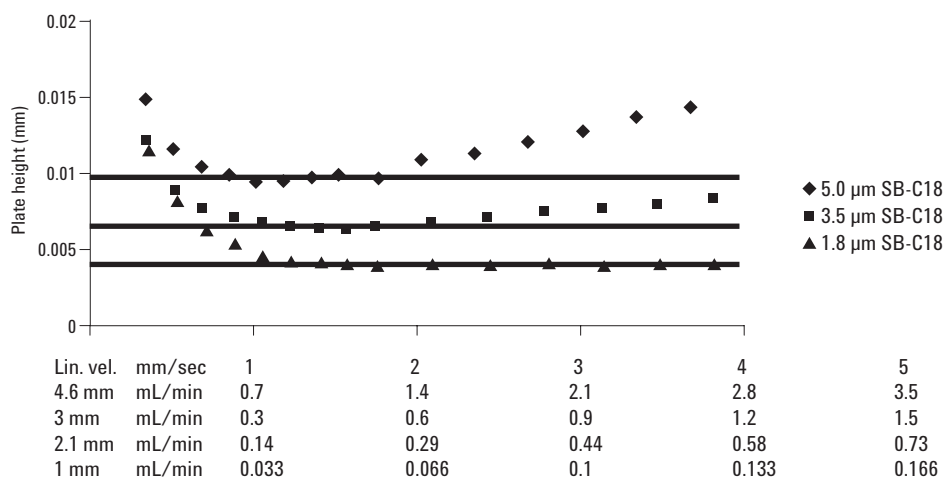


Figure 1. van Deemter plot with various flow rates and particle sizes.

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

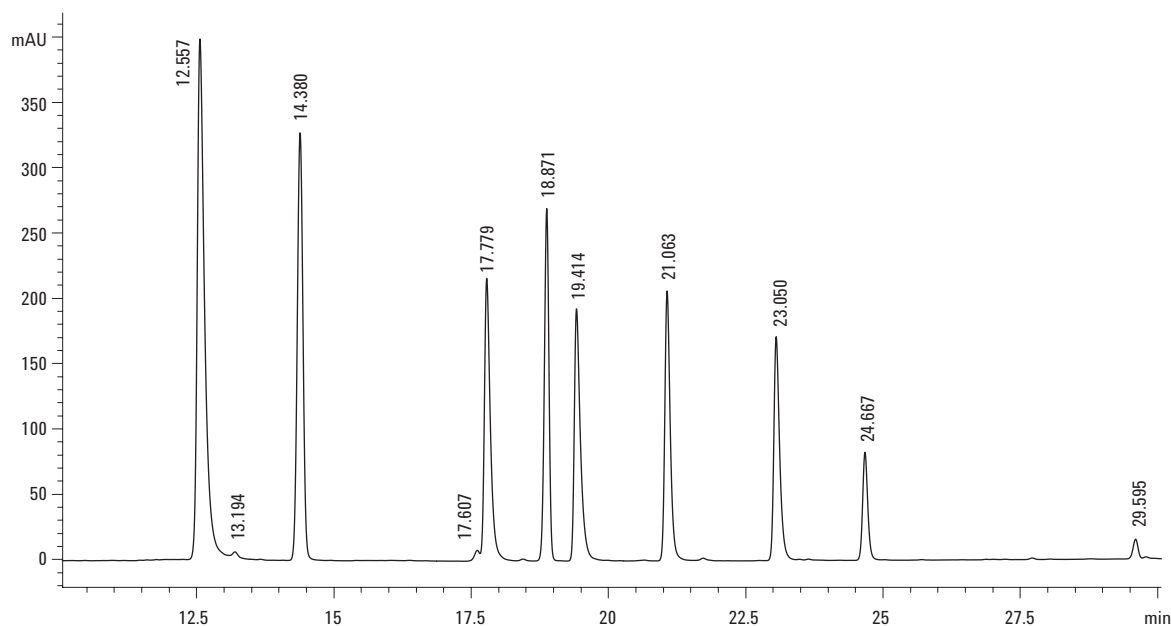
Standard mixture of chlorinated phenoxy acid herbicides,
 100 μg/mL in methanol

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 H₃PO₄

Gradient slope: 7.8% ACN/column volume

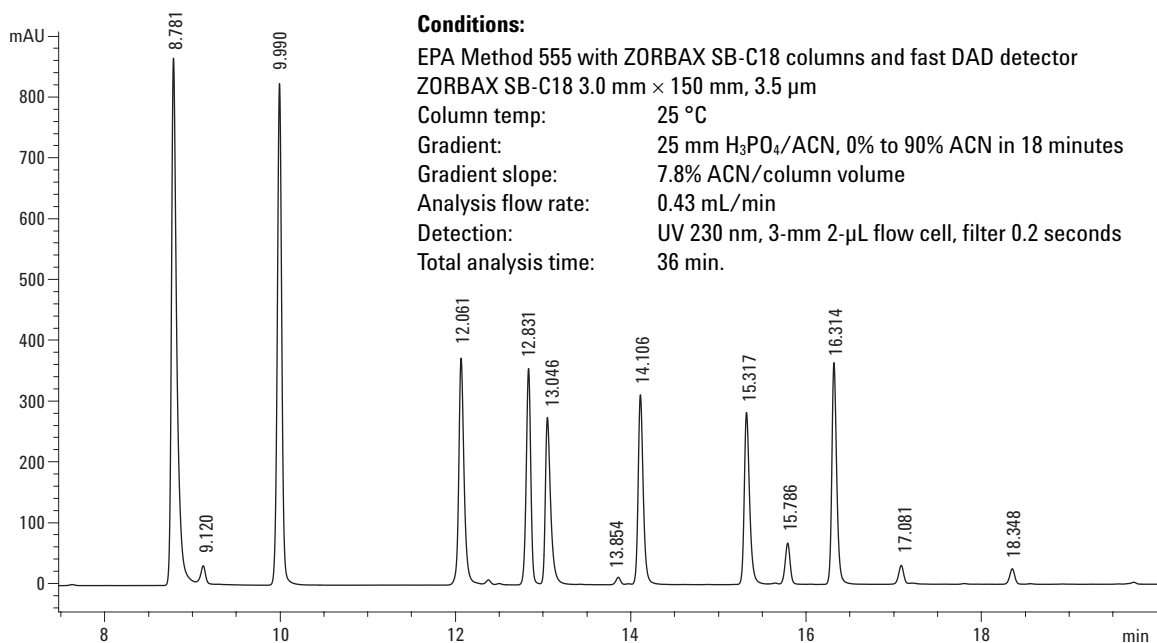
Analysis flow rate: 1 mL/min

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 H₃PO₄/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.

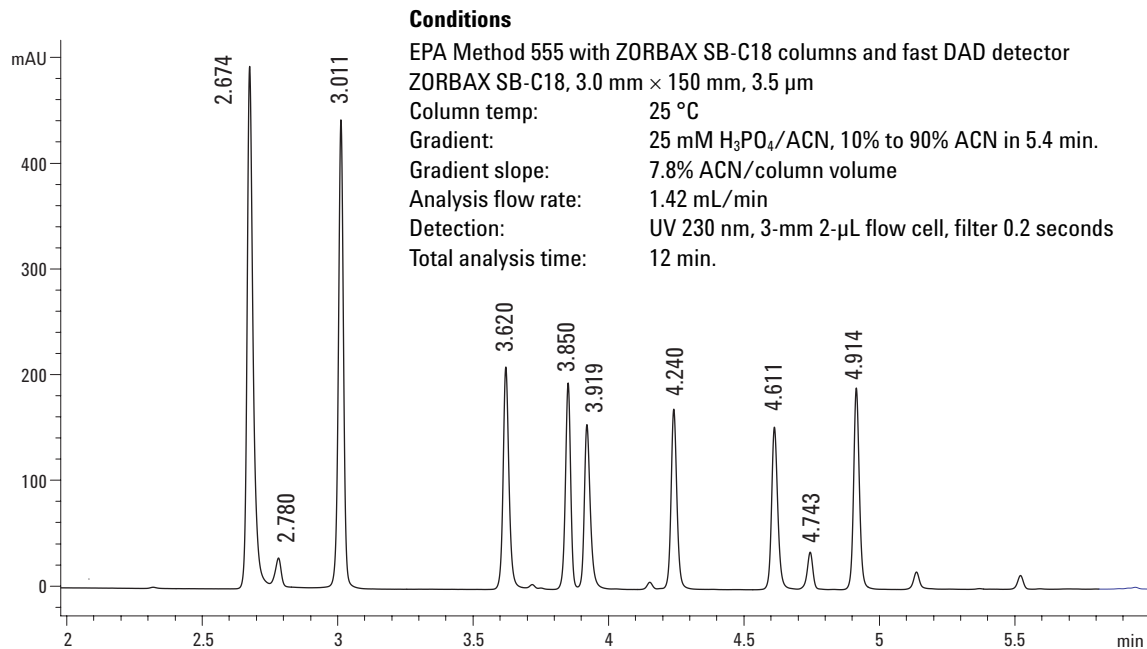


Figure 4. High speed gradient separation of herbicides on 3.0 × 150 mm, 3.5-μm ZORBAX SB-C18.

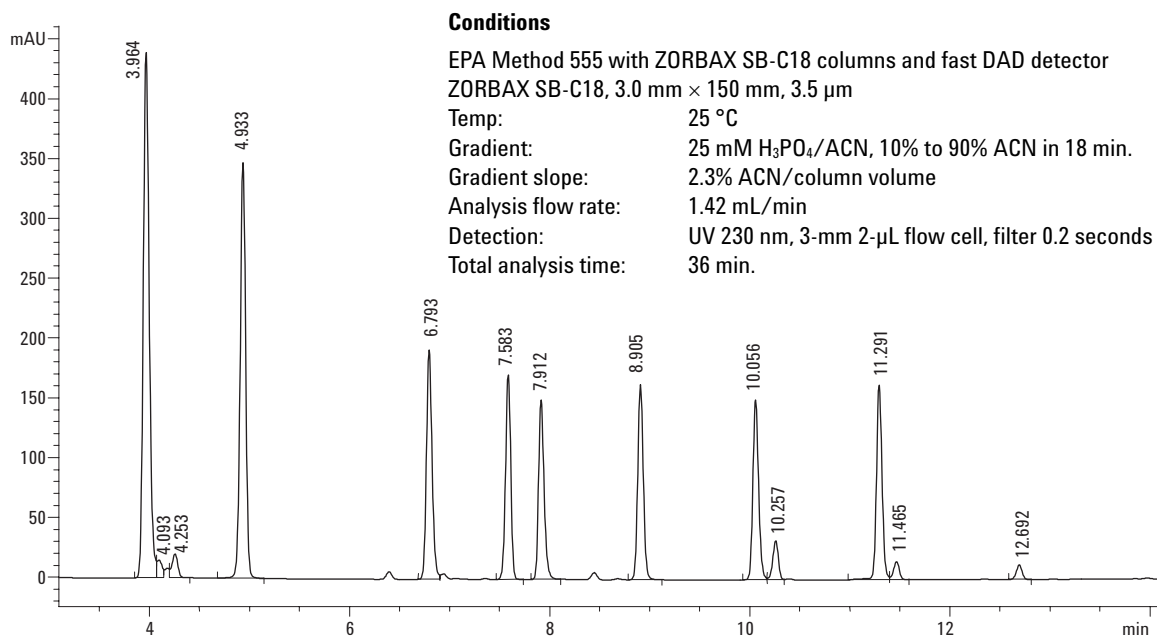


Figure 5. Reduced slope gradient separation of herbicides on 3.0 × 150 mm, 3.5-μm ZORBAX SB-C18.

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- μ L injection of dilute actone

Table 1. Volumetric Measurements of Various Flow Cells

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

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- μ L to the 13- μ L flow cells is 11 μ L, we observe an increase of 15 to 16 μ L because of the larger diameter inlet tubing integral to the larger volume flow cells.

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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Agilent Technologies

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, μ ECD, 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

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.

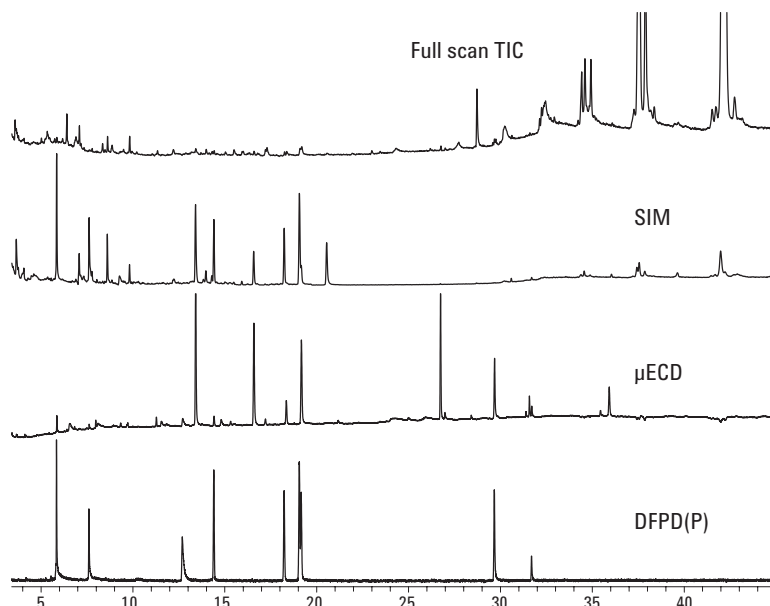


Figure 1. Four chromatograms collected simultaneously from a single injection of a milk extract.



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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

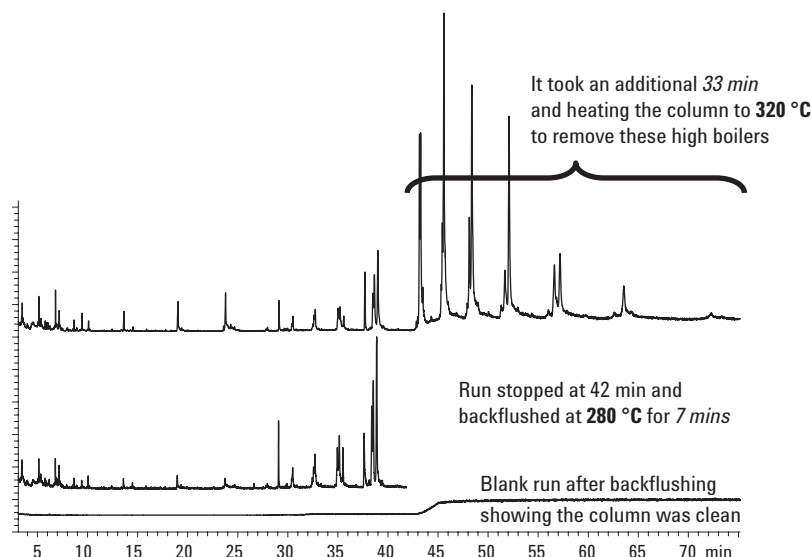


Figure 2. Three total ion chromatograms comparing the results with and without backflush.

of 320 °C. A column effluent splitter or QuickSwap is required to do the backflush.

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Acknowledgement

Milk extract is courtesy of Dr. Steven Lehotay from USDA Agricultural Research Service in Wyndmoor, Pennsylvania, USA.

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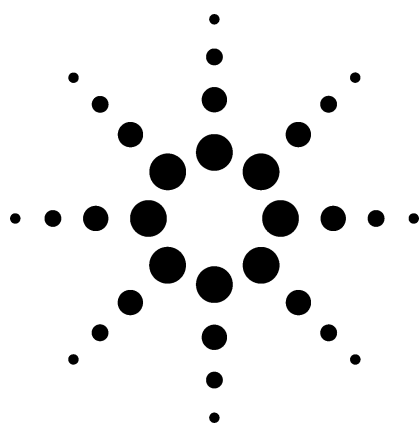
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A Column-Flow Independent Configuration for QuickSwap



Application

Authors

Matthew S. Klee and Bruce Quimby
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

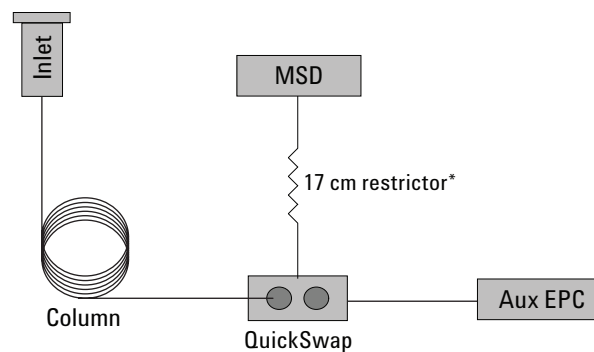
Abstract

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.



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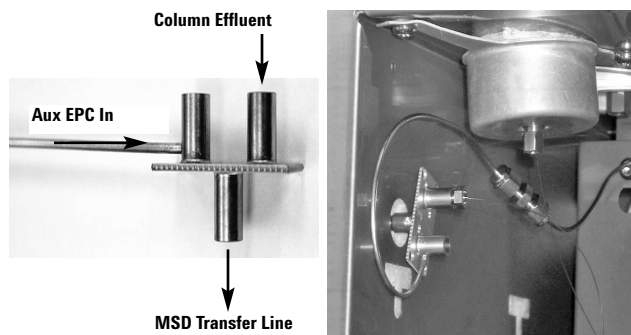


Figure 2. QuickSwap is pictured on the left showing permanent (Aux EPC In) and temporary connections. A picture of a normal QuickSwap installation is shown on the right.

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.

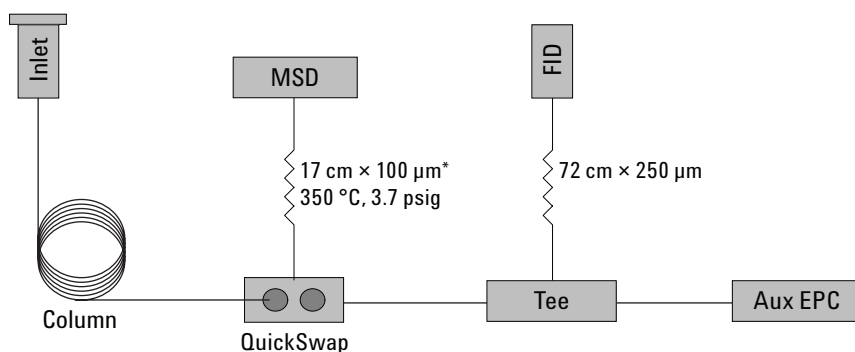
In general, when flow to the MSD changes,

- 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.

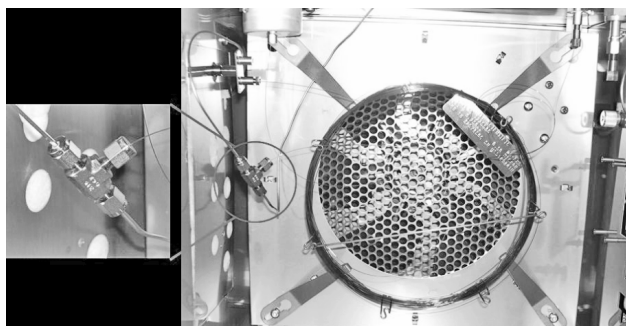
- Simplifies retention time locking applications with QS
- Allows pressure pulse injections without having to change QS restrictor
- Allows more aggressive backflush conditions than if larger restrictors were used
- Allows method translation and speed up without having to change QS restrictor
- Allows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

tions 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.

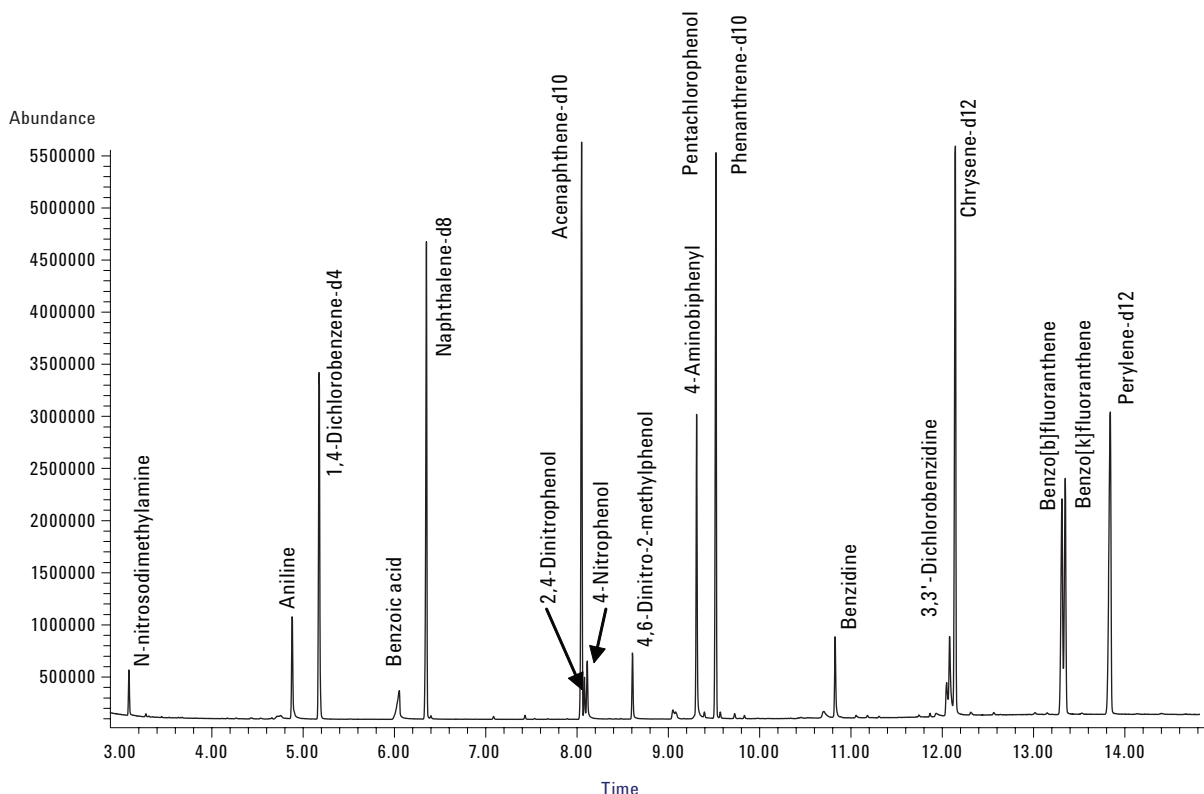


Figure 4. Reference chromatogram for Fast 8270 method.

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 Corresponding to the Optimal Flow Rate Range of the MSD

QuickSwap restrictor id (μm)	QuickSwap pressure (psig)	Transfer line temperature ($^{\circ}\text{C}$)	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 semi-volatiles 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) $\rightarrow$ 350°C (3 min) @ $20^{\circ}\text{C}/\text{min}$; 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
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).

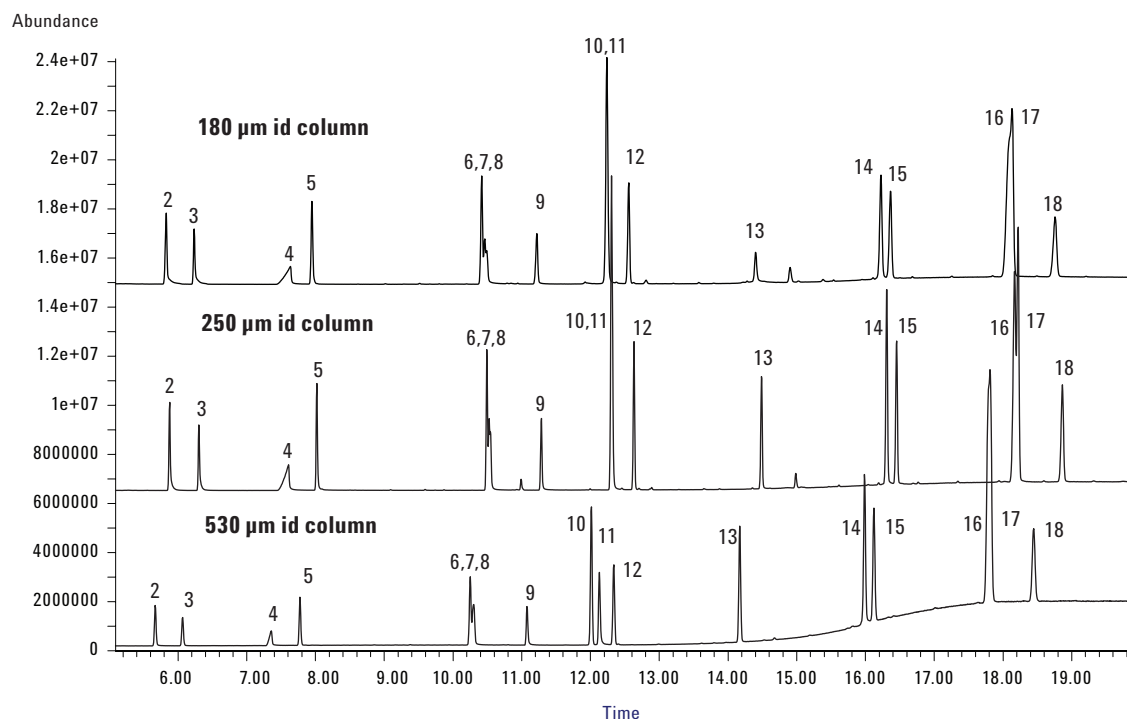


Figure 5. Constant pressure mode analysis with three different column dimensions; 0.5- μL splitless injections of 80-ppm semi-volatiles test sample, with flow conditions from Table 2.

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- μ m id column flow exceed 1 mL/min, so there is nothing vented and no FID signal. For the 250- μ m 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- μ m 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.

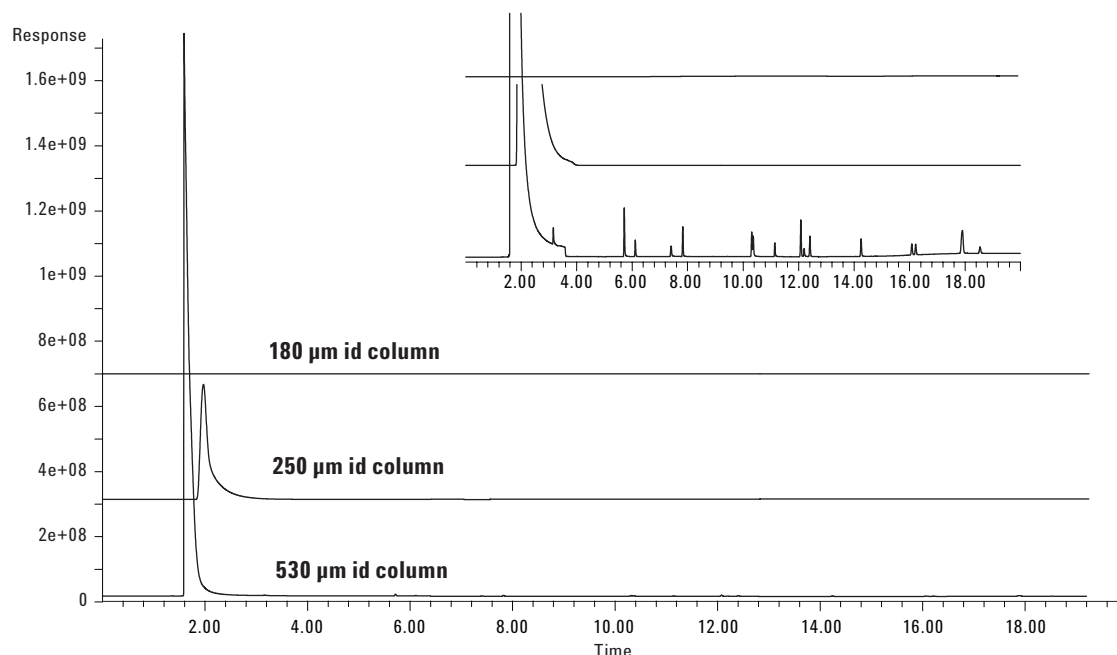


Figure 6. FID signal of vent stream shows what is vented when column flow exceeds flow to MSD.

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

Dimensions	Outlet flow
20 m X 180 μ m	0.72 mL/min
20 m X 180 μ m	1.44 mL/min
30 m X 250 μ m	2.5 mL/min
30 m X 250 μ m	1.0 mL/min
30 m X 530 μ m	2.1 mL/min
30 m X 530 μ m	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- μ m and 180-mm id columns, no column effluent is split to the FID. Since the flow rate of the 530- μ m id column is approximately 2X the flow the MSD, half of the column effluent is split to the FID.

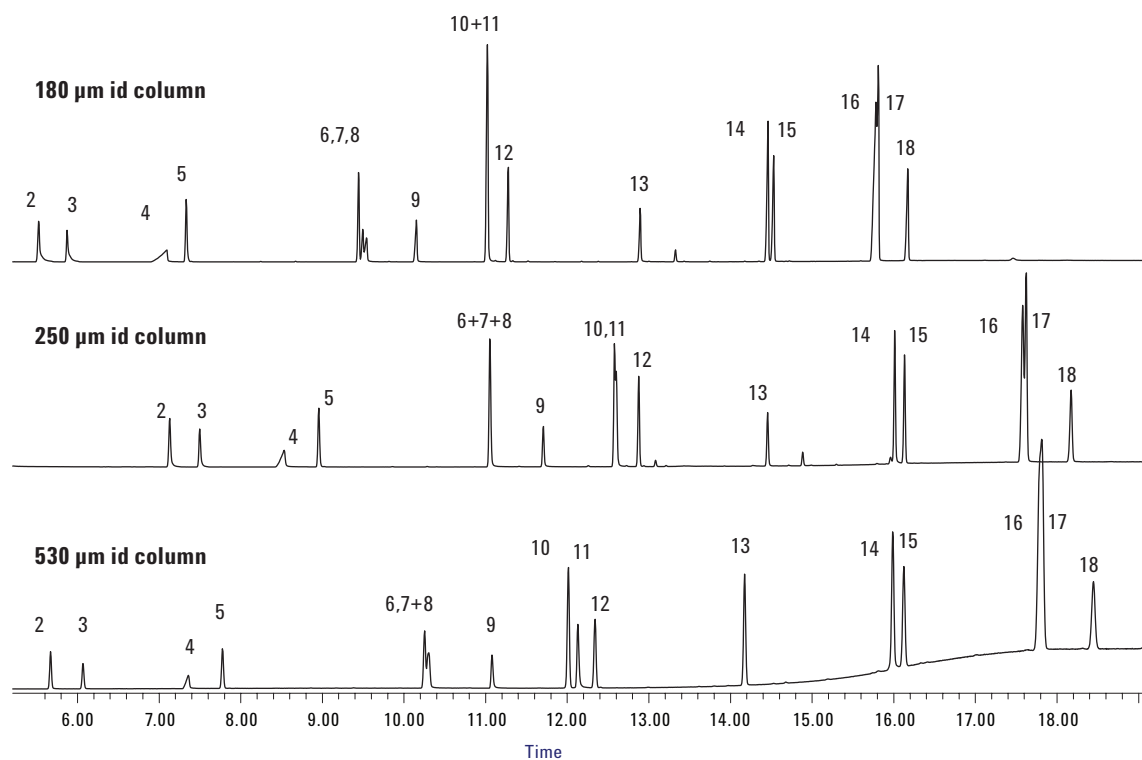


Figure 7. TIC chromatograms for the three columns under optimal constant flow mode conditions.

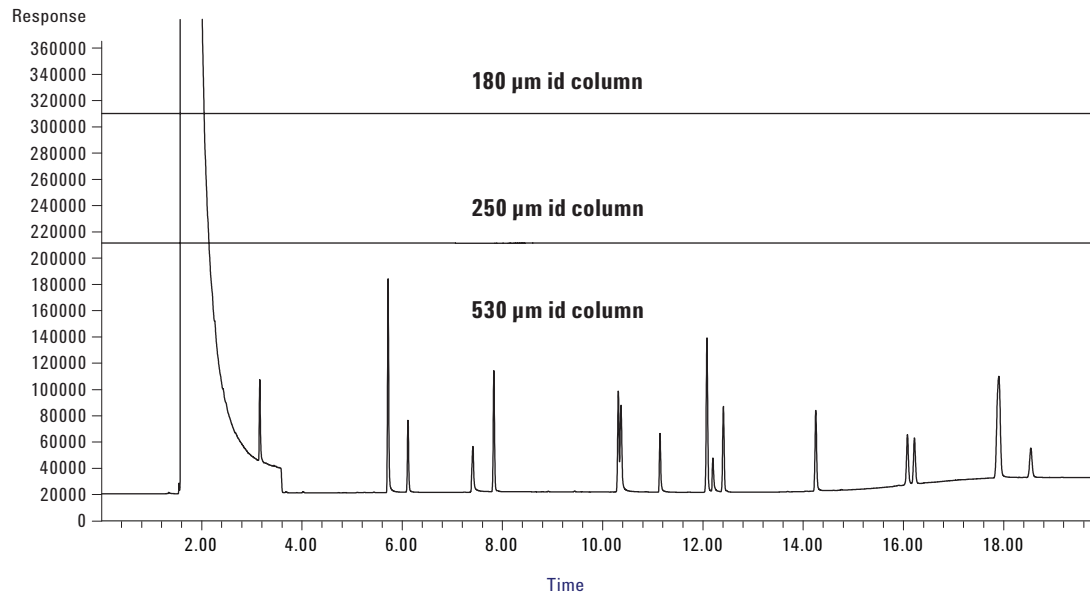


Figure 8. FID vent signal for three columns under optimal flow conditions. Only the 530-µm id column has a flow that exceeds the 1 mL/min flow to the MSD.

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.

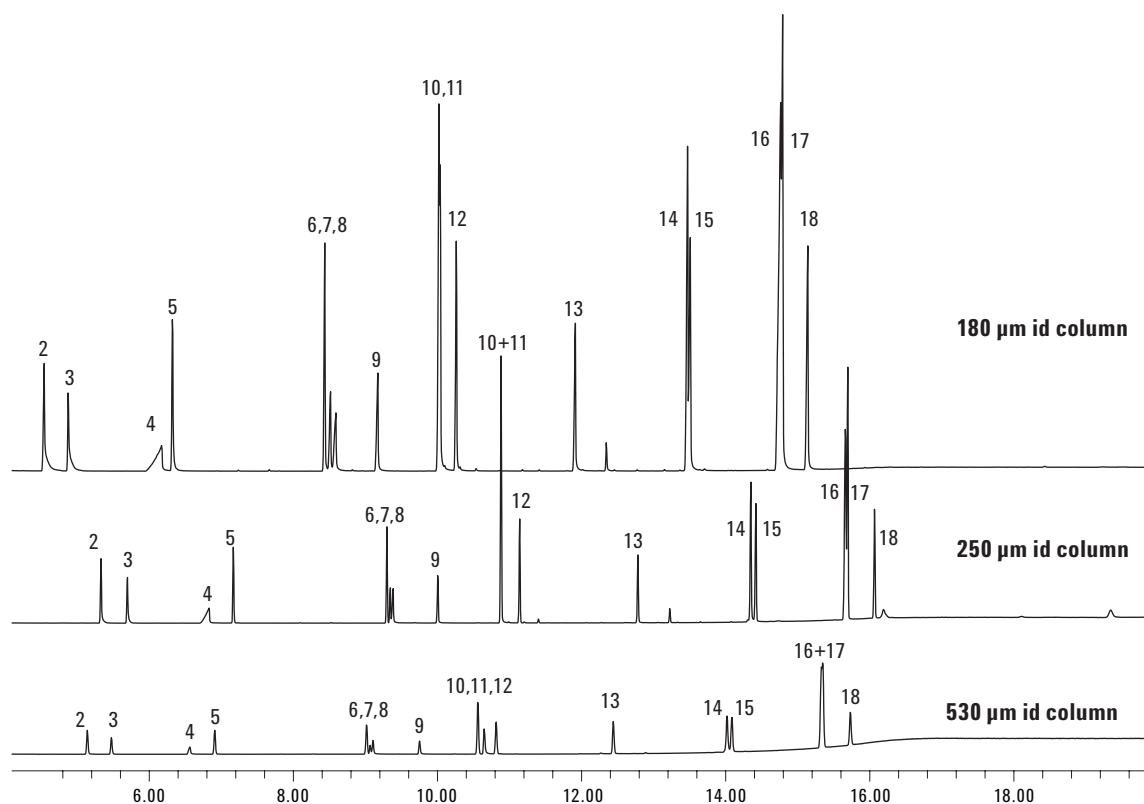


Figure 9. Comparison of MSD TIC chromatograms for three columns run at 2X optimal constant flow mode. Scale is constant for the three, showing the absolute amount of sample reaching the MSD.

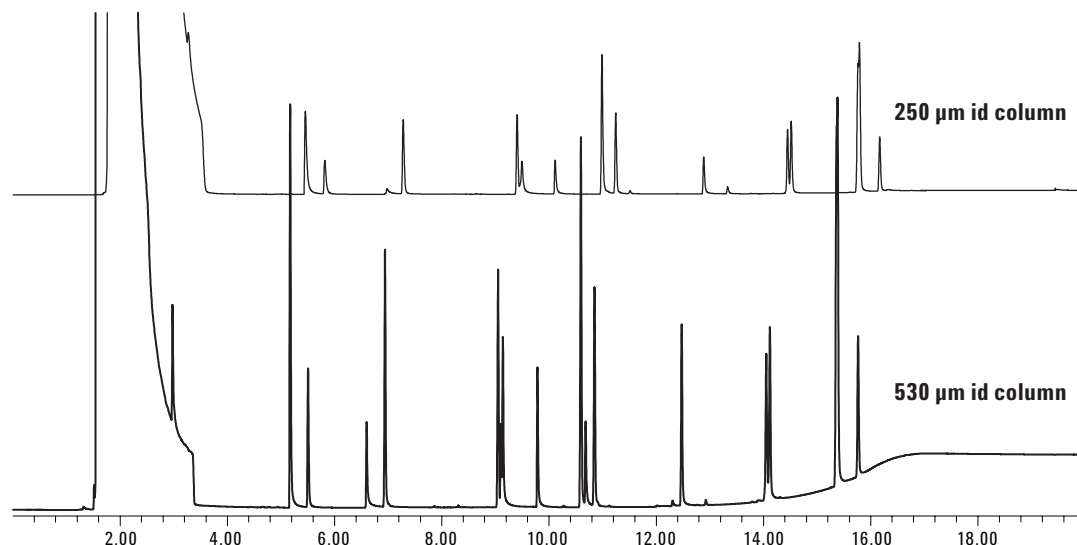


Figure 10. FID vent signals for the two largest columns operated at 2X optimal constant flow rate conditions.

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.

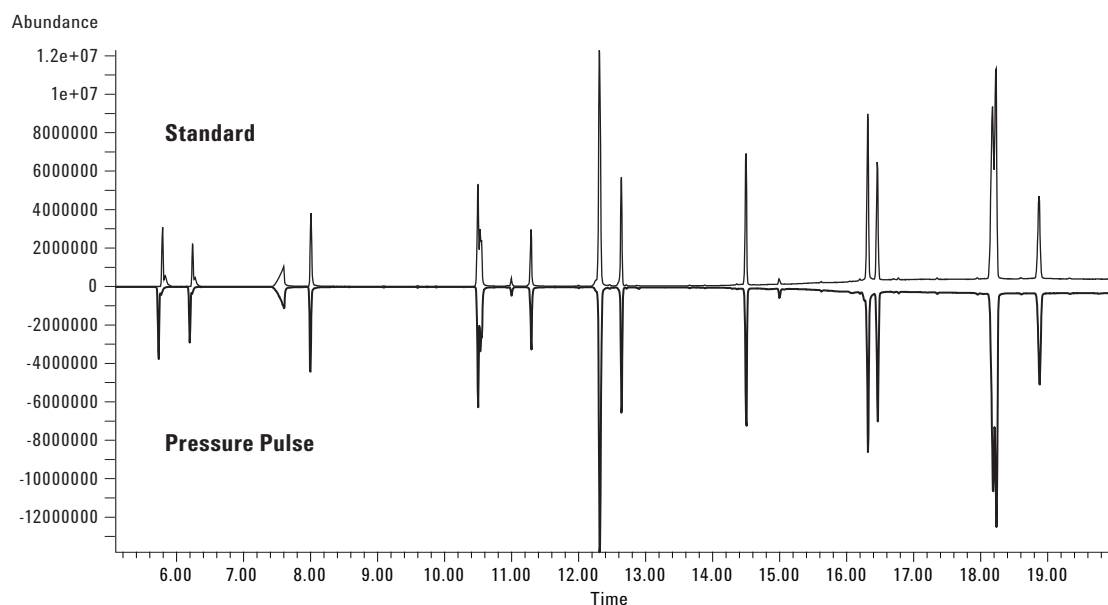


Figure 11. Comparison of standard and pressure-pulse injection modes. No adjustment of QuickSwap pressure was required for the pressure-pulse mode—a benefit of using QuickSwap split configuration.

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.

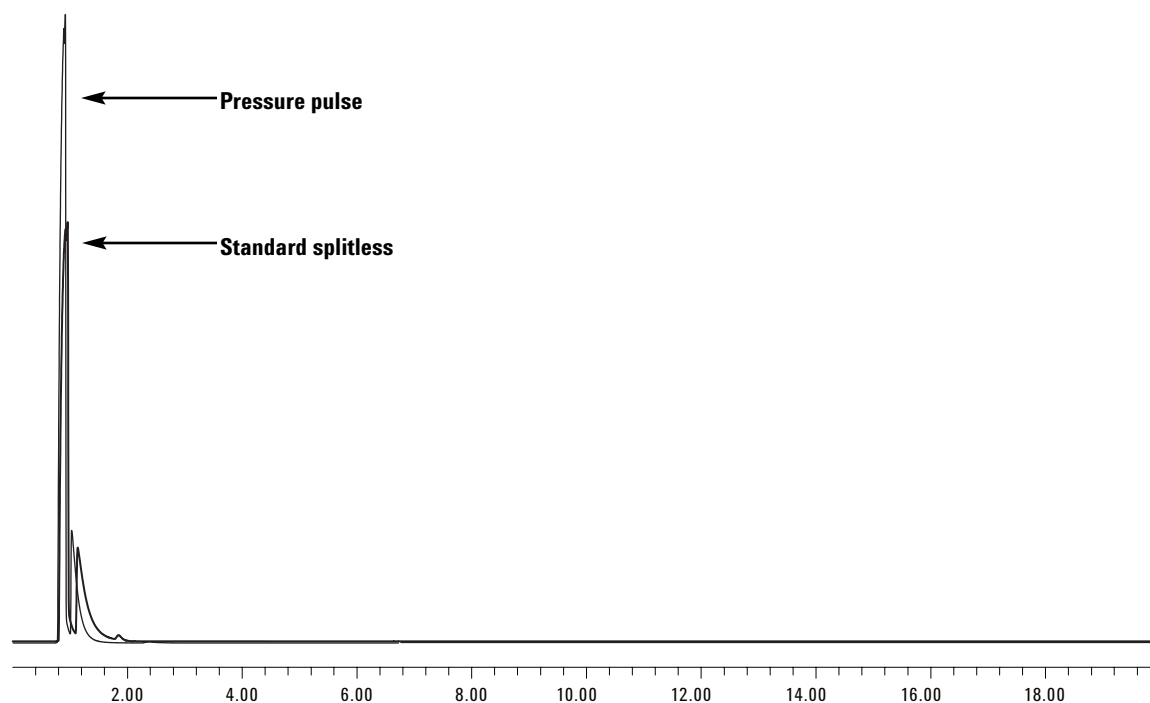


Figure 12. FID vent signal for pressure-pulse injection versus standard splitless injection.

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

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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.
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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 column connections	250 µm	5188-5361
	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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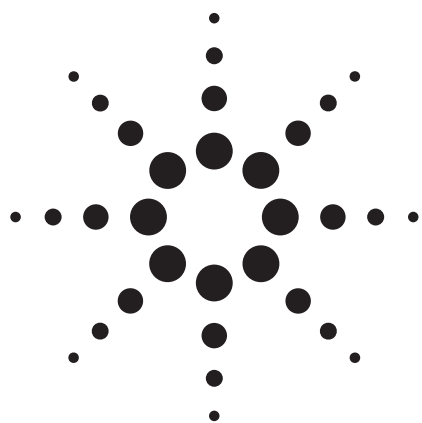
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Parallel GC for Complete Refinery Gas Analysis



Application

Hydrocarbon Processing

Author

Chunxiao Wang
Agilent Technologies (Shanghai) Co. Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
China

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 O₂, N₂, CO, CO₂, H₂S, 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 nC₅, C₆+ 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 back-



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flush 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 DB1 column, 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.

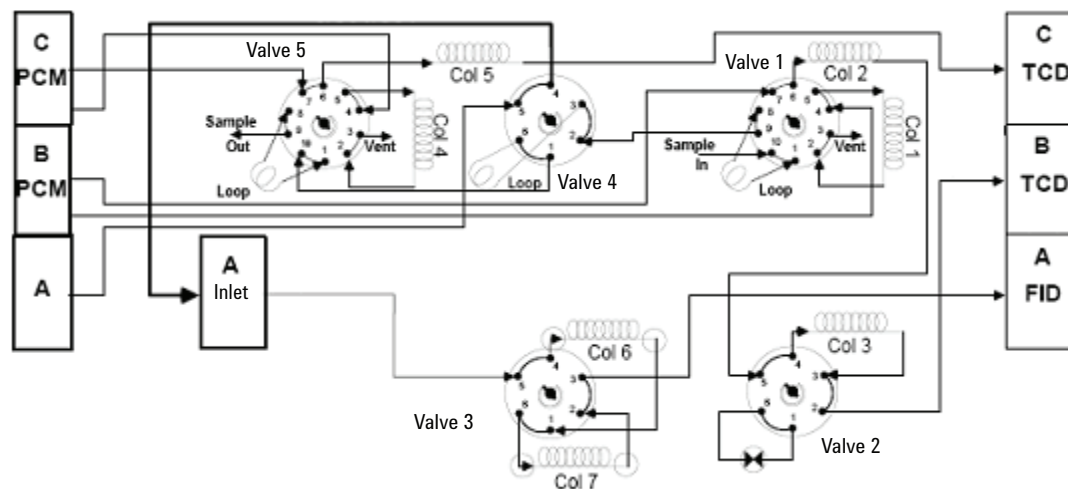
A new tube connector based on capillary flow technology is used to connect the valve to the capillary column to enhance the hydrocarbons analysis by improving the peak shape.

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 development 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
Procolum 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
Procolum 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 connector. With the new union connector 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.

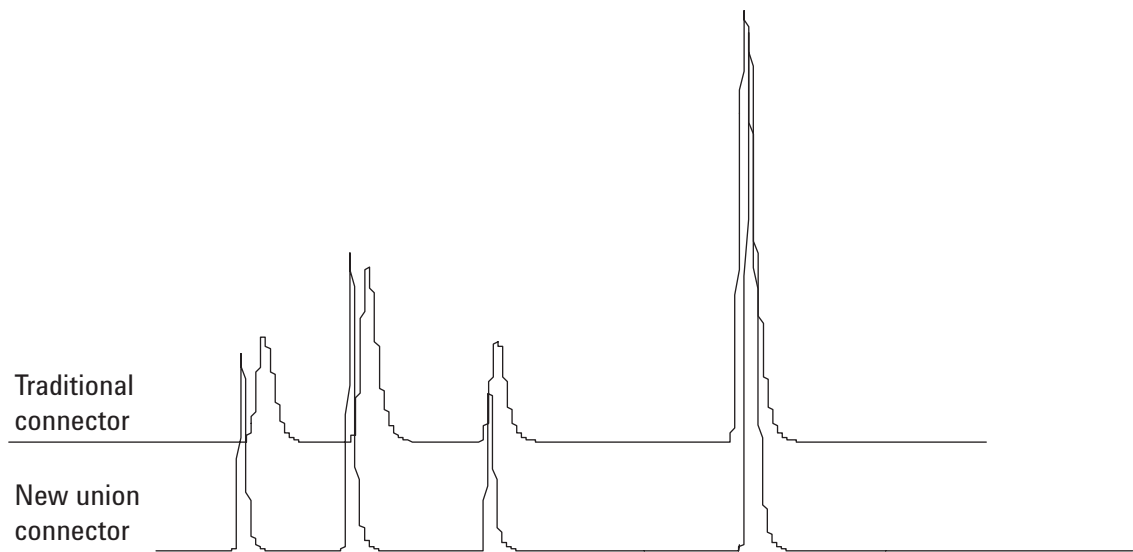


Figure 2. Hydrocarbon peaks obtained from traditional tube connector and new union connector.

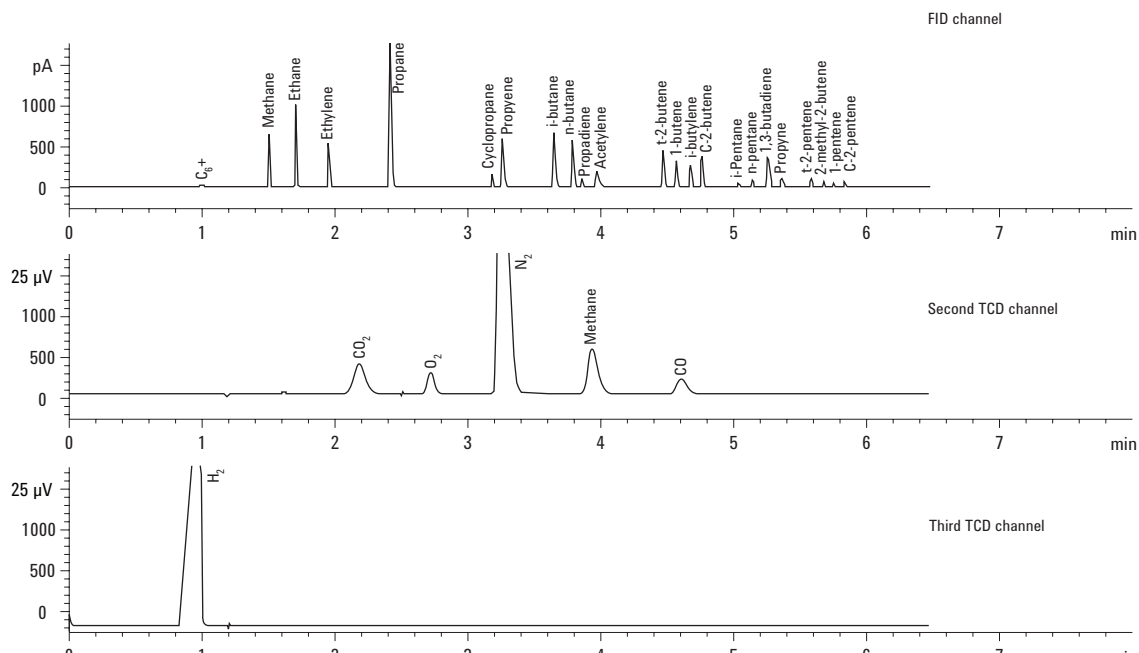


Figure 3. Refinery gas calibration standards analysis. The concentrations for each compound are shown in Table 2.

The top chromatogram (FID channel) is the hydrocarbon analysis. The PLOT alumina column provides excellent separation of hydrocarbons from C₁ to nC₅, including 22 isomers. Components heavier than nC₆ are backflushed early as a group (C₆+) 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

Compounds	Retention time			Average	Area	
	Average	Std. dev.	RSD%		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
Propylene	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 C₆+ followed by individual C₁ to C₅ hydrocarbons as mentioned in fast RGA, or C₇+ followed by individual C₁ to C₆ hydrocarbons, or no backflush to separate C₁ to C₉ individual hydrocarbons. The top chromatogram in Figure 5 is the result with backflush group of C₆+, the middle one is that of C₇+, 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.

H₂S and COS Analysis

H₂S 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 H₂S 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 H₂S 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 H₂S analysis to minimize corrosion.

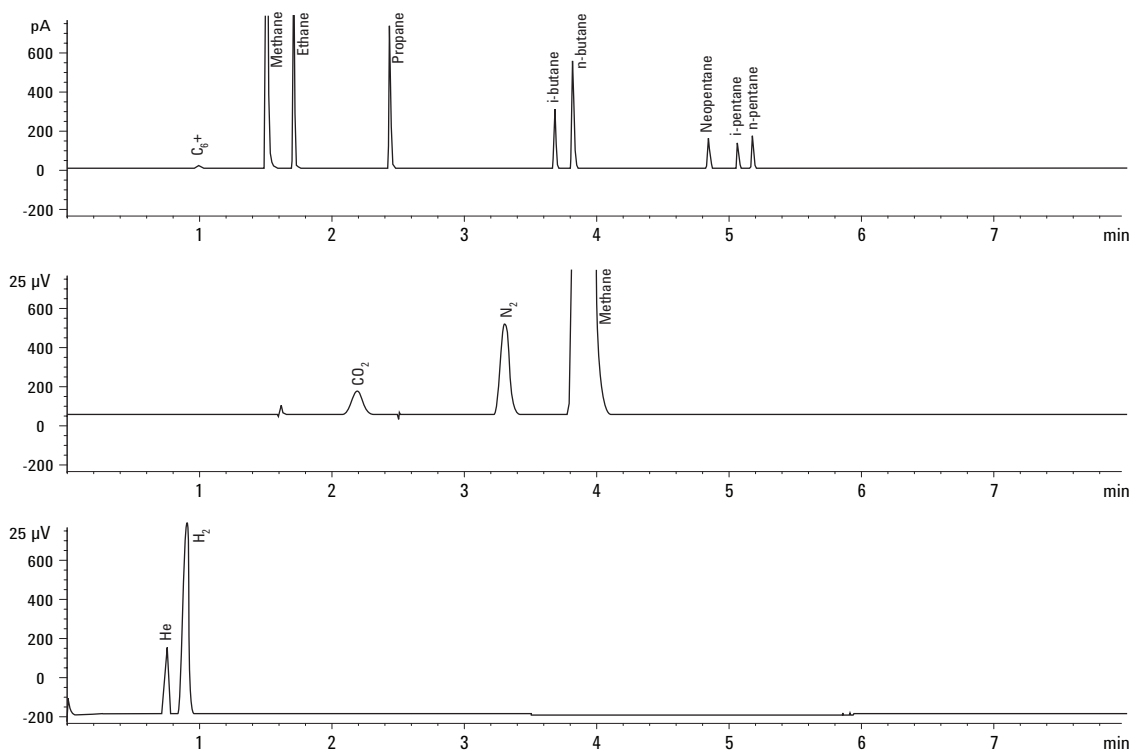


Figure 4. Natural gas analysis of a calibration gas.

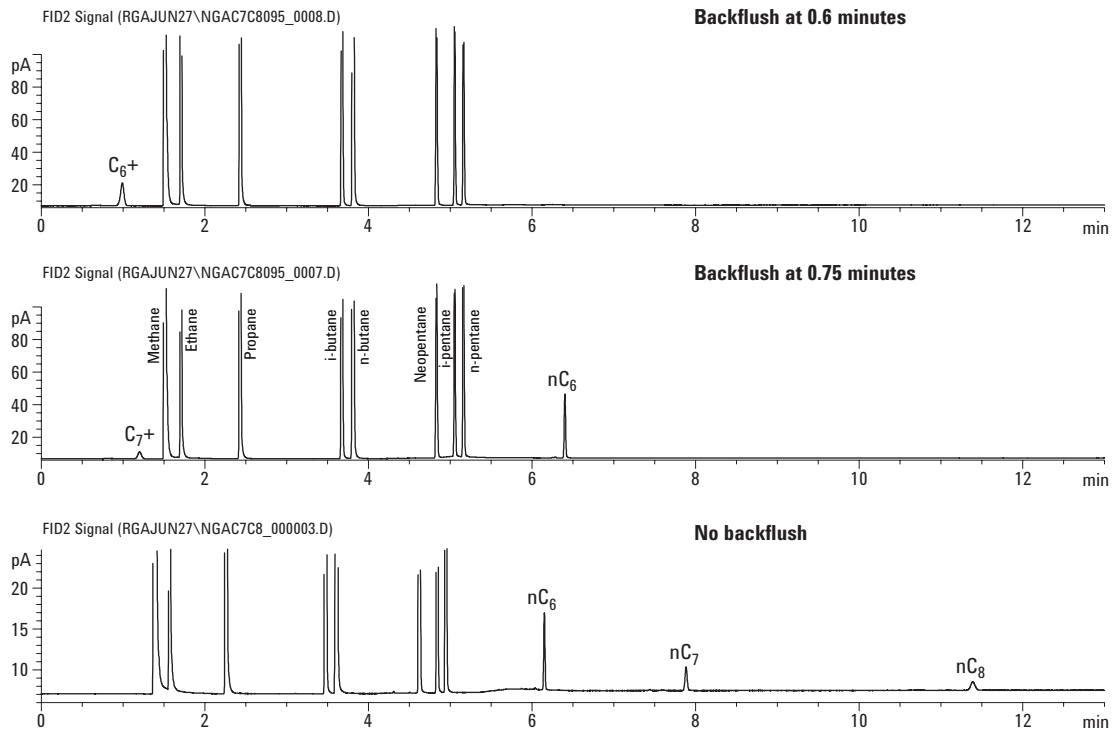


Figure 5. Chromatograms of light hydrocarbons on FID channel with different backflush times .

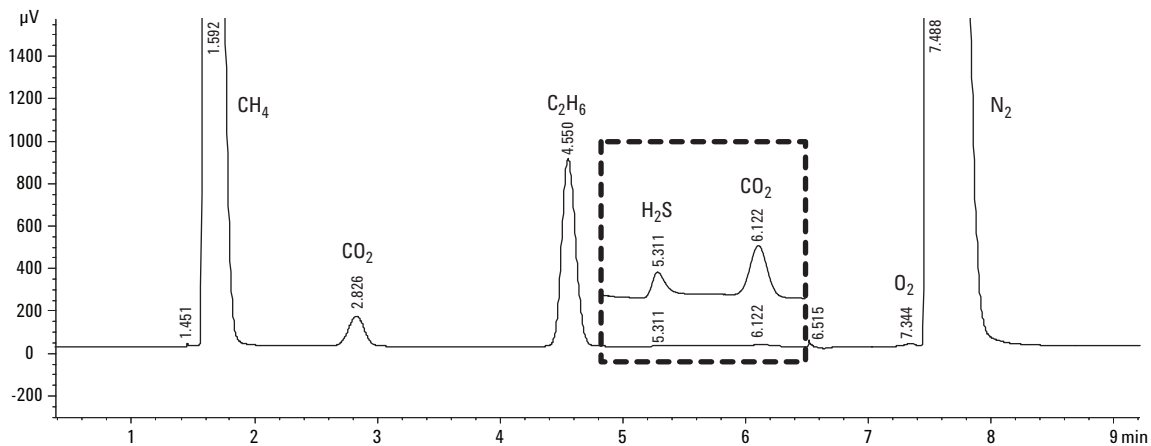


Figure 6. H₂S at approximately 500 ppm and COS 300 ppm on second TCD channel.

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 C₅ and C₆+ 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 C₆+ or C₇+, or no backflush to separate C₁ to C₁₀ individual hydrocarbons. In these cases, the analysis time is increased by 6 minutes. H₂S 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.

References

1. ASTM D1945-03, "Standard Test Method for Analysis of Natural Gas by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
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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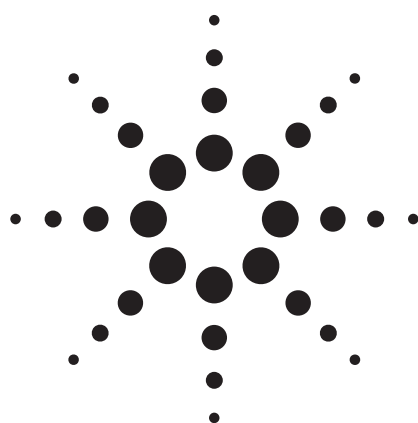
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Agilent Technologies

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 H₂ analysis using N₂ or Ar as carrier gas to improve H₂ detectability and linearity. The updated configuration uses a 10-port valve with a pre-column for backflushing late-eluting components while H₂ 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,

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 H₂S containing samples on the 7890A.

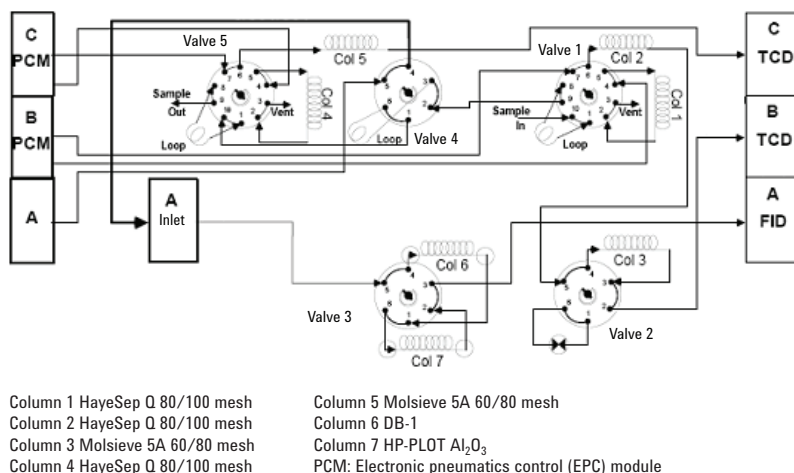


Figure1. RGA valve system.



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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 AL203 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). H₂S 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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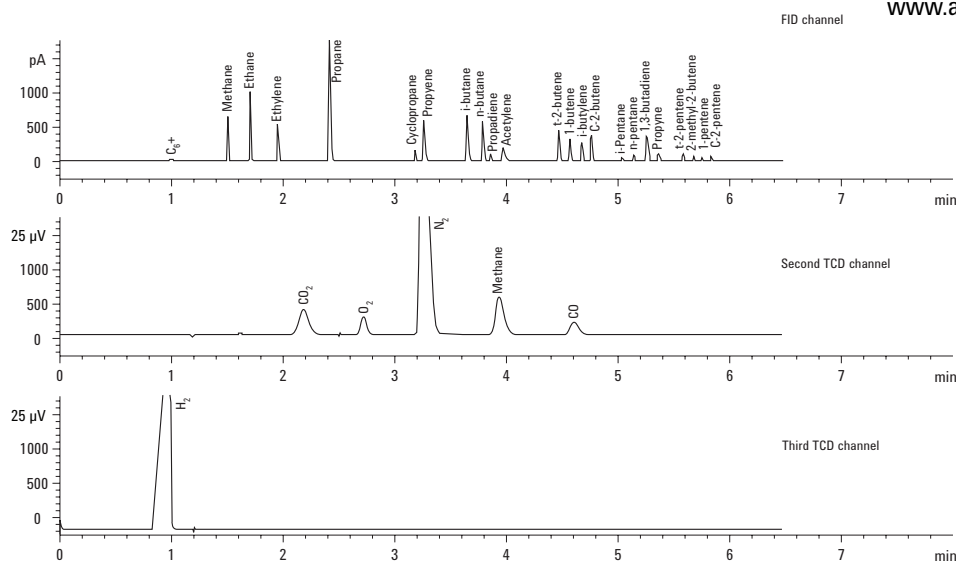


Figure 2. Refinery gas calibration standards analysis.

Reference

1. Chunxiao Wang, "Parallel GC for Complete RGA Analysis," Agilent application brief, 5989-6103EN, January 19, 2007
2. ASTM D1945-03, "Standard Test Method for Analysis of Natural Gas by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
3. 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.
4. UOP Method 539, "Refinery Gas Analysis by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428, USA.

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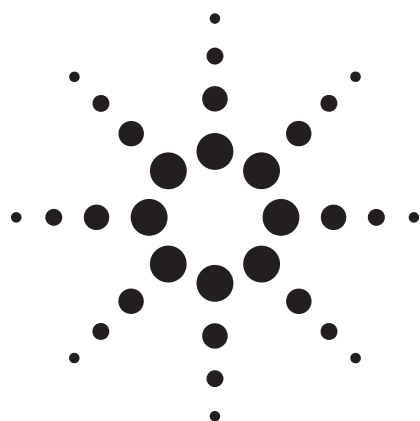
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Fast Analysis of Aromatic Solvent with 0.18 mm ID GC column



Application

Gas Chromatography

Authors

Yun Zou
Agilent Technologies (Shanghai) Co. Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
P.R. China

Zhenxi Guan
Agilent Technology
3 Wangjing Bei Lu
Chao Yang District
Beijing 100102
P.R. China

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.



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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 μ m Carbowax	Capillary 50 m $\times$ 0.25 mm	wt% of individual C8 HC
D2360	Std test for trace impurities in monocyclic hydrocarbons	0.32 μ m Carbowax	Capillary 60 m $\times$ 0.32 mm	wt% of individual aromatic impurities, total impurities, purity
D3760	Std test for cumene	0.25 μ m Carbowax	Capillary 50 m $\times$ 0.32 mm	wt% of individual impurities, cumene purity (wt%)
D3797	Std test for o-xylene	0.5 μ m Carbowax	Capillary 60 m $\times$ 0.32 mm	wt% of individual impurities, o-xylene purity (wt%)
D3798	Std test for p-xylene	0.25 μ m Carbowax	Capillary 50 m $\times$ 0.32 mm	wt% of individual impurities, total impurities, p-xylene purity (wt %)
D4492	Std test for benzene	0.25 μ m Carbowax	Capillary 50 m $\times$ 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 $\times$ 3.175 mm	wt% of benzene
D5060	Std test for impurities in ethylbenzene	0.5 μ m Carbowax	Capillary 60 m $\times$ 0.32 mm	wt% of individual impurities, ethylbenzene purity
D5135	Std test for styrene	0.5 μ m Carbowax	Capillary 60 m $\times$ 0.32 mm	wt% of individual impurities, styrene purity
D5917	Std test for trace impurities in monocyclic hydrocarbons (ESTD Cal)	0.25 μ m Carbowax	Capillary 60 m $\times$ 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- μ L 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 $\times$ 0.32 mm $\times$ 0.5 μ m 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 $\times$ 0.32 mm $\times$ 0.50 μ m
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 μ L

The experiment was then repeated with a high-efficiency 20 m $\times$ 0.18 mm $\times$ 0.18 μ m 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 modi-

fications 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 $\times$ 0.18 mm $\times$ 0.18 μ m
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 (1 min)
Detector	FID at 250 °C
Data acquisition rate	At 50 Hz
Injection size	0.2 μ L

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 (R_s = 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 $\times$ 0.18 mm $\times$ 0.18 μ m
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 μ L

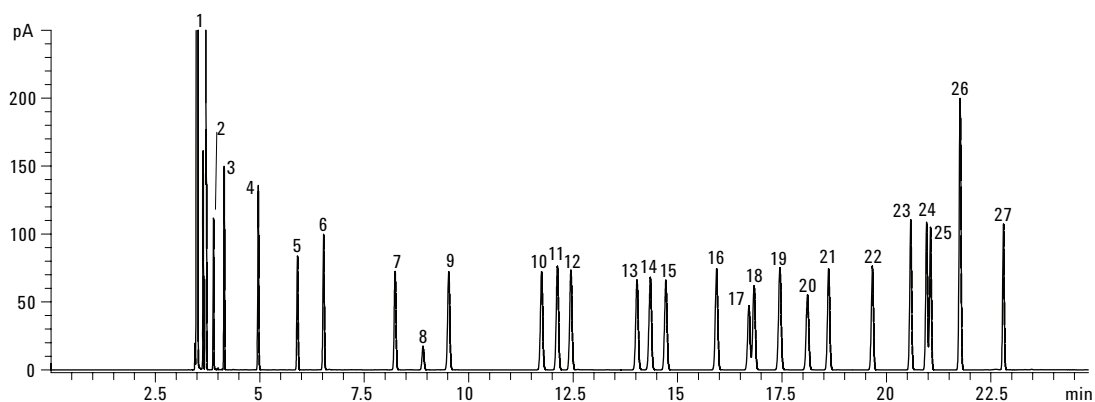


Figure 1. Unified aromatic solvent method with a 60 m × 0.32 mm × 0.5 μm HP-INNOWax column.

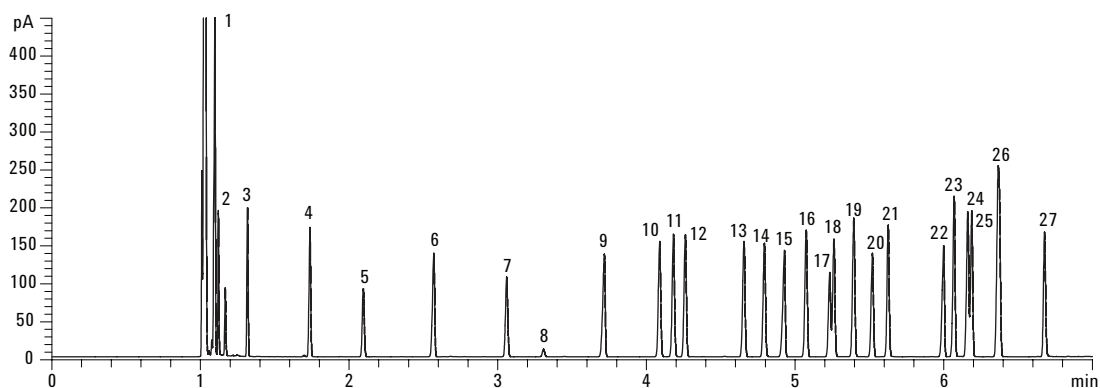


Figure 2. Separation of the same aromatic solvent with a 20 m × 0.18 mm × 0.18 μm HP-INNOWax column.

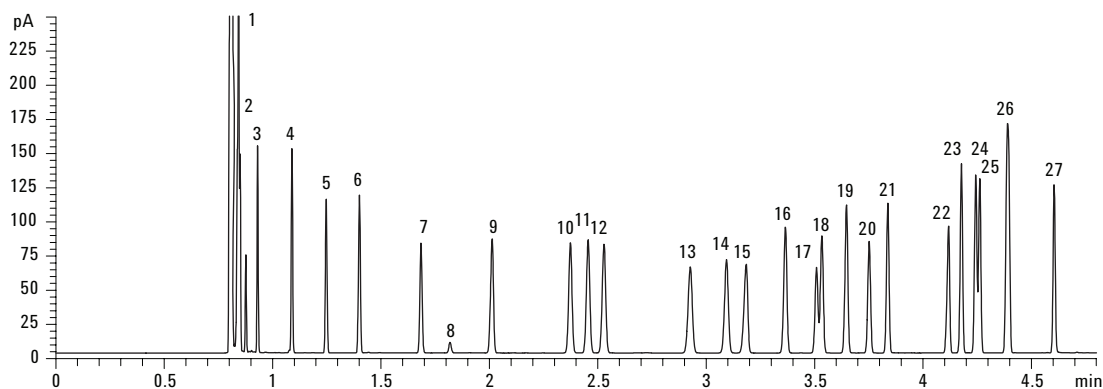


Figure 3. Optimized unified aromatic solvent method with a 20 m × 0.18 mm × 0.18 μm HP-INNOWax column.

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

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.

Original Method				Translated Method			
Column Length, m	60		60				
Internal Diameter, μm	320		320				
Film Thickness, μm	0.500		0.500				
Phase Ratio	160.0		160.0				
Carrier Gas	Helium		Nitrogen				
Head Pressure, psi	20		7.518				
Flow Rate, mL/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		3-ramp Program				
	Ramp Rate	Final Temp	Final Time		Ramp Rate	Final Temp	Final Time
	°C/min	°C	min		°C/min	°C	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

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

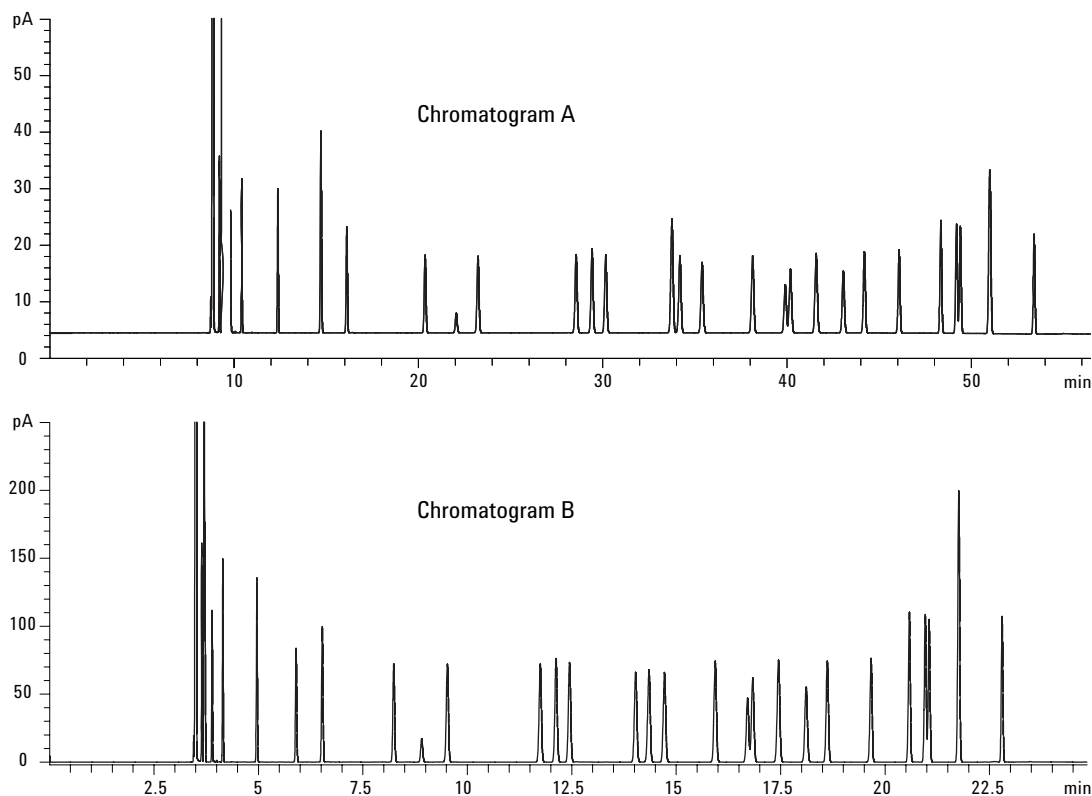


Figure 5. Comparison of unified aromatic solvent analysis using nitrogen and helium carrier gases with a 60 m × 0.32 mm × 0.5 µm HP-INNOWax column. 5a. Nitrogen carrier gas (Method 4). 5b. Helium carrier gas (Method 1).

Hydrogen vs. Helium Carrier Gas

A faster analysis can be achieved by switching the carrier gas from helium to hydrogen on the same column. 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 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, mL/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			
	Ramp Rate °C/min	Final Temp. °C	Final Time min	
Initial	70	70	3	
Ramp 1	45	145.00	0.5	
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

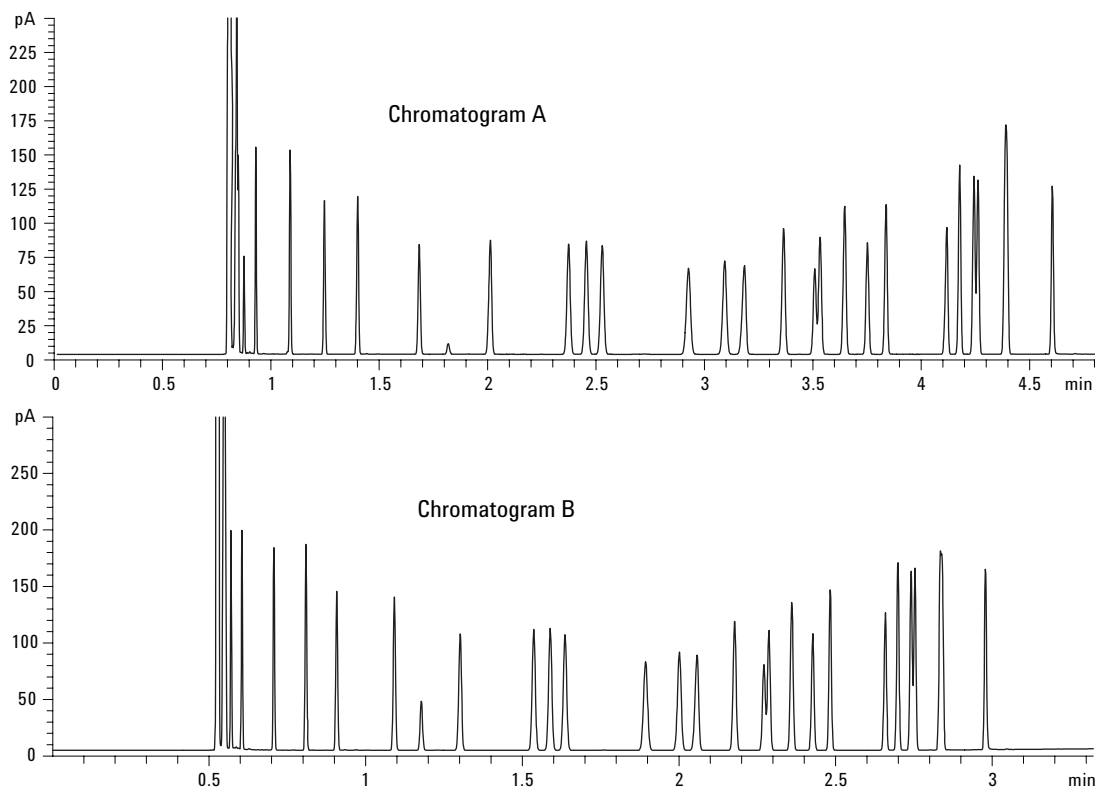


Figure 7. Comparison of unified aromatic solvent analysis using helium and hydrogen carrier gases with a $20\text{ m} \times 0.18\text{ mm} \times 0.18\text{ }\mu\text{m}$ HP-INNOWax column. 7a. Helium carrier gas (Method 5). 7b. Hydrogen carrier gas (Method 3).

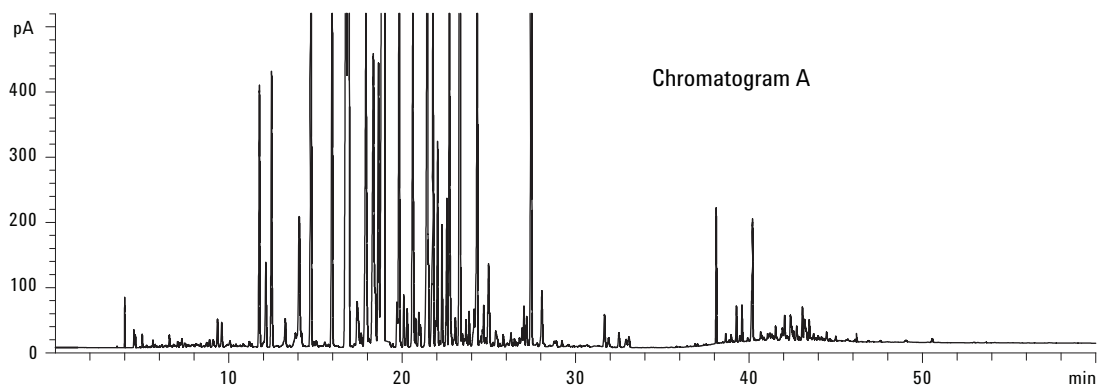
Complex Matrix Sample

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.

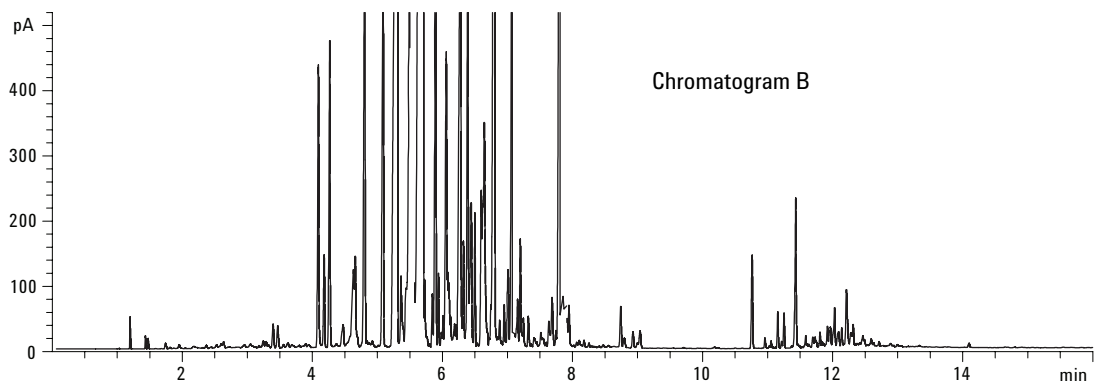
Although the analysis time is a bit longer with Method 2 compared to Method 3, the overall resolution obtained is slightly better for Method 2 (see

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.

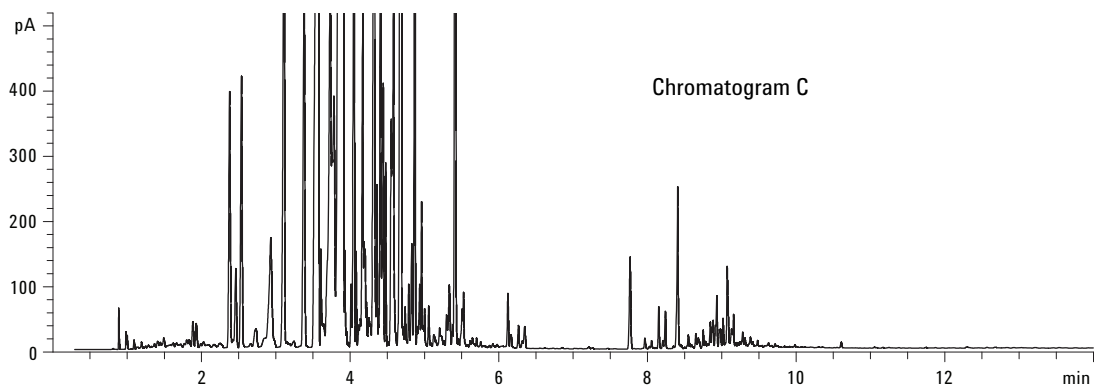
For complex matrix samples, a balance between speed and resolution must be selected according to the laboratory goals. In this case, it demonstrates that a complex matrix sample can be separated well on a high-efficiency 0.18 mm id GC column, where a more than 3x improvement in run time was accomplished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



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



Column HP-INNOWax, 20 m $\times$ 0.18 mm $\times$ 0.18 μ m
 Carrier gas Helium at 25.00 psi constant pressure mode
 Inlet Split/splitless at 250 $^{\circ}$ C; 150:1 split ratio
 Oven temp 50 $^{\circ}$ C (2 min); 15 $^{\circ}$ C/min to 90 $^{\circ}$ C (0 min); 20 $^{\circ}$ C/min to 145 $^{\circ}$ C (3 min), 80 $^{\circ}$ C/min to 220 $^{\circ}$ C (8 min)
 Detector FID at 250 $^{\circ}$ C
 Injection size 0.2 μ L



Column HP-INNOWax, 20 m $\times$ 0.18 mm $\times$ 0.18 μ m
 Carrier gas Helium at 33.00 psi constant pressure mode
 Inlet Split/splitless at 250 $^{\circ}$ C; 150:1 split ratio
 Oven temp 70 $^{\circ}$ C (3 min); 45 $^{\circ}$ C/min to 145 $^{\circ}$ C (3 min), 80 $^{\circ}$ C/min to 220 $^{\circ}$ C (8 min)
 Detector FID at 250 $^{\circ}$ C
 Injection size 0.2 μ L

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.

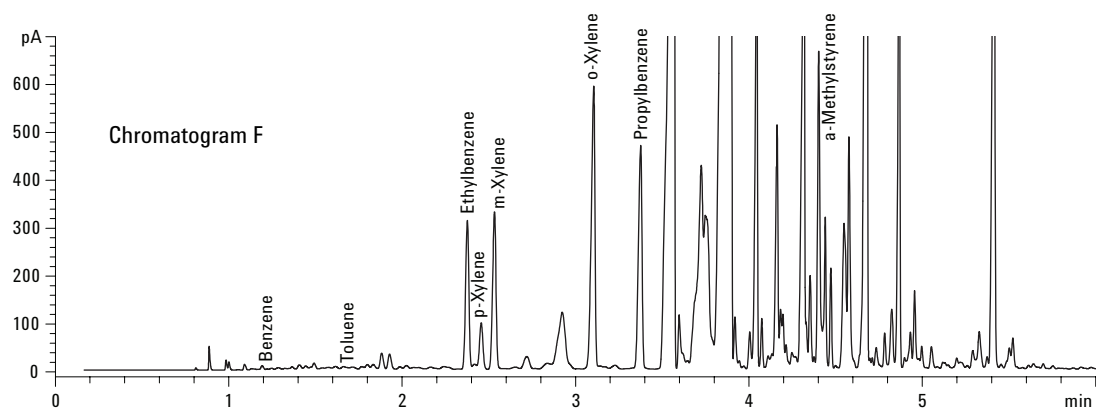
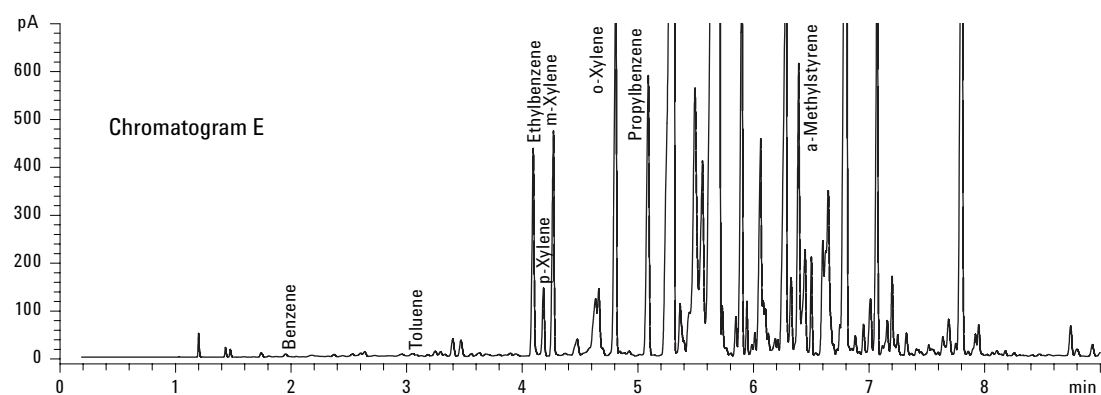
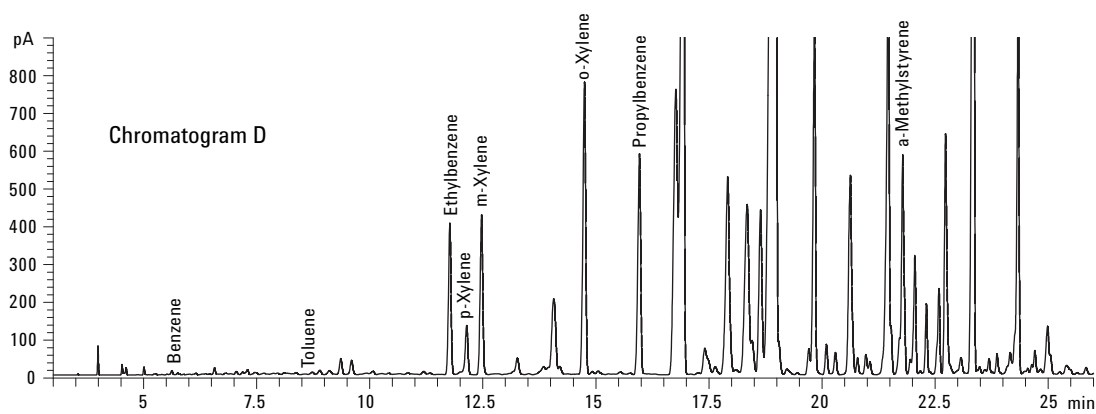


Figure 8. Comparison of real aromatic solvent sample separations (a) and (d) Method 1, (b) and (e) Method 2, and (c) and (f) Method 3. (continued)

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 μ L 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).

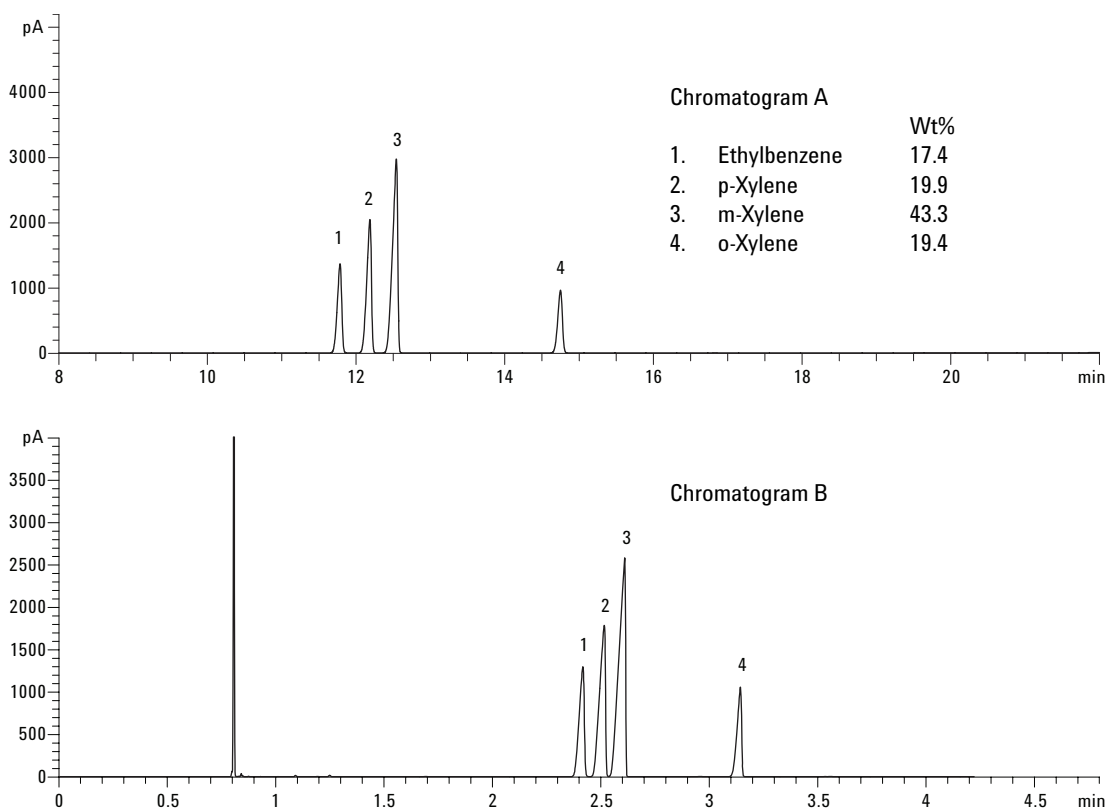


Figure 9. ASTM D2306 C8 aromatic hydrocarbon quantitative calibration standards (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (method 3).

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 μ L 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).

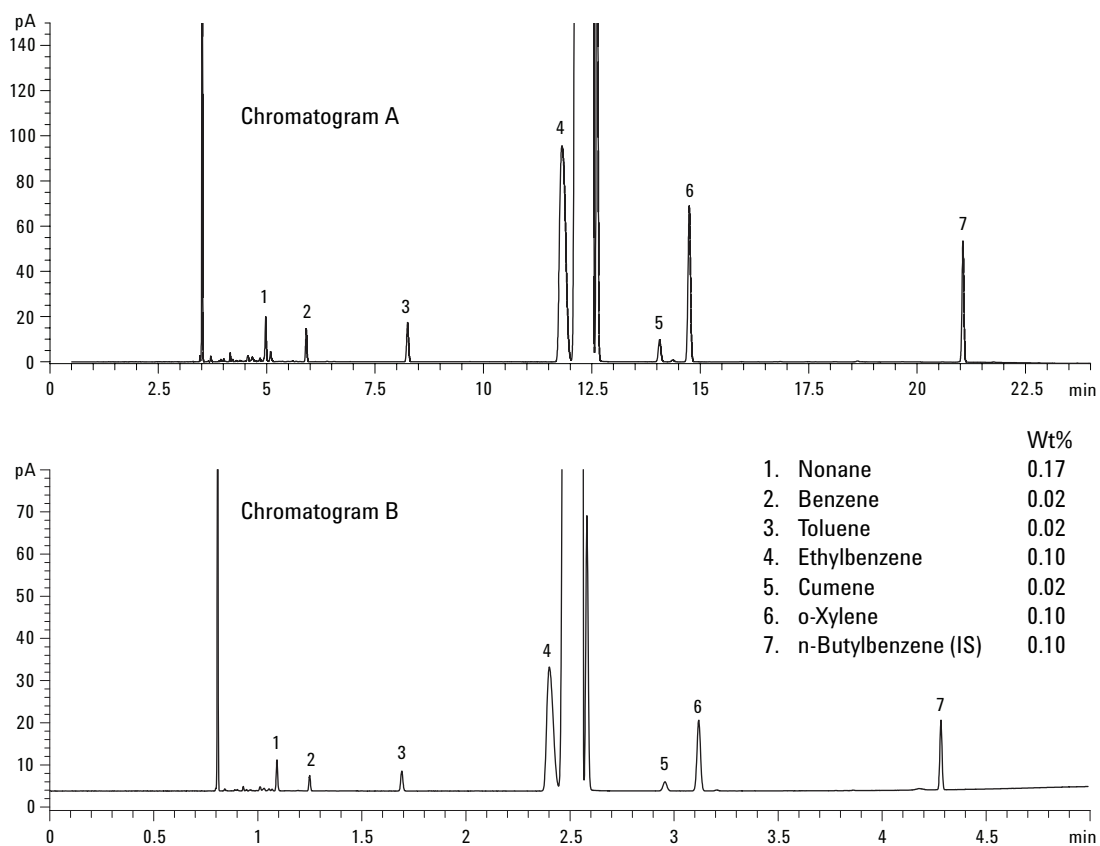
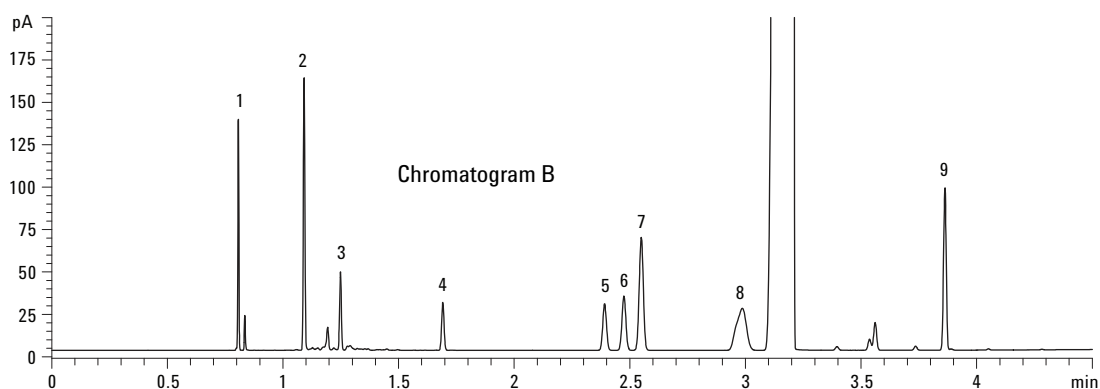
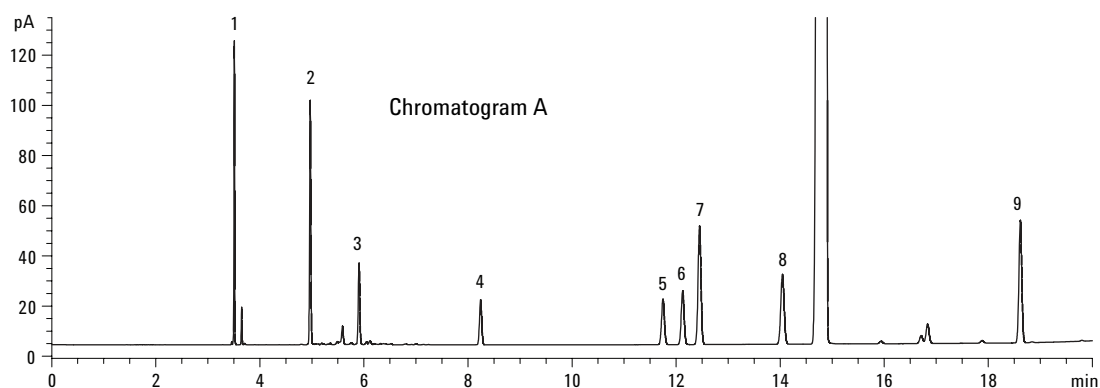


Figure 10. ASTM D2360 monocyclic hydrocarbon quantitative calibration standard run (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (Method 3).

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 μ L 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 μ L 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.

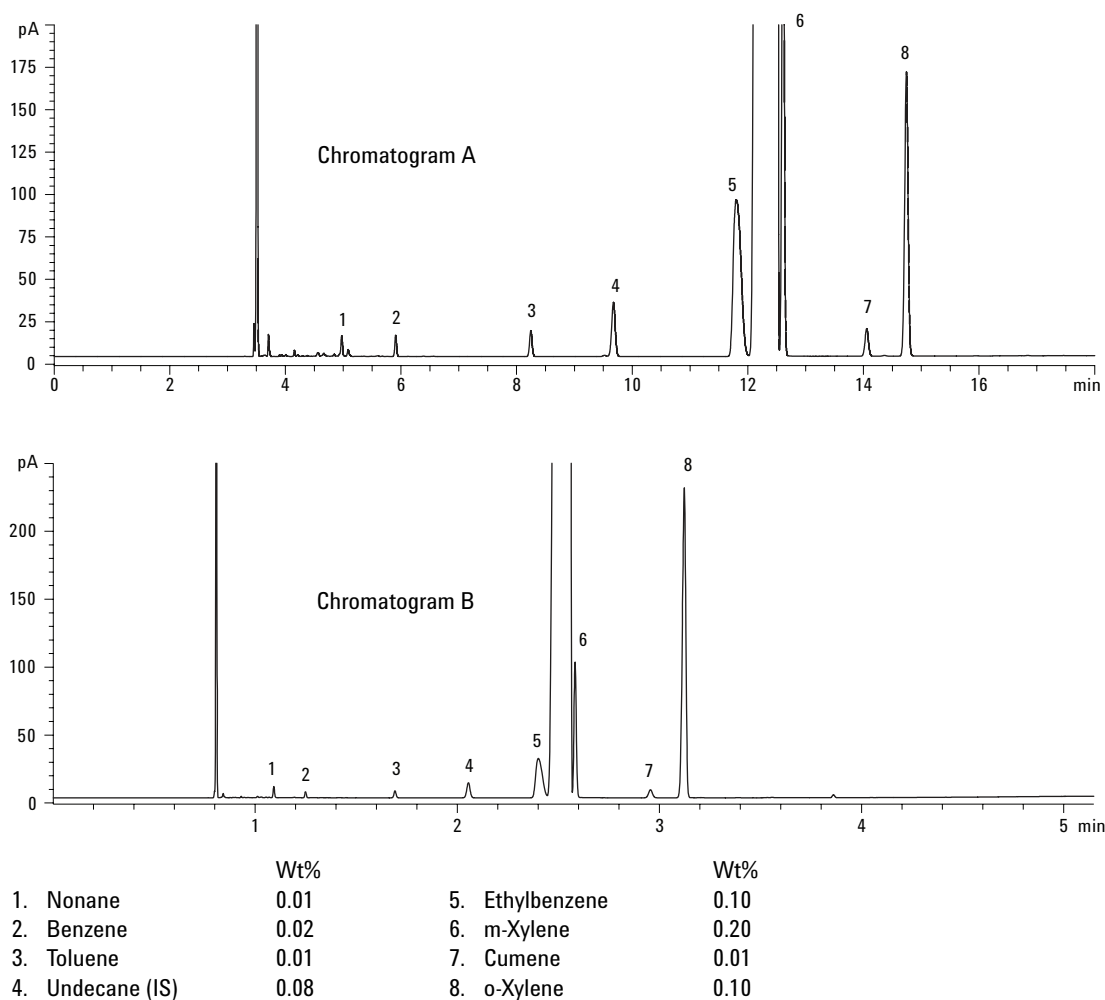


Figure 12. p-Xylene standard run (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (Method 3).

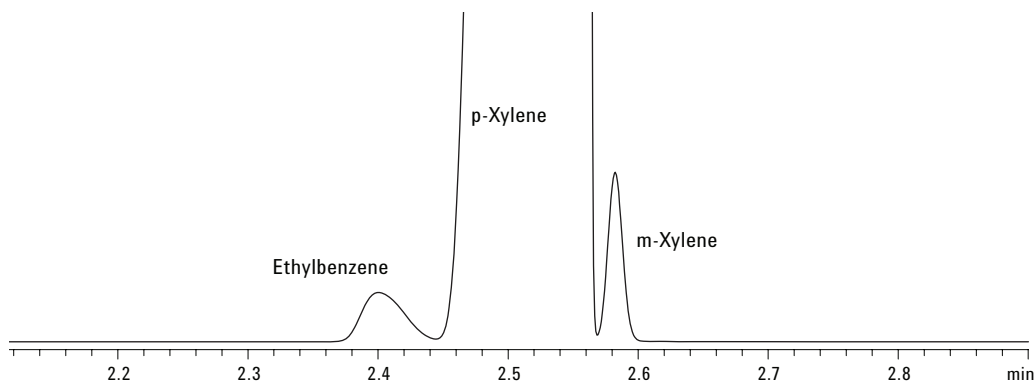


Figure 13. Expanded view from Figure 7 shows excellent separation of m-Xylene peak from p-Xylene peak using the fast GC method.

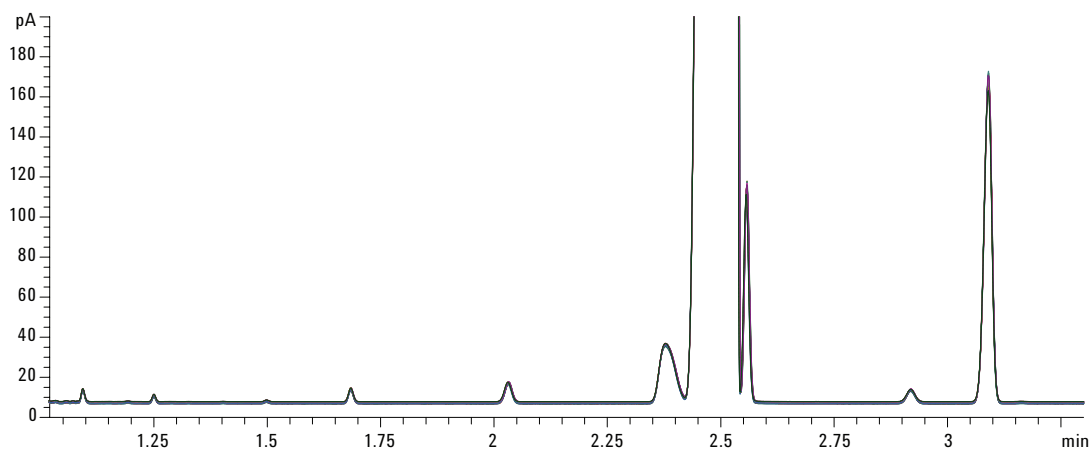


Figure 14. D3798 standard 30th run overlaid using a high-efficiency GC column.

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 μ L 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.

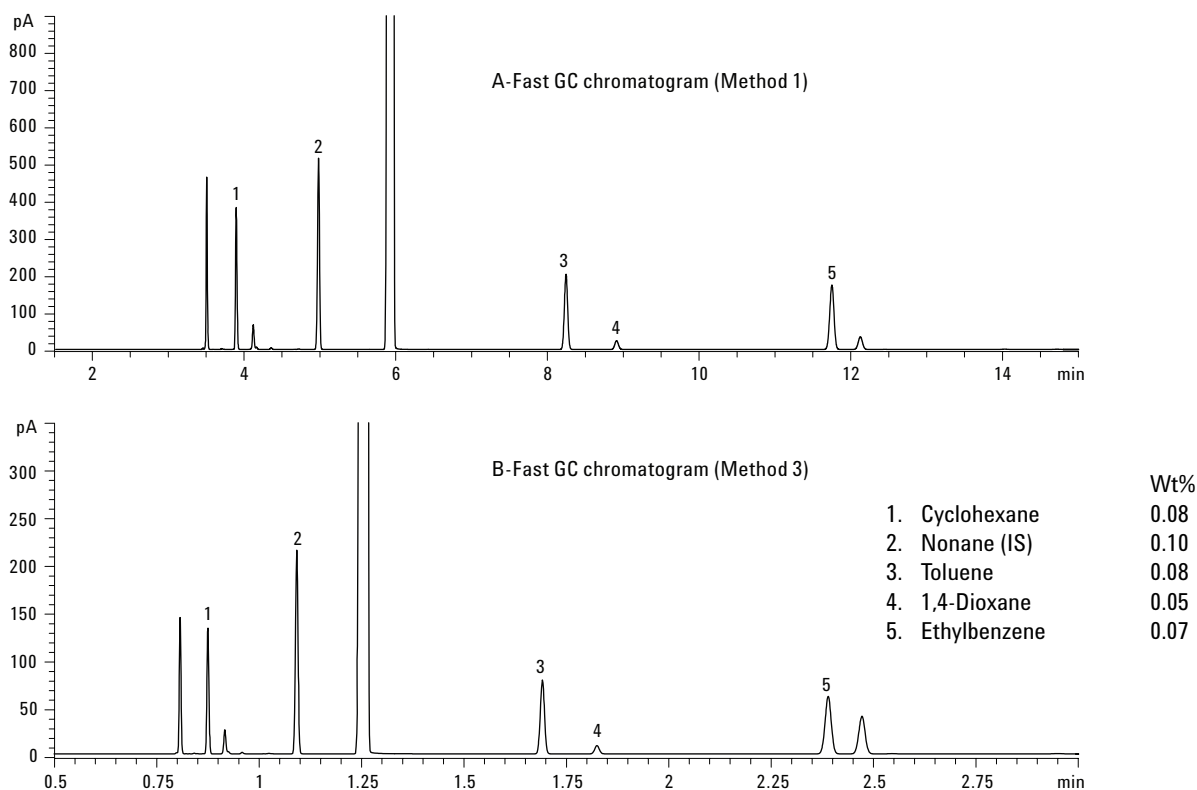


Figure 15. ASTM D4492 benzene quantitative calibration standard run (a) on a standard column (Method 1) and (b) on a high-efficiency GC column (Method 3).

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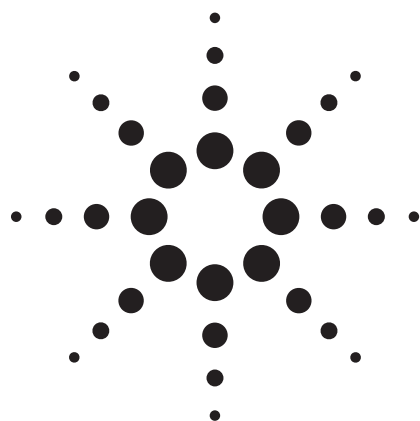
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Investigation of the Unique Selectivity and Stability of Agilent GS-OxyPLOT Columns



Application

Gas Chromatography

Authors

Yun Zou and Min Cai
Agilent Technologies (Shanghai) Co. Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
P.R. China

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 back-flush 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 split/splitless injection liners (Agilent p/n 5183-4711). Injections were done using 10- μ L 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



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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.

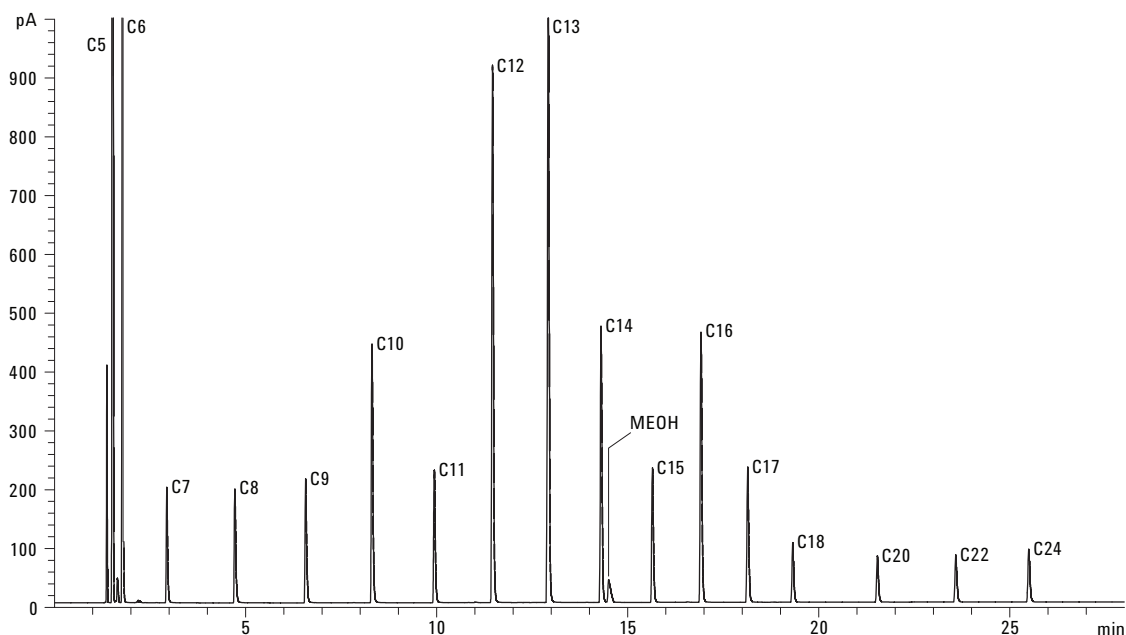


Figure 1. Analysis of methanol and normal hydrocarbons on a GS-OxyPLOT column, 10 m × 0.53 mm × 10 µm.

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

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

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.

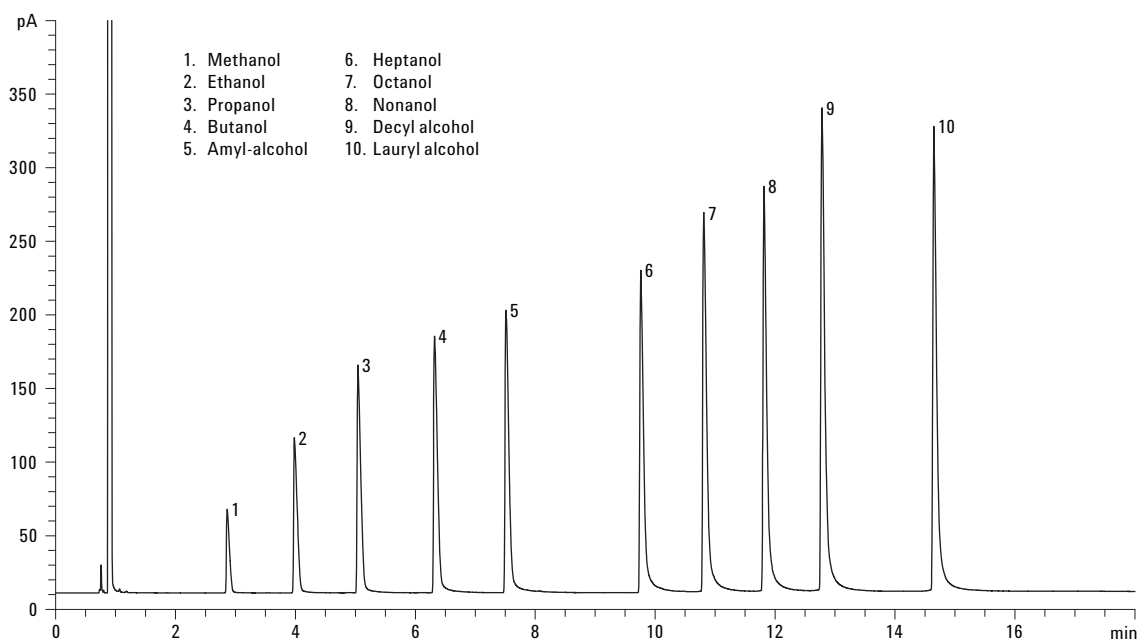


Figure 2. Separation of alcohols using GS-OxyPLOT, 10 m × 0.53 mm × 10 µm.

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, I_x , was calculated using the following equation:

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

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 retention 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 by 14.4% 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.

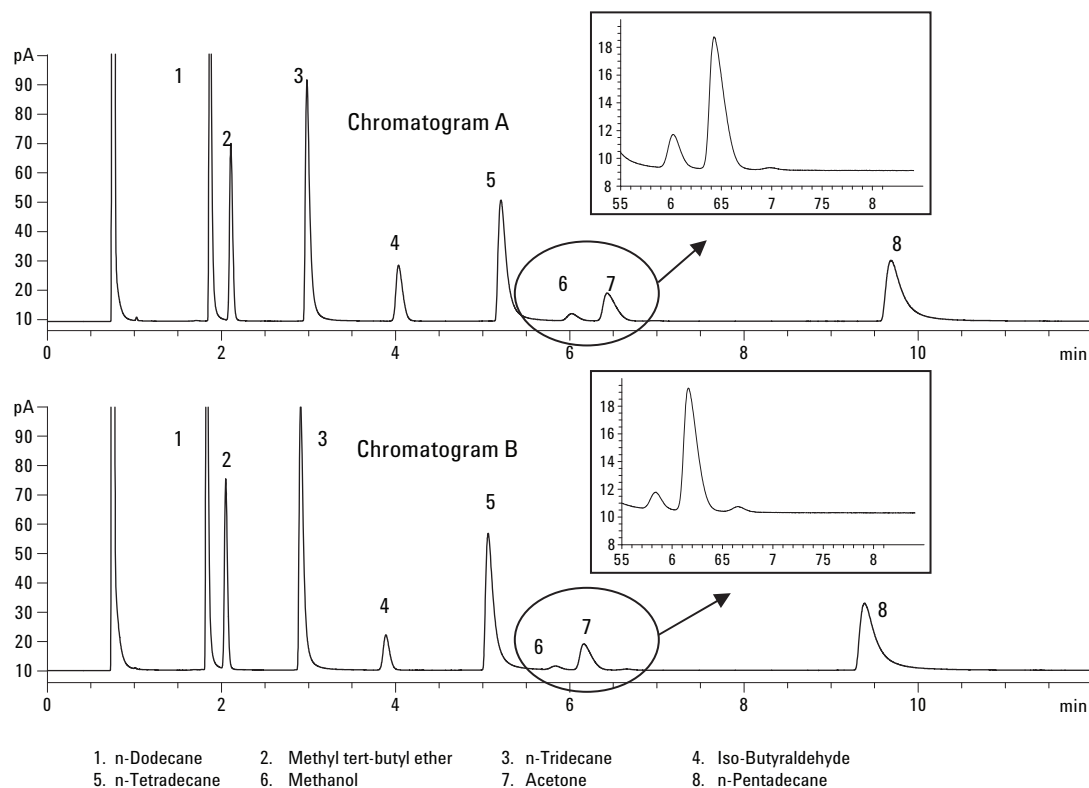


Figure 3. Comparison of test mixture separation before (A) and after (B) 100 injections of water.

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.

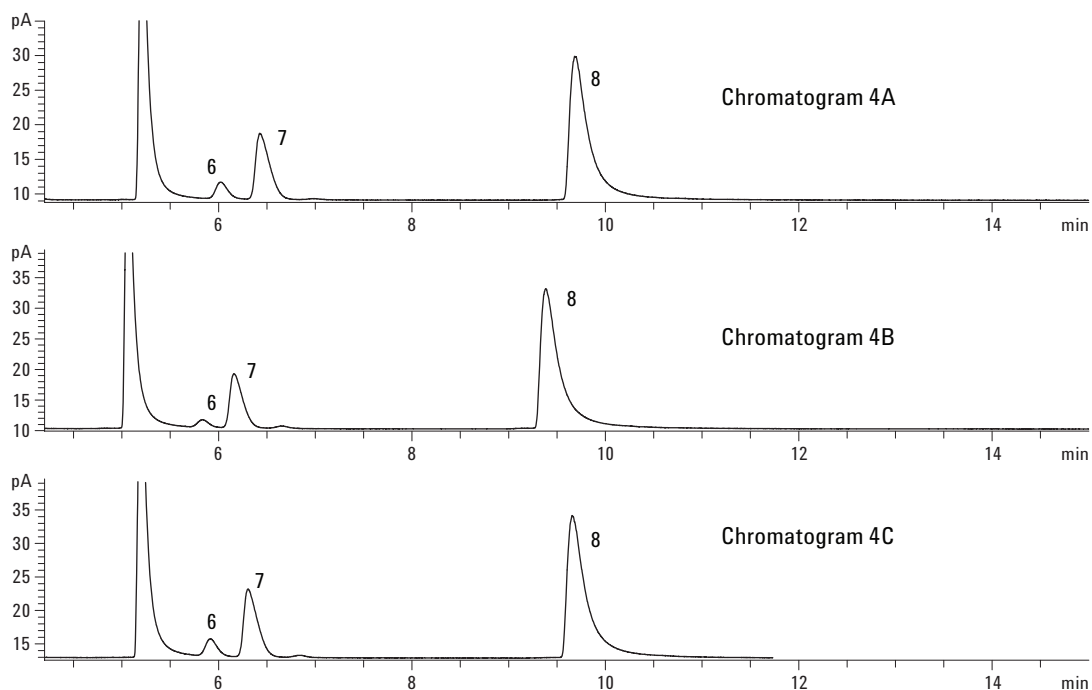


Figure 4. Expanded view shows comparison of test mixture separation on GS-OxyPLOT.
4A. Before injection of water. 4B. After 100 injections of water. 4C. After conditioning the column.

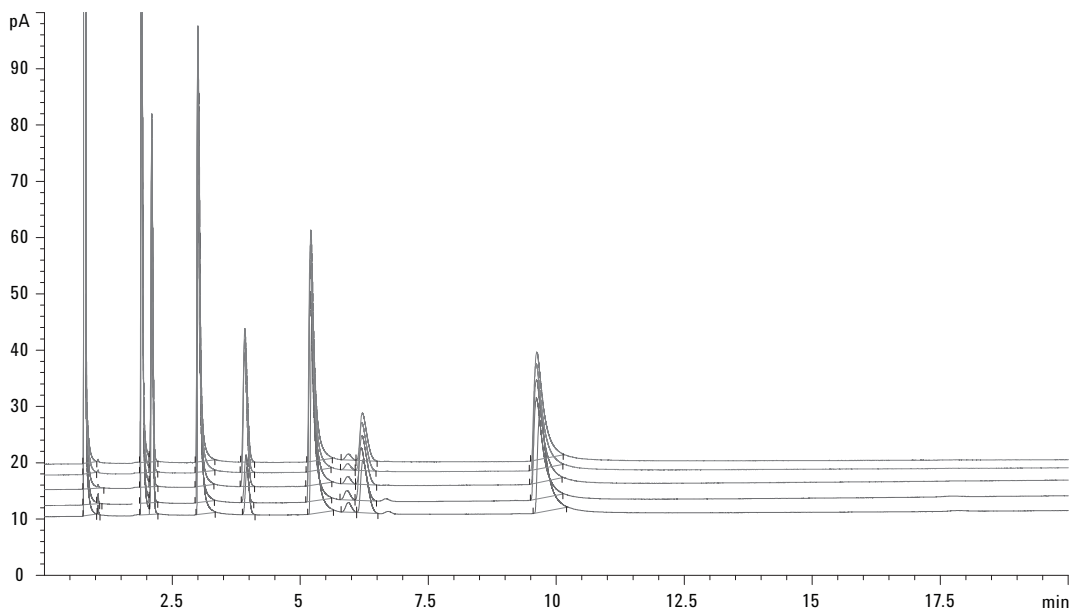
Table 6. Comparison of Test Mixture Separation

	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 calibra-
tion 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

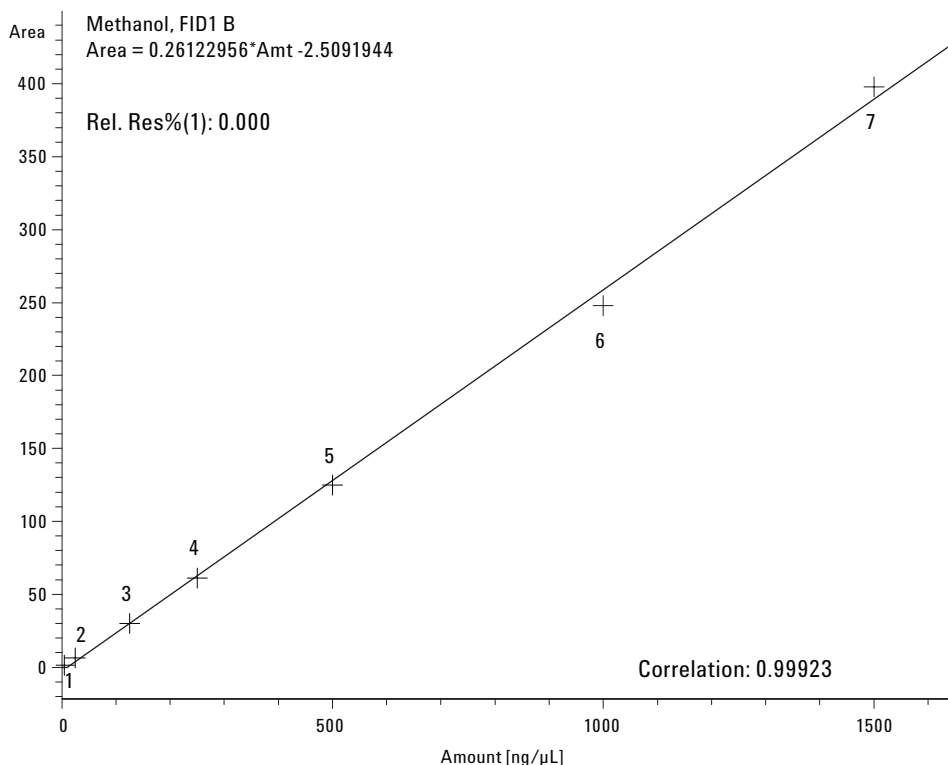


Figure 6. The calibration curve of methanol in toluene.

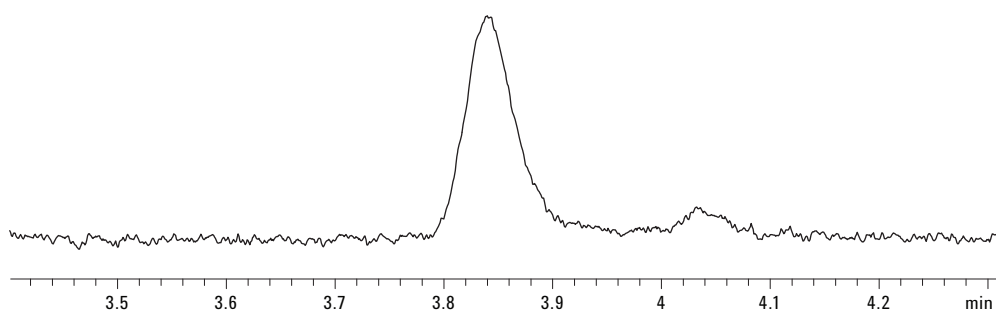


Figure 7. Test mixture of 5 ppm methanol in toluene.

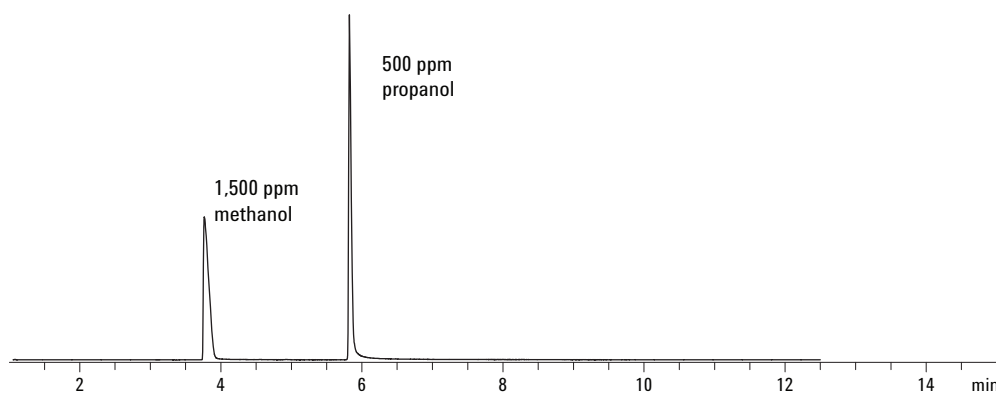


Figure 8. Test mixture of 1,500 ppm methanol in toluene.

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	

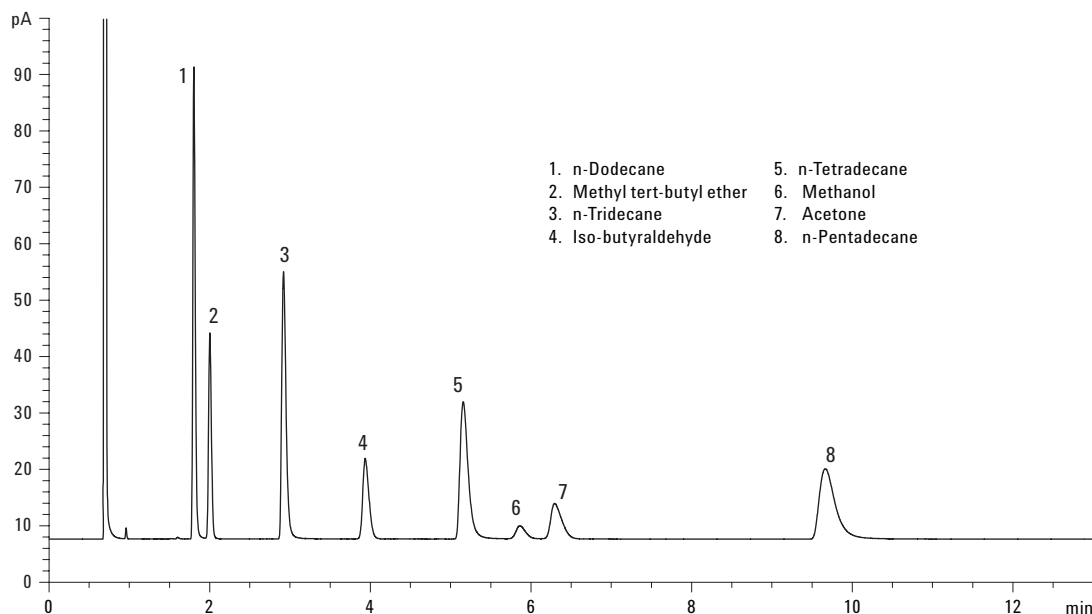


Figure 9. Chromatogram of performance mixture after 1,500 injections.

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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4. Standard test method for the determination of methanol in crude oils by multidimensional gas chromatography, ASTM D7059-04, July 2004

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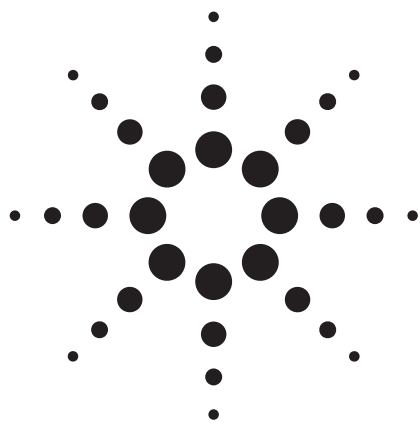
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Fast Hydrocarbon and Sulfur Simulated Distillation Using the Agilent Low Thermal Mass (LTM) System on the 7890A GC and 355 Sulfur Chemiluminescence Detector

Application Note

Hydrocarbon Processing

Authors

ChunXiao Wang
Agilent Technologies Co., Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
China

Roger Firor and Paul Tripp
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington DE 19808
USA

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 cool-down. 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.



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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 chosen, 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\$+dadatfile\$+"\AIB2B.CH")=1

```
rename dadatapath$+dadatfile$+"\\AIB2B.ch",dadat-  
path$+dadatfile$+"\\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 employs 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.

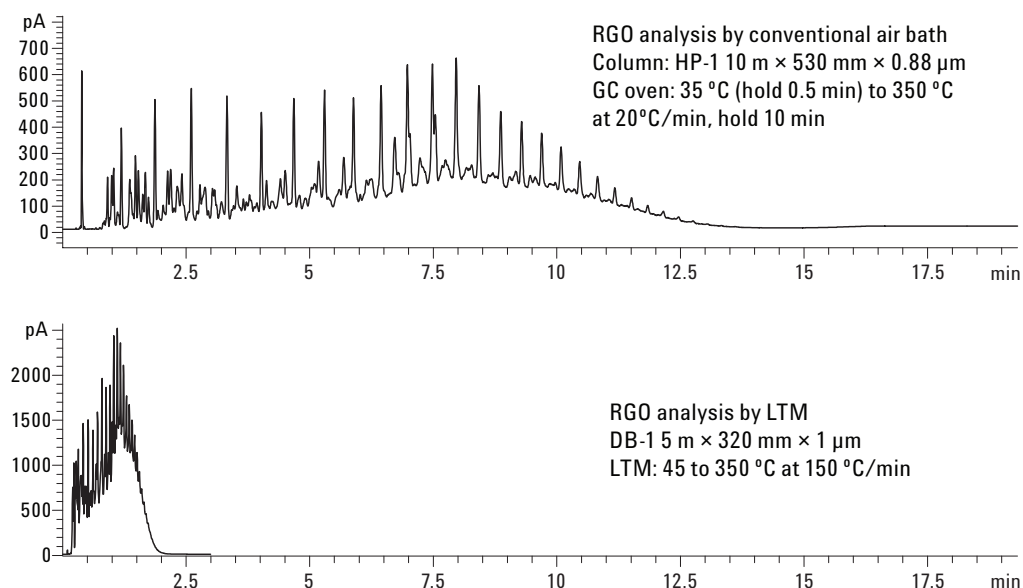


Figure 1. Comparison of RGO analysis by LTM and air bath GC ovens.

Table 2. RGO SimDis Results with the LTM System

ASTM D2887 Values			Observed Value													Average	Difference	RSD%
	BP, °C	Allowable difference	1	2	3	4	5	6	7	8	9	10						
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.

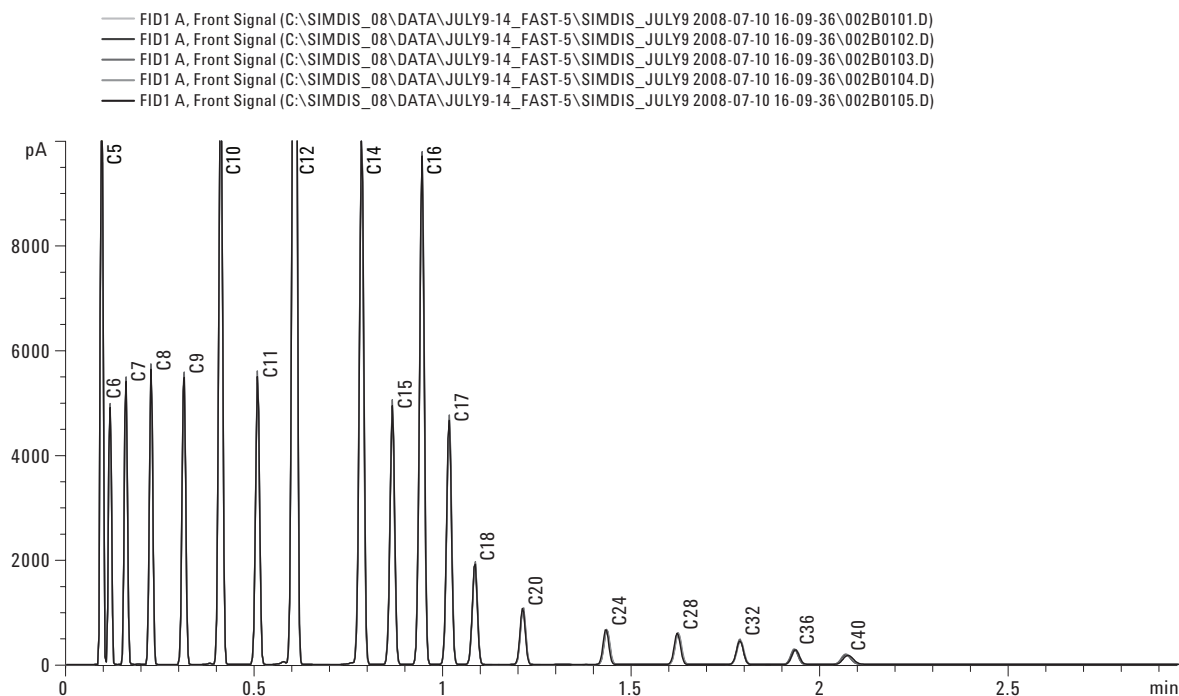


Figure 2. Overlays of five consecutive runs of the C5 to C40 calibration mixture. Chromatographic overlay shows outstanding repeatability. LTM: 45 to 350 °C at 150 °C/min.

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 acquisition. 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/ μ L (ppm). The calibration curve is displayed in Figure 3, giving a correlation coefficient above 0.999.

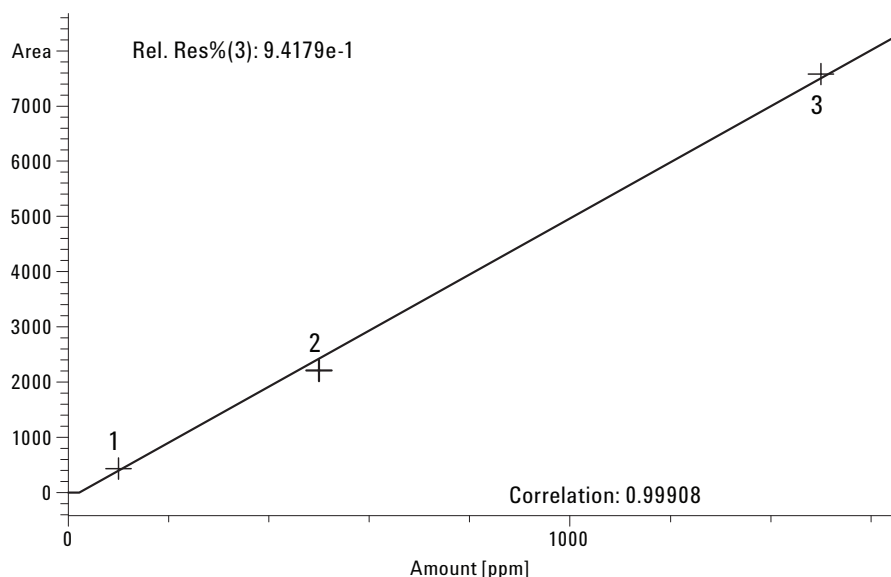


Figure 3. Linearity of sulfur with the SCD and LTM system.

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).

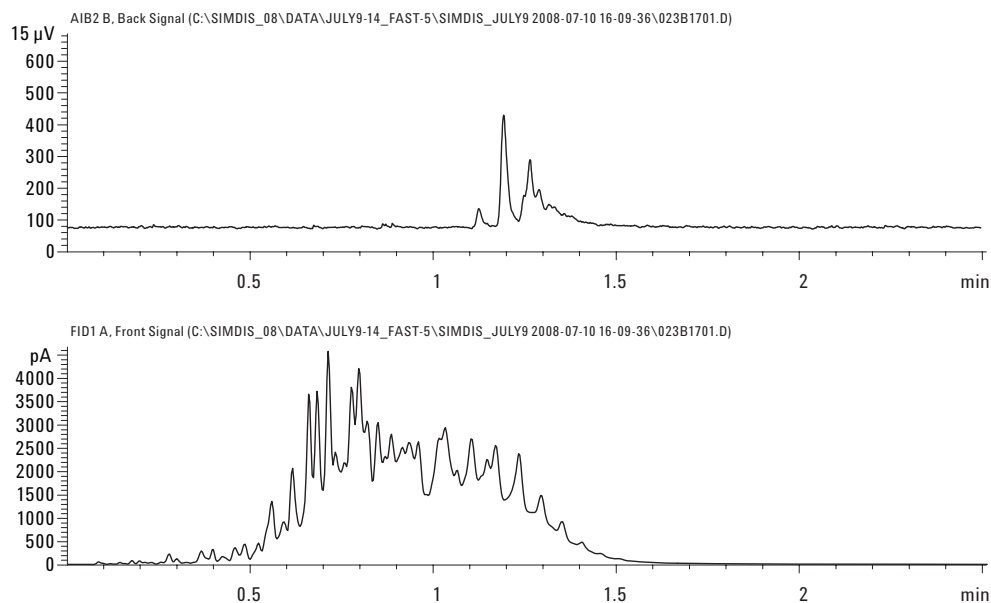


Figure 4. Chromatograms for sulfur and carbon. Sulfur top chromatogram.

Table 4. Hydrocarbon and Sulfur SimDis Results for Light Cycle Oil

Hydrocarbon SimDis												
	BP, °C										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, °C											
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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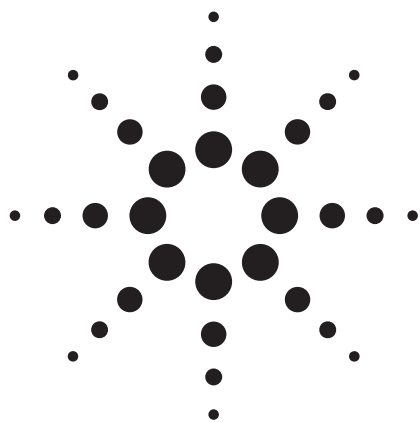
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Dual Channel Simulated Distillation of Carbon and Sulfur with the Agilent 7890A GC and 355 Sulfur Chemiluminescence Detector

Application Note

Hydrocarbon Processing

Authors

ChunXiao Wang
Agilent Technologies (Shanghai) Co., Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
China

Roger Firor and Paul Tripp
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington DE 19808
USA

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.



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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$+dadatfile$+"\AIB2B.CH")=1
rename dadatapath$+dadatfile$+"\AIB2B.ch",dadatapath$+dadatfile$+"\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.

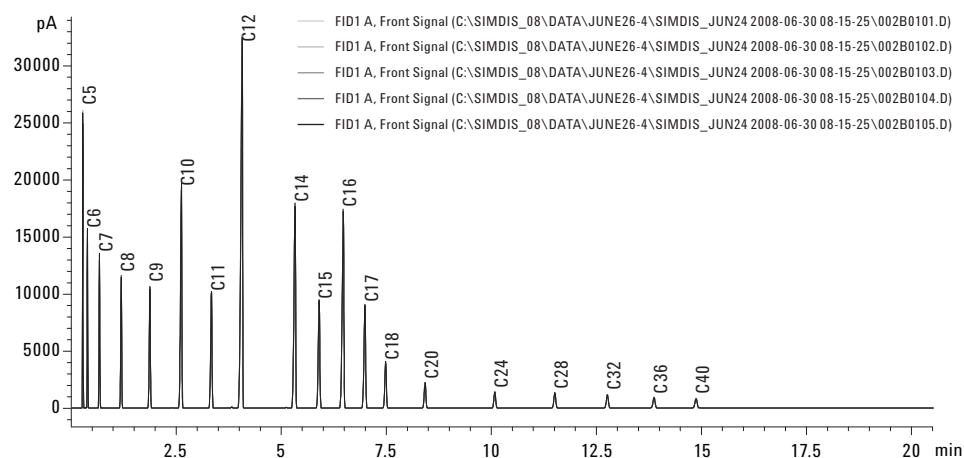


Figure 1. Overlay of five consecutive runs of C5 to C40 calibration mix, vial heated to 80 °C for 3 min prior to injection. GC conditions are listed in Table 1, items (1).

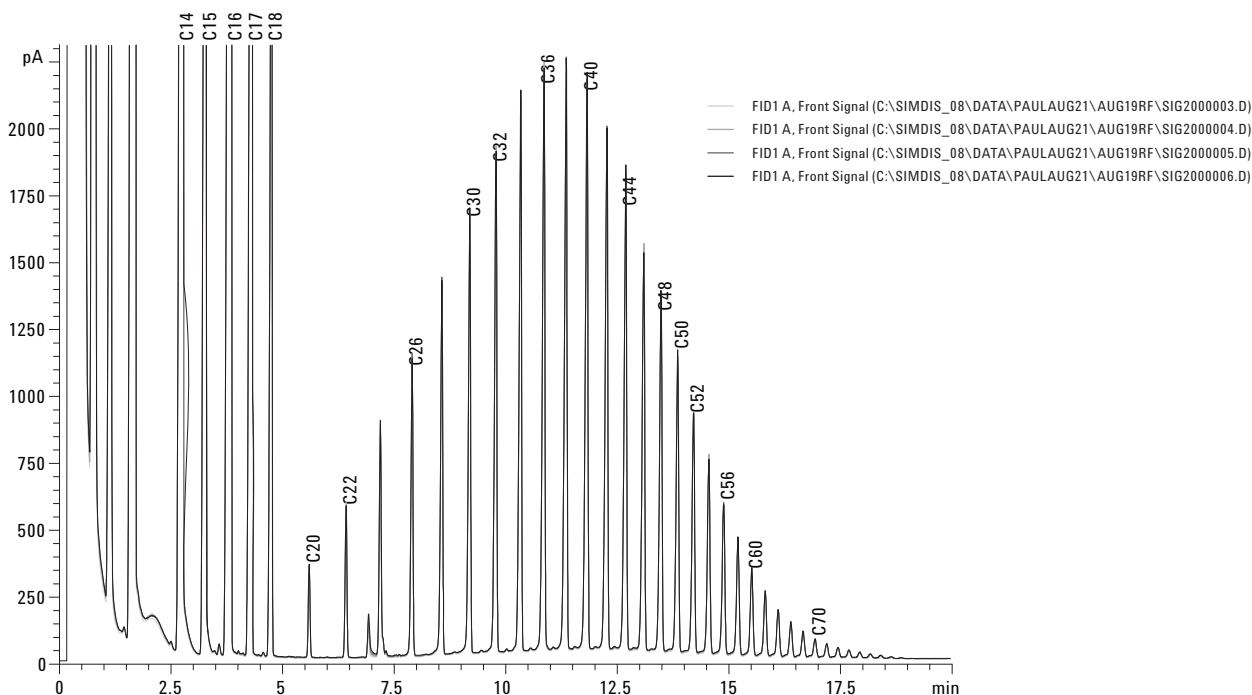


Figure 2. Overlay of four consecutive runs of Polywax 500 plus C5–C18. GC conditions are listed in Table 1, items (2).

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

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

Table 3. 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

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-

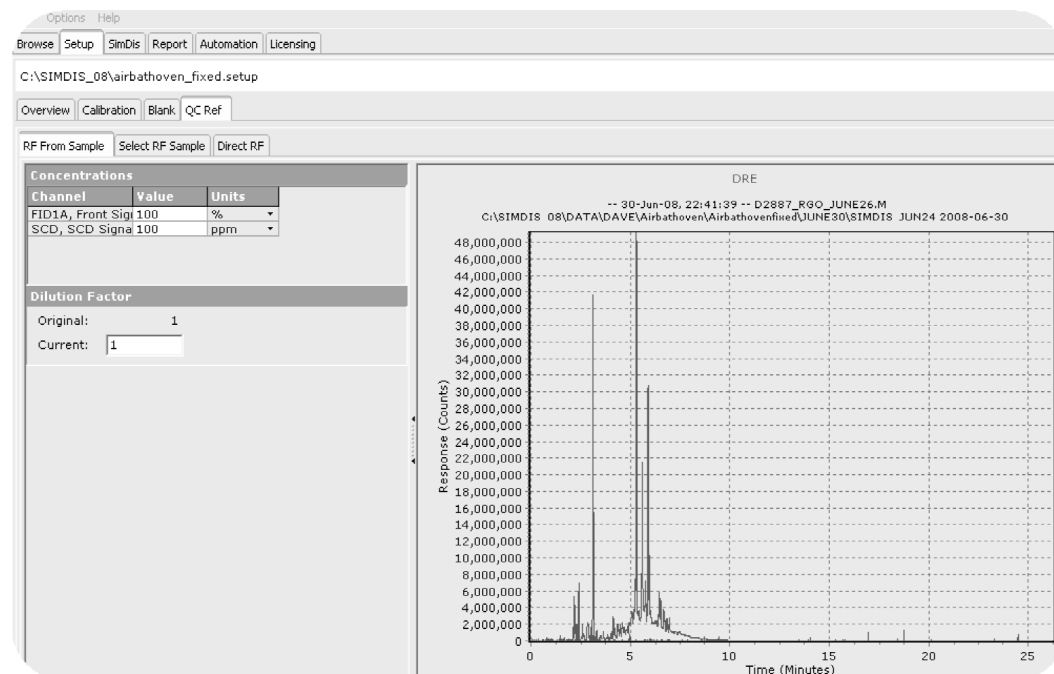


Figure 3. QC reference setup. GC conditions are listed in Table 1, items (1).

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.

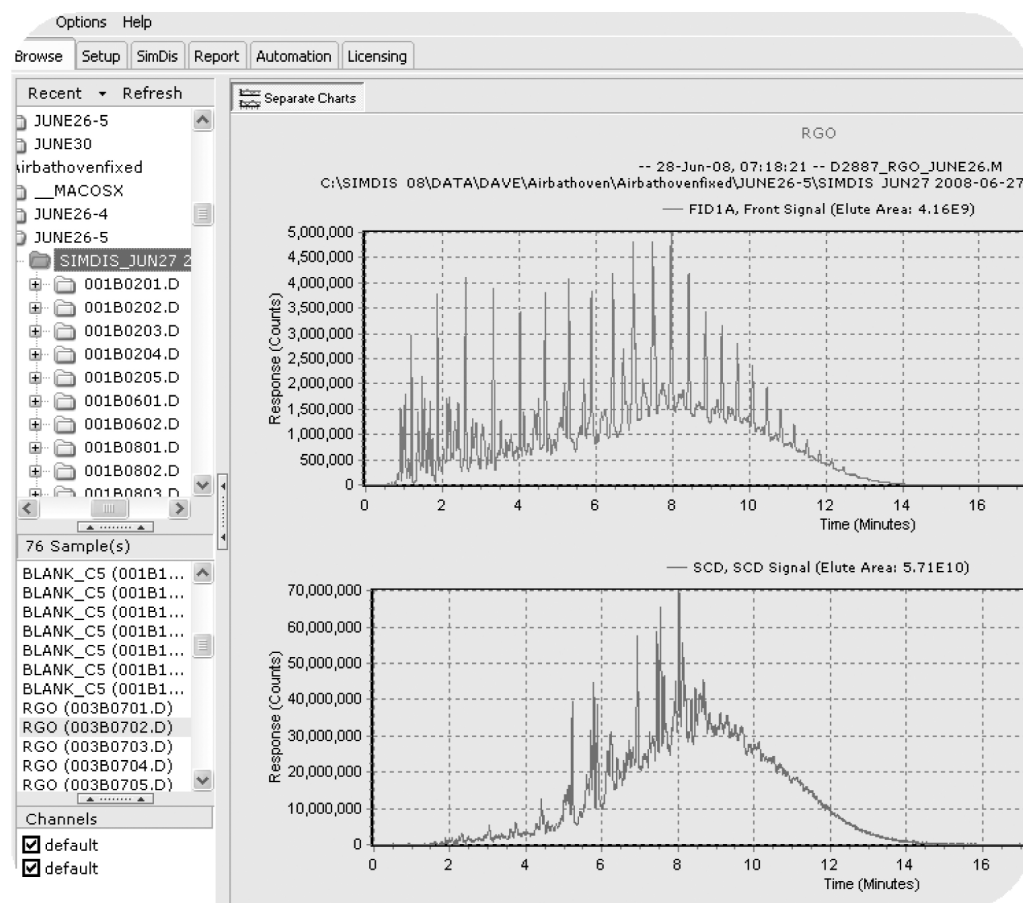


Figure 4. Chromatograms of RGO for hydrocarbon and sulfur channels. GC conditions are listed in Table 1, items (1).

Table 4. Hydrocarbon SimDis Results for Reference Gas Oil (Six runs shown.)

ASTM D2887 Values												
OFF %	BP, °C	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.

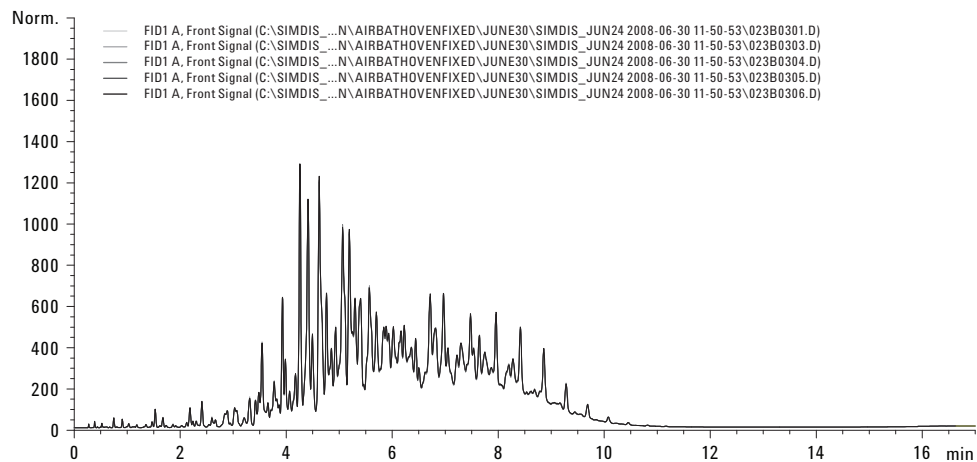


Figure 5a. Carbon SimDis of LCO. Five-run overlay.

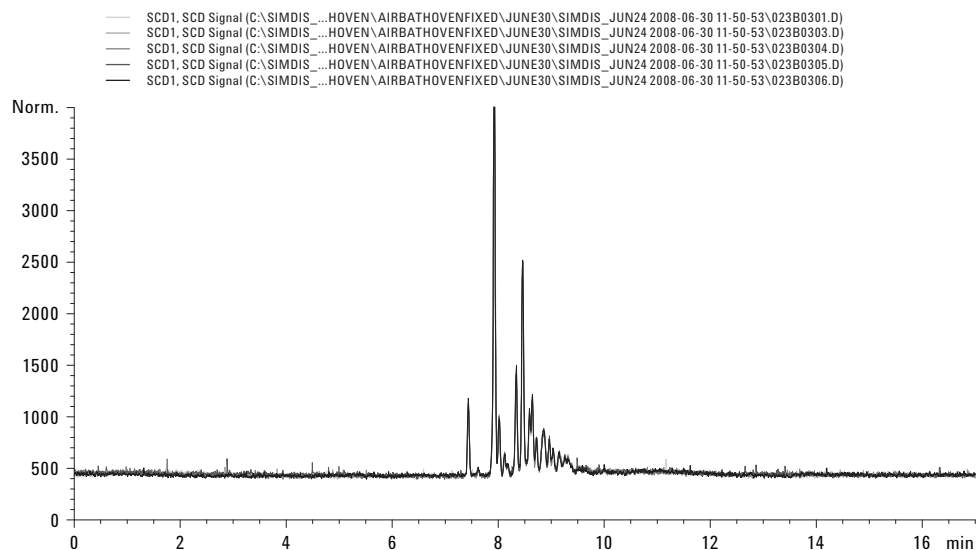


Figure 5b. Sulfur SimDis of LCO. Five-run overlay.

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.

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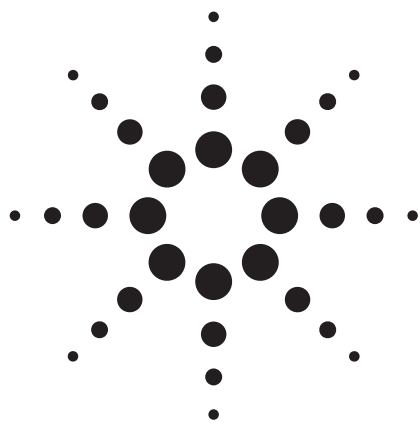
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Analysis of Trace Hydrocarbon Impurities in Benzene by Agilent 7820A Gas Chromatograph

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 many 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
H ₂ flow	40 mL/min
Air flow	400 mL/min
Make up (N ₂)	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.

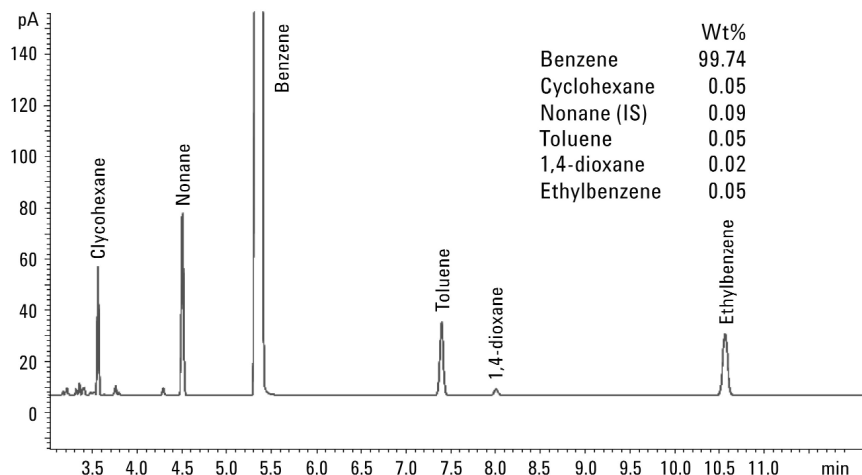


Figure 1. ASTM D4492 benzene calibration standard. Oven temperature program: 75 °C (10 min); 3 °C/min to 100 °C. Sample size: 0.5 µL, Split ratio: 100:1.

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.

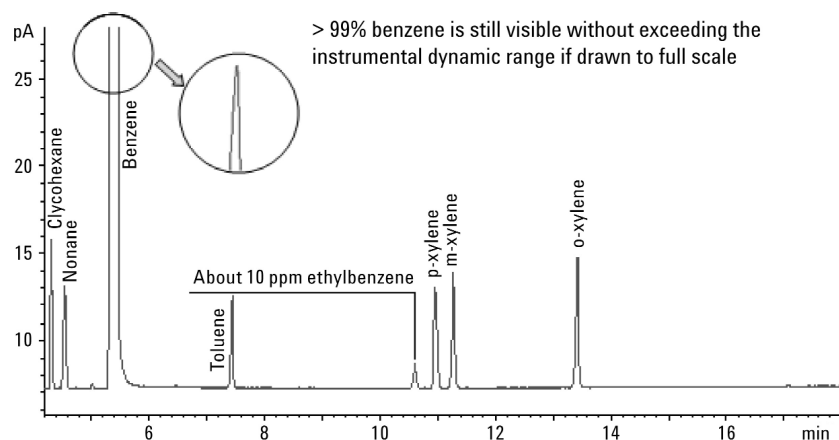
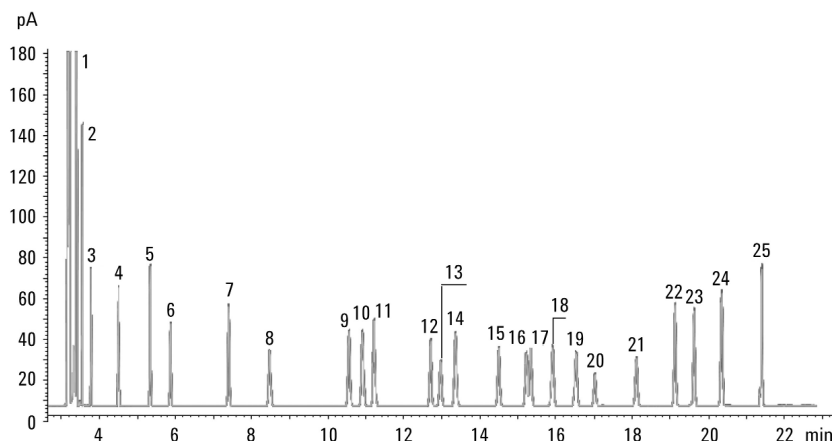


Figure 2. Analysis of trace impurities spiked in benzene. Oven temperature program: 75 °C (10 min); 3 °C/min to 100 °C. Sample size: 0.5 µL, Split ratio: 30:1.

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 | 7. Toluene | 13. Dodecane | 19. s-butylbenzene |
| 2. Cyclohexane | 8. Undecane | 14. o-xylene | 20. Styrene |
| 3. Octane | 9. Ethylbenzene | 15. Propylbenzene | 21. Tridecane |
| 4. Nonane | 10. p-xylene | 16. p-ethyltoluene | 22. Diethylbenzene |
| 5. Benzene | 11. m-xylene | 17. m-ethyltoluene | 23. n-butylbenzene |
| 6. Decane | 12. Cumene | 18. t-butylbenzene | 24. a-methylstyrene |
| | | | 25. Phenylacetylene |

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.

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Chunxiao Wang and Wenmin Liu and
 are application chemist based at
 Agilent Technologies (Shanghai), Co.
 Ltd., 412 Ying Lung Road, Waigaoqiao
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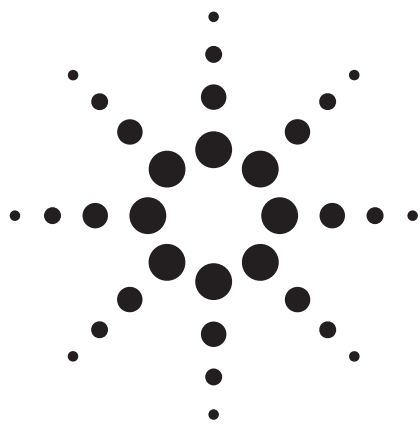
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Automated Preparation of Simulated Distillation Samples for ASTM Methods D2887, D7213, D7398 and D6352 using a Dual Tower 7693A and Tray System

Application Note

Hydrocarbon Processing

Authors

Roger L. Firor
Agilent Technologies, Inc.
2850 Centerville Rd
Wilmington, DE 19808
USA

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 μ L syringe while the back tower is equipped with a 250 or 500 μ L 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 CS₂ for sample dilution while D6352 may use CS₂ 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 CS₂ 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 CS₂ 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 CS₂ and toluene are commonly used, and

Table 2. Sample prep procedure for D2887

Sampler program steps	
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 μ L 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

Sampler program steps
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 μ L from vial 'Wash A2' to vial Sample 1 on the Back tower
Dispense 5 μ L 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

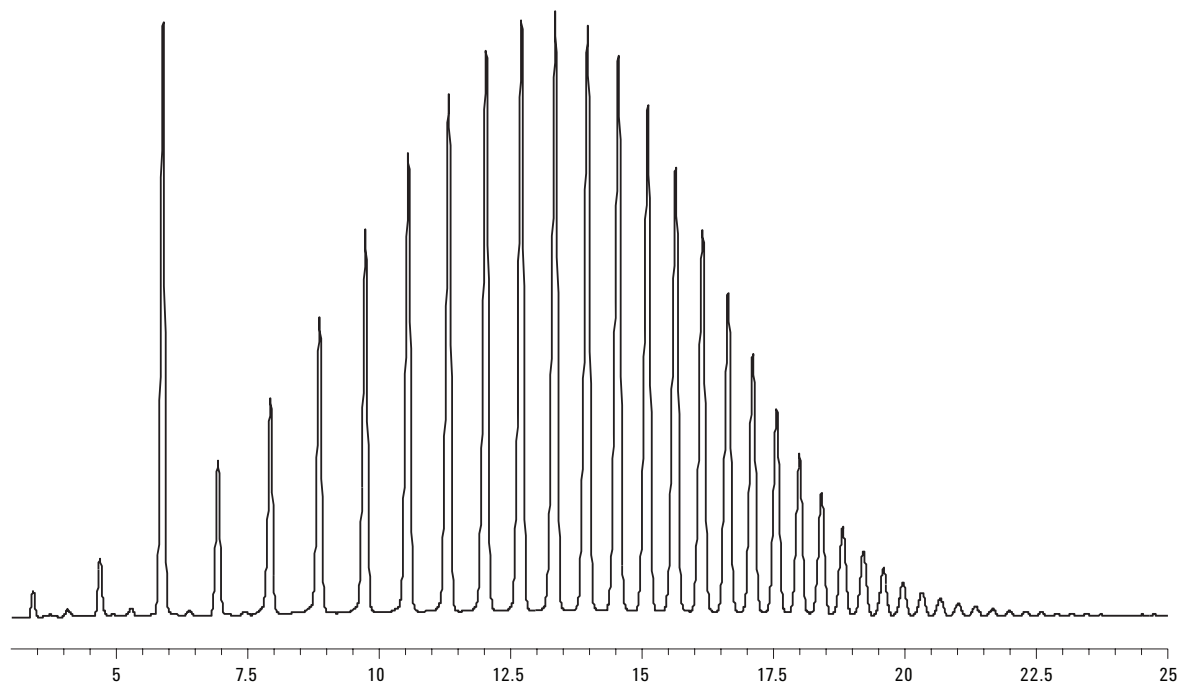


Figure 1. Polywax 500 with C20 marker. Multimode inlet with 7890A oven.

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 μ L) of C5-C18 mix was added to the Polywax 655/toluene solution as part of the automated procedure.

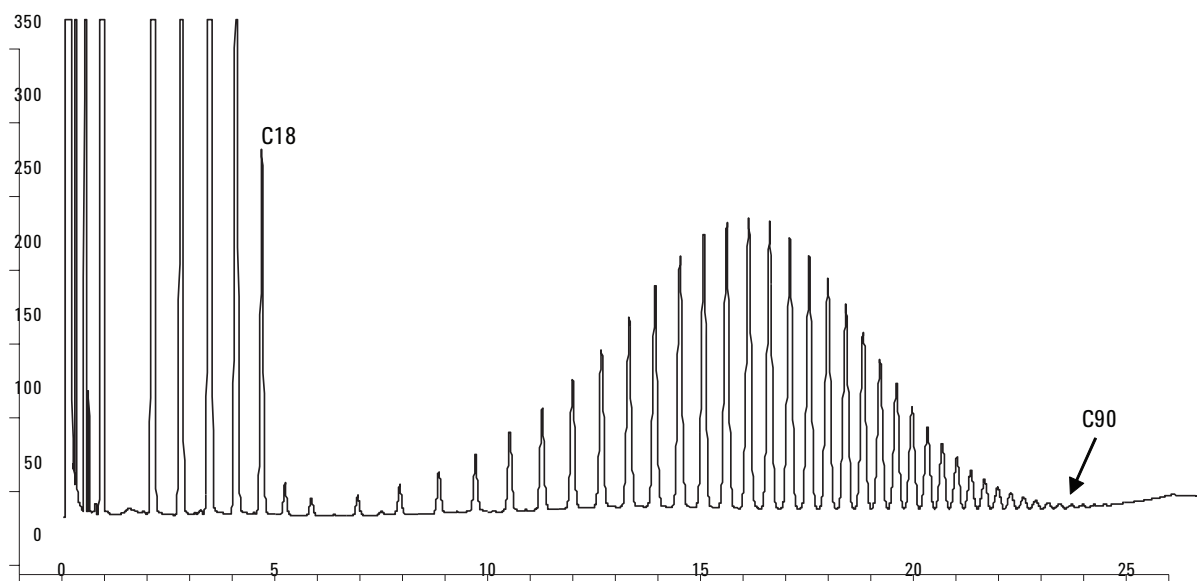


Figure 2. Chromatogram of Polywax 655.

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.

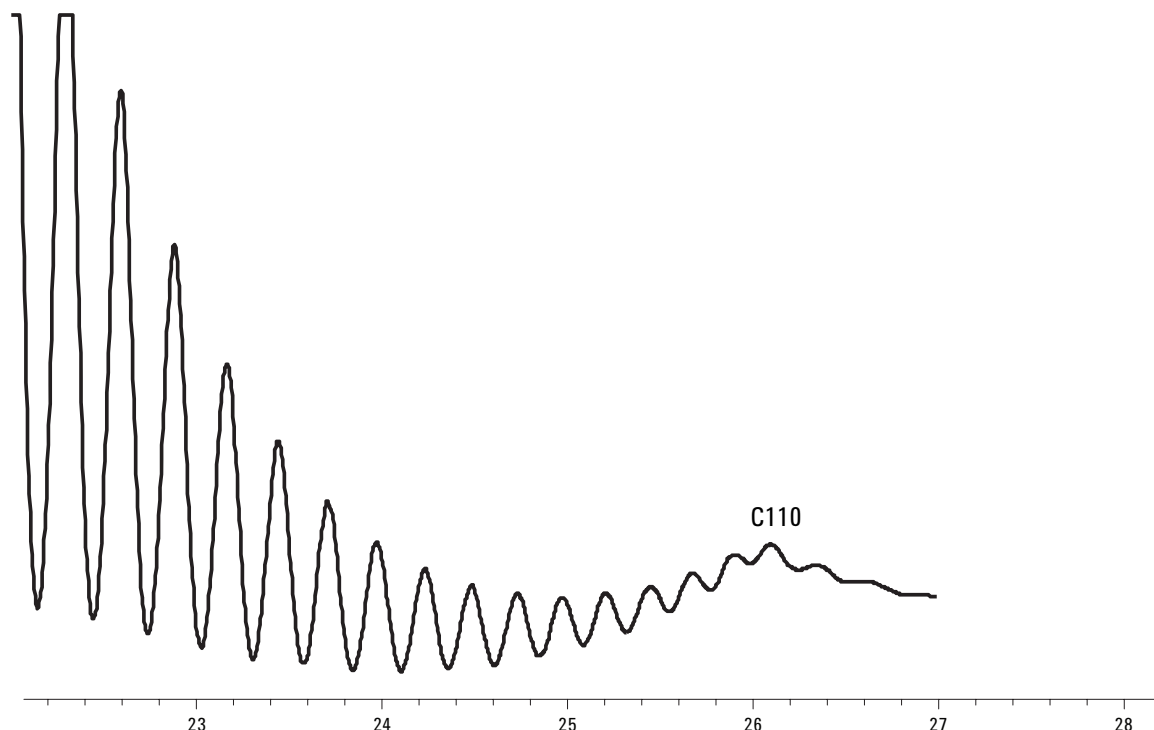


Figure 3. Polywax 655 to C110. Multimode inlet program: 150 °C (0 min) to 430 °C (hold until end of run) at 200 °C/min. 7890A oven: 40 °C (0 min) to 430 °C (5 min) at 15 °C/min. 3 µL injection. Solvent is toluene.

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.

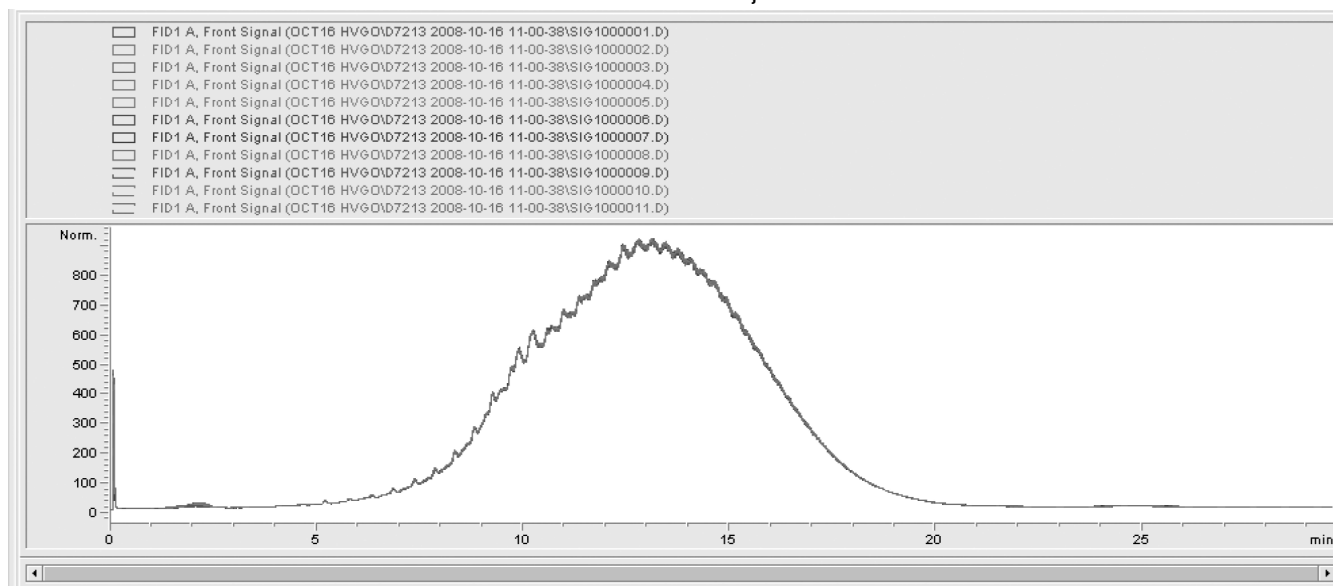


Figure 4. Overlay of 11 runs of HVGO, each prepared using 7693A towers and tray.

Table 4. Preparation of HVGO for injection. CS_2 is used as the solvent.

Sampler program steps
Move vial from front sample vial offset by -1 vial(s) to back turret position #1
Dispense 600 μ L 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 μ L 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 μ L 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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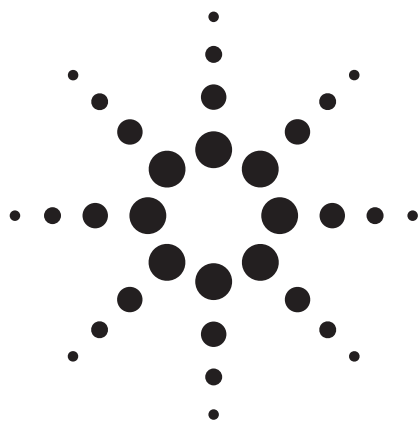
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Agilent Technologies



Achieving Lower Detection Limits Easily with the Agilent Multimode Inlet (MMI)

Application Note

All Industries

Authors

Bill Wilson and Chin-Kai Meng
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

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- μ L hot splitless, 10- μ L cold splitless and 25- μ L solvent vent illustrates the improvement in signal-to-noise ratios using LVI.



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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.

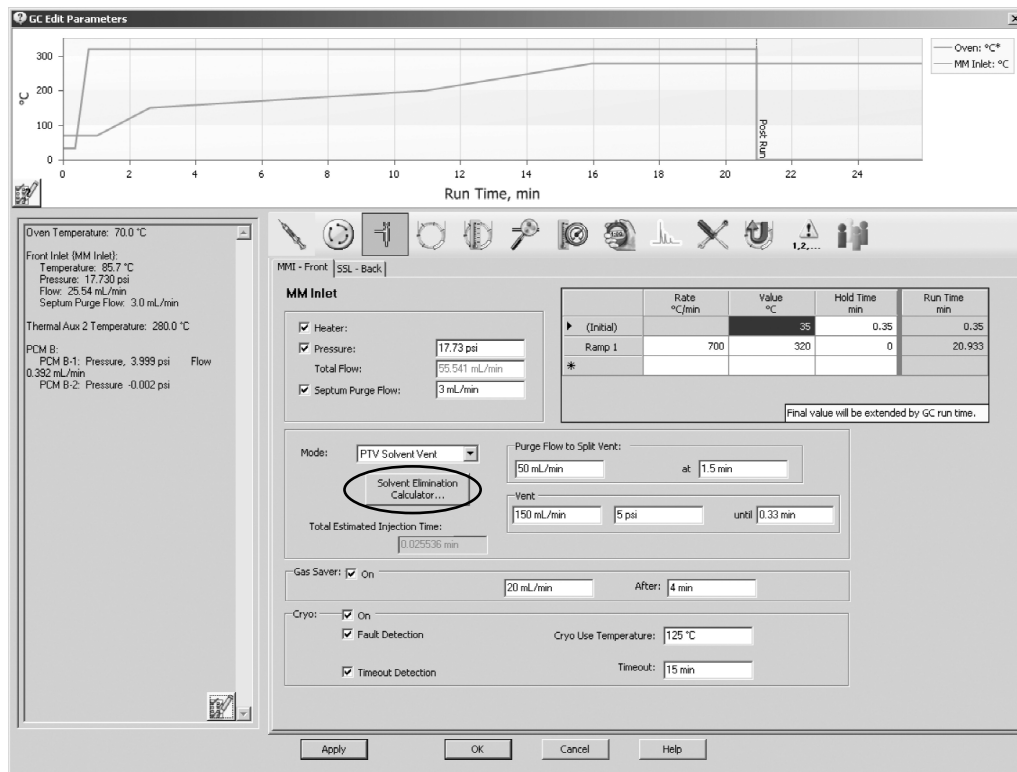


Figure 1. Multimode Inlet "Solvent Elimination Calculator" imbedded in ChemStation for easy method development.

Solvent Elimination Calculator

Agilent
Solvent Elimination
Calculation Wizard

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 uL

Boiling Point of first eluting analyte (°C)
150 °C

LVI Method Help Next Cancel Help

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.

Solvent Elimination Calculator

Agilent
Solvent Elimination
Calculation Wizard

Calculated values will change each time an input parameter is modified.

Elimination Rate (µL/min) 149.80 Suggested Injection Rate (µL/min) 74.90 Suggested Vent Time (min) 0.33

Inlet Temperature (°C) 35 Vent Pressure (gauge) 5.000 ☐ kPa
 Vent Flow (mL/min) 150 Outlet Pressure (gauge) 0.000 ☒ psi
 Injected Volume (µL) 25.0 ☐ bar

Solvent acetone

LVI Method Help Previous Next Cancel Help

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

Buttons at the bottom: LVI Method Help, Previous, Confirm and Copy, Cancel, Help.

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- μ L hot splitless injection. Some of the 40-ppb pesticides are barely visible (80 pg each on column). The middle TIC is from a 10- μ L 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- μ L 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- μ L injection volume. This implies that the solvent was mostly eliminated during the injection.

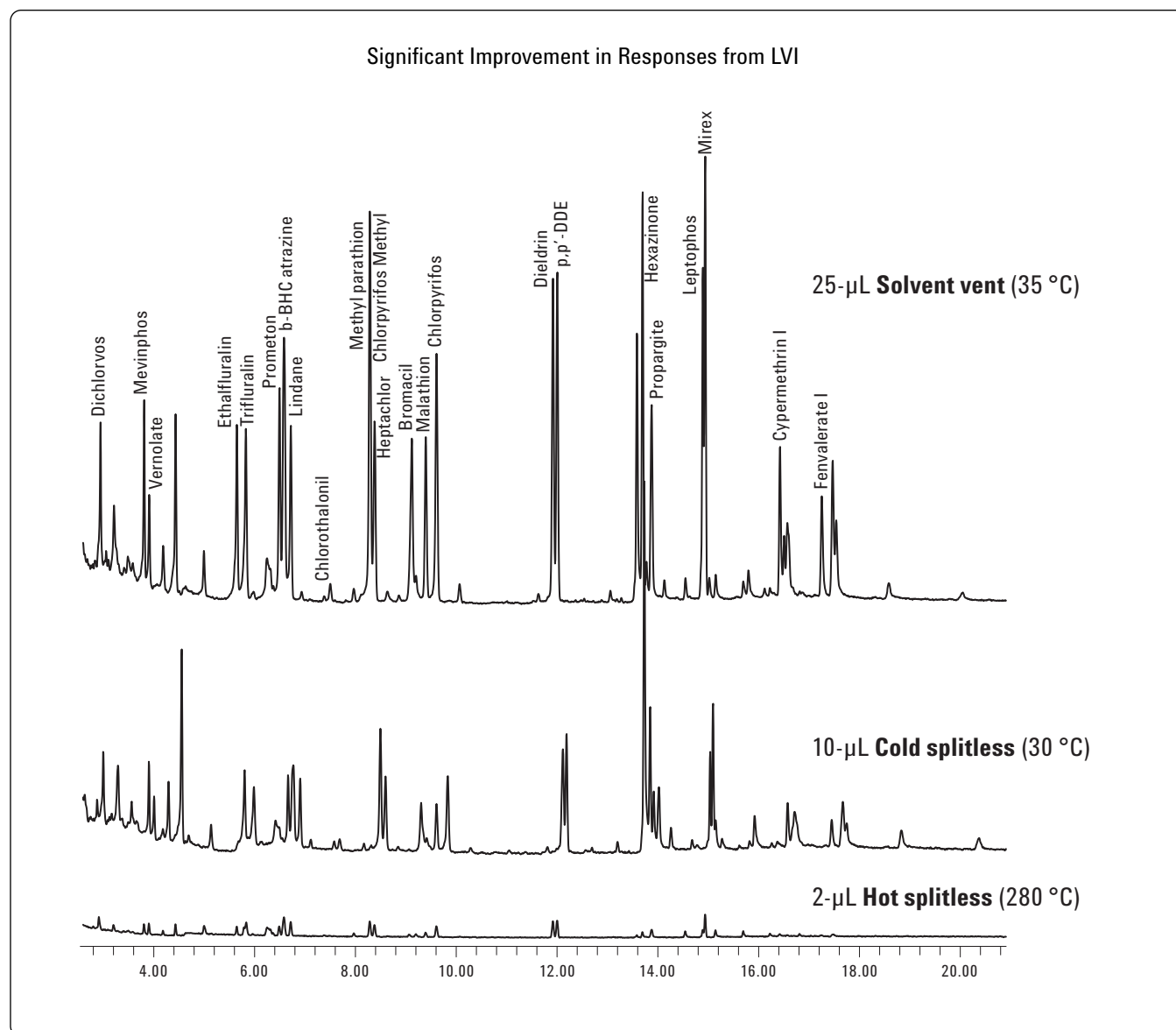


Figure 5. Overlay of total ion chromatograms (TICs) from three injection modes, plotted on the same scale.

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- μ L solvent vent injection to the 2- μ L 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.
2. Chin-Kai Meng, "Improving Productivity and Extending Column Life with Backflush," Agilent Technologies publication, 5989-6018EN, December 2006.
3. Matthew Klee, "Simplified Backflush Using Agilent 6890 GC Post Run Command," Agilent Technologies publication, 5989-5111EN, June 2006.
4. J. Stanieski and J. Rijks, *Journal of Chromatography* 623 (1992) 105-113.

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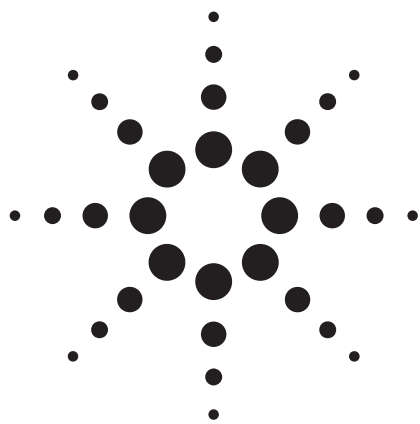
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Implementation of the Pressure Controlled Tee for Backflushing for the 7000 Series Triple Quadrupole Mass Spectrometer: Implications for Sensitivity

Application Note

Environmental, Drug testing, Forensics and Metabolomics

Author

Harry Prest
Agilent Technologies, Inc.
Santa Clara, CA
USA

Abstract

The 7000 Series Triple Quadrupole Mass Spectrometer is designed to provide the most sensitive and specific analytical determinations in gas chromatography. The enhanced specificity of GC/MS/MS analysis encourages a more relaxed or minimized sample preparation strategy with the aim of higher sample throughput and sample turnaround time. However these more complex samples can rapidly degrade the gas chromatograph (GC) and mass spectrometer (MS) performance. Applying backflushing helps maintain the GC and the MS source by removing later eluting compounds from the column before reaching the MS, and prior to the next sample injection. This note cites the results of the Pressure Controlled Tee (PCT) configuration for rapid and universal GC/MS backflushing applied to selected reaction monitoring experiments on the Agilent 7890 GC used with the Agilent 7000 Series Triple Quadrupole Mass Spectrometer. The results show no loss in sensitivity and precision as measured for the peak area, height or signal-to-noise ratio in the 272→241 m/z for octafluoronaphthalene. This means that rapid backflushing and quick column and inlet maintenance without venting the MS system can be incorporated without a loss in detection limits using a simple PCT configuration.



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Introduction

Agilent's GC Capillary Flow Technologies (CFTs) have greatly expanded the capability and flexibility of gas chromatographic analysis. CFT can provide rapid column and inlet maintenance without MS venting as well as backflushing of the accumulated sample matrix preventing carryover which compromises the column performance. One such CFT arrangement, the Pressure Controlled Tee [1], has been shown to provide rapid backflushing and enhance analytical robustness in GC/MSD single quadrupole analysis in a very challenging sample matrix [2]. The expectation of reduced sample preparation steps for analyses using GC/MS/MS suggests that backflushing is essential to prevent source and column fouling and maintain sample throughput. In fact, MS/MS analysis of complex hydrocarbon samples has already demonstrated rising baselines and carryover in the absence of comprehensive backflushing [3]. However, concerns exist that implementing additional "plumbing" may compromise the signal and therefore the detection limits in MS/MS analysis. This note presents sensitivity results for the 7000A Triple Quadrupole GC/MS in multiple reaction monitoring (MRM) mode using the Pressure Controlled Tee (PCT) configuration.

Experimental

The target compound is the checkout compound, octafluoronaphthalene (OFN), which represents a model compound for demonstrating MRM detection thresholds. Studies were conducted at concentrations of 100 fg using the Pressure Controlled Tee (PCT) configuration.

The experimental arrangement is shown schematically in Figure 1. The typical 30-m analytical column is replaced by two 15-m columns joined by the Purged Ultimate Union. Makeup gas can be supplied by either an Auxiliary Electronic Pneumatic Control (Aux EPC) or Pressure Control module (PCM) but here an Aux EPC was used. The installation and use of the PCT are described in the G1472A kit and included documents [4]. It should be noted that the PCT is a very flexible configuration and many column combinations are possible. The one in this demonstration is the simplest to illustrate.

The same method MRM acquisition parameters were applied for the OFN as the standard instrument checkout method however the GC parameters were altered to include a backflushing period and to terminate the GC at 200 °C (Table 1). This shortened the runtime by about one third compared with the standard method. Data was also collected using a continuous 30-m column as in the checkout with the same tune file and standard checkout GC parameters.

Table 1. GC Parameters for OFN Testing with Backflush

Configuration:	(the actual arrangement is two – 15-m columns but the GC is configured as follows)
Column 1:	Front Inlet to MSD Outlet: HP-5ms 30 m × 0.25 mm, 0.25 µm film, helium carrier at 1.20 mL/min.
Column 2:	AUX EPC Channel 4 to MSD Outlet: HP-5ms 15 m × 0.25 mm, 0.25 µm film, helium carrier at 1.22 mL/min.
GC oven:	45 °C for 2.25 min, 40 °C/min to 195 °C (6 minutes runtime)
Post run:	200 °C for 2 minutes
Column 1:	0.25 mL/min (flow is actually reversed)
Column 2:	5 mL/min

Results

Replicate injections showed no statistically significant difference between the peak areas or heights for the 272 *m/z* → 241 *m/z* transition (Table 2). Further, retention time reproducibility was unaffected by addition of the PCT and a standard deviation of less than 0.1 secs was achieved both with and without the PCT. (The absolute retention times can shift slightly due to a slight difference in the absolute flows and lengths). Signal-to-noise was also indistinguishable between the two configurations although noise is uniformly low in selected reaction mode so variation in the signal-to-noise ratio can be high. The degree of correspondence is best illustrated in Figure 2.

Conclusions

Since part of the strategy for sample analysis by MRM is minimized sample cleanup to increase sample throughput, protecting the mass spectrometer source integrity and GC column phase through backflushing will help achieve system robustness. Introducing the Pressure Controlled Tee configuration into the 7890 GC combined with the 7000 Series MS maintains signal height and area without degrading compound retention time reproducibility or other performance metrics. This means that rapid backflushing and service of the injection port and column (without venting the mass spectrometer) can be introduced without compromising analytical integrity. In this way the PCT is a powerful addition to the analytical strategy for tandem mass spectrometry.

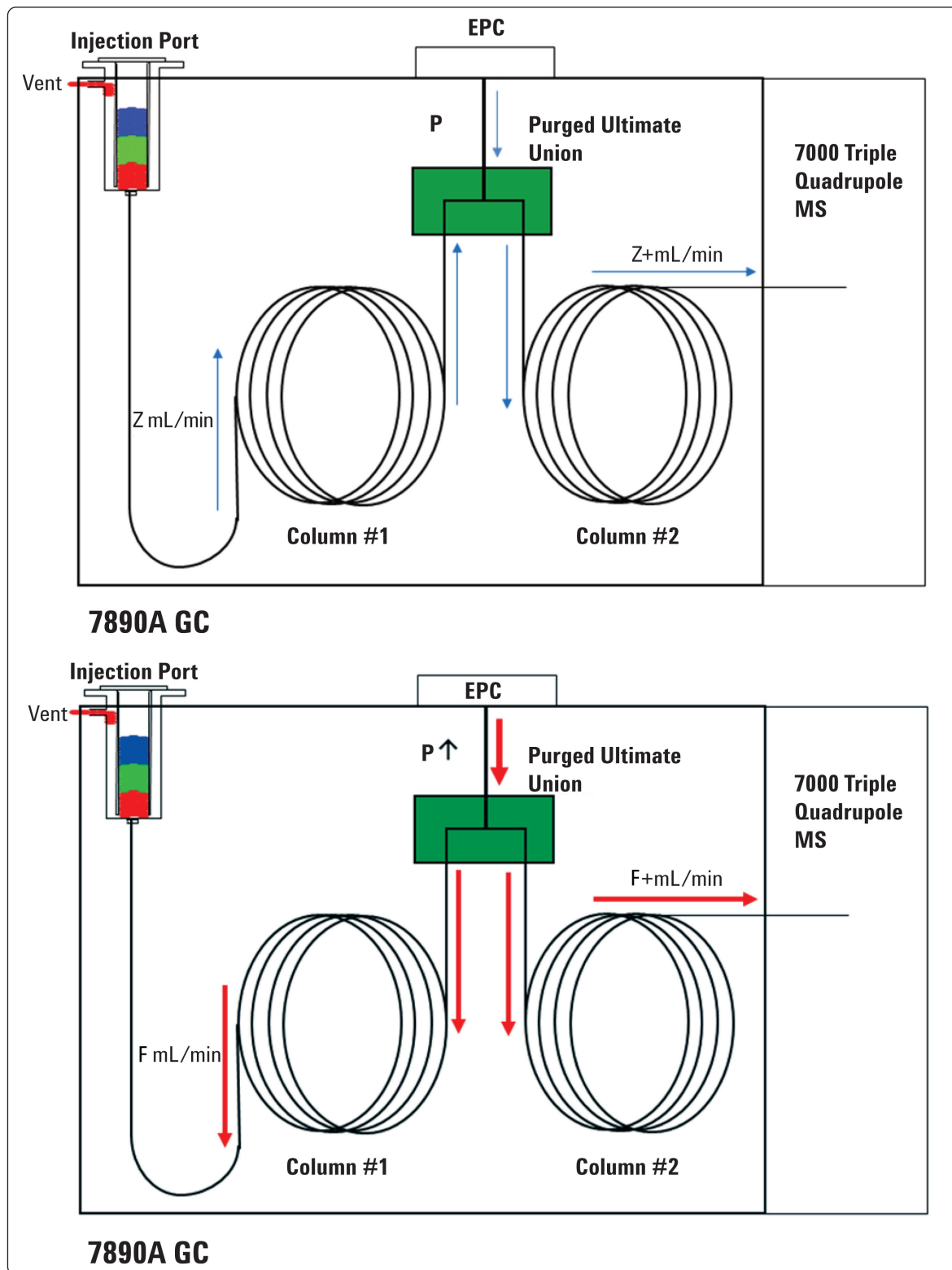


Figure 1 The Pressure Controlled Tee arrangement. Upper panel shows the forward flow during analysis and the lower panel shows the column flows during backflushing.

Table 2. Comparison between PCT and Continuous Column configurations for MRM 272→241 m/z transition for octafluoronaphthalene (OFN). To simplify the comparison, the results for the peak area, height and signal-to-noise (S/N) ratio have been normalized against the standard configuration.

GC configuration	RT variation (s)	Normalized MRM Signal area	Normalized MRM RSD (%)	Normalized MRM Signal height	Normalized MRM RSD (%)	Normalized MRM S/N
Continuous column without PCT	0.063	1	14	1	15	1
With PCT	0.098	1.1	15	1.0	16	1.2

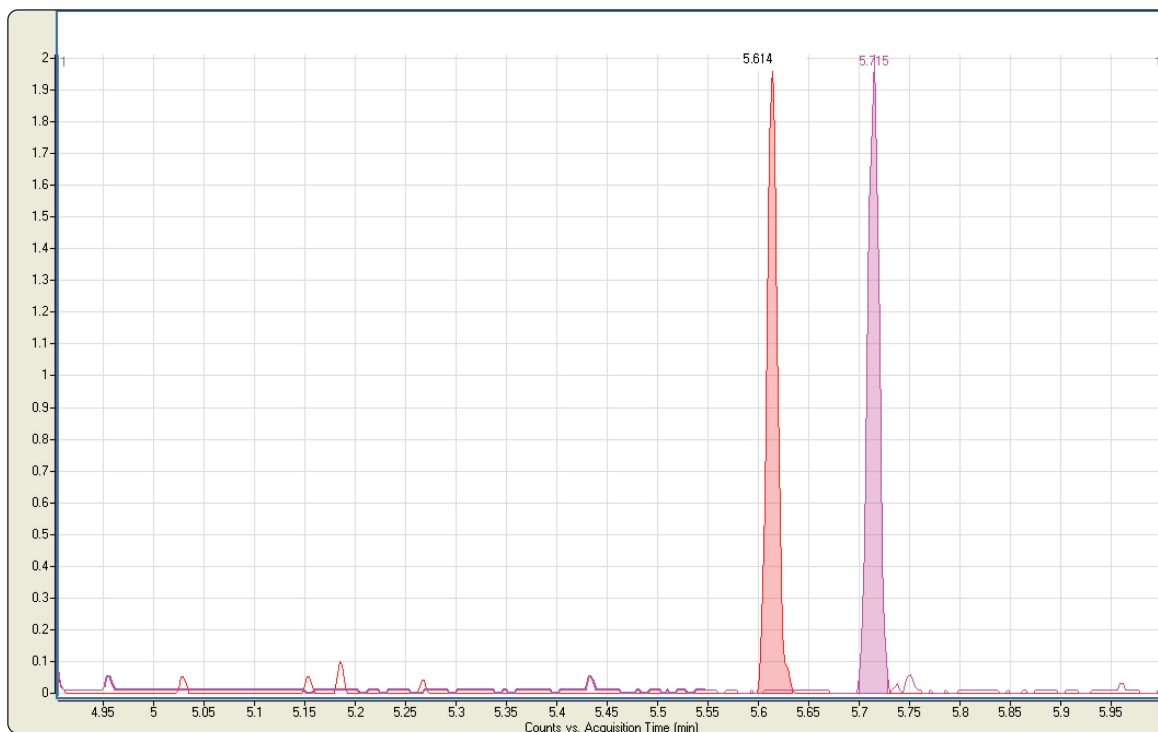


Figure 2. OFN 272 → 241 m/z transition without the PCT (5.614 min) and using the PCT (5.715 min). The same absolute abundance scale is applied to both.

References

- 1 "Capillary Flow Technology for GC/MS: A Simple Tee Configuration for Analysis at Trace Concentrations with Rapid Backflushing for Matrix Elimination," Agilent Technologies publication 5989-8664EN
- 2 "Capillary Flow Technology for GC/MS: Efficacy of the Simple Tee Configuration for Robust Analysis Using Rapid Backflushing for Matrix Elimination," Agilent Technologies publication 5989-9359EN
- 3 "Enhanced Sensitivity for Biomarker Characterization in Crude Oil by GC-SRM," in press
- 4 "The Rapid Universal GC/MS Backflushing Kit," part number G1472A and contains the manual (G1472-90001) which describes this configuration and operation for 5973 or 5975 or 7000 series Mass Selective Detectors.

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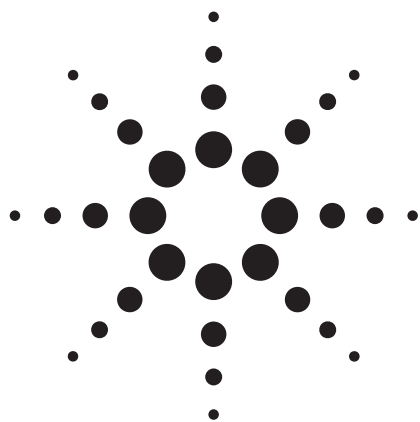
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Analysis of Permanent Gases and Light Hydrocarbons Using Agilent 7820A GC With 3-Valve System

Application Note

HPI

Authors

Xiaohua Li

Agilent Technologies (Shanghai) Co., Ltd.

412 Ying Lun Road

Waigaoqiao Free Trade Zone

Shanghai 200131 P.R.China

Zhenxi Guan

Agilent Technologies Co., Ltd.(China)

No.3, Wang Jing Bei Lu,

Chao Yang District,

Beijing, China,100102

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 $\times$ 0.53 mm) is used to measure all hydrocarbons (C1~C6) including CH_4 .



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Introduction

Analysis of permanent gases and light hydrocarbons has been widely employed in the petrochemical, chemical and energy industries. These permanent gases, such as O₂, N₂, CH₄, CO, and CO₂ 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.

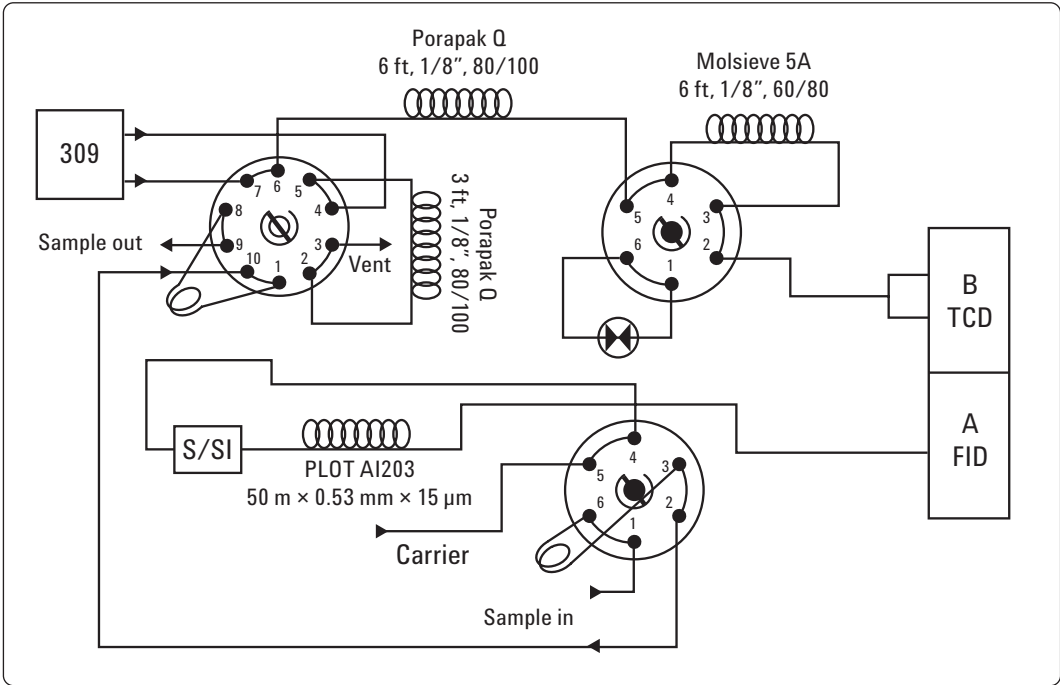


Figure 1. Valve diagram for dual-channel natural gas analysis.

Table 3. Concentrations of the Standard Gases

Components	H ₂	O ₂	N ₂	CO	CO ₂	CH ₄	C ₂ H ₆	C ₃ H 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 Al₂O₃ 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.

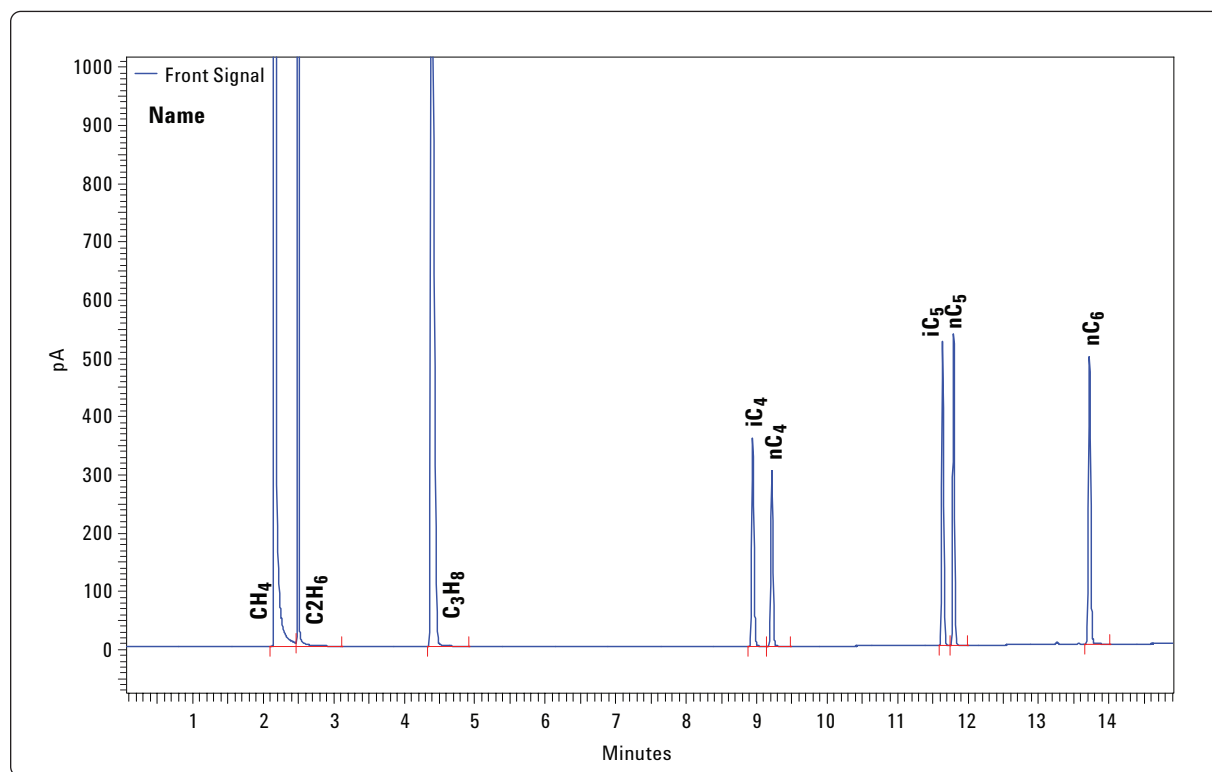


Figure 2. FID Channel chromatogram of CH₄, C₂H₆, C₃H₈, iC₄, nC₄, iC₅, nC₅, and nC₆.

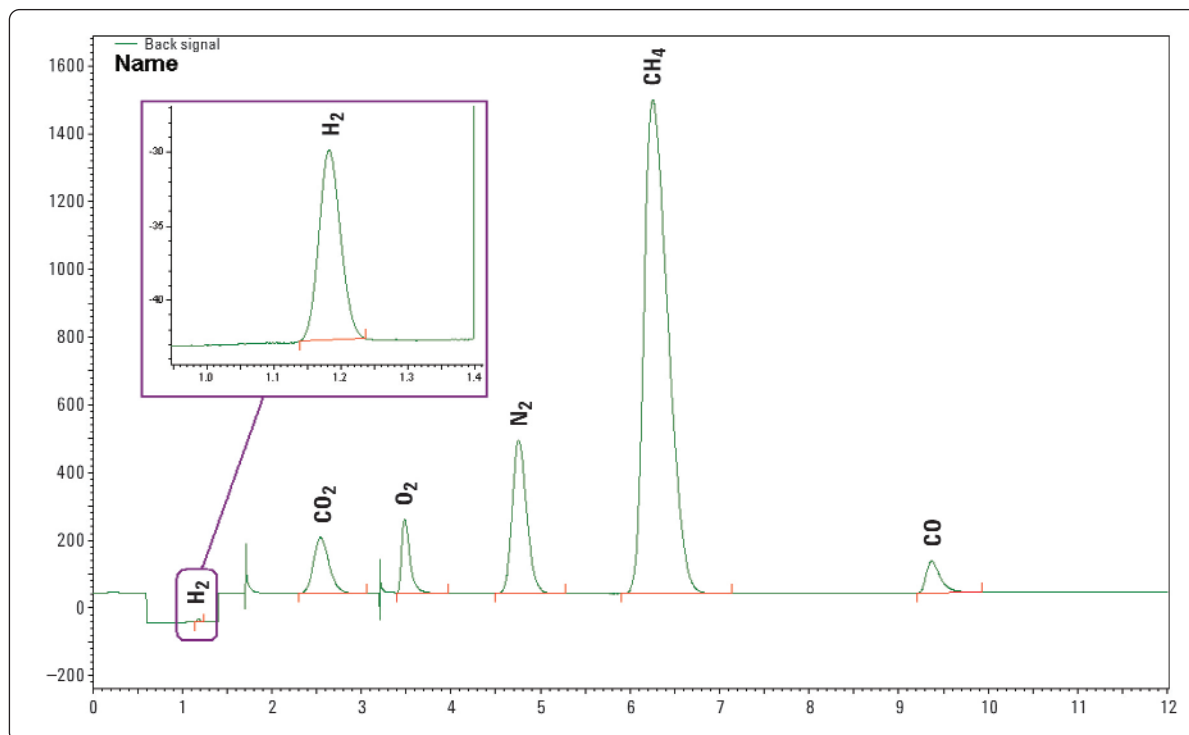


Figure 3. TCD Channel chromatogram of H₂, O₂, CO₂, N₂, CH₄, CO.

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 H₂, CO₂, O₂, N₂, CH₄, 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

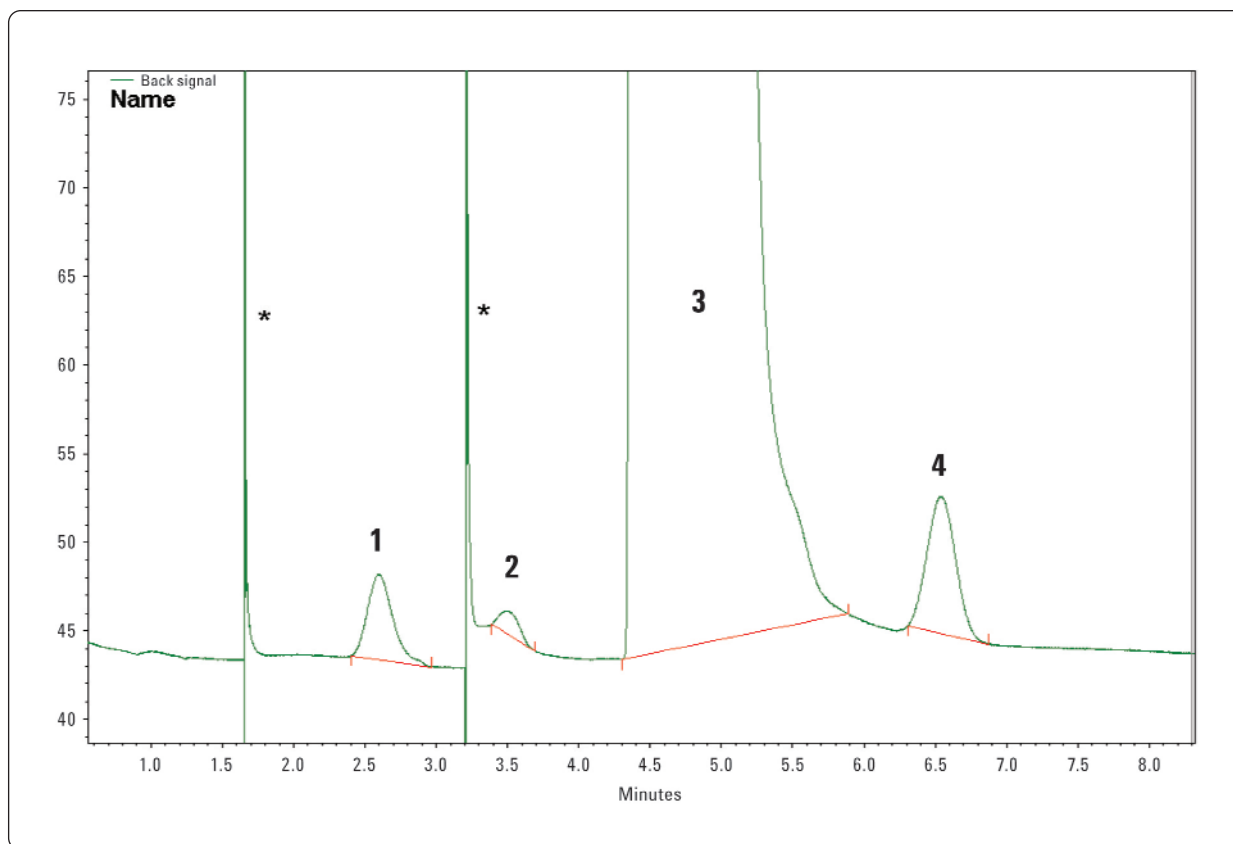


Figure 4. Chromatogram of low level permanent gas standard mix.

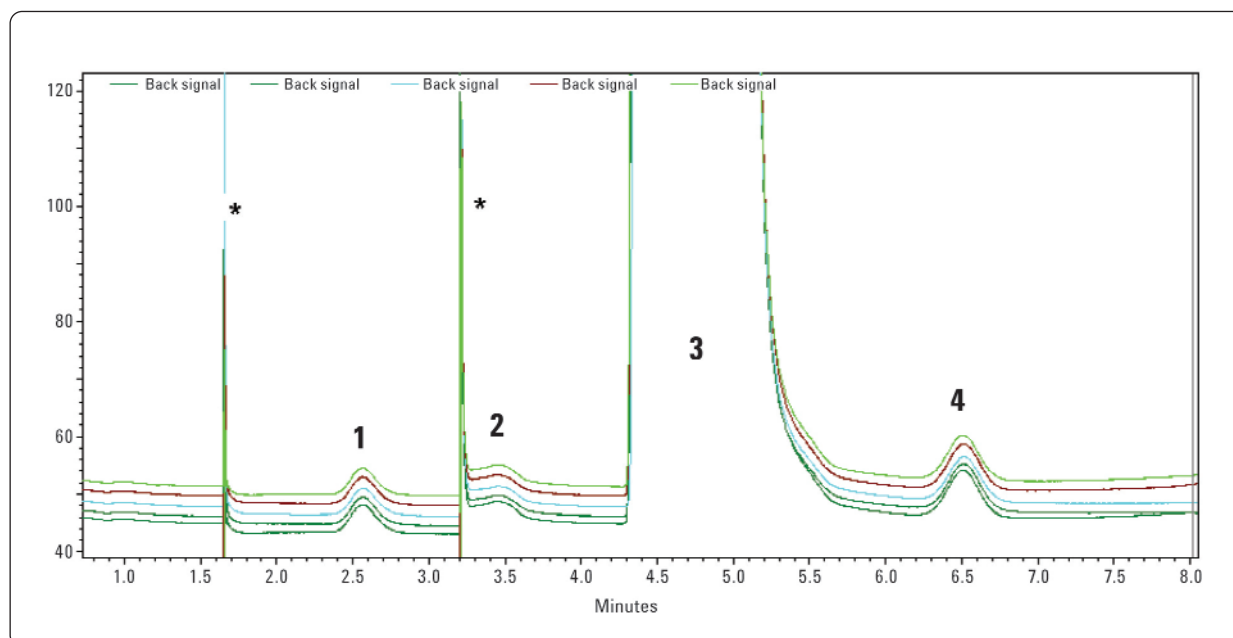


Figure 5. Overlapped chromatograms of five runs.

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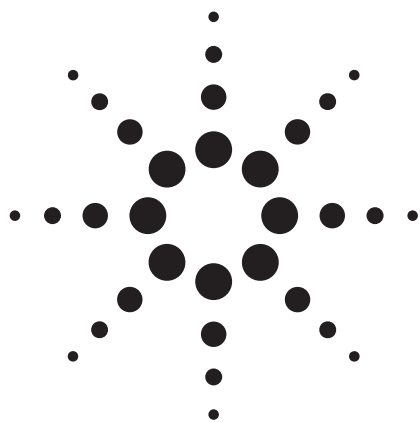
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Enhanced Sensitivity for Biomarker Characterization in Petroleum Using Triple Quadrupole GC/MS and Backflushing

Application Note

Environmental

Authors

Melissa Churley
Agilent Technologies, Inc.
5310 Stevens Creek Blvd.
Santa Clara, CA 95051
USA

Harry Prest
Agilent Technologies, Inc.
5310 Stevens Creek Blvd.
Santa Clara, CA 95051
USA

David A. Zinniker
Department of Geological and
Environmental Sciences
Stanford University
Stanford, CA 94305-2115
USA

Celso Blatt
Agilent Technologies Brasil Ltda
Sao Paulo 06455-940
Brazil

Abstract

A rapid, reliable method for the routine detection and quantification of biomarkers in petroleum was developed using the Agilent 7890A/7000A Series Triple Quadrupole GC/MS with backflushing using a Pressure Controlled Tee configuration. In a single run, diverse biomarkers from several transitions can be detected, confirmed, and quantified at levels as low as 2 ppm, with RSDs well below 5%. This method is suitable for "fingerprinting" of petroleum samples and the deconvolution of oil mixtures in complex, multisource petroleum systems.



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Introduction

Petroleum biomarkers are complex molecular fossils derived from once living organisms [1]. These compounds provide unique clues to the identity of source rocks from which petroleum samples are derived. This information includes the biological source organisms which generated the organic matter, the environmental conditions that prevailed in the water column and sediment at the time, the thermal history of both the rock and the oil, and the degree of microbial biodegradation. Biomarkers are used in conjunction with other geochemical parameters to help solve oil exploration, development, and production problems. They provide much more detailed information about petroleum source and history than nonbiomarker analysis (bulk isotopes, elemental analysis, and so forth) alone.

High resolution mass spectrometry (HRMS) is often used to analyze biomarkers in petroleum, due to its ability to provide quantitative data for compounds present in complex mixtures. However, HRMS requires a significant financial investment as well as highly trained operators to assure valid results. Triple Quadrupole GC/MS offers a viable alternative for the rapid, routine analysis of biomarkers in petroleum, providing excellent precision, sensitivity, selectivity, and dynamic range. Implementing GC backflushing in the acquisition method improves data quality robustness, due to the very complex and varied nature of petroleum samples.

Experimental

Standards and Samples

STANFORD-1 is a new external standard for quantitative biomarker analysis. It is a mixture of pure biomarker standards and paraffin-free saturate fractions from Paleozoic, Mesozoic,

Cenozoic, biodegraded, terrestrially-influenced, carbonate/evaporate-sourced, and open-marine sourced petroleum samples. It contains known quantities of most, if not all, commonly used biomarkers and two internal standards, BTI-6 and 5- β cholane, which are useful for quantifying hopane and sterane biomarkers across diverse GC/MS systems.

C30 sterane fractions were prepared using standard normal phase liquid chromatography techniques, n-alkane removal, and proprietary molecular sieve and HPLC techniques for the final enrichment of target compounds. Two compounds which coelute with n-propylcholestane (4-methylstigmastane and hopane) were completely removed from the sample to avoid known interference with the m/z 414 $\rightarrow$ 217 transition.

Instruments

The experiments were performed on an Agilent 7890A gas chromatograph equipped with a split/splitless inlet, an Agilent 7000A Triple Quadrupole GC/MS with Triple-Axis Detector, and an Agilent 7683B automatic liquid sampler (ALS). The split/splitless inlet is fitted with a deactivated, helical double taper injection liner (p/n 5188-5398). Injections were made using a 10- μ L syringe (p/n 9301-0713). A variety of configurations was explored to examine possible improvements in analysis time. Ultimately, two configurations were used for the experiments, and the instrument conditions and specific configurations are listed in Table 1.

MS SRM Parameters

The MS/MS parameters used in the analysis of the petroleum samples are shown in Tables 2 and 3 and in the Figure 6 legend. Experience with HRMS metastable transitions was used to select these precursor and product ions, and an extensive study of product ions was not performed.

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

GC Run Conditions	60 m Configuration	40 m Configuration
Column	Two 30 m x 0.25 mm x 0.25 µm DB-1MS Ultra Inert columns (p/n123-0132UI)	Two 20 m x 0.18 mm x 0.18 µm DB-1MS Ultra Inert columns (p/n 121-0122UI)
Inlet temperature	325 °C	325 °C
Inlet pressure	19.197 psi	17.13 psi
Carrier gas	Helium, constant flow mode	Hydrogen, constant flow mode
Flow rate	Column 1: 1.15 mL/min; Column 2: 1.20 mL/min	Column 1: 0.95 mL/min; Column 2: 1.0 mL/min
Injection mode	Pulsed splitless (50 psi until 1 min)	Pulsed splitless (50 psi until 0.75 min)
Oven program	50 °C (1 min hold), then 40 °C/min to 140 °C for 0 min, then 2 °C/min to 313.5 °C for 0 min	40 °C (0.6 min hold), then 40 °C/min to 140 °C for 0.5 min, then 3.4 °C/min to 300 °C for 1 min
Column velocity	Column 1: 27.636; Column 2: 39.923 cm/s	Column 1: 45.449; Column 2: 65.944 cm/s
Injection volume	1 µL	1 µL
Transfer line temperature	325 °C	325 °C
GC Post-Run Conditions		
Backflush device	Purged Ultimate Union (p/n G3186-60580) controlled by a Electronic Pneumatic Control (EPC) (p/n G3470A)	Purged Ultimate Union (p/n G3186-60580) controlled by a Electronic Pneumatic Control (EPC) (p/n G3471A)
Backflush conditions	–4 mL/min at 325 °C for 7 min	–4 mL/min at 325 °C for 5 min
MS Conditions		
Tune	Autotune	Autotune
Delta EMV	70 eV	70 eV
Acquisition parameters	El; selected reaction monitoring	El; selected reaction monitoring
Solvent delay	5 min	3 min
MS temperatures	Source 250 °C; Quadrupoles 150 °C	Source 250°C; Quadrupoles 150 °C

Table 2. Analysis Parameters for Precision Experiments*

Compound	Transition (m/z)
Stigmastane	400.4 → 217.2
Homohopane (22S)	426.4 → 191.2
n-propylcholestane	414.4 → 217.2
27-nordiacholestane (13β,17α(H),20S)	358.4 → 217.2
27-norcholestane	358.4 → 217.2
4-methylstigmastane	414.4 → 231.2
Dinosterane	414.4 → 98.1
Hopane	412.4 → 369.4
5β-Cholane (ISTD)	330.3 → 217.2

*The method contained 17 transitions in total. The dwell time and collision energy used for each transition was 50 msec and 5 eV, respectively, using the 60 m configuration.

Results and Discussion

Backflushing with a Pressure Controlled Tee Configuration

Backflushing was used to remove higher boiling substances from the column prior to each subsequent run. Using this technique, late eluting peaks are flushed out of the inlet split flow vent instead of driving them through the entire length of column and into the mass spectrometer. Backflushing reduces accumulated chemical noise due to carryover (which can be observed even in SRM mode as a rising baseline) and the cycle time of the analysis, thus increasing throughput. System uptime is also increased, due to reduced maintenance of the columns and MS detector. The suite of Agilent Capillary

Flow Technology modules comprises a proprietary solution that enables easy and rapid backflushing with minimal dead volumes for maintaining chromatographic resolution. It also uses ferrules and fittings that eliminate leaks. All Capillary Flow Technology modules require the use of an Auxiliary Electronic Pneumatic Control (EPC) module or a Pneumatic Control Module (PCM) to provide a precisely-controlled second source of gas that directs the column flow to the appropriate column or detector. During analysis, the EPC module supplies a pressure slightly above the pressure of the carrier gas through the column. When backflushing, the inlet pressure is dropped and the EPC module pressure is increased, forcing the flow to reverse through the column and out the split vent.

A quick and simple approach to backflushing is to use a Capillary Flow Technology device in the middle of the analytical column [2–4]. As an example employed here, instead of using a 40-m column, two 20-m columns are used and connected by an ultralow dead volume Purged Ultimate Union in a Pressure Controlled Tee (PCT) configuration (Figure 1). The EPC module adds just enough makeup gas to match that from the first column, so there is very little flow addition and subsequent decrease in sensitivity due to suboptimal carrier gas flows into the mass spectrometer. As a general rule, the flow for column 2 is set to be 0.02 to 0.05 mL/min greater than that for column 1. Backflushing in this configuration is accomplished simply by reducing the flow or pressure in the first column and increasing it in the second column.

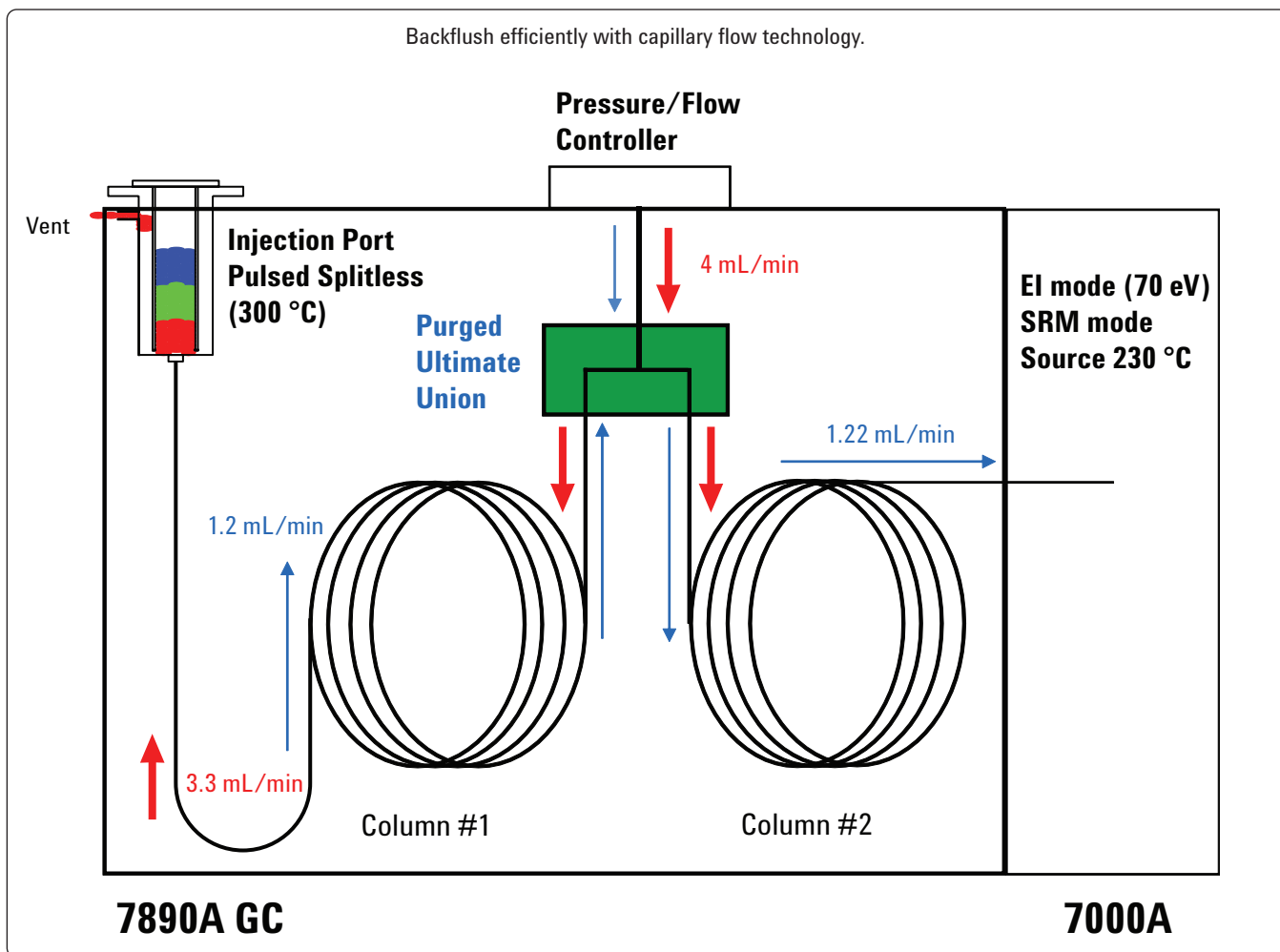


Figure 1. Schematic of the Pressure Controlled Tee GC/MS configuration. The narrower (blue) lines indicate the forward flow during analysis and the thicker (red) lines indicate the backflushing post-run state.

Figure 2 illustrates the advantages of backflushing with the PCT configuration. Typical hydrocarbon GC/MS analysis requires long cycle times due to long hold times at high oven temperatures to avoid contaminating subsequent analyses with carryover of high-boiling components (top chromatogram). Using backflush, targeted volatile components, in this case those eluting within 25 minutes, can be analyzed with significantly shorter cycle times, eliminating the need for column baking and extended GC run times (bottom chromatogram). High boiling hydrocarbons are not retained and column degradation by "permanently" absorbed components and high temperature hold times is decreased. In the example shown, cycle times are reduced from over 100 minutes to less than 30 minutes, and a blank injection after backflushing reveals no high-boiling components and only the baseline rise associated with column bleed.

Faster Analysis of Biomarkers

Run times can be accelerated 30 minutes per cycle without loss in chromatographic resolution or substantial loss in signal by switching from a 60-m (0.25-mm id) column with helium carrier gas to a 40-m (0.18-mm id) column with hydrogen carrier gas (Figure 3). The speed of the 7000A Triple Quadrupole mass spectrometer in SRM mode required only a change in dwell time from 50 to 20 msec to record the required 17 transitions with the same number of scans over the peaks. Because the 7000A Triple Quadrupole MS allows dwell times as short as 1 msec, even faster analysis is possible. An experimental comparison with an uninterrupted 60-m column (results not shown) demonstrated that the insertion of the PCT configuration results in no degradation in chromatography due to the low dead-volume of the Purged Ultimate Union.

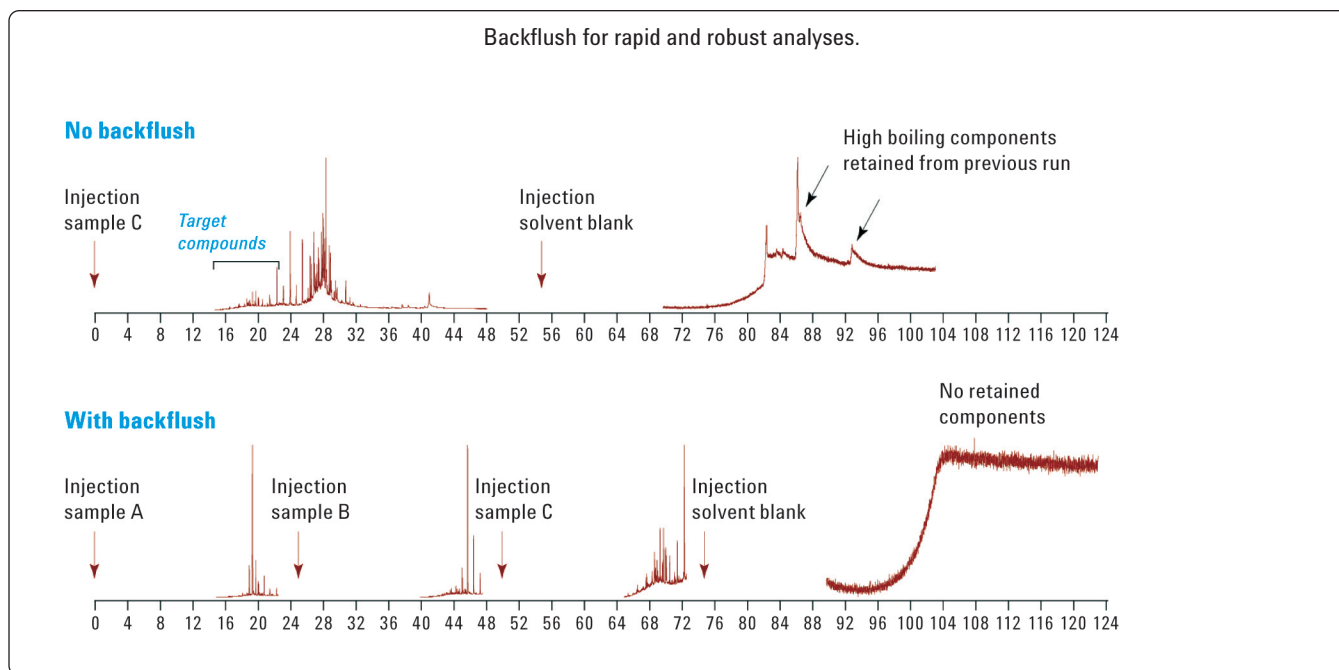


Figure 2. Petroleum samples, including one from Williston Basin source rocks (Sample C) which contains many late eluting, high molecular weight hydrocarbons, were analyzed without (top) and with (bottom) backflushing (40 m configuration). The target compounds comprise a subset of the total number of possible compounds in any injected sample and are indicated by brackets in the top chromatogram. As in a typical analysis, a sequence of samples was analyzed from three sources using the backflushing method in the bottom trace, followed by a solvent blank injection which demonstrated the lack of retained components.

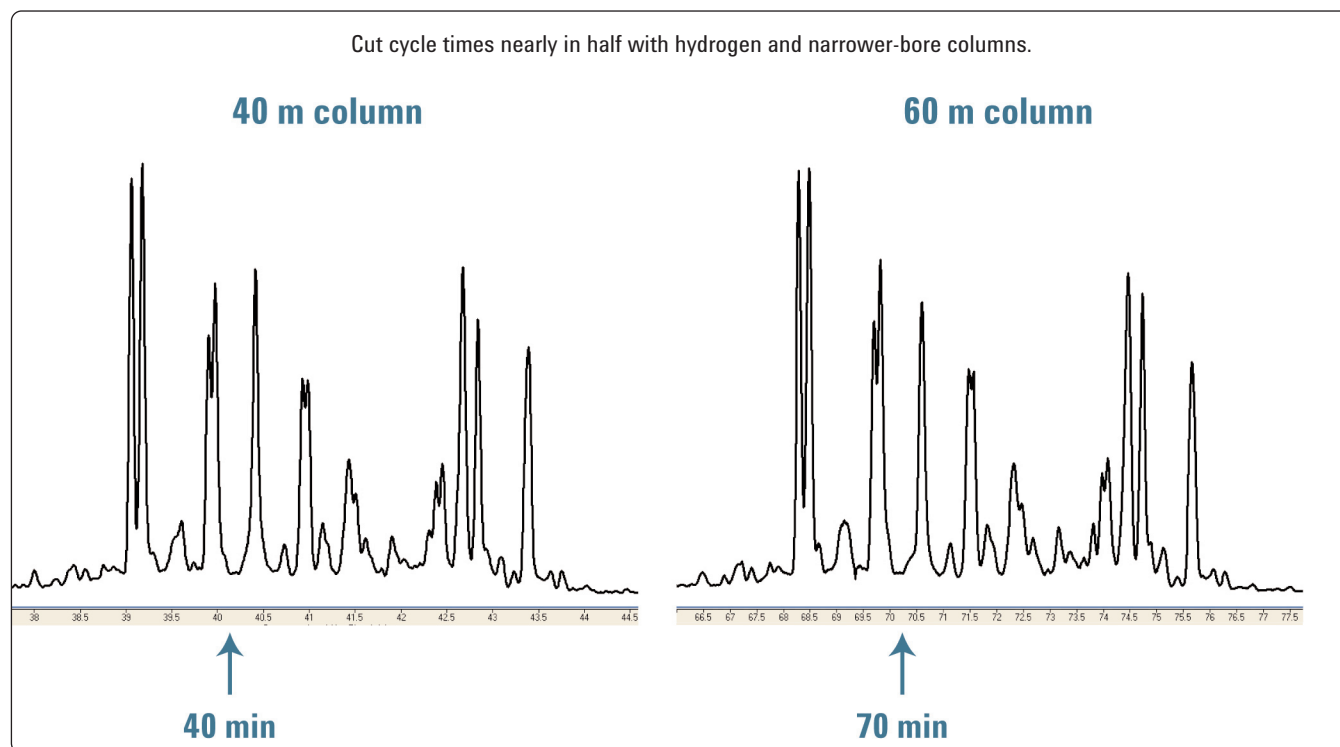


Figure 3. C28 steranes were analyzed using m/z transition 386→217 on either a 60 meter, 0.25 μm column and helium carrier gas, or a 40 meter, 0.18 μm column with hydrogen carrier gas. Employing hydrogen and the smaller bore column reduces analytical time significantly without loss in compound resolution.

Sensitivity, Selectivity and Precision

Routine biomarker analysis in petroleum samples requires precise determination of the abundance of a large number of individual compounds which can vary over a large range of concentrations in these complex mixtures. This precision allows the distinction of differences between petroleum samples with subtly different source or post-generation history. Results for ten sequential runs of the STANFORD-1 standard demonstrate that calculated concentrations of eight different compounds using several different transitions with widely varying concentrations is quite precise (Table 2, Figure 4a).

Most relative standard deviations (RSDs) were well below 5%. The only compound that gave an RSD higher than 5% (dinosterane) was present at a very low concentration (~2 ppm) and required manual integration for quantification. In addition, the calculated concentrations of the compounds were within a few percent of the expected concentration across all ten runs, except for the manually integrated dinosterane (Figure 4b). This precision demonstrates the ability of the Triple Quadrupole GC/MS system to distinguish subtle variations in petroleum composition for traditional biomarker studies, reservoir partitioning studies, and three-dimensional basin modeling.

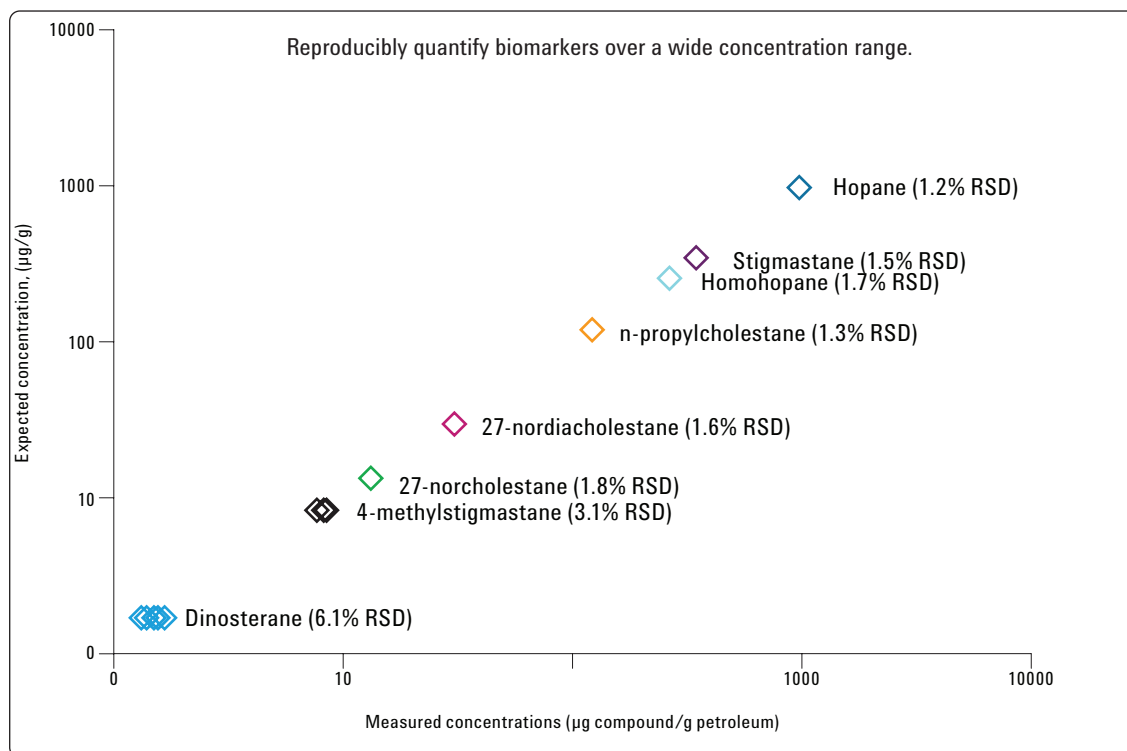


Figure 4a. Precision experiment results for eight biomarkers of widely varying concentrations contained within the STANFORD-1 standard. Ten sequential analyses were performed over a 15 hour period using the 60-m column PCT configuration. See Table 3 for transitions.

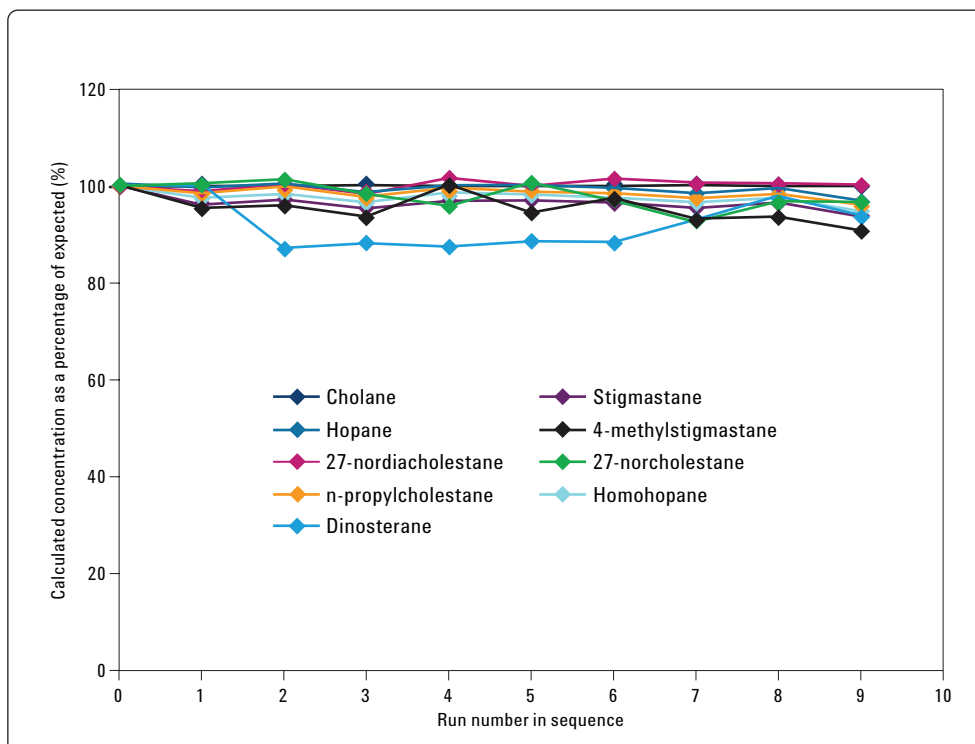


Figure 4b. The data from the analysis described in Figure 4a were plotted as calculated concentration of each biomarker versus the expected concentration over 10 analyses.

Deconvolving Oil Mixtures

A sophisticated understanding of petroleum systems requires the recognition and deconvolution of oil samples derived from more than one source rock. This problem is common where stacked source rocks exist in sedimentary basins (Figure 5). For this work a series of laboratory mixtures consisting of a marine petroleum endmember and a lacustrine endmember were analyzed for stigmasterane, a ubiquitous component present in petroleum from both sources, and n-propylcholestane, a compound unique to oil from marine source rock.

As the ubiquitous component must be measured on a different SRM transition and is an order of magnitude more abundant in the marine oil, transition ratio stability and a large instrumental dynamic range are necessary to accurately identify small marine petroleum inputs in lacustrine source rock samples. The data demonstrate that mixtures as low as 0.2% (v/v) in the minor marine component can be accurately determined (Figure 6).

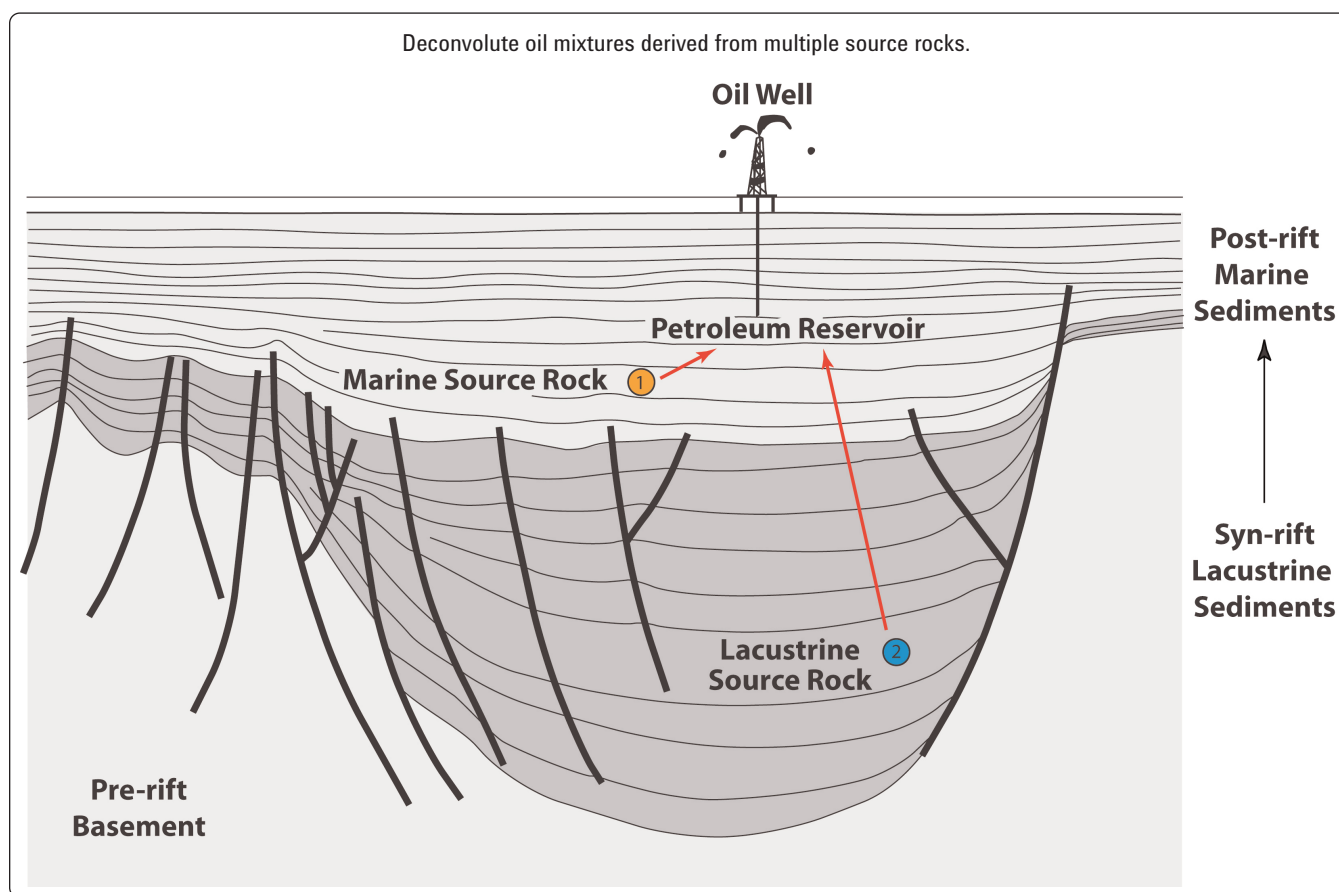


Figure 5. Diagram of an oil deposit containing source rocks from both marine (1) and lacustrine (2) sources.

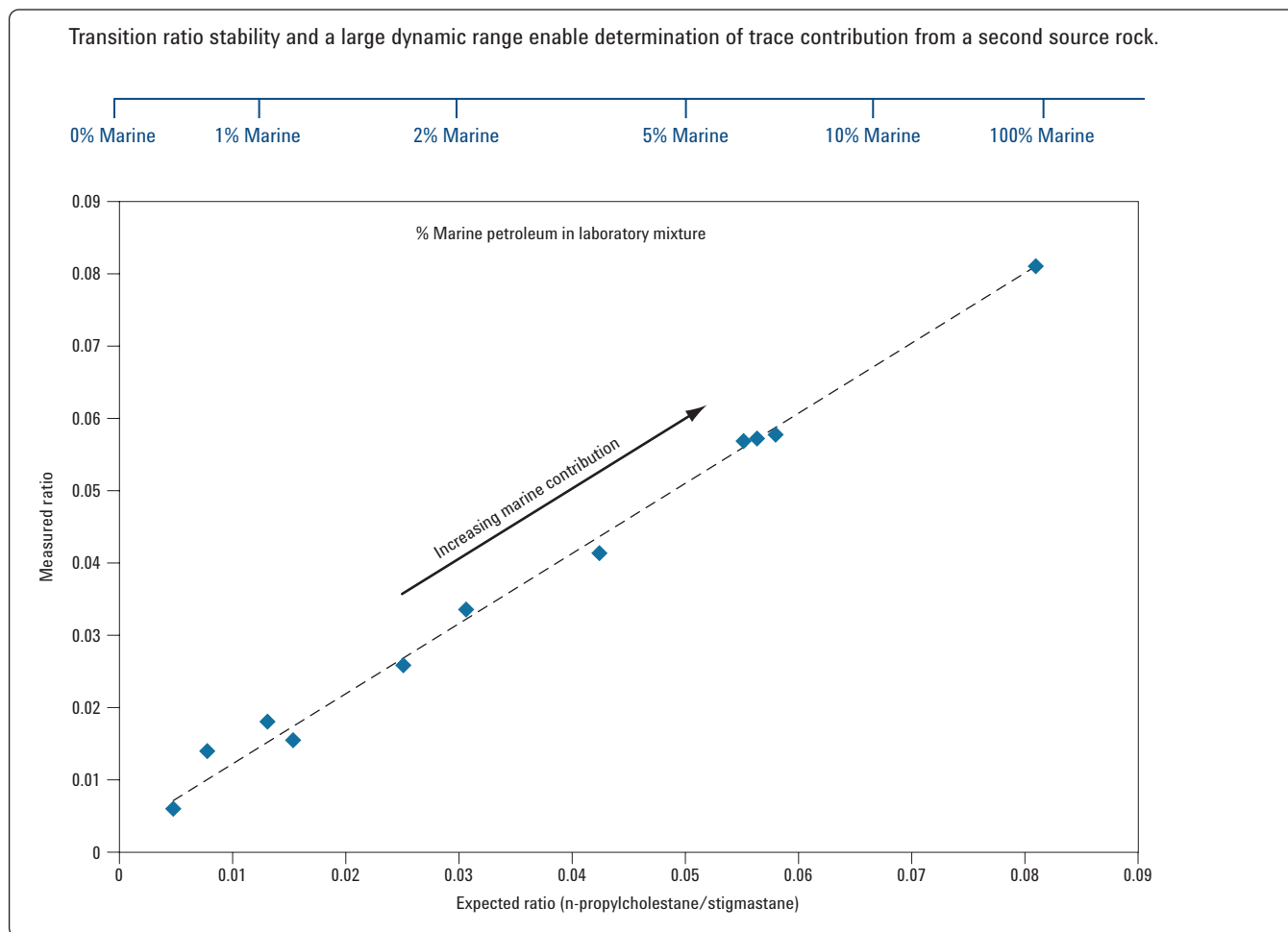


Figure 6. A series of laboratory mixtures consisting of various percentages of a marine petroleum sample in a lacustrine sample were analyzed for stigmastane, a ubiquitous component present in petroleum from both sources, and n-propylcholestane, a compound unique to oil from lacustrine source rock. The measured ratio of the two compounds was then plotted versus the expected ratio. Transitions monitored were: n-propylcholestane, m/z 414.4 $\rightarrow$ 217.2; stigmastane, m/z 400.4 $\rightarrow$ 217.2.

Conclusions

The Agilent 7000A Triple Quadrupole MS with 7890 GC using backflushing is a viable approach to the routine analysis of petroleum biomarkers, providing increased sensitivity, better selectivity and the potential to greatly reduce analysis time versus traditional GC/MS analysis. Column backflush provides higher sample throughput with lower carryover and source maintenance, and the use of hydrogen carrier gas and

narrower bore columns reduces run times nearly two-fold at no significant loss in chromatographic resolution. The SRM speed, linearity, dynamic range and transition ratio stability of the 7000A Triple Quadrupole mass spectrometer enable quantitative characterization for the fingerprinting of petroleum samples and the deconvolution of complex petroleum mixtures.

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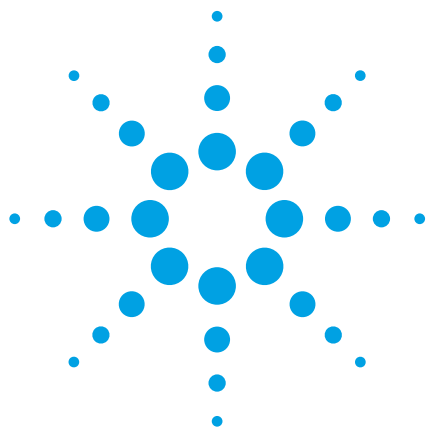
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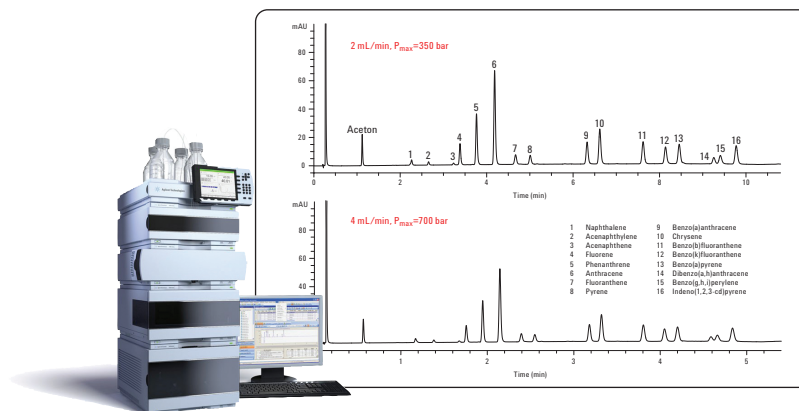
Fast analysis of polyaromatic hydrocarbons using the Agilent 1290 Infinity LC and Eclipse PAH columns

Application Note

Environmental

Author

Gerd Vanhoenacker
Research Institute for Chromatography
Kennedypark 26, B-8500 Kortrijk,
Belgium



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.



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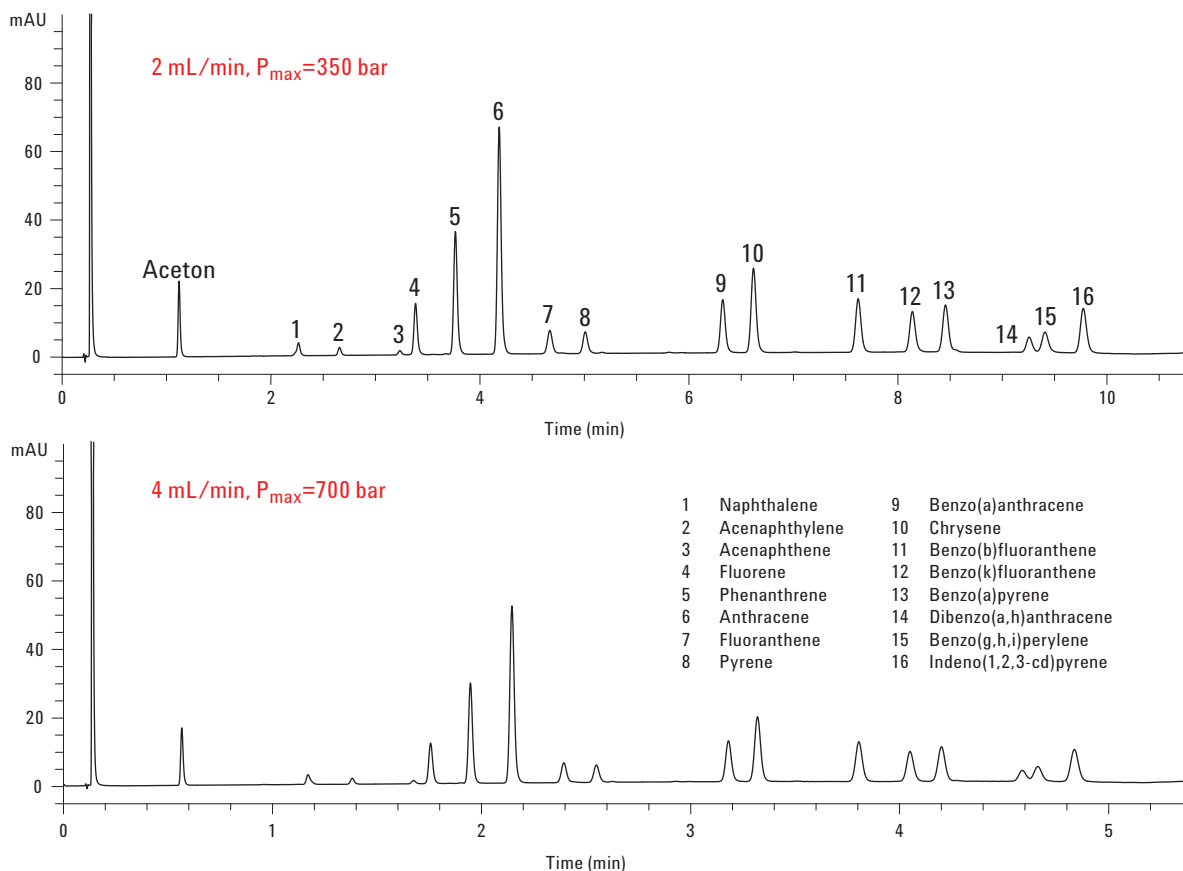


Figure 1

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:

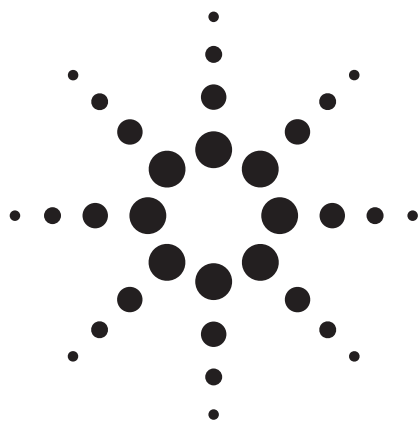
Column: ZORBAX Eclipse PAH 4.6 mm × 50 mm, 1.8 µm
 Mobile phase: A = water, B = acetonitrile
 Flow rate and gradient: 2 mL/min 0–0.33 min 40% B
 0.33–10 min 40–100% B
 4 mL/min 0–0.17 min 40% B
 0.17–5 min 40–100% B
 Injection volume: 0.2 µL
 Detector: Sig = 254/10 nm, Ref = off, 40 Hz
 Temperature: 25 °C

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Prefractionator for Reliable Analysis of the Light Ends of Crude Oil and other Petroleum Fractions

Application Note

Hydrocarbon Processing

Author

Roger L Firor
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

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.



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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.

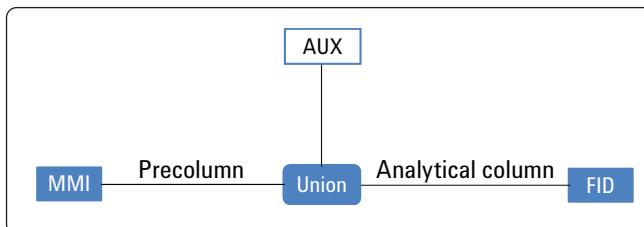


Figure 1. Basic precolumn backflush configuration with purged union.

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 × 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 × 0.53 mm deactivated retention gap
Column 1 Flow:	9 mL/min
Column 2:	5 m × 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.

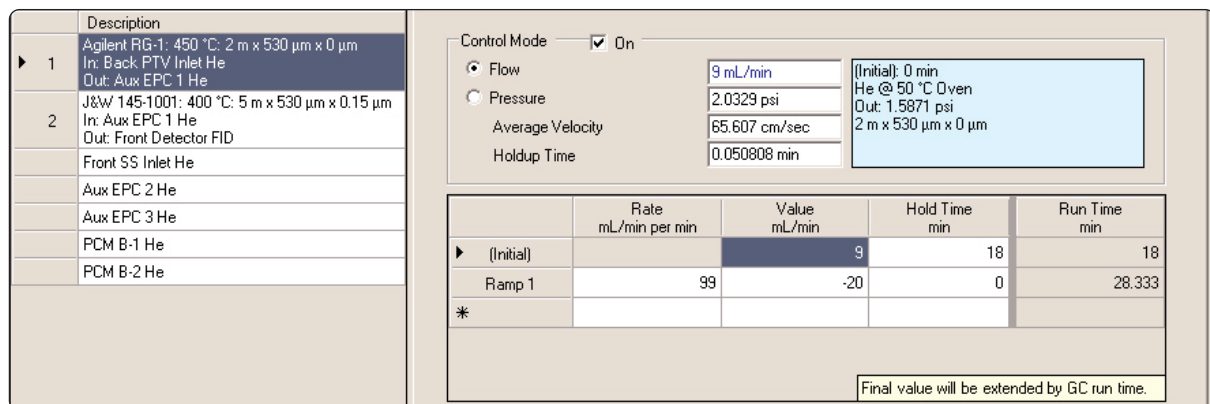


Figure 2A. Precolumn flows. Backflush starts at 18 min in this example.

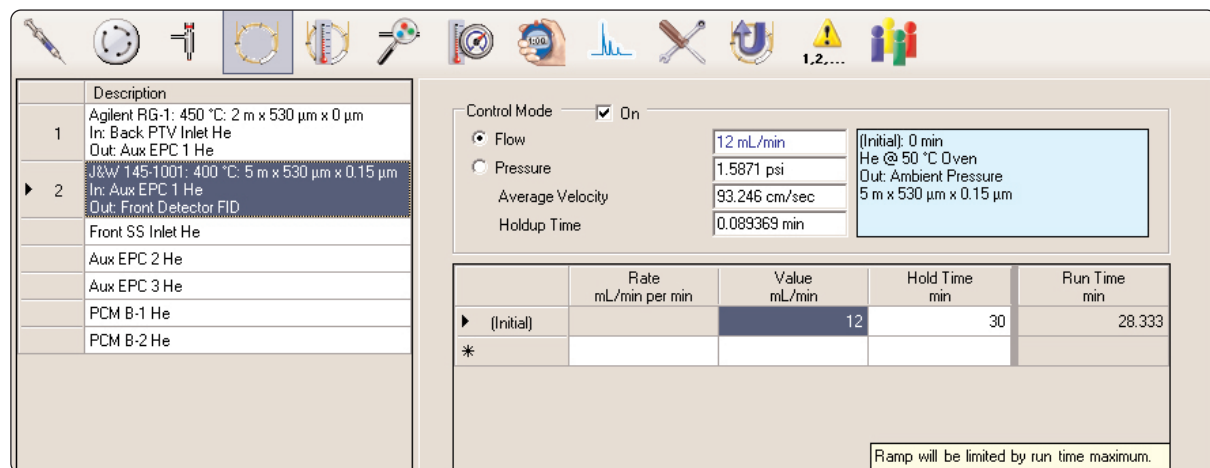


Figure 2B. Analytical column flow set at 12 ml/min for the entire run.

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).

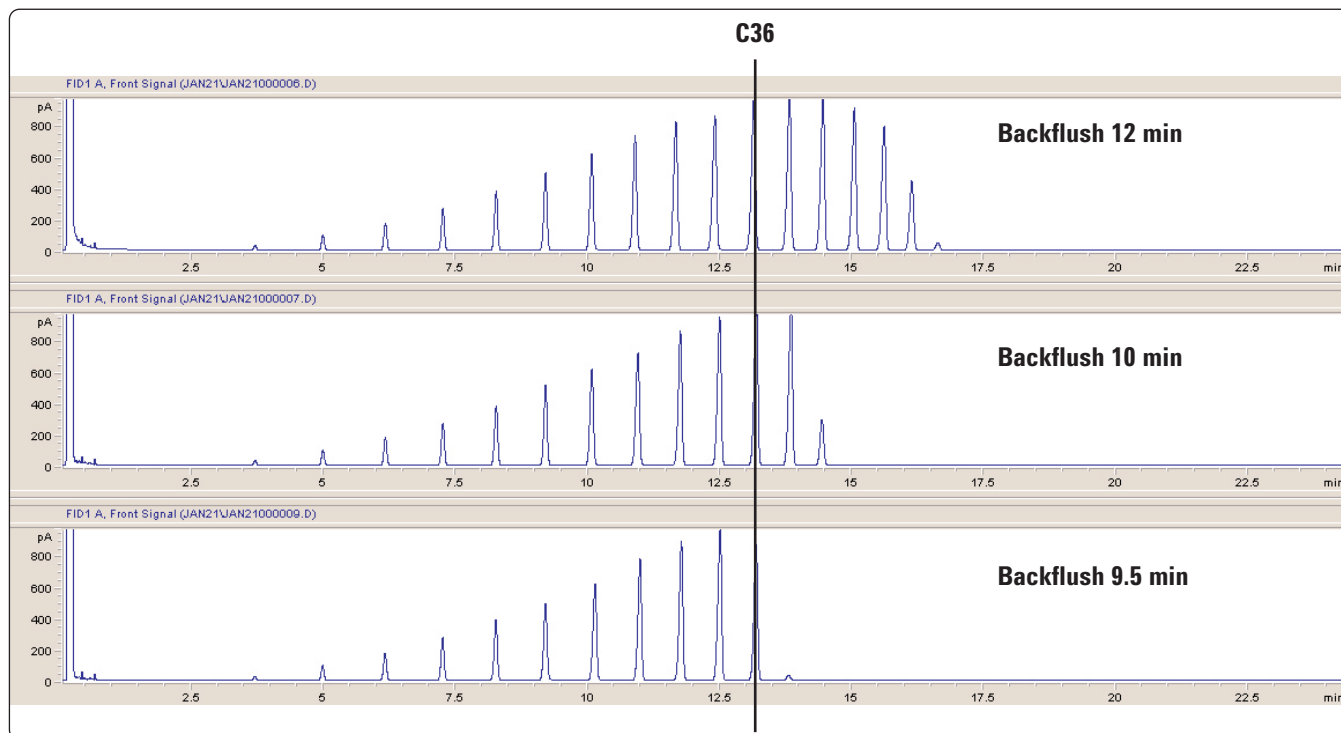


Figure 3. Polywax 500 chromatograms at three backflush times.

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

$$\text{BF Time} = (\text{Carbon number} - 5.56)/3.68$$

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 application 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.

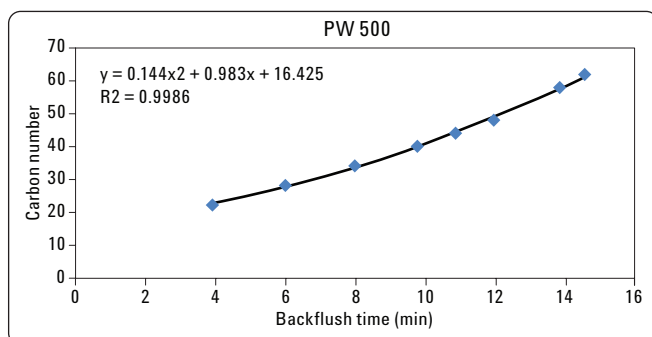


Figure 4A. Polynomial fit.

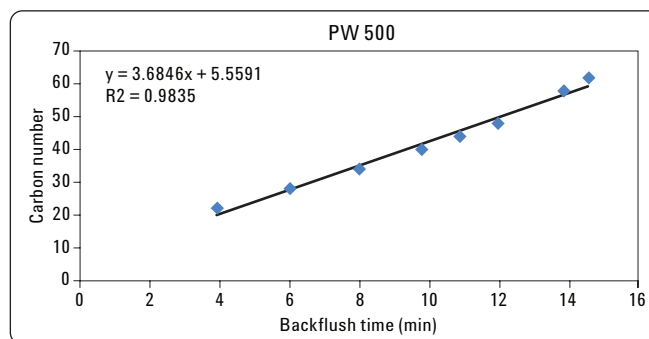


Figure 4B. Linear regression.

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).

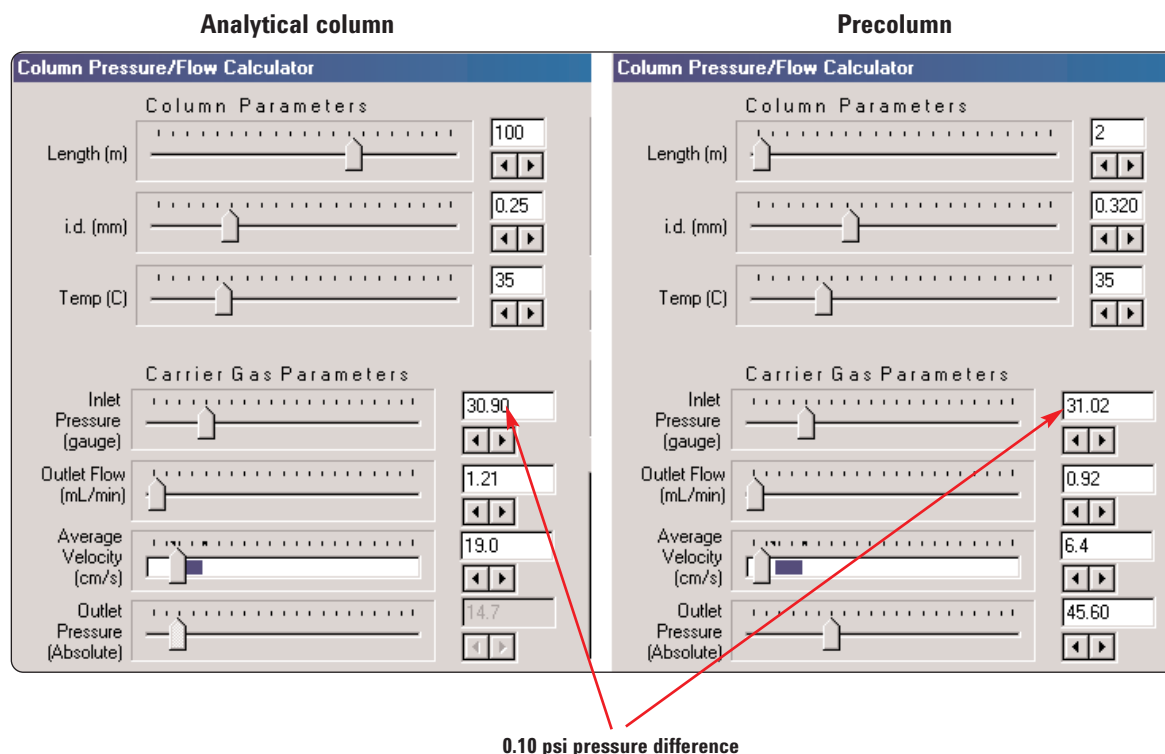


Figure 5. Pressure and flow setting for the analytical column (left pane) and precolumn (right pane).

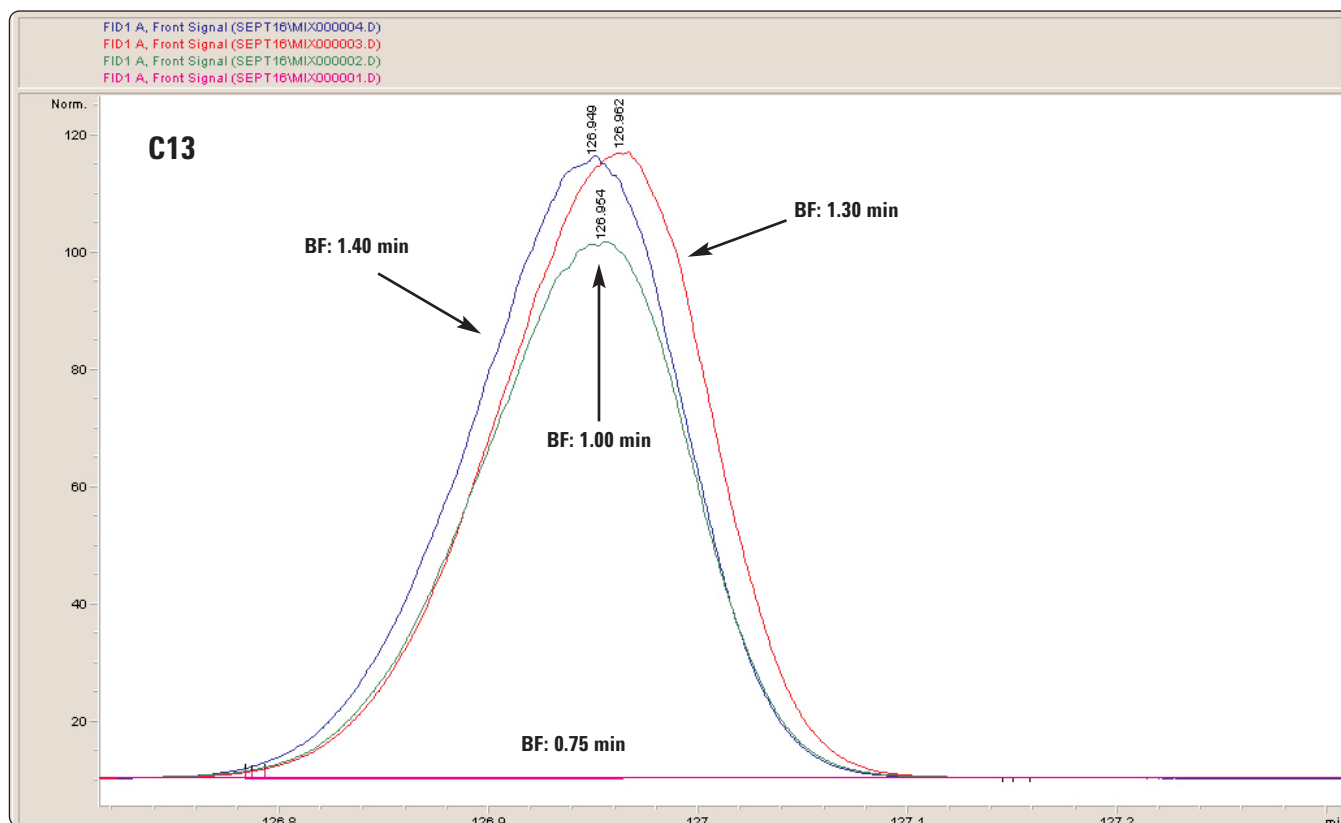


Figure 6. Fine tuning backflush time for ending transfer at C13. Trace at baseline: BF = 0.75 min, Peak at height of 100pa: BF = 1.00 min, Peaks at 117 pa: BF = 1.3 min and 1.4 min.

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 heavier 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
☐ Pressure
Average Velocity
Holdup Time

1.2 mL/min
30.859 psi
19.043 cm/sec
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 time.

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.

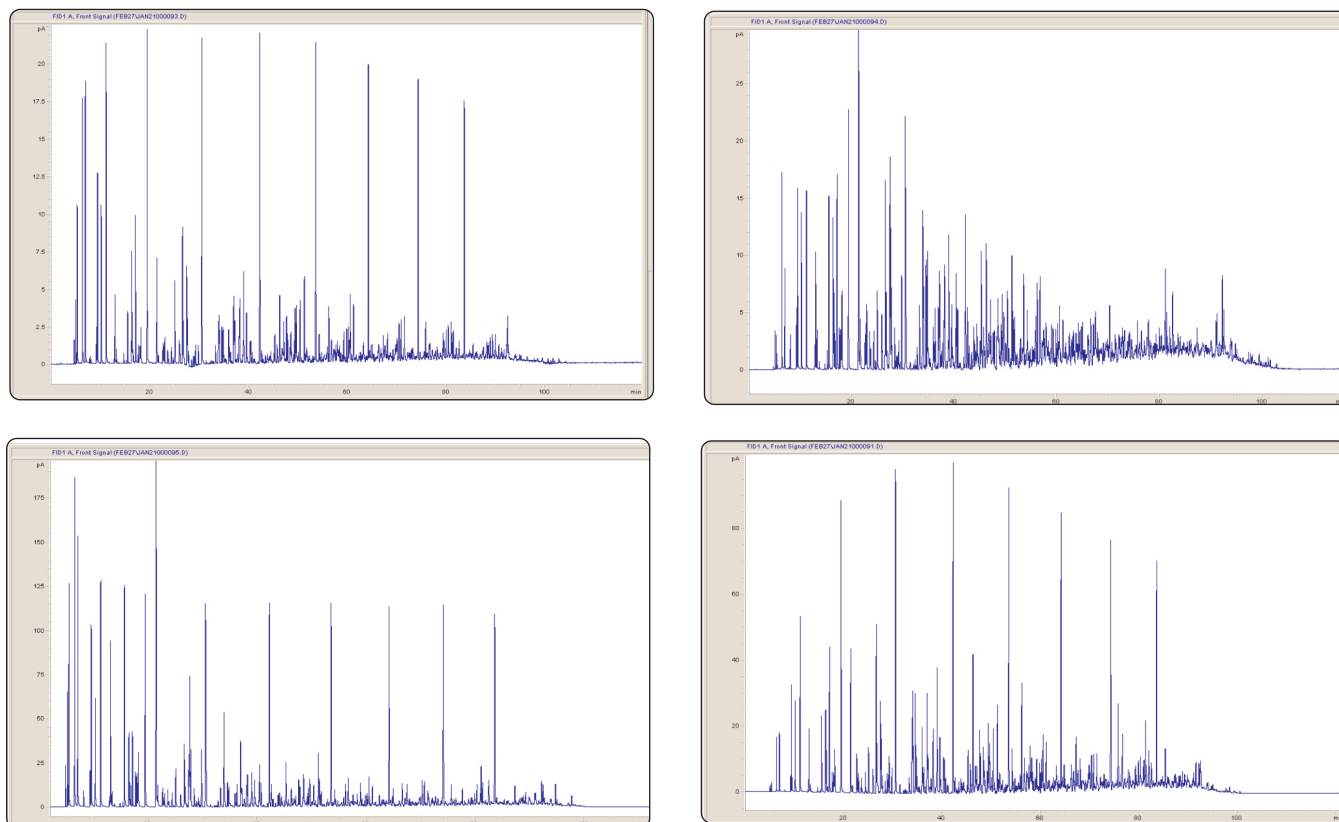


Figure 8. Four crude oils from different regions. Backflushed between C12 and C13.

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.

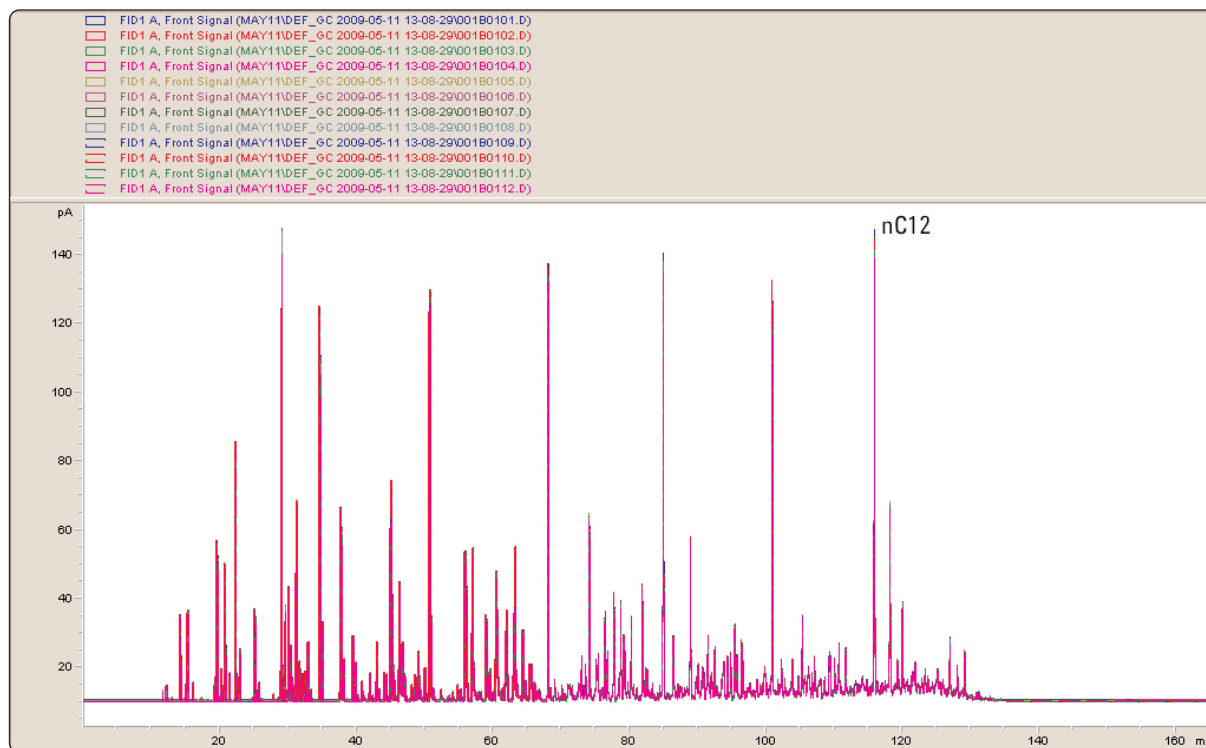


Figure 9. Overlay of twelve runs of crude oil backflushed between C12 and C13.

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 software: www.agilent.com/chem/flowcalculator

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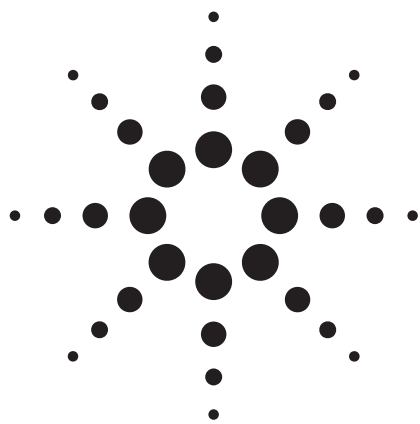
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Automated Preparation of Simulated Distillation Standards and Samples for ASTM Methods D2887, D7213, D7398 and D6352 using the 7693A System with Easy SamplePrep Software

Application Note

Hydrocarbon Processing

Author

Roger L. Firor
Agilent Technologies, Inc.
2850 Centerville Rd
Wilmington, DE 19808
USA

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- μ L syringe while the back tower is equipped with a 250- μ L 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 CS₂ for sample dilution while D6352 may use CS₂ 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.



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Experimental

The Agilent 7890A GC system was equipped with two Agilent 7693A towers and 150 sample tray. The front tower used a standard 5- μ L or 10- μ L syringe and the rear tower was equipped with the optional large syringe carriage with a 250- μ L 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 $\times$ 0.53 mm, 3.0 μ m DB-2887
Oven	40 $^{\circ}$ C (0 min) to 350 $^{\circ}$ C (5 min) @ 15 $^{\circ}$ C/min
Inlet	Multimode (MMI), G3510, 100 $^{\circ}$ C (0 min) to 340 $^{\circ}$ C (to end of run) @ 250 $^{\circ}$ 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 $\times$ 0.53 mm, 0.15 μ m DB-HT SimDis
Oven Program	35 $^{\circ}$ C (0 min) to 400 $^{\circ}$ C (5 min) @ 10 $^{\circ}$ C/min
Inlet	Multimode (MMI), 100 $^{\circ}$ C (0 min) to 400 $^{\circ}$ C (20 min) @ 250 $^{\circ}$ 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 $\times$ 0.53 mm, 0.15 μ m DB-HT SimDis
Oven Program	35 $^{\circ}$ C (0 min) to 435 $^{\circ}$ C (2 min) @ 10 $^{\circ}$ C/min
Inlet	Multimode (MMI), 100 $^{\circ}$ C (0 min) to 430 $^{\circ}$ C (hold to end of run) @ 250 $^{\circ}$ C/min
Split ratio	5 to 1
Flow	15 mL/min, constant flow mode
Agilent 7693A system	
Front tower	5 μ L syringe, G4513A
Back tower	250 μ L 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 μ L 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 poly-wax 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 CS₂ is shown in Figure 2.

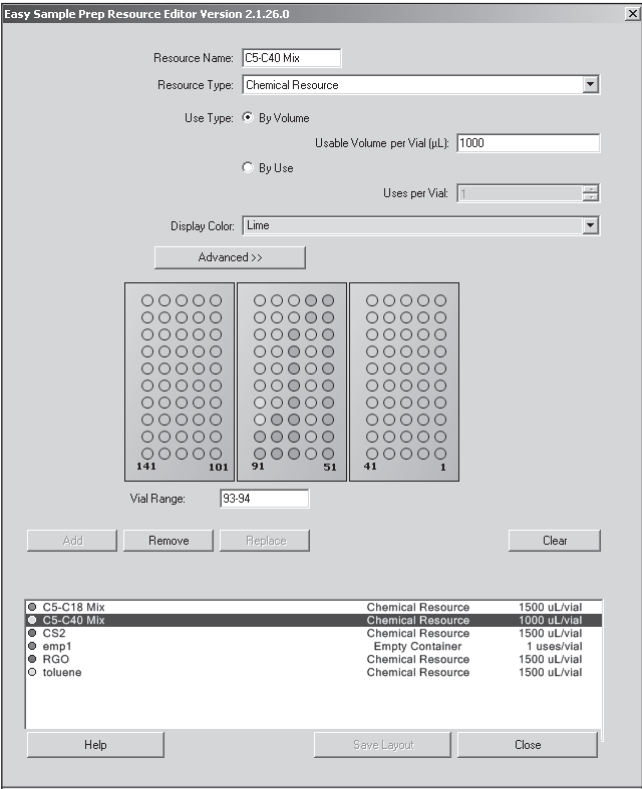


Figure 1. Example resource layout for various simulated distillation procedures. Each resource is assigned a unique color.

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.

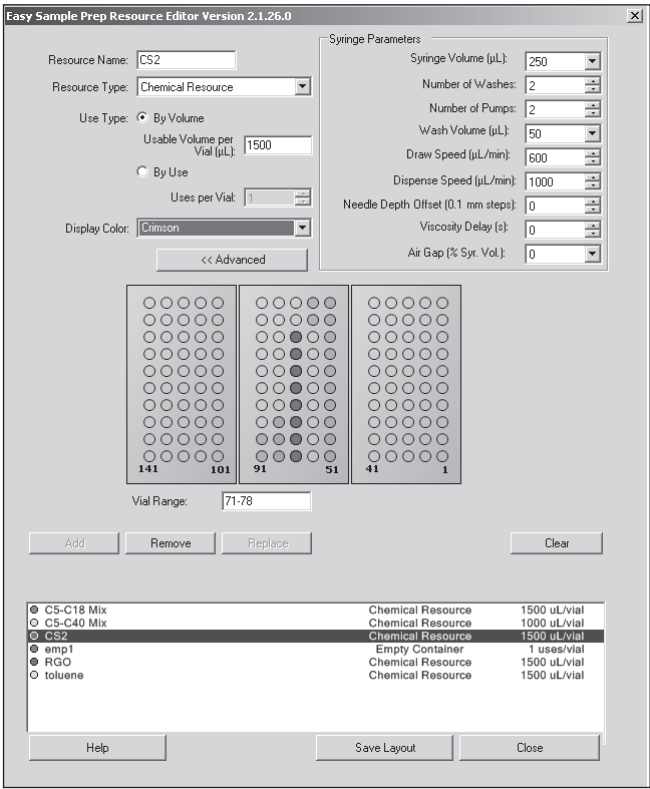


Figure 2. Advanced parameters shown (upper right box) for chemical resource CS₂.

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.

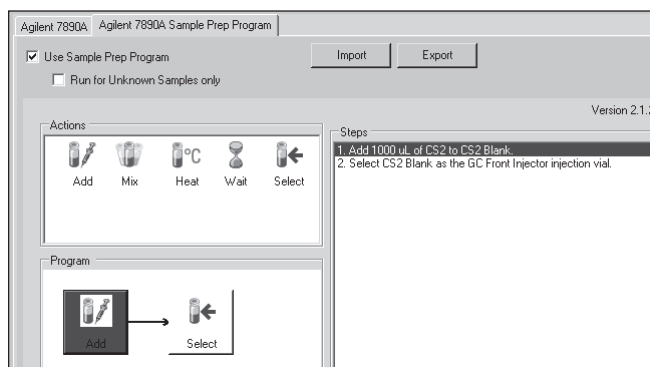


Figure 4. Easy Sample Prep program for the preparation of a CS_2 blank. An empty tray vial has been assigned the name "CS2 Blank". The select icon indicates that the prepared vial is to be injected.

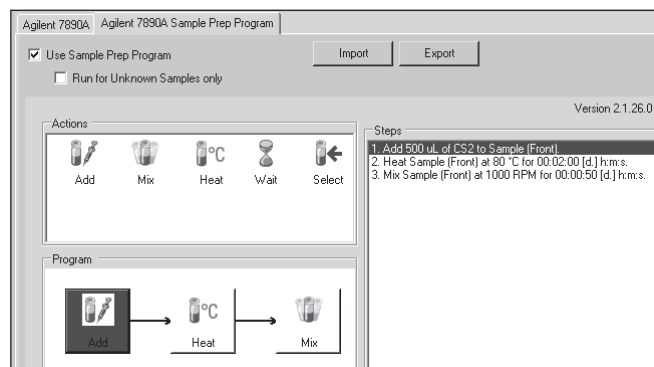


Figure 5. Easy Sample Prep program for preparation and injection of the C5 to C40 calibration mix. The "sample [front]" label defines sequence vials for the front tower.

A

Resource Name	Resource Type	Uses/Vial	Vial Ran
C5-C18 Mix	Chemical Resource	10	91-100
Empty	Empty Container	1	41-42

B

C

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.

Figure 6c. 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- μ L 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.

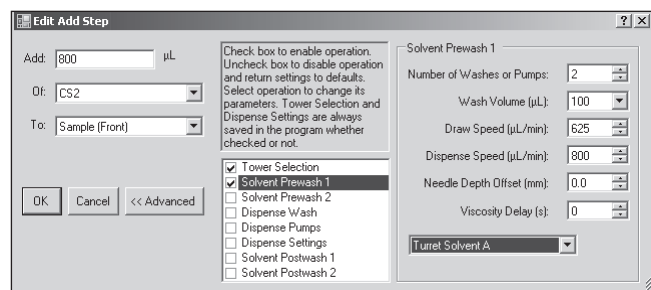


Figure 7. An example using solvent wash vial 1 (5 mL) in the turret of tower A.

Preparation of polywax standards for the higher temperature SimDis methods can be challenging due to their low solubility. Solvents such as CS₂ 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 μ L 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).

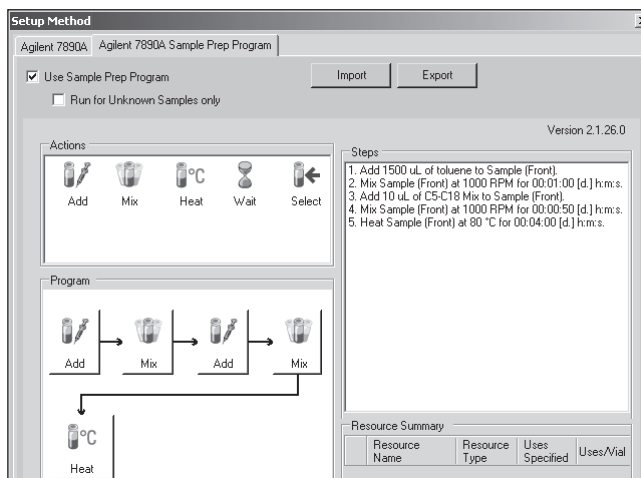


Figure 8. Polywax 500 prep procedure.

A resulting chromatogram for the injection of the prepared PW500 (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 μ L) of C₅-C₁₈ 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.

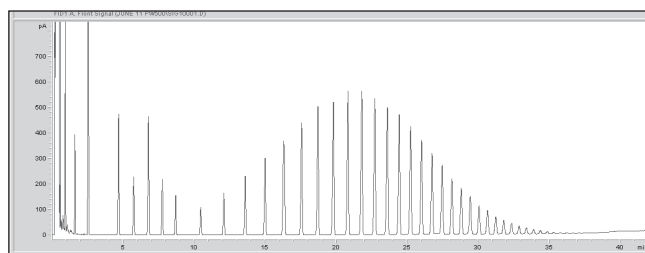


Figure 9. Polywax 500 with C₅-C₁₈ added. Multimode inlet, 2.5- μ L injection.

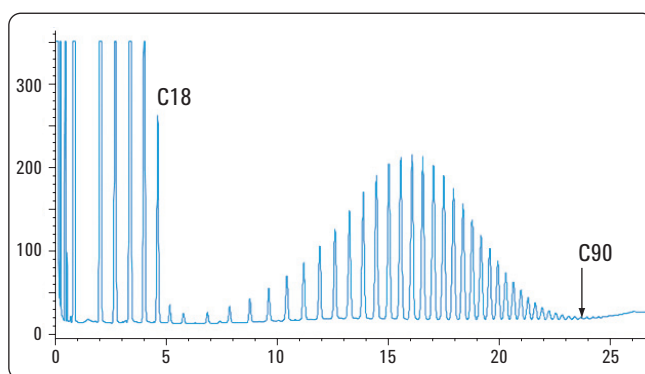


Figure 10. Chromatogram of PW 655.

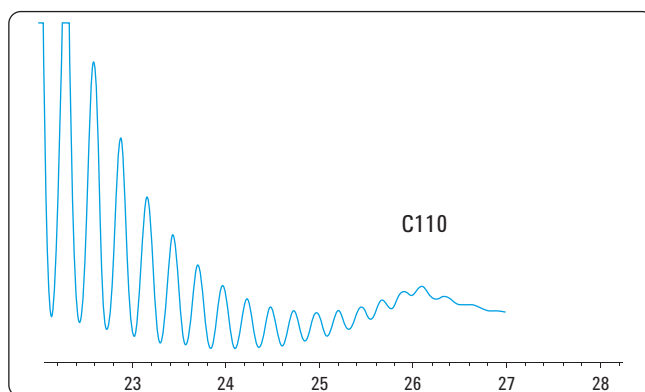


Figure 11. Polywax 655 to C110. Multimode inlet program: 150 $^{\circ}$ C (0 min) to 430 $^{\circ}$ C (hold to end of run) @ 200 $^{\circ}$ C/min. 7890A oven: 40 $^{\circ}$ C (0 min) to 430 $^{\circ}$ C (5 min) @ 15 $^{\circ}$ C/min. 3- μ L injection. Solvent is toluene.

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)

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.

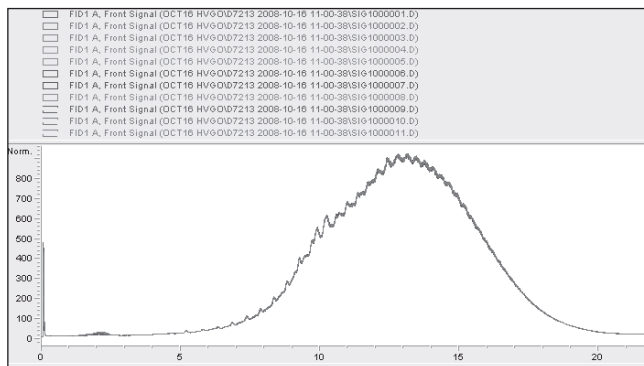


Figure 12. Overlay of 11 runs of HVGO, each prepared by using a Easy Sample Prep program.

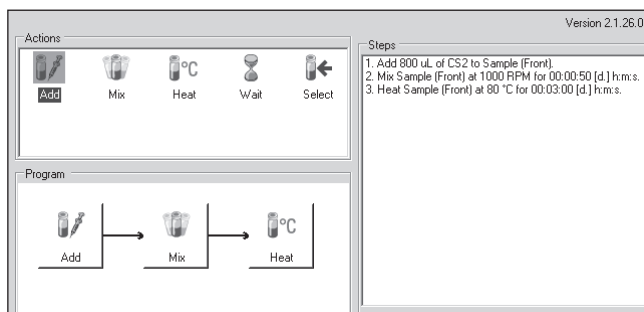


Figure 13. Preparation of HVGO for injection. CS_2 is used as the solvent.

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.

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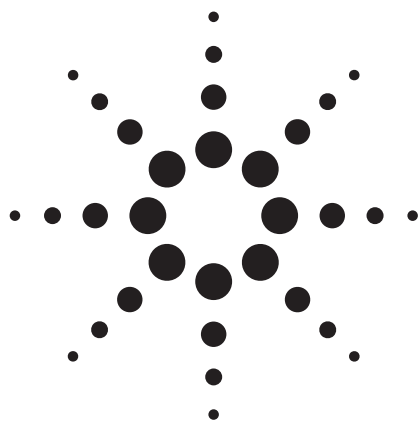
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Evaporation from 2-mL Vials on the Agilent 7696A Sample Prep WorkBench: Septa Unpierced, Septa Pierced with a Syringe Needle, Septa with an Open Hole

Application Note

Author

W. Dale Snyder
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

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.



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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).

Table 1. Average Evaporation Rates from Vials with the Different Septa

Solvent: hexane, bp = 70 °C

	Septum:	A		B		C	
		%loss	%loss/hr	%loss	%loss/hr	%loss	%loss/hr
After:							
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	
		%loss	%loss/hr	%loss	%loss/hr	%loss	%loss/hr
After:							
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

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.

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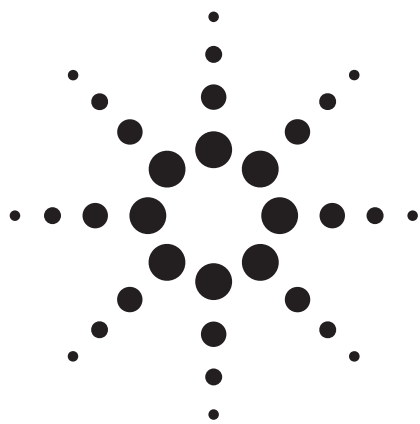
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Agilent 7696A Sample Prep WorkBench: How to Automate Preparation of a Sample Set by Serial Dilution for Measurement of Flame Ionization Detector Performance

Application Note

Author

W. Dale Snyder
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

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.



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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- μ L syringe (p/n G4513-60561). The front injector used a standard syringe carriage containing a 100- μ L 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 μ L solvent + 100 μ L sample and the second used half these amounts: 450 μ L solvent + 50 μ L 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 μ L C_{13} to a 1 mL volumetric and diluting to mark.*

The first sequence prepared the 1 mL sample (900 μ L + 100 μ L) by adding 900 μ L solvent to an empty vial (see Appendix for syringe parameters). The sequence specified vials 2 through 9.

* 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.

The second sequence specified sample dilutions according to the following steps. (see Appendix for syringe parameters):

Step	Function
1	Add 100 μ L of Sample (Front) to vial #2
2	Mix vial #2 at 1500 RPM for 0 min 5 sec
3	Add 100 μ L of vial #2 to vial #3
4	Mix vial #3 at 1500 RPM for 0 min 5 sec
5	Add 100 μ L of vial #3 to vial #4
6	Mix vial #4 at 1500 RPM for 0 min 5 sec
7	Add 100 μ L of vial #4 to vial #5
8	Mix vial #5 at 1500 RPM for 0 min 5 sec
9	Add 100 μ L of vial #5 to vial #6
10	Mix vial #6 at 1500 RPM for 0 min 5 sec
11	Add 100 μ L of vial #6 to vial #7
12	Mix vial #7 at 1500 RPM for 0 min 5 sec
13	Add 100 μ L of vial #7 to vial #8
14	Mix vial #8 at 1500 RPM for 0 min 5 sec
15	Add 100 μ L 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 μ L, 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 μ L. The volume increase of the last sample was 100 μ L or 50 μ L 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.

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

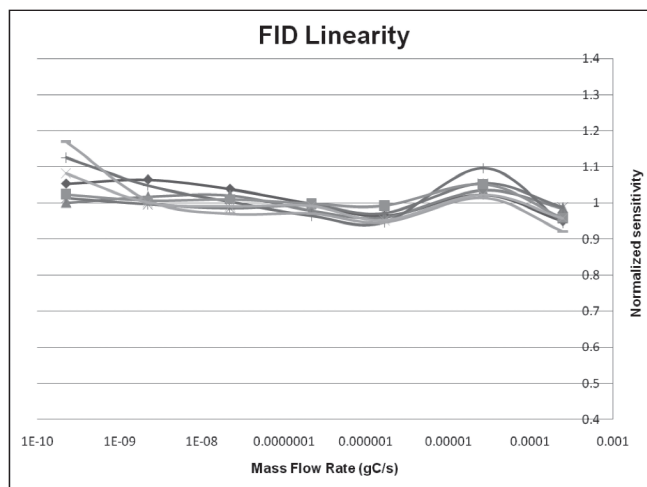


Figure 1. Linearity Plots for all eight runs overlaid.

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 μ L 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 (μ L)					50			
Draw speed (μ L/min)					1250	1250		
Dispense speed (μ L/min)					3000	3000		
Needle depth offset (mm)					0	0		
Viscosity delay(s)					2	2		
Turret solvent								
Air gap (% syr.vol.)						0		

100 μ L 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 (μ L)		10		20	10			
Draw speed (μ L/min)		300		300	300	300		
Dispense speed (μ L/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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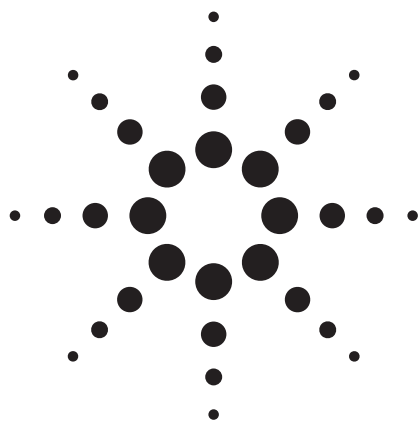
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Improved Data Quality Through Automated Sample Preparation

Application Note

Authors

Rebecca Veeneman and Dale Snyder
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

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.



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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 $^{\circ}\text{C}$ 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).

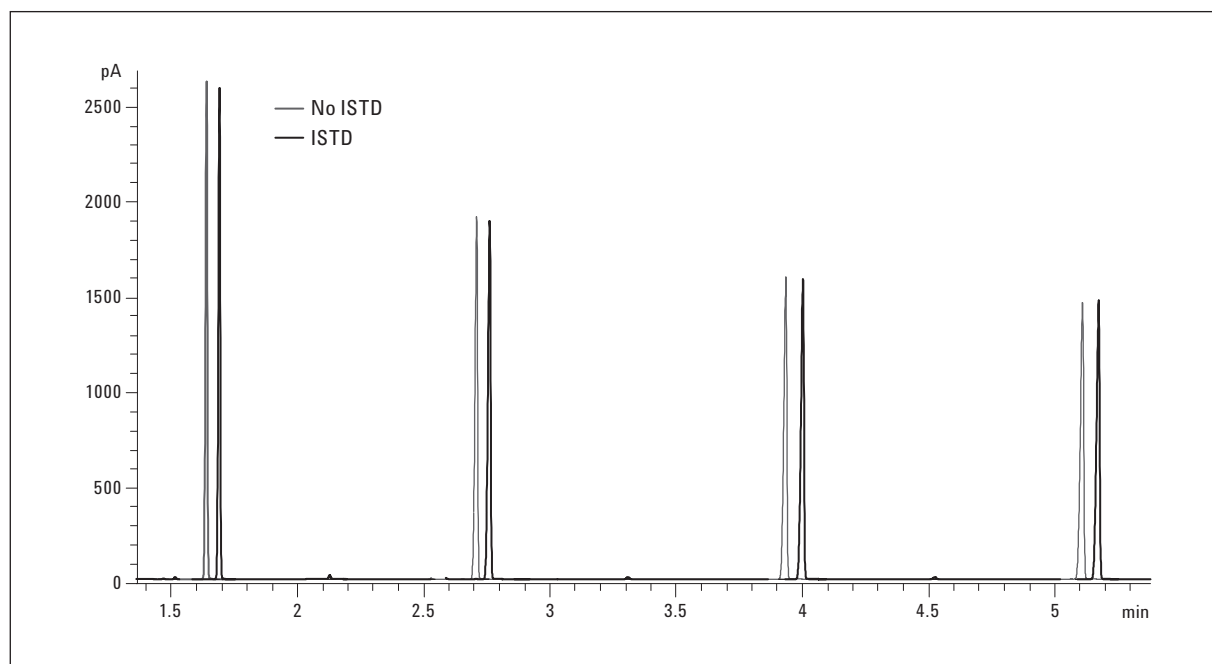


Figure 4. GC chromatograms (slightly offset) are shown for a standard solution dispensed and diluted with and without an ISTD added. No difference in peak areas are observed.

For the 10 samples diluted for LC analysis, similar results were obtained. Dispensing all three volumes with a 250 μ L 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 con-

trast, 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%.

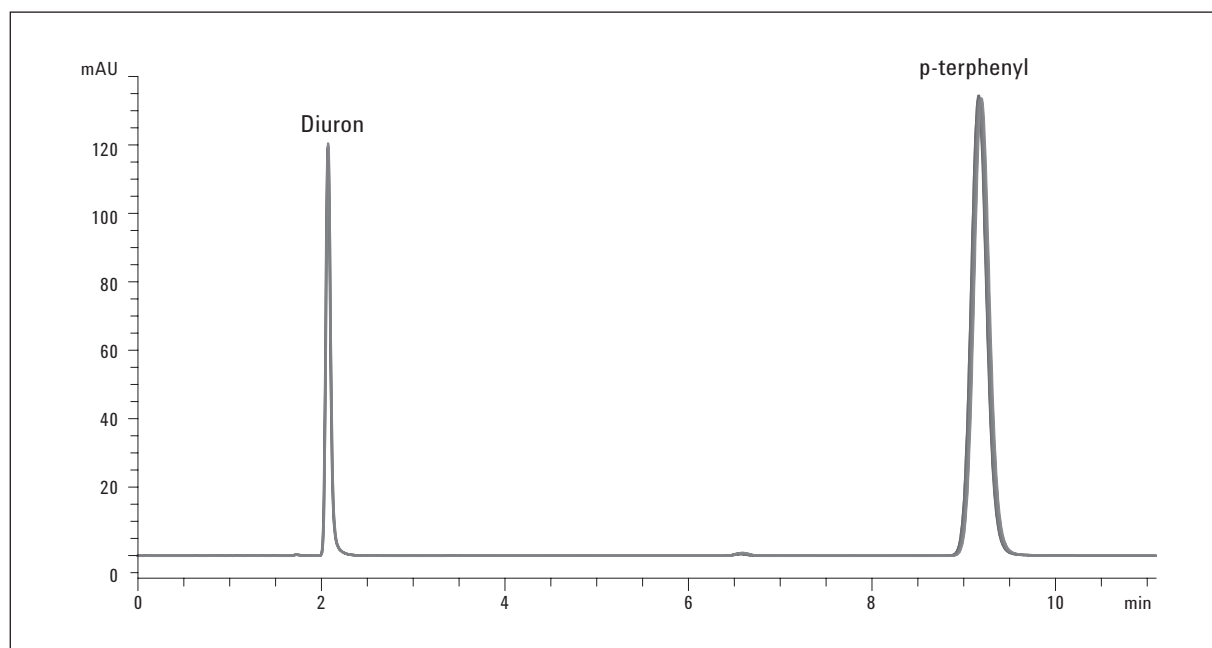


Figure 5. LC Chromatograms are shown for a diluted pesticide standard with an ISTD added. Excellent reproducibility was observed for the five samples shown.

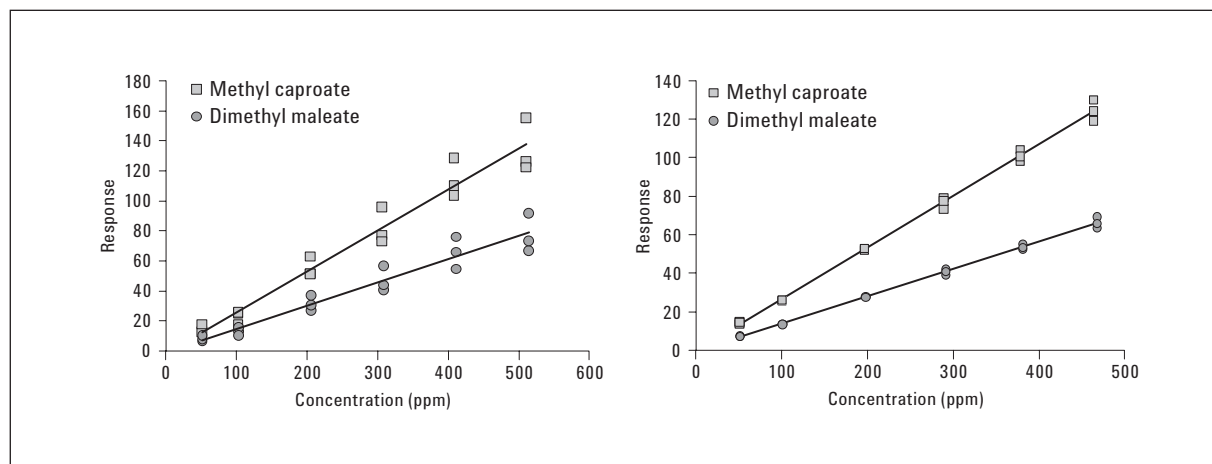


Figure 6. Two calibration curves are shown for two representative analytes. The curves on the right, prepared with the Agilent 7696 Sample Prep WorkBench, are visibly more reproducible than the curves made manually on the left.

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 μ L of solvent was used, excluding the wash vials. This can result in substantial cost savings for laboratories. Additionally, calibration 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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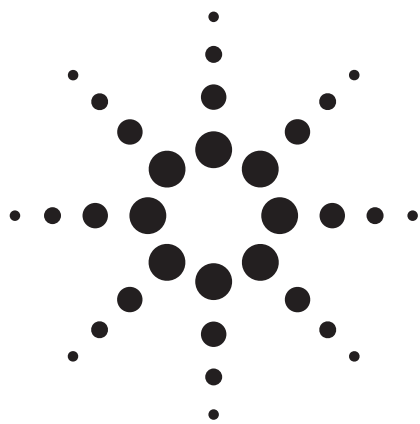
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GC Analysis of Sulfur Components in Propylene using a Pulsed Flame Photometric Detector

Application Note

Hydrocarbon Processing

Author

Helena Jacobse
Agilent Technologies
Herculesweg 8
4338 PL Middelburg
The Netherlands

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.



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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 ₂ S, COS, and CH ₃ SH
Injection volume:	1 mL
Injection:	Gas sampling valve

Results and Discussion

The stationary phase shows good selectivity between H₂S, 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 H₂S, COS, and CH₃SH 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.

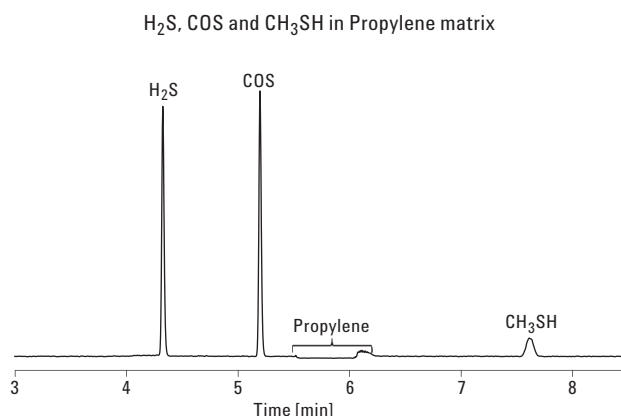


Figure 1. Chromatogram of sulfur compounds H₂S, COS and CH₃SH in a propylene matrix, using the Agilent J&W Select Low Sulfur with GC-PFPD.

Conclusion

The Agilent J&W Select Low Sulfur used in a GC with a sulfur specific detector, such as a PFPD, can detect H₂S, COS and CH₃SH 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 H₂S, 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.

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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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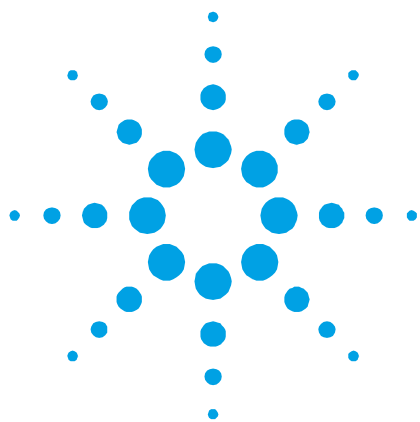
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Onsite additive depletion monitoring in turbine oils by FTIR spectroscopy

Fast, easy antioxidant measurement

Application Note

Author

Frank Higgins

Agilent Technologies,
Connecticut, USA



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.



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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.

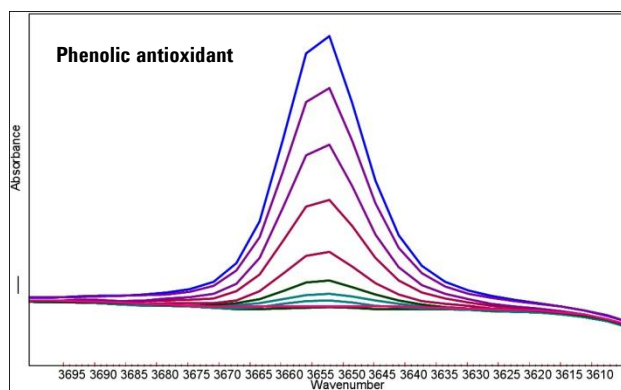


Figure 1. FTIR spectral overlay of the phenolic antioxidant functional group bands depleting as a function of time. The strongest band (light blue) is that of new ISO 32 turbine oil and the weakest absorbance (light green) is from turbine oil that has started to show some oxidation.

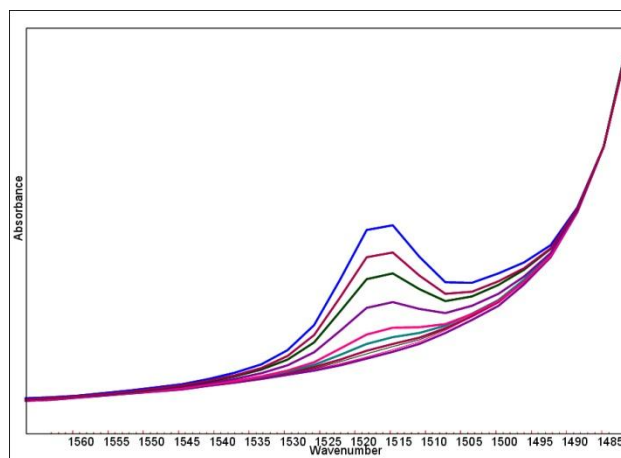


Figure 2. FTIR spectral overlay of the aminic antioxidant functional group depleting as a function of time. The strongest absorbance (red) is aminic antioxidant in new ISO 32 turbine oil and the weakest bands (blue and green) are from turbine oil with spent antioxidant.

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.

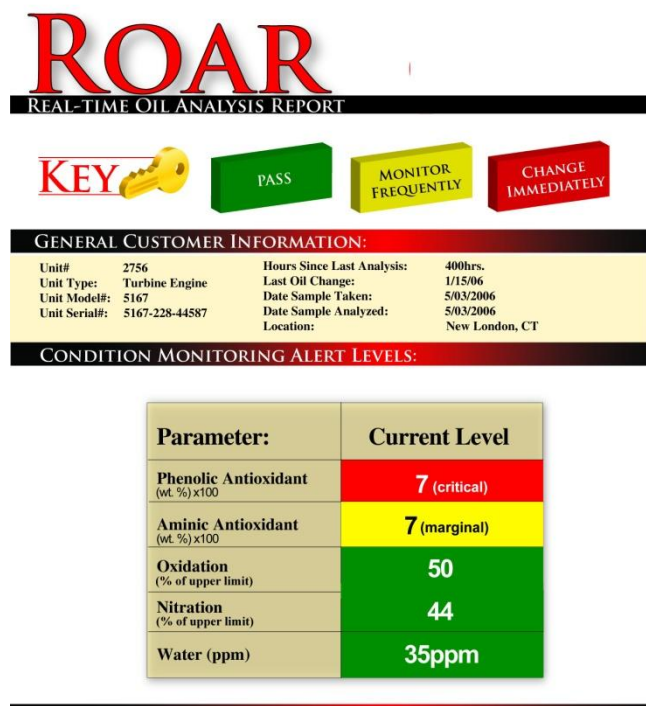


Figure 3. Agilent 5500t FTIR software presents the user with the specific concentration of phenolic and aminic antioxidants as well as crucial information about oxidation by-products and level of water contamination

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.

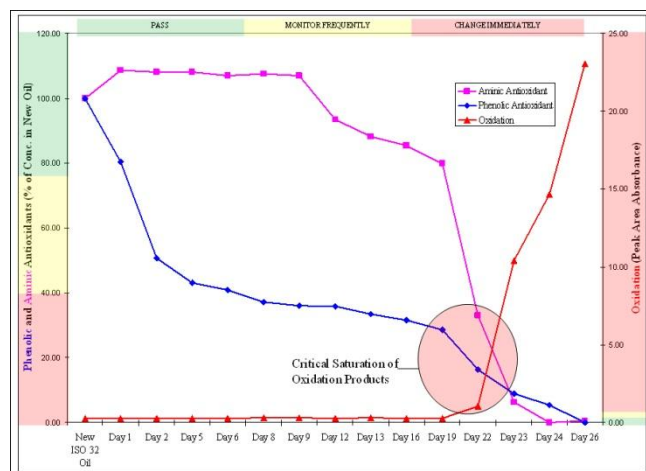


Figure 4. The additive depletion (% relative to new oil concentrations, left scale) and oxidation formation (right scale) trend analysis in thermally stressed ISO 32 turbine oil generated using the Agilent 5500t FTIR spectrometers

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.

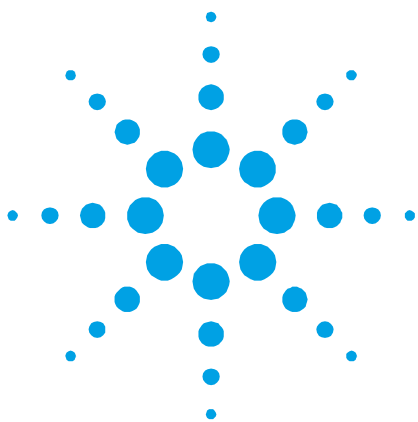
The capability of measuring additives in turbine oil by FTIR spectroscopy eliminates the issues associated with other measurements, including the need for sample preparation, calibrating, and maintaining electrodes based on voltammetric systems. The measurements are more rapid than electrode based antioxidant 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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Onsite quantitative FTIR analysis of water in turbine oil

Application Note

Author

Frank Higgins

Agilent Technologies,
Connecticut, USA



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.



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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 $R^2=0.977$ 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 $R^2=0.996$.

Therefore, this calibration is optimized for the low levels of water (<500 ppm), but is still quite accurate for predictions of higher water levels above 500 ppm if necessary.

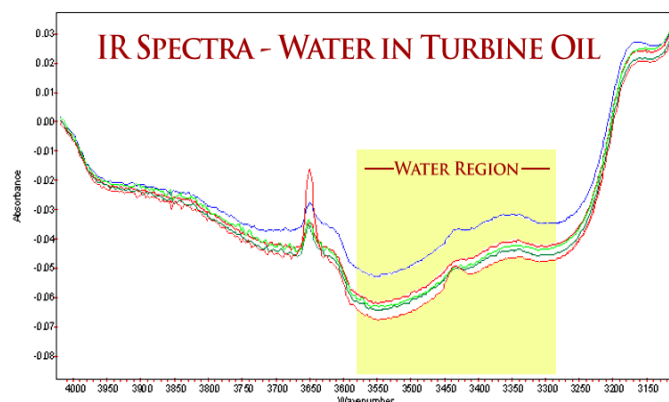


Figure 1. The overlaid IR spectra of turbine oil with the water absorbance region expanded, water values from bottom to top are 30 ppm (red), 80 ppm (dark green), 217 ppm (light green), 533 ppm (red), and 1460 ppm (blue)

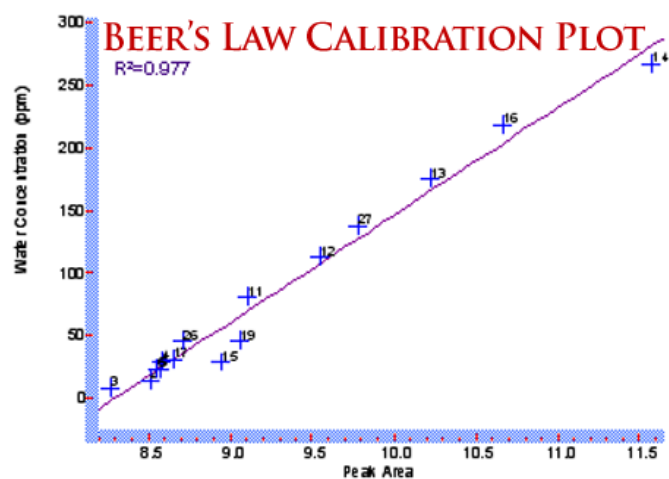


Figure 2. The calibration plot of KF water values (ppm) versus peak absorbance area for water in turbine oil using a Beer's Law peak area method

PLS model

The PLS chemometric model uses more sophisticated mathematics 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 $R^2=0.990$.

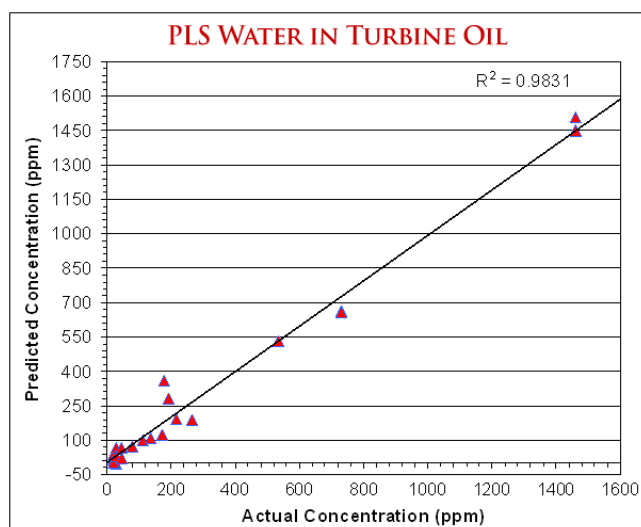


Figure 3. The PLS predicted versus actual plot of KF values using Agilent 4500 Series FTIR spectrometer

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.

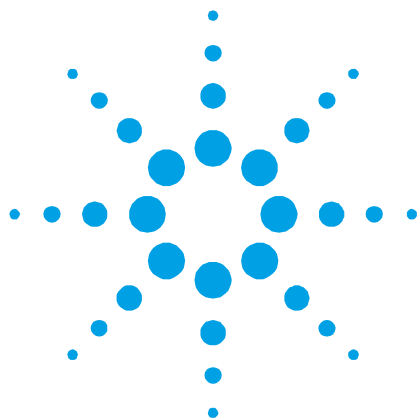


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Agilent Technologies



Returning to Fixed Pathlength Infrared Spectroscopy: Gaining Detail and Removing the Obstacles

Author

John Coates

Coates Consulting, Newtown,
CT

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 an 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).



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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} / $2.0\text{ }\mu\text{m}$ to $25\text{ }\mu\text{m}$)
- 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 ($<200\text{ }\mu\text{m}$, $<0.2\text{ mm}$)
- 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 $10\text{ }\mu\text{m}$ to $25\text{ }\mu\text{m}$, 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, fulfilling 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.

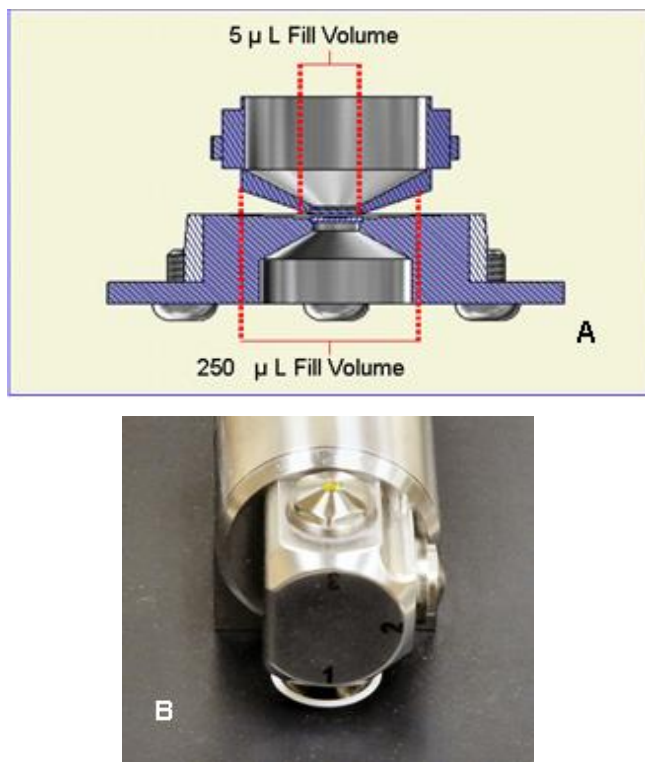


Figure 1. The 5500 DialPath FTIR sampling point concept (A); provides a user selectable pathlength, with one of three fixed/calibrated optical paths, designated 1, 2 and 3 (B)

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} .

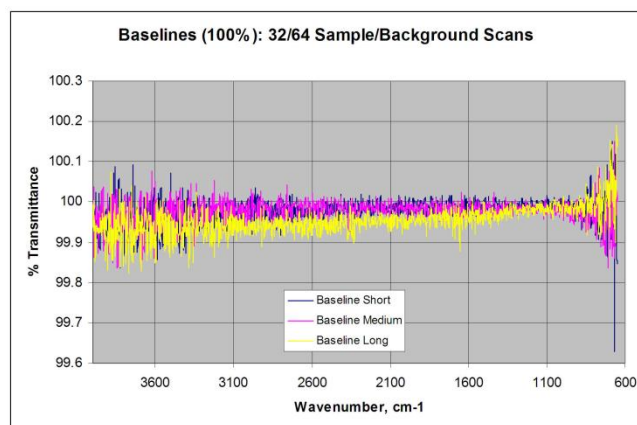


Figure 2. 100% Baseline performance; spectra from long, medium and short pathlengths presented with an average SNR of 8000:1 (2100 cm^{-1} to 1100 cm^{-1})

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.

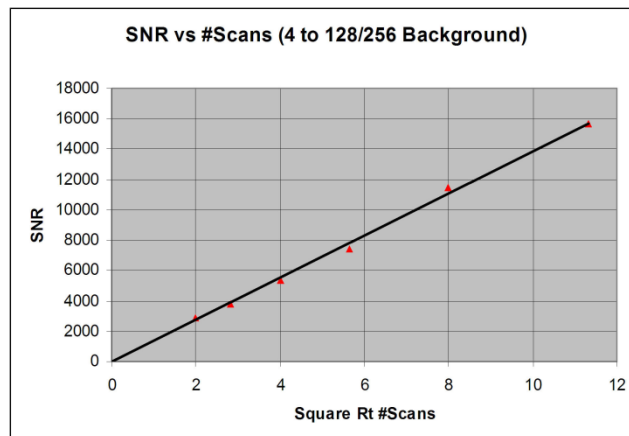


Figure 3. The adherence of the measurement system to the square root law of measured SNR

It is appropriate to compare the spectral data from a standard diamond ATR system with the fixed pathlength (5500 DialPath) measurement (Figure 4).

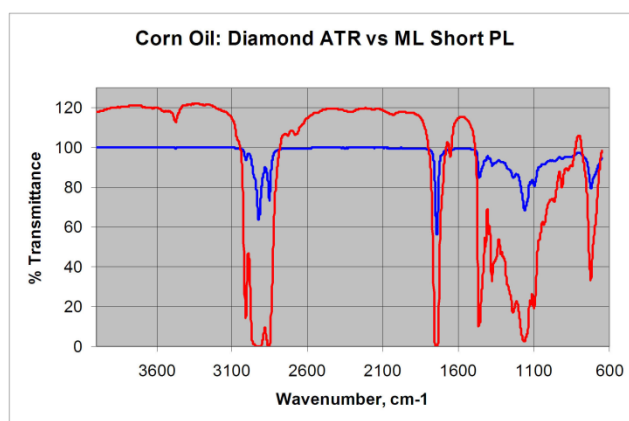


Figure 4. Comparison of the effective pathlength of a diamond ATR integrated system with the short fixed pathlength ($\sim 30 \mu\text{m}$) transmission spectrum for corn oil

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 (30 μ m, 50 μ m and 100 μ m). 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 μ m, medium = 52.6 μ m, and long = 114.7 μ m.

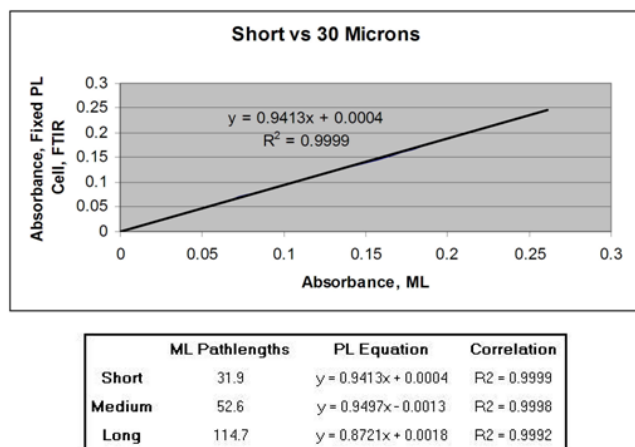


Figure 5. Example calibration for the short pathlength (No 1) of the Agilent 5500 DialPath FTIR system based on comparisons with a calibrated fixed pathlength cell for a series of xylene solutions

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 μ m 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).

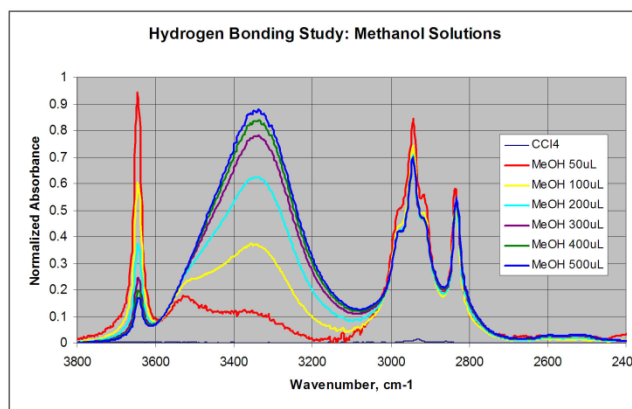


Figure 6: Dilute solutions of methanol in carbon tetrachloride; a study of the effects of hydrogen bonding in non-polar solvents

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+ μ m 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 ($100+\text{ }\mu\text{m}$ pathlength).

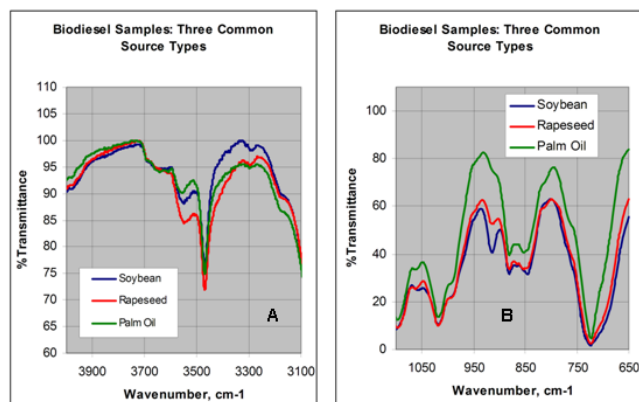


Figure 7. Detailed information from the base ester components used in the production of biodiesel methyl esters; hydroxyl (A) and unsaturation (B) functionalities

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.

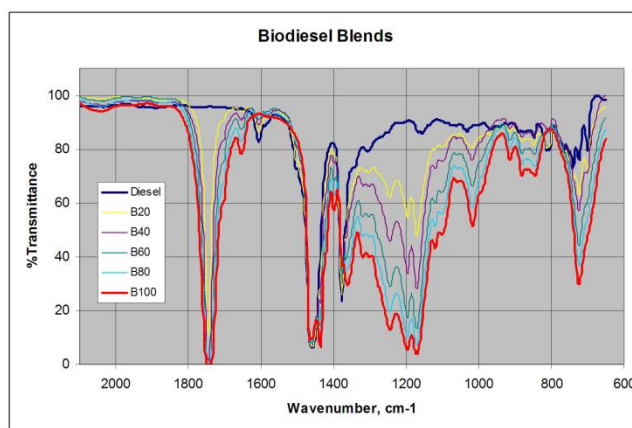


Figure 8. Measurement of biodiesel blends, experimental data from B0 (diesel fuel) to B100 (biodiesel) and intermediate biodiesel/diesel blends

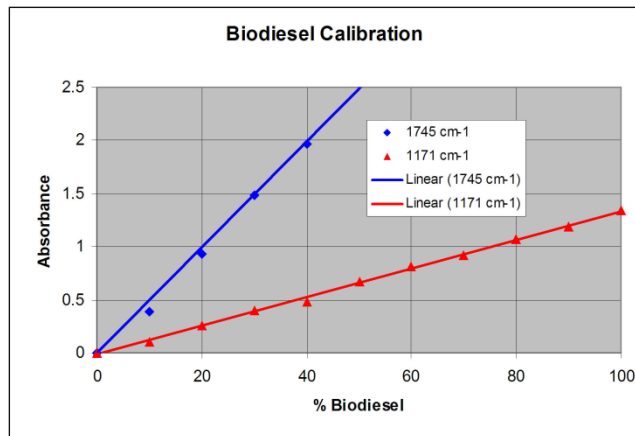


Figure 9. Quantitative measurement of biodiesel blends, B0, B10 to B90 and B100

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.

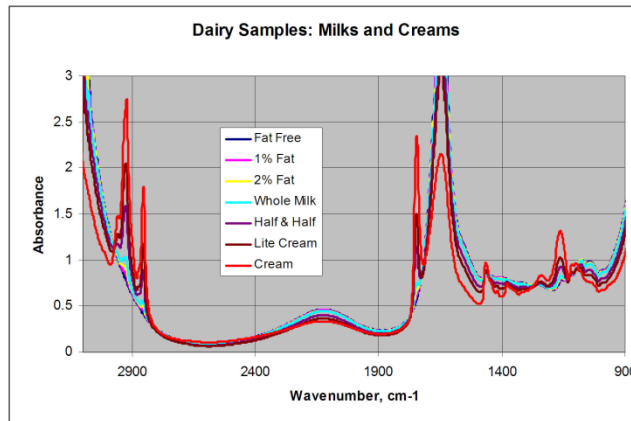


Figure 10. Dairy product spectra; short fixed pathlength (~30 mm), from fat free skim milk to standard heavy cream

Summary of the role and benefits of a “fixed” dial-a-pathlength system

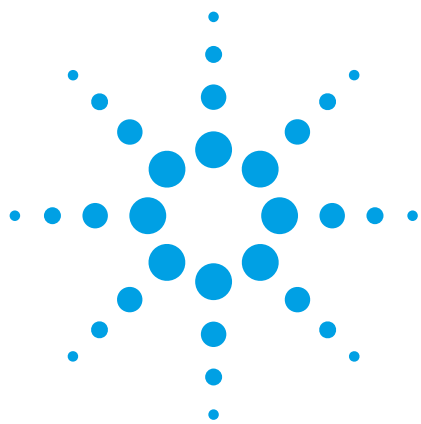
This article has reintroduced the concept of making fixed pathlength mid-infrared transmission measurements without the complexity or the difficulties of the traditional sample handling method. A two-step approach summarized as “drop it on” and “wipe it off” is proposed, where the sample is put in place 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

Authors

J. Moffett and G. Russell

Agilent Technologies
Melbourne, Australia

J. P. Lener

Agilent Technologies
Massy Cedex, France



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.



Agilent Technologies

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.

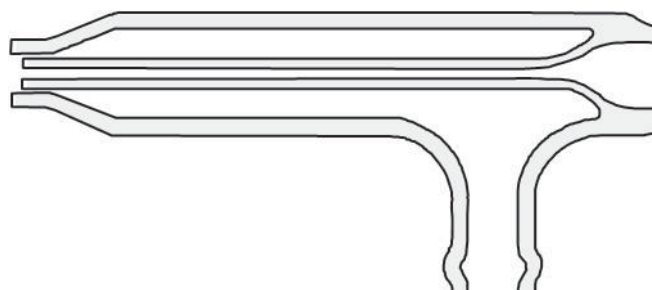


Figure 2. Concentric glass nebulizer

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 (Table 1). 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.

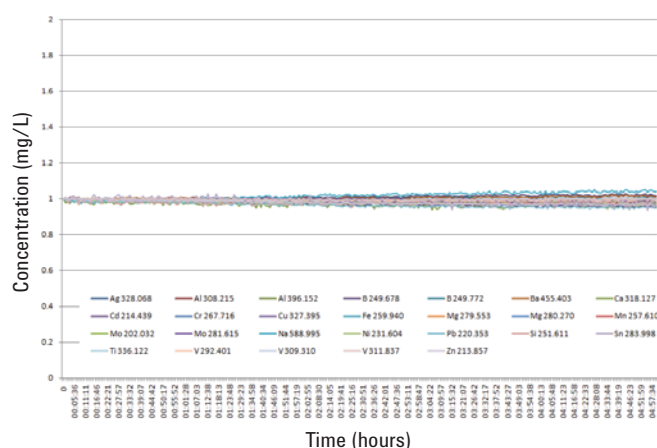


Figure 3. Long-term stability of the OneNeb nebulizer with diisobutyl ketone

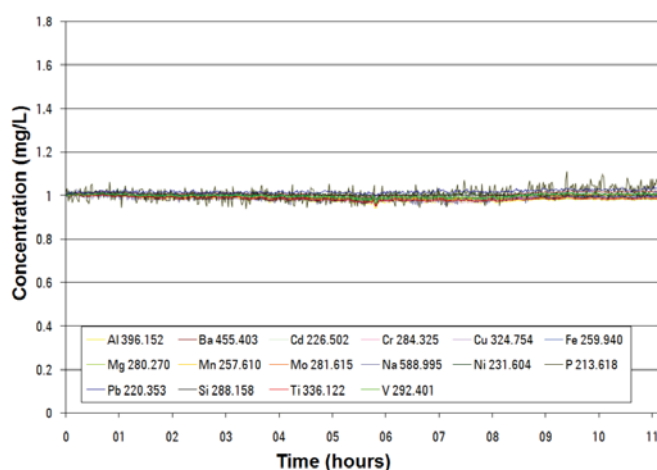


Figure 4. Long-term stability of the OneNeb nebulizer with ShellSol

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
Ti 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 $\mu\text{L}/\text{min}$, potentially allowing the analysis of volume limited samples.

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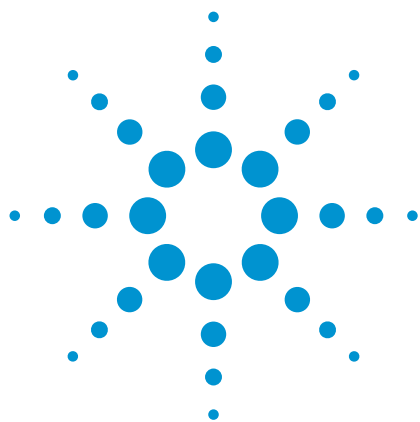
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Agilent Technologies



Using a Dual LTM Series II System with Flow Modulated Comprehensive GCxGC

Application Note

Application Area Identifier

Author

Roger L Firor
Agilent Technologies, Inc.
2850 Centerville Rd
Wilmington, DE
19808

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 $\times$ 0.18 mm $\times$ 0.25 μ m DB5ms for the first dimension, a 7 m $\times$ 0.25 mm $\times$ 0.2 μ m HP-INNOWax for LTM module 1 and a 5 m $\times$ 0.25 mm $\times$ 0.15 μ m 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.

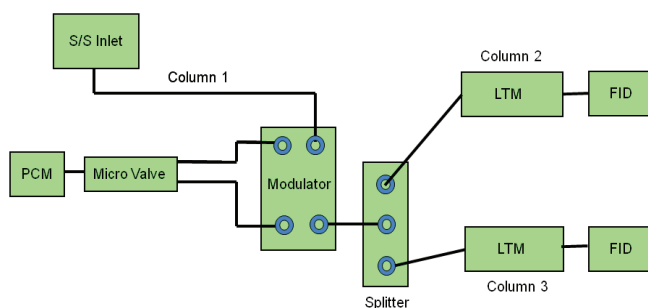


Figure 1. Diagram of the dual LTM GCxGC system.

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 overflow 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.

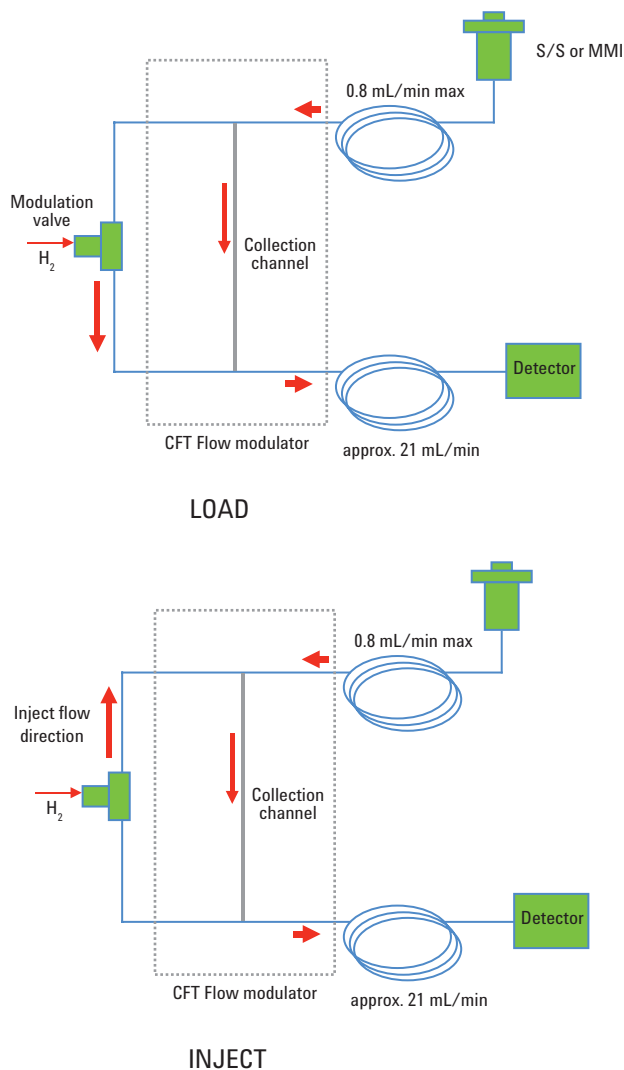


Figure 2. Operational detail of the flow modulator showing load and inject states.

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.

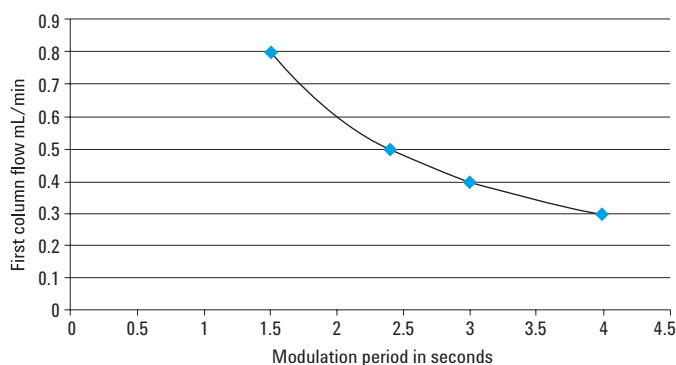


Figure 3. Relationship between modulation period and first dimension column flow rate.

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	7 m × 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.

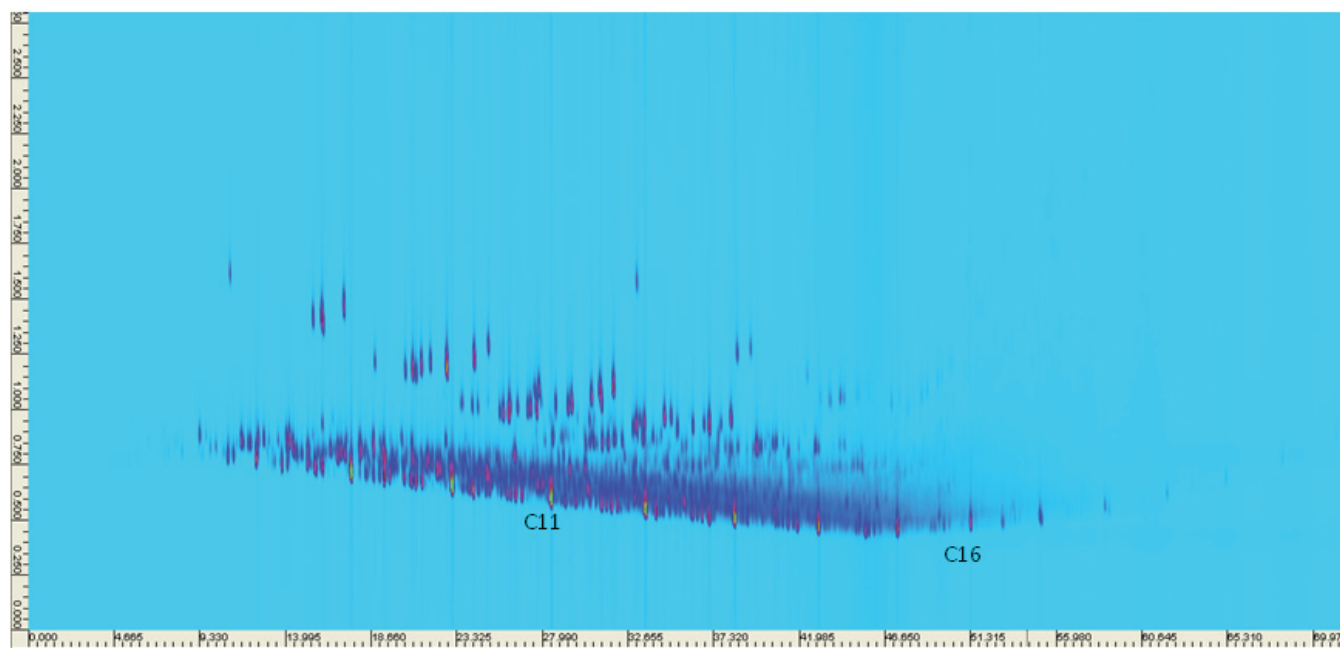


Figure 5a. Jet fuel 2D image. 7 m $\times$ 0.25 mm $\times$ 0.24 μ m HP-INNOWax, LTM program: 55 $^{\circ}$ C (3 min) to 270 $^{\circ}$ C @ 5 $^{\circ}$ C/min. 7890A program: 35 $^{\circ}$ C (2 min) to 280 $^{\circ}$ C @ 3 $^{\circ}$ C/min.

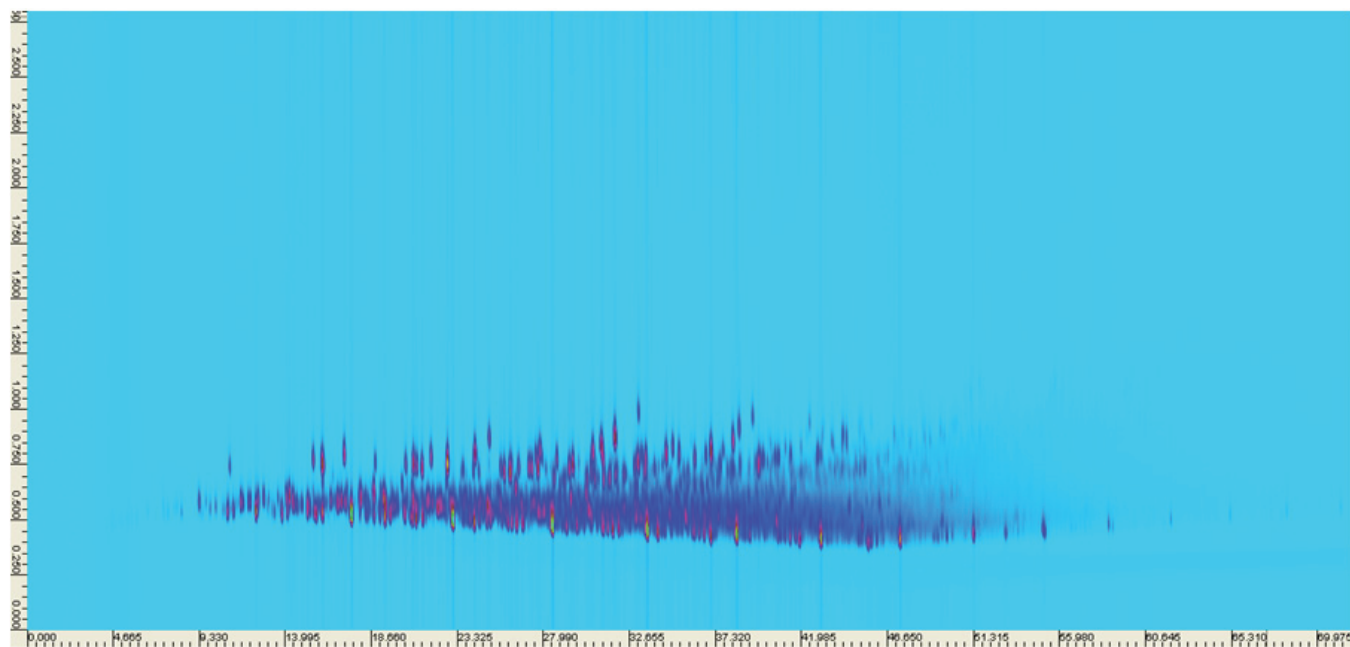


Figure 5b. Jet fuel on 5 m $\times$ 0.25 mm $\times$ 0.15 μ m DB17HT, LTM program: 60 $^{\circ}$ C (5 min) to 300 $^{\circ}$ C @ 3 $^{\circ}$ C/min. 7890A program: 35 $^{\circ}$ C (2 min) to 280 $^{\circ}$ C @ 3 $^{\circ}$ C/min.

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-cyclohexyl 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 $\times$ GC - 5975C MSD system.

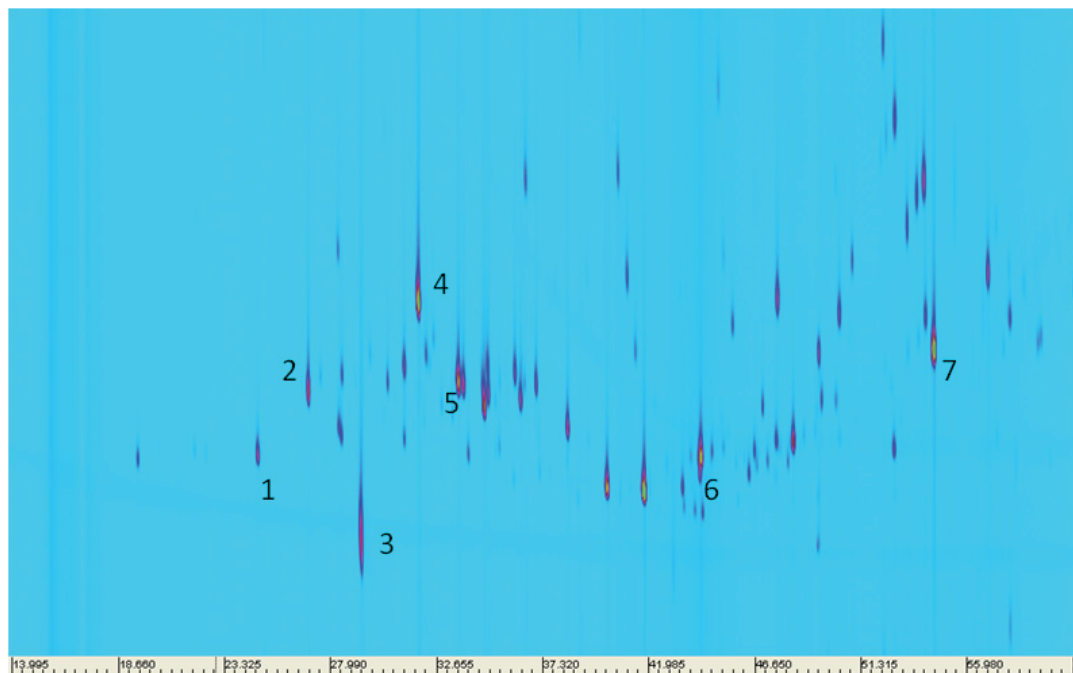


Figure 6a. Fragrance additive using 7 m INNOWax for 2nd dimension, LTM program: 55 °C (3 min) to 270 °C @ 5 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min. 1. Alpha Pinene, 2. Limonene, 3. 2,6 dimethyl 7-octen-2-ol, 4. Phenethyl acetate, 5. Terpenol, 6. Bicyclopentadiene, 7. 4-tert-butylcyclohexyl acetate.

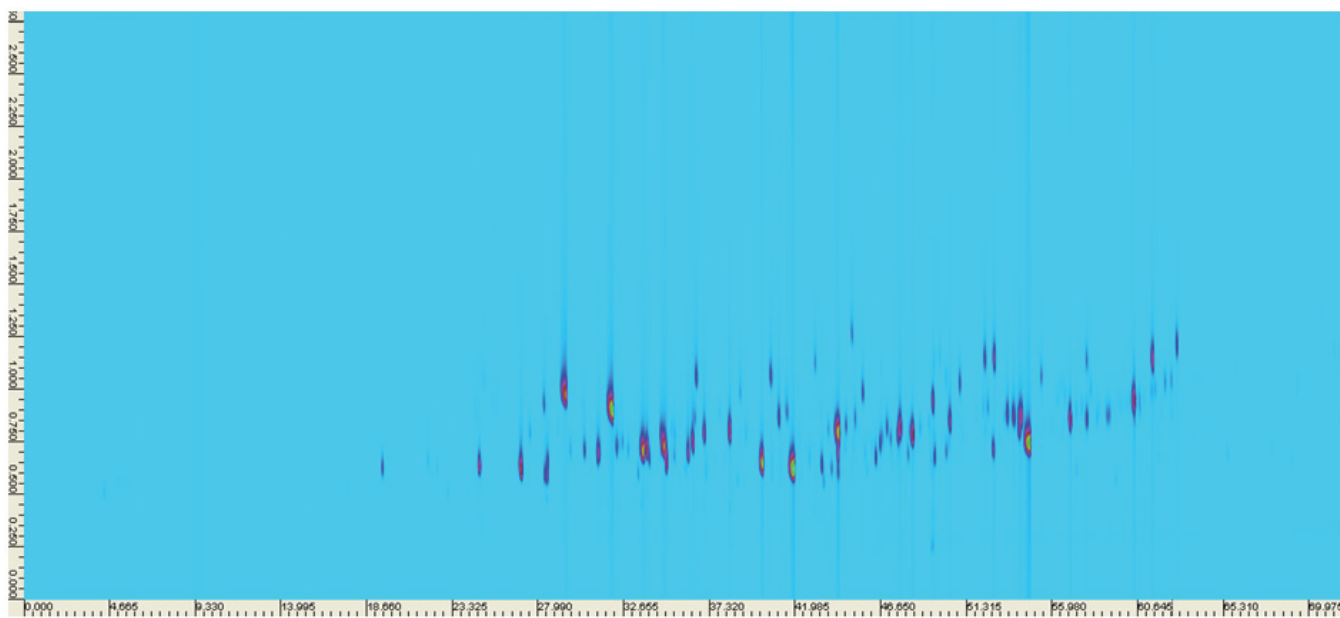


Figure 6b. Fragrance additive using 5m DB17HT for 2nd dimension separation. LTM program: 60 °C (5 min) to 300 °C @ 3 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min.

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.

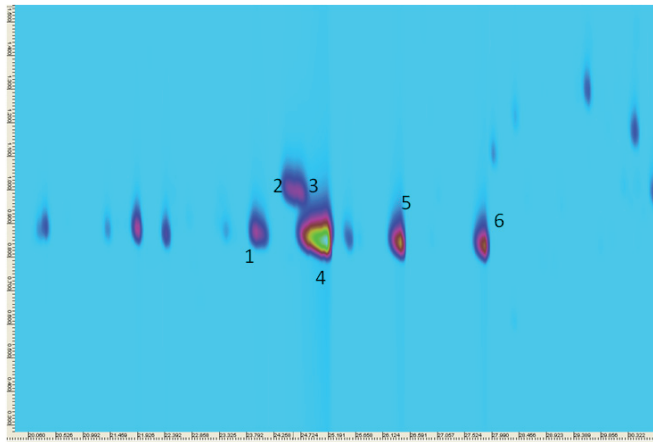


Figure 7a. Lime oil on the 7 m INNOWax. LTM program: 55 °C (3 min) to 270 °C @ 5 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min. 1. Alpha Pinene, 2. Limonene, 3. 2,6 dimethyl 7-octen-2-ol, 4. Phenethyl acetate, 5. Terpenol, 6. Bicyclopentadiene, 7. 4-tert-butylcyclohexyl acetate 1.beta pinene, 2. 1,4 Cineol, 3. m-cymene, 4. Limonene, 5. Terpinen, 6. Terpinolen

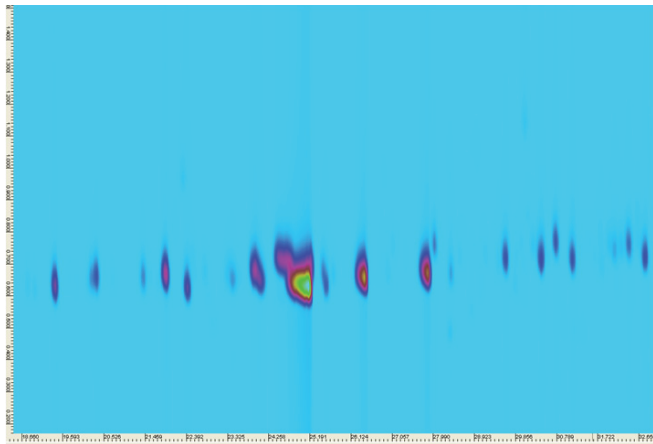


Figure 7b. Lime oil on the 5 m DB17HT. LTM program: 60 °C (5 min) to 300 °C @ 3 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min.

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.

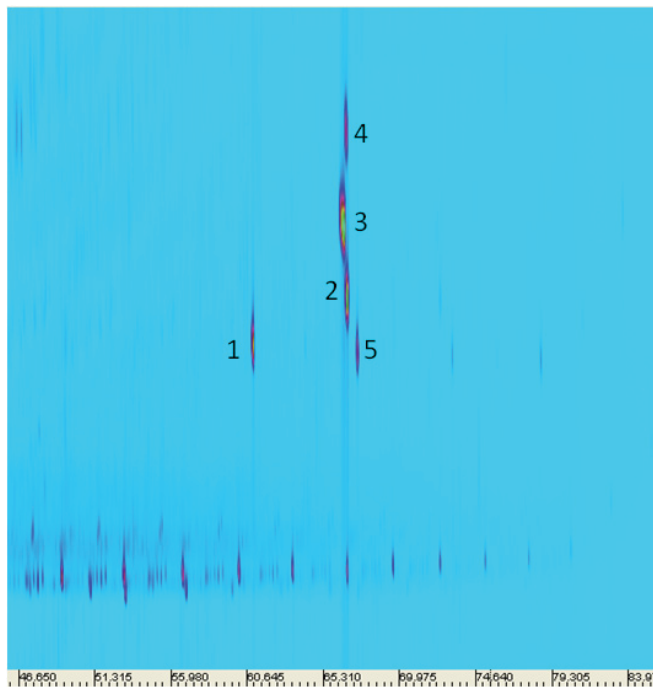


Figure 8. Separation of C16 and C18 fatty acid methyl esters in B20 biodiesel on a 5 m × 0.25 mm × 0.15 μm LTM INNOWax column in the 2nd dimension. LTM program: 30 °C (0 min) to 270 °C (5 min) @ 3 °C/min. 1. C16:0, 2. C18:1, 3. C18:3, 4. C18:3, 5. C18:0.

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.

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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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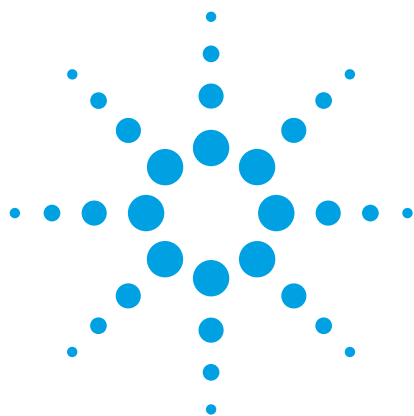
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Asphalt Analysis with Agilent PLgel Columns and Gel Permeation Chromatography

Application Note

Materials Testing and Research, Polymers

Authors

Greg Saunders and Ben MacCreath
Agilent Technologies (UK) Ltd
Essex Rd
Church Stretton
SY6 6AX
UK

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.



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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

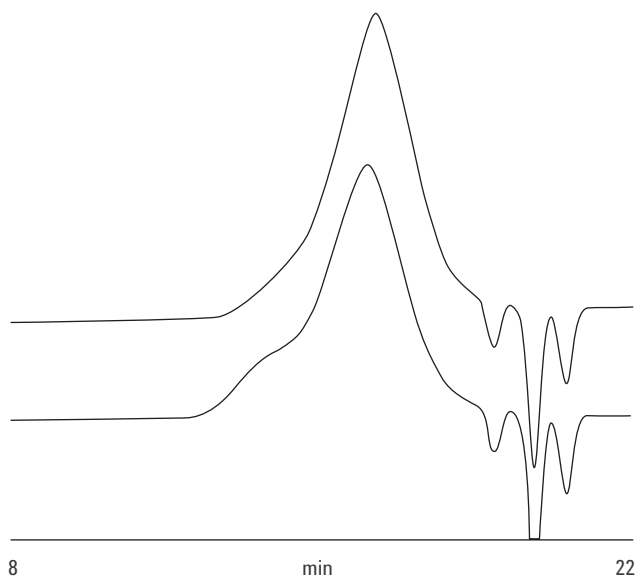


Figure 1. Comparing two batches of asphalt using an Agilent PLgel 5 µm MIXED-D two-column set with tetrahydrofuran as eluent.

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

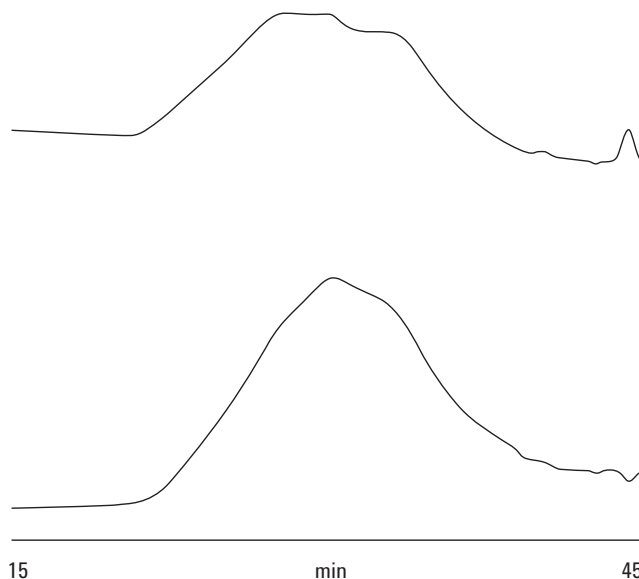


Figure 2. Comparing two batches of asphalt using an Agilent PLgel 5 µm MIXED-E two-column set with o-xylene as eluent.

Figure 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.

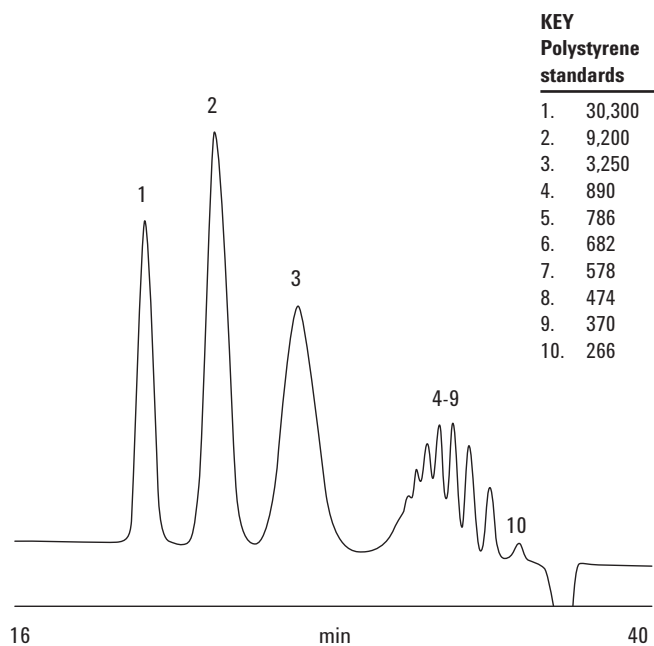


Figure 3. Separation of low molecular weight polystyrene standards on Agilent PLgel 3 μ m MIXED-E columns.

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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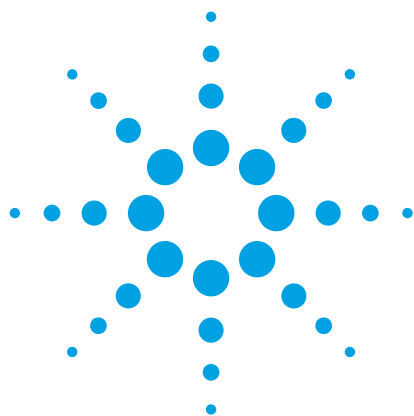
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Petroleum Analysis with Agilent PLgel Columns and Gel Permeation Chromatography

Application Note

Materials Testing and Research, Polymers

Authors

Greg Saunders and Ben MacCreath
Agilent Technologies (UK) Ltd
Essex Rd
Church Stretton
SY6 6AX
UK

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.



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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

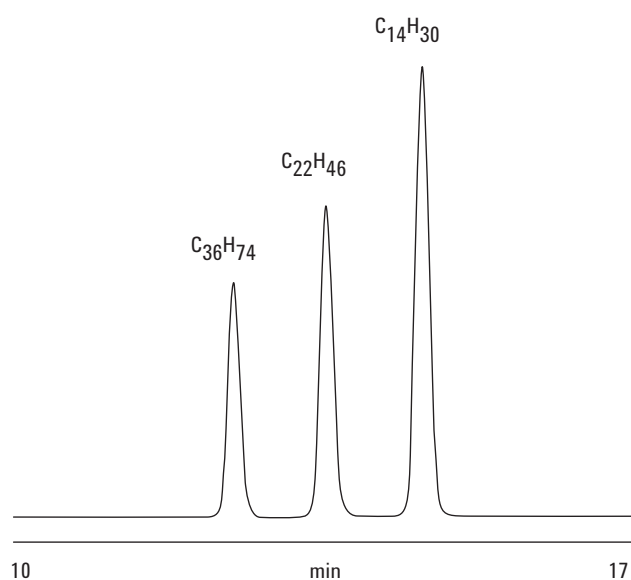


Figure 1. Low molecular weight linear hydrocarbons resolved to base line using an Agilent PLgel 5 µm two-column set.

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 processability 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

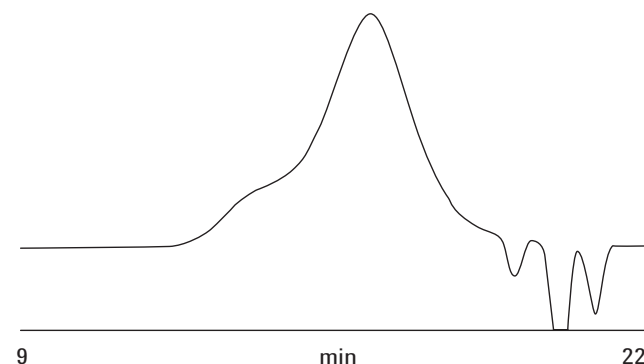


Figure 2. Asphalt separation on an Agilent PLgel 5 µm MIXED-D two-column set.

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

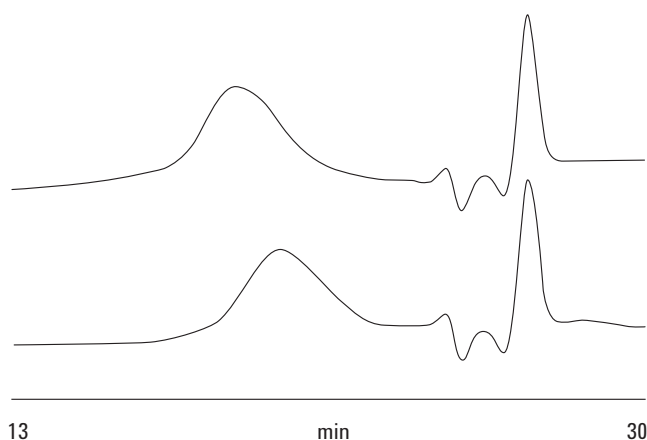


Figure 3. Polyethylene and polypropylene separated on an Agilent PLgel 20 µm MIXED-A three-column set.

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.

For More Information

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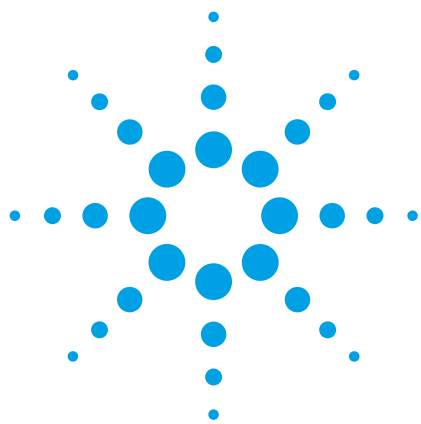
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Determination of major and minor elements in geological samples using the 4100 MP-AES

Application note

Geochemistry, metals and mining

Authors

Craig Taylor and Elizabeth Reisman

Agilent Technologies
Melbourne, Australia



Introduction

Establishing the elemental composition and grade of base metal ores is carried out at different stages of mining and processing. It is used in advanced exploration to confirm the feasibility of mining the ore, and in the assay of the ore concentrate. The determination of the concentration of base metals requires a technique with good accuracy and precision that is capable of generating and managing data from the analysis of large numbers of samples. Consequently, there are also very high expectations in terms of sample throughput and reliability.

In addition, ore-grade samples contain a range of concentrations. It would not be unusual to see high percentage level analytes present alongside low parts per million level analytes. A sample with 40% copper would not be unexpected, and as such, any analysis technique used needs to be able to cope with this range of concentrations.



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Typically, the determination of major and minor elements in geological samples is performed using flame atomic absorption spectroscopy (FAAS) and/or inductively coupled plasma optical emission spectroscopy (ICP-OES). Agilent has developed a new instrument, the 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES), that out-performs FAAS in terms of analytical performance, and offers lower operating costs and unattended overnight operation. The 4100 MP-AES is a highly automated multi-element system with high matrix tolerance and high sample throughput. This ensures that challenging samples can be analyzed quickly and reliably with little operator training and minimal method development.

Experimental

Instrumentation

The 4100 MP-AES is a fast sequential multi-element analytical technique that uses a microwave-induced plasma to provide analysis of liquid sample using a conventional sample introduction system. As MP-AES relies on the generation of a microwave plasma using nitrogen, no flammable gases such as acetylene are required. This reduces running costs and improves lab safety. Nitrogen can be supplied from bottled gas or the Agilent 4107 Nitrogen Generator. This alleviates the difficulty and costs in sourcing gases such as acetylene, specially in remote locations.

The potential of the Agilent 4100 MP-AES for the analysis of ore-grade base metal samples was investigated following preparation of the samples by a four-acid digestion procedure.

Samples and sample preparation

Ore-grade samples require different digestion techniques to geochemical exploration samples in order to dissolve the high metal concentrations and retain them in solution. As a result, dilution factors are greater than with geochemical exploration samples, resulting in higher detection limits, and also higher upper limits.

The preparation method used involves taking 0.4 g of sample and performing a four-acid (HNO_3 - HClO_4 -HF-HCl) digestion. The process is completed by further addition of hydrochloric acid and deionized water, followed by cooling to room temperature. The resulting solution

was diluted to 100 mL with de-ionized water resulting in a final matrix of 30% HCl. This represents a 250-fold sample dilution.

The 4100 MP-AES operating parameters were optimized as shown in Table 1.

Table 1. Agilent 4100 MP-AES operating parameters

Instrument parameter	Setting
Nebulizer pressure	80–240 kPa
Read time	3 s (10 s for Ag)
Stabilization time	15 s
Background correction	Auto

Results and discussion

Method detection limits (MDLs)

Method detection limits (MDLs) for silver, copper, molybdenum, nickel, lead, and zinc were determined. Table 2 shows that excellent MDLs can be obtained using the 4100 MP-AES.

Table 2. MDLs for digestions of ore-grade base metal samples

Analyte	Wavelength (nm)	MDL (ppm)
Ag	328.068	0.04
Cu	327.395	0.1
Mo	379.398	0.7
Ni	352.453	0.4
Pb	405.781	0.4
Zn	213.857	0.7

Quantitative analysis

A batch of base metal ore sample digests were prepared using the sample preparation method. These sample were analysed by the 4100 MP-AES using a blank and three matrix-matched standard solutions.

Accuracy

The results obtained by the 4100 MP-AES for Ag, Cu, Mo, Ni, Pb and Zn were plotted against the expected results — see Figures 1 to 7. The graphs show good correlation (accuracy) over the calibration range, up to ~4% for copper, indicating that MP-AES is a suitable technique for the application.

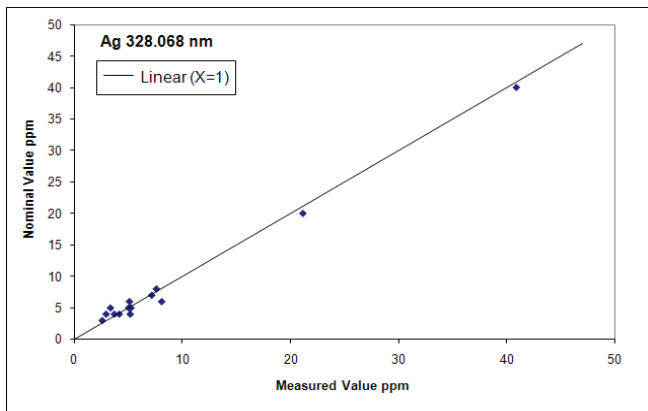


Figure 1. MP-AES measured results for Ag compared to nominal values

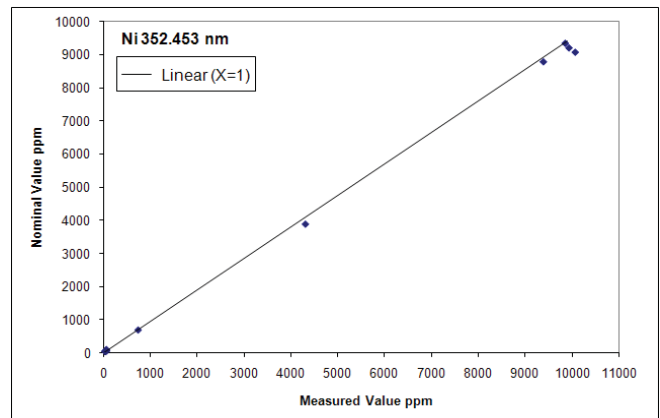


Figure 4. MP-AES measured results for Ni compared to nominal values

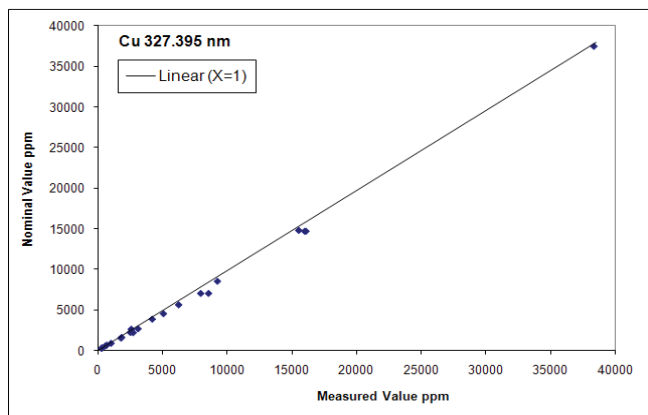


Figure 2. MP-AES measured results for Cu compared to nominal values

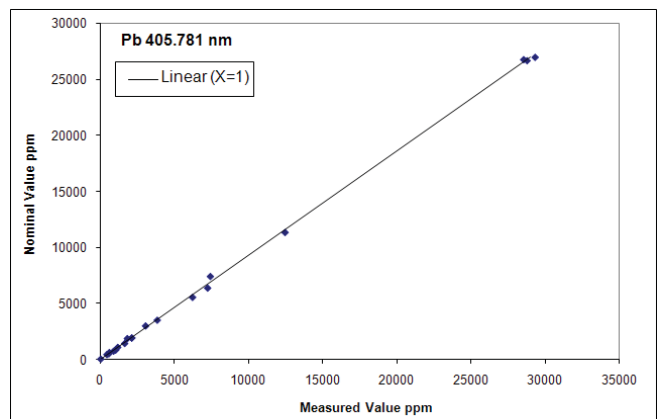


Figure 5. MP-AES measured results for Pb compared to nominal values

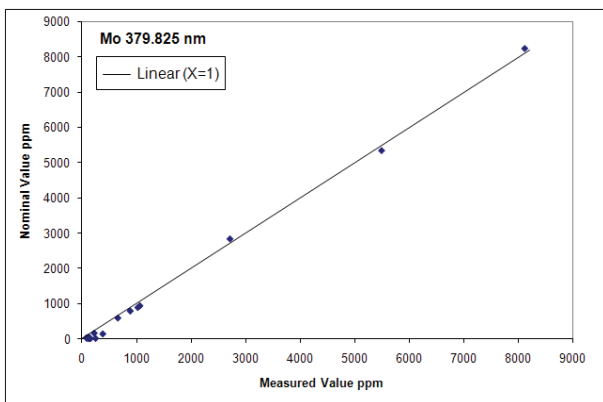


Figure 3. MP-AES measured results for Mo compared to nominal values

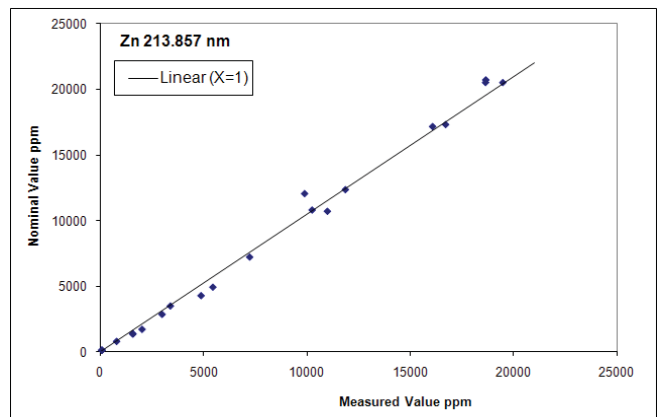


Figure 6. MP-AES measured results for Zn at the 213.857 nm wavelength compared to nominal values

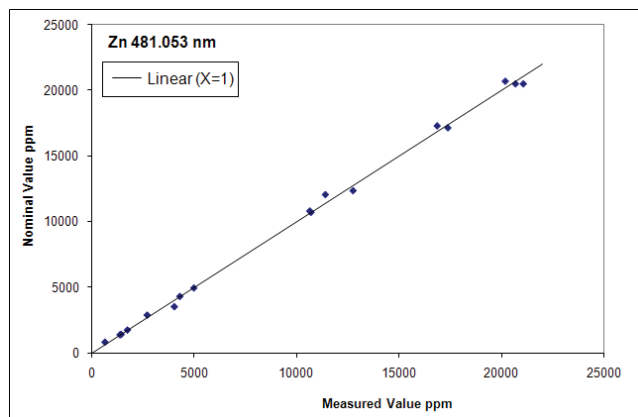


Figure 7. MP-AES measured results for Zn at the 481.053 nm wavelength compared to nominal values

Conclusions

A series of geological samples has been successfully analyzed using the Agilent 4100 MP-AES, following a sample preparation procedure that is commonly used to prepare base metal ores for analysis by geochemical laboratories. Quantitative results were obtained for 6 elements present in a batch of 23 base metal ore samples, with measured concentrations ranging from less than 1 ppm to 29%. The comparative results for Ag,

Cu, Mo, Ni, Pb and Zn obtained using MP-AES show that the 4100 MP-AES is well suited to this application. It also offers additional benefits over comparative techniques such as flame AAS, through lower operating costs, improved safety and the ability to perform the analysis using unattended overnight operation.

Operating costs can be further reduced by directly generating nitrogen from compressed air using an Agilent 4107 Nitrogen Generator. This is particularly advantageous in areas where gas supplies are expensive, difficult to obtain or pose logistics challenges in transporting bulk cylinders to site. The 4100 MP-AES also offers the possibility of installations in remote locations. This enables laboratories to analyze samples locally at the source rather than transporting the samples to a central laboratory for analysis, as is the current practice. 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.

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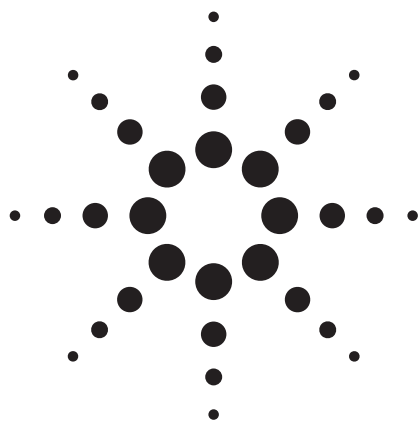
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Obtaining Optimum Performance When Using the SIPS Accessory

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.



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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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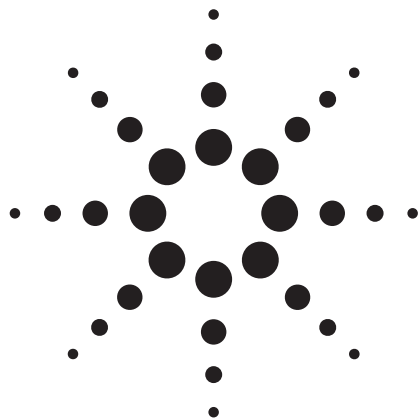
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Routine Maintenance for Atomic Absorption Spectrophotometers

Application Note

Atomic Absorption

Author

Margaret A. Cunliffe

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



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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 m³/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 in the 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 block-

age, 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% HNO₃, 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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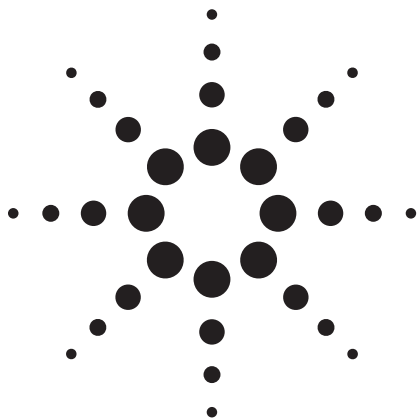
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Guidelines for Using Non-Aqueous Solvents in Atomic Absorption Spectrometry

Application Note

Atomic Absorption

Author

Jonathan Moffett

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.



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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
Tetrahydronaphthalene (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):

$$\% \text{ Recovery} = (\text{SSR} - \text{SR}) / \text{SA} \times 100$$

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 $\mu\text{g/g}$ 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 $500 \mu\text{g/g}$ 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.

$$\text{mass salt} = \frac{MC}{10,000 P} \text{ grams} \quad (1)$$

where M is mass of oil standard required (g)
 C is concentration of analyte in oil ($\mu\text{g/g}$)
 P is percent analyte in salt

Example 1: Prepare a $500 \mu\text{g/g}$ 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.

$$\text{mass oil standard} = \frac{MC}{S} \text{ grams} \quad (2)$$

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 $120 \mu\text{g/g}$ Cu and $300 \mu\text{g/g}$ Al starting with $5000 \mu\text{g/g}$ standards.

Using equation 2,

$$\begin{array}{ll} \text{Cu} & \text{Al} \\ m = \frac{10 \times 120}{5000} & m = \frac{10 \times 300}{5000} \\ = 0.2400 \text{ g} & = 0.6000 \text{ g} \end{array}$$

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.

$$\begin{array}{ll} \text{Method 1:} & 1.5\% \text{ Zn} = 1.5 \times 10,000 \mu\text{g/g Zn} \\ \text{From equation 1:} & m = \frac{20 \times 1.5 \times 10,000}{10,000 \times 16.18} = 1.854 \text{ g} \end{array}$$

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:

$$\text{From equation 2} \quad m = \frac{20 \times 150}{5000} = 0.600 \text{ g}$$

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 naphthenates, sulphonates or cyclobutyrate.

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 analytes 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
- Suitably 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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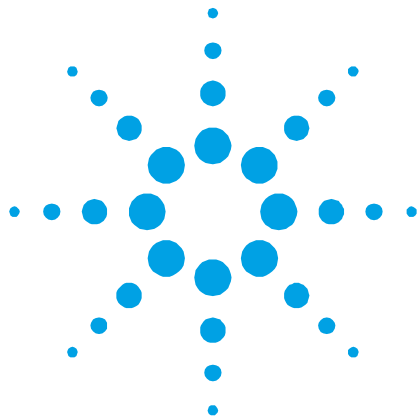
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Agilent Oil Analyzer: customizing analysis methods

Application Note

Author

Alexander Rzhevskii &
Mustafa Kansiz
Agilent Technologies, Inc.

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 advantages¹:

- 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.



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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/JPS 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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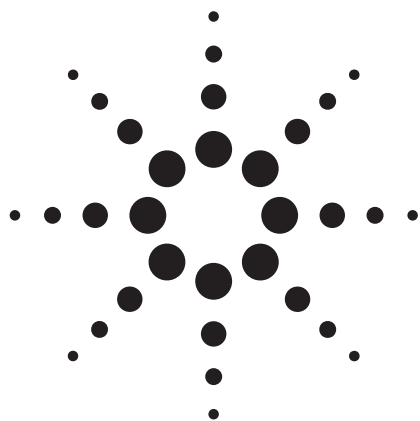
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AA or ICP – Which Do You Choose?

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

Geoff Tyler

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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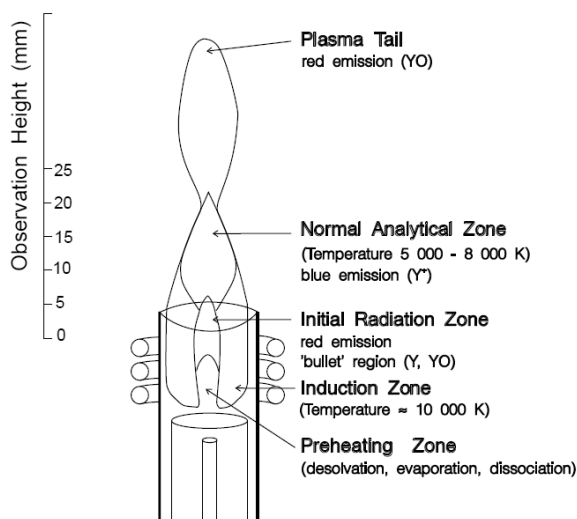


Figure 1. A plasma used for emission spectrometry. The regions refer to those seen when a Yttrium solution is introduced.

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	0.3 – 2%	0.1 – 1%	0.5 – 5%
Short term	Less than 5%		
Long term (over 8 hrs)			
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

Element		AA λ (nm)	ICP λ (nm)	ICP Detection limit µg/L	Flame AA Characteristic conc µg/L	Detection limit µg/L	Flame type	Zeeman Furnace AA Characteristic*** conc** µg/L	Mass pg	MSR %	EI
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 ₂ O	0.25	5	100	Al
Arsenic	As	193.7	188.985	12	500	300	N ₂ O	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 ₂ O	43	855*	70	B
Barium	Ba	553.6	455.403	0.07	200	20	N ₂ O	0.85	17	100	Ba
Beryllium	Be	234.9	313.042	0.2	15	1	N ₂ O	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 ₂ O	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 ₂ O			–	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 ₂ O	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 ₂ O	2.3	45	100	Dy
Erbium	Er	400.8	337.271	0.7	500	50	N ₂ O	5	100	100	Er
Europium	Eu	459.4	381.967	0.3	300	1.5	N ₂ O	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 ₂ O			–	Gd
Germanium	Ge	265.1	265.118	13	1000	200	N ₂ O	0.45	9*	100	Ge
Hafnium	Hf	307.3	264.141	4	10000	2000	N ₂ O			–	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)

Element		AA λ (nm)	ICP λ (nm)	ICP Detection limit µg/L	Flame AA Characteristic conc µg/L	Detection limit µg/L	Flame type	Zeeman Furnace AA Characteristic*** conc** µg/L	Mass pg	MSR %	EI
Holmium	Ho	410.4	345.600	0.5	700	40	N ₂ O			—	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 ₂ O			—	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 ₂ O			—	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 ₂ O	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 ₂ O			—	Nb
Neodymium	Nd	492.5	401.225	2	6000	1000	N ₂ O			—	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 ₂ O			—	Os
Phosphorous	P	213.6	177.499	18	120000	40000	N ₂ O	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 ₂ O			—	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 ₂ O			—	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 ₂ O			—	Sc
Selenium	Se	196.0	196.026	37	1000	500	N ₂ O	0.7	14*	92	Se
Silicon	Si	251.6	251.611	5	1500	300	N ₂ O	0.75	15	100	Si
Samarium	Sm	429.7	442.434	7	6000	1000	N ₂ O			—	Sm
Tin	Sn	235.5	242.949	15	700	100	N ₂ O	0.5	10*	93	Sn
Strontium	Sr	460.7	407.771	0.02	40	2	N ₂ O	0.1	2	94	Sr
Tantalum	Ta	271.5	268.517	9	10000	2000	N ₂ O			—	Ta
Terbium	Tb	432.7	350.917	5	7000	700	N ₂ O	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 ₂ O	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 ₂ O			—	Tm
Uranium	U	358.5	385.958	18	100000	40000	N ₂ O			—	U
Vanadium	V	318.5	309.311	2	700	100	N ₂ O	1.1	22	79	V
Tungsten	W	255.1	239.709	17	5000	1000	N ₂ O			—	W
Yttrium	Y	410.2	371.030	0.2	2000	200	N ₂ O			—	Y
Ytterbium	Yb	398.8	328.937	0.3	60	4	N ₂ O	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 ₂ O			—	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:

$$CM_n = CM_z \times MSR (\%)/100 \quad CC_n = CC_z \times MSR (\%)/100$$

where:

CM_n = Characteristic Mass for Deuterium Furnace Systems

CM_z = Characteristic Mass for Zeeman Furnace Systems (from Table 1)

MSR = Magnetic Sensitivity Ratio (as % from Table 1)

CC_n = Characteristic Concentration for Deuterium Furnace Systems

CC_z = Characteristic Concentration for Zeeman Furnace Systems (from Table 1).

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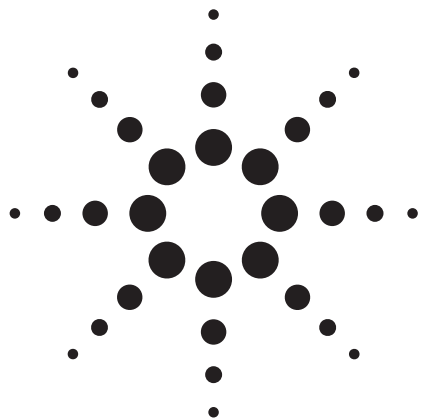
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Improving Throughput for Oils Analysis by ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

Ingrid Szikla

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.



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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 spray-chamber 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	
Auxiliary 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
Zn 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 compromise 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 peristaltic 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	Actual 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

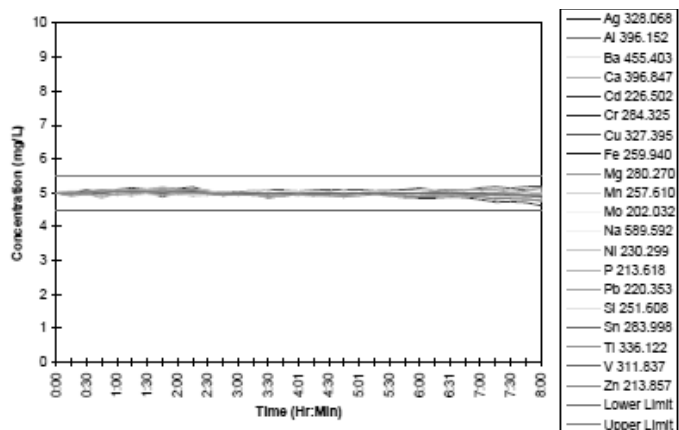


Figure 1. Stability of the Vista-PRO radial instrument over 8 hours. Results remained within $\pm 10\%$ for all elements in the 5 mg/L S21 kerosene solution without internal standardization or recalibration.

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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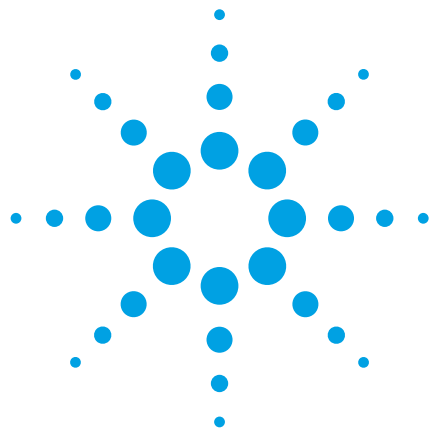
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Separation of Permanent Gases on a Liquid Phase

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

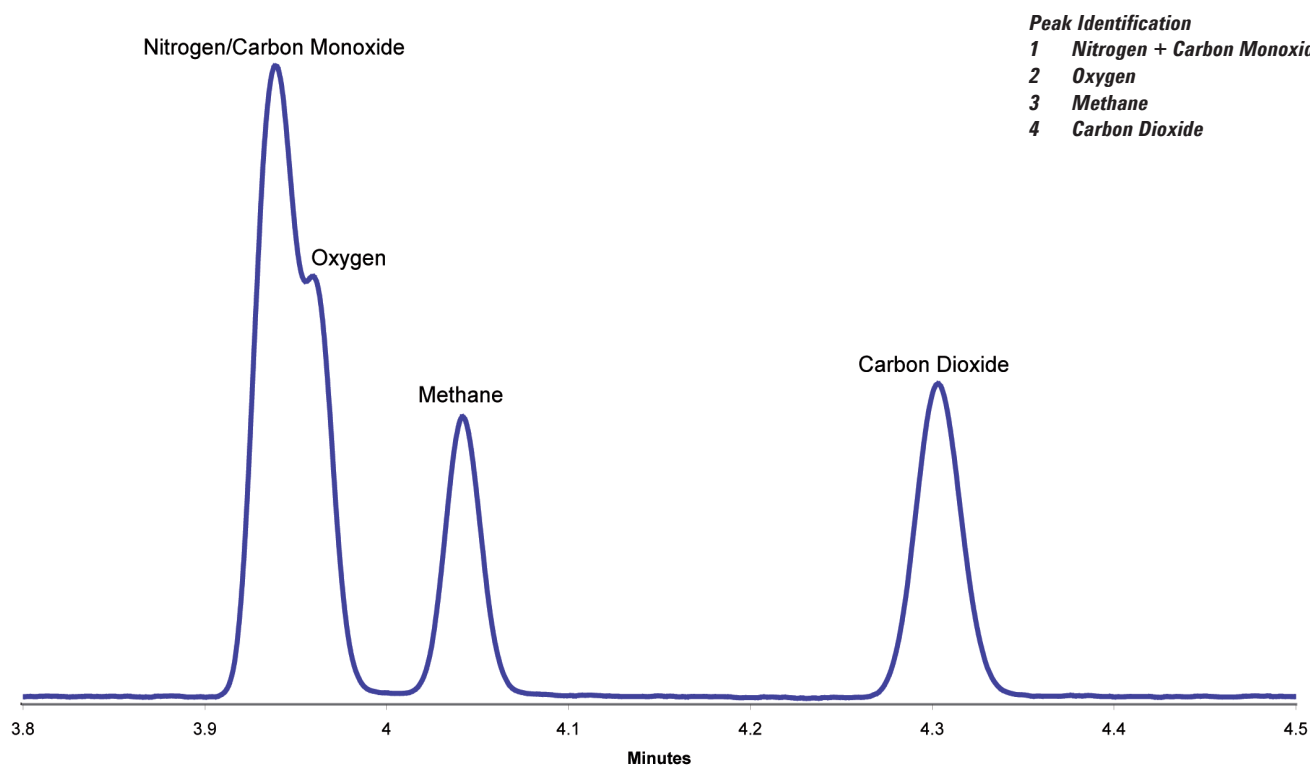
Normally permanent gases are separated by PLOT (porous layer open tubular) columns with their high retentive phases. With WCOT (wall coated open tubular) columns sub-ambient temperatures are normally necessary. Thick films, like the 8 μm film thickness of the Agilent J&W Select CP-Sil 5CB for Formaldehyde, 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.



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Materials and Methods

Technique:	GC-Capillary Medium Bore	Carrier Gas:	Helium at 25 psi (170 kPa)	Detector:	Thermal Conductivity Detector at 220 °C (Filament Temp. 280 °C)
Instrument:	GC Gas Chromatograph	Temp Program:	35 °C isothermal	Sample:	All Gases 1% in Helium
Column:	CP-Sil 5 CB for Formaldehyde, 0.32 mm x 60 m, df=8 µm (part number CP7475)	Injector:	Split/Splitless-Injector (1177) at 250 °C		
		Inj Volume:	500 µL (split ratio 1:20)		



Analysis of permanent gases at 35°C

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Fast Refinery Gas Analysis Using the 490 Micro GC QUAD

Application Note

Authors

Coen Duvekot
Agilent Technologies, Inc.

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.



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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	Bal
3	Oxygen	
4	Nitrogen	
5	Methane	
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.

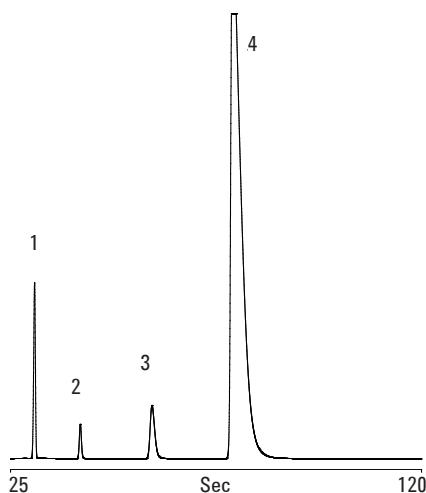


Figure 1. Standard gas on the Molsieve column, channel 1

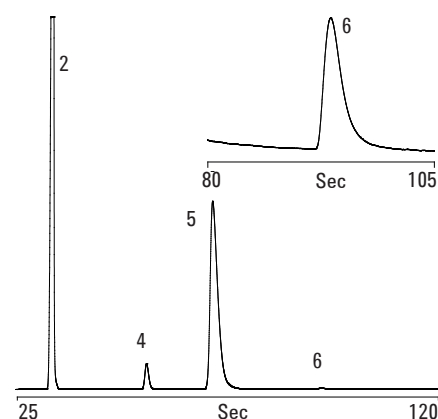


Figure 2. Refinery gas on the Molsieve column, channel 1

Hydrogen or helium, oxygen, nitrogen methane and carbon monoxide were separated and analyzed. Later eluting components were back flushed to vent.

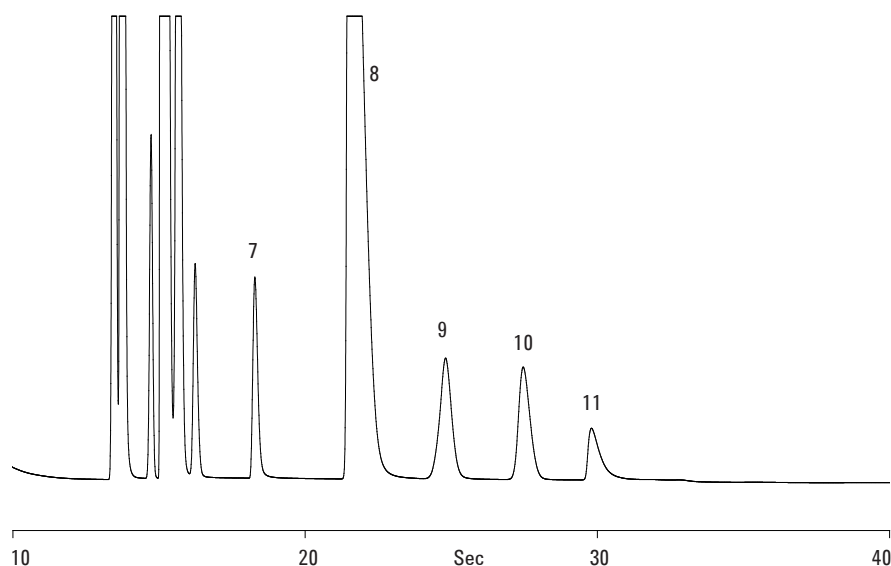


Figure 3. Refinery gas on the CP-PoraPLOT U column, channel 2

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.

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.

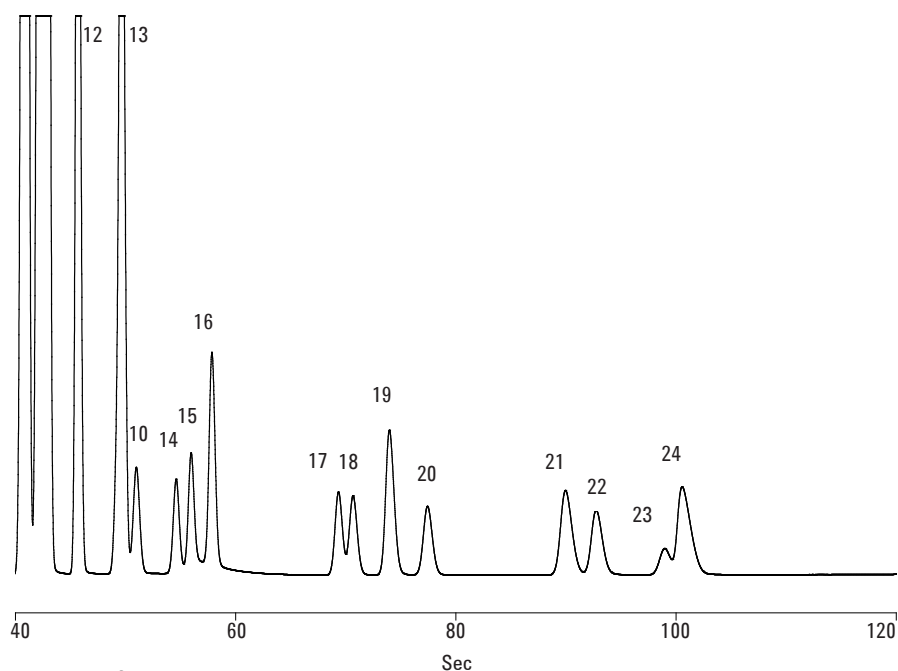


Figure 4. Refinery gas on the aluminium oxide column, channel 3

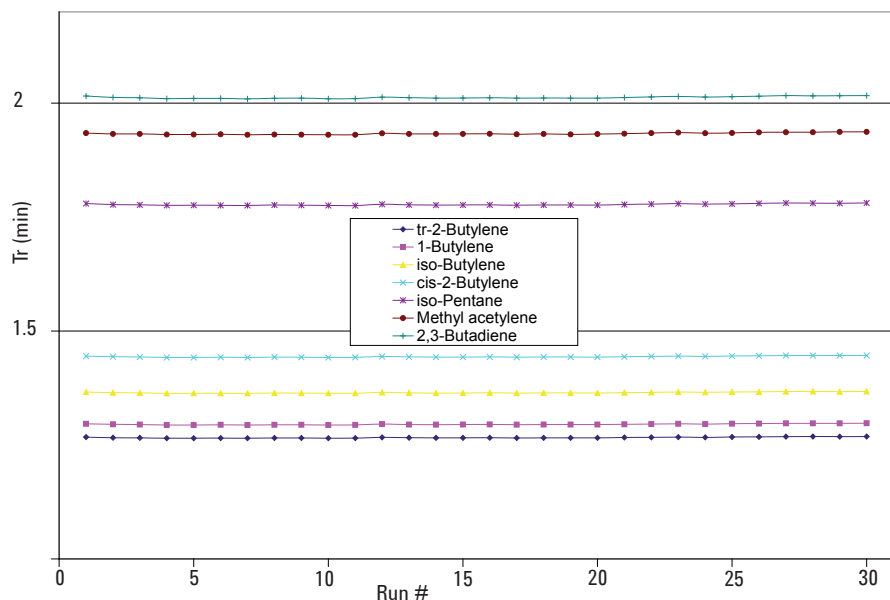


Figure 5. Repeatability figures for the aluminium oxide channel, channel 3

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.

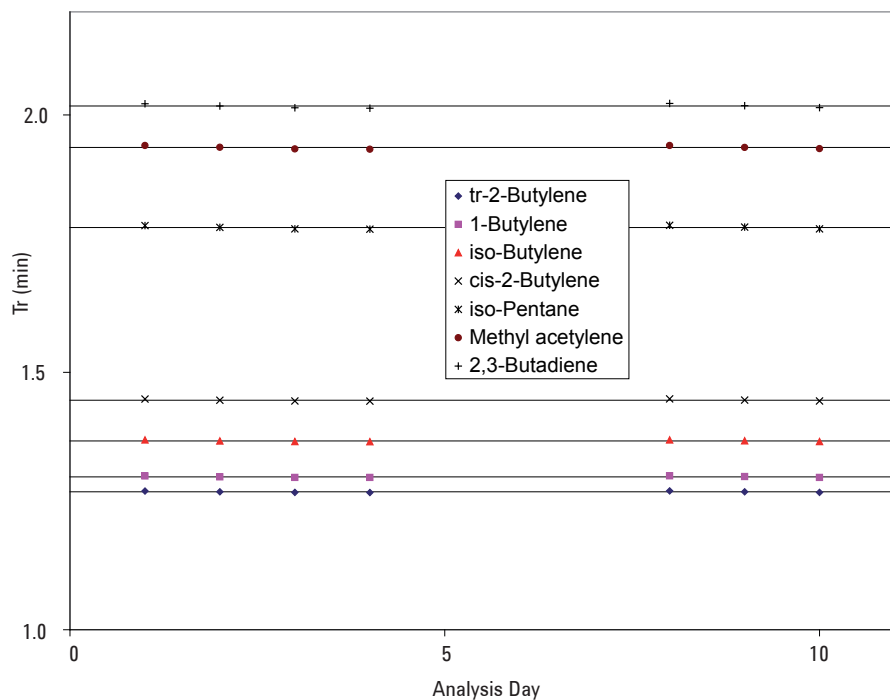


Figure 6. Reproducibility of the aluminium oxide channel, channel 3

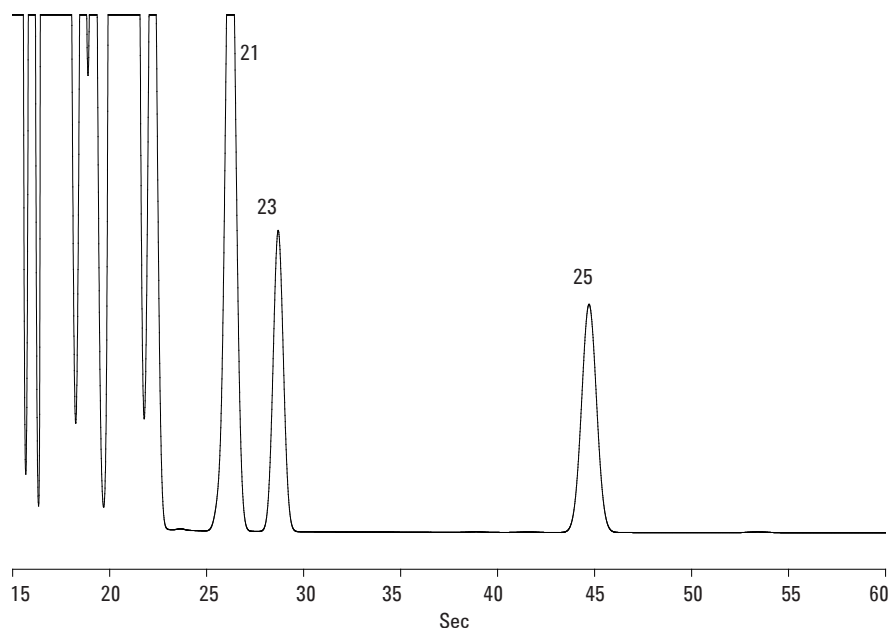


Figure 7. Refinery gas on the CP-Sil 5 CB column, channel 4

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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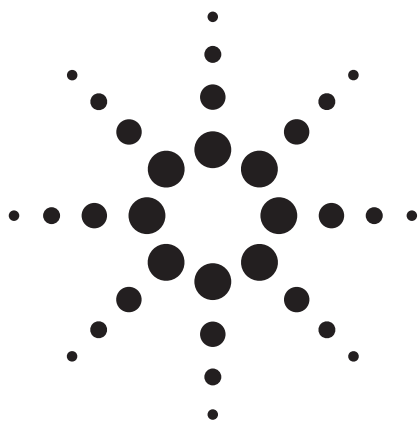
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SI-02233



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



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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.

PEAK ABSORBANCE PEAK HEIGHT	NEBULIZER CONCENTRATION (sec)	SAMPLER AUTOMIX 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)	0.999	

Figure 1. The Agilent Mark-VI spraychamber: (1) nebulizer, (2) ceramic faceplate, (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.

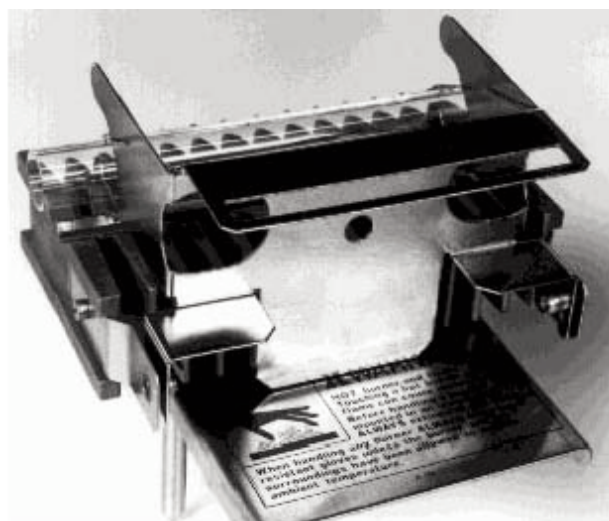


Figure 2. The ACT 80 Atom Concentrator Tube.

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 spray-chamber 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 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

Element	Literature FAAS	Characteristic concentration			Literature FAAS	Detection limit		
		Standard FAAS (Ht=10)	Act-80 FAAS (Ht=3)	Act-80 improvement factor		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.

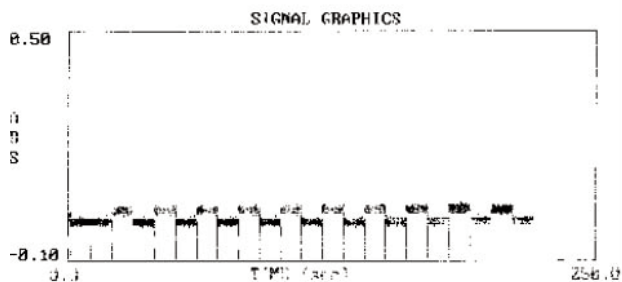


Figure 3(a). Pb signal compared to blank without ACT-80 tube.

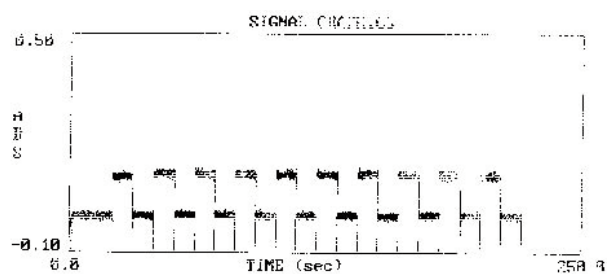


Figure 3(b). Pb signal compared to blank with ACT-80 tube.

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.

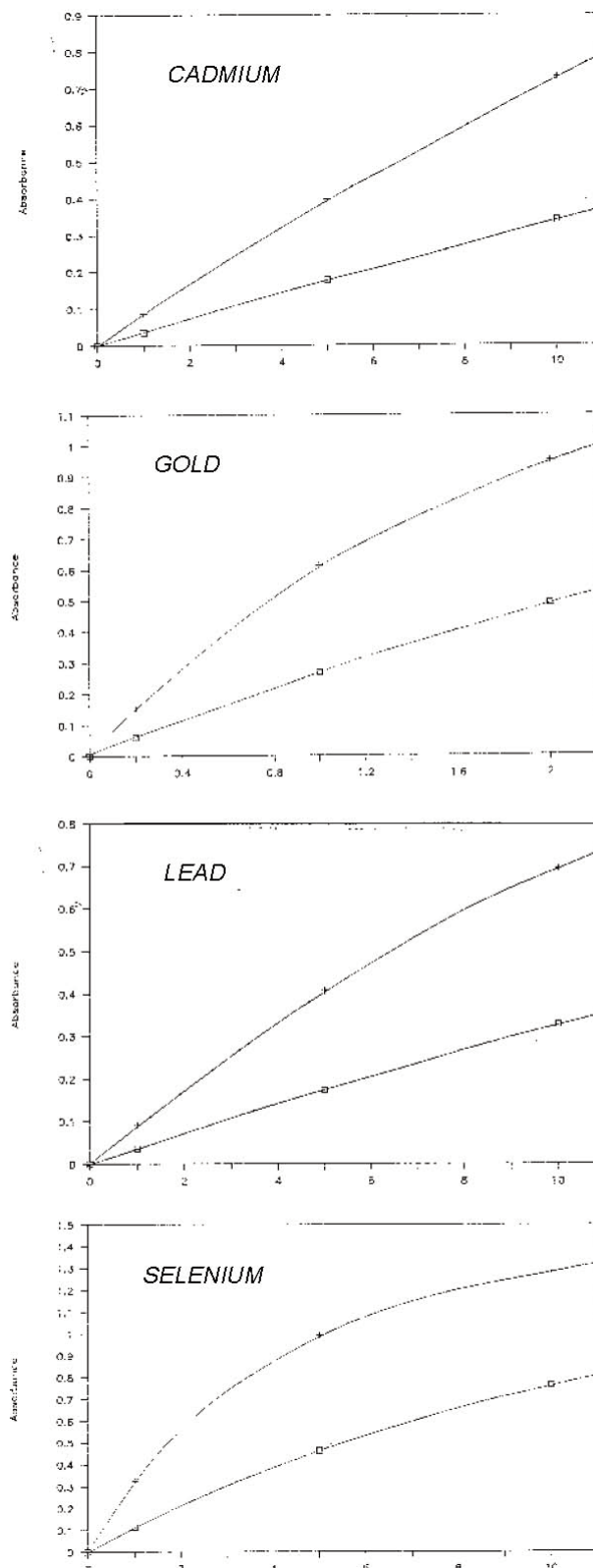


Figure 4. Calibration graphs of selected elements showing improvement in sensitivity. (+ = ACT-80, □ = normal FAAS)

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.

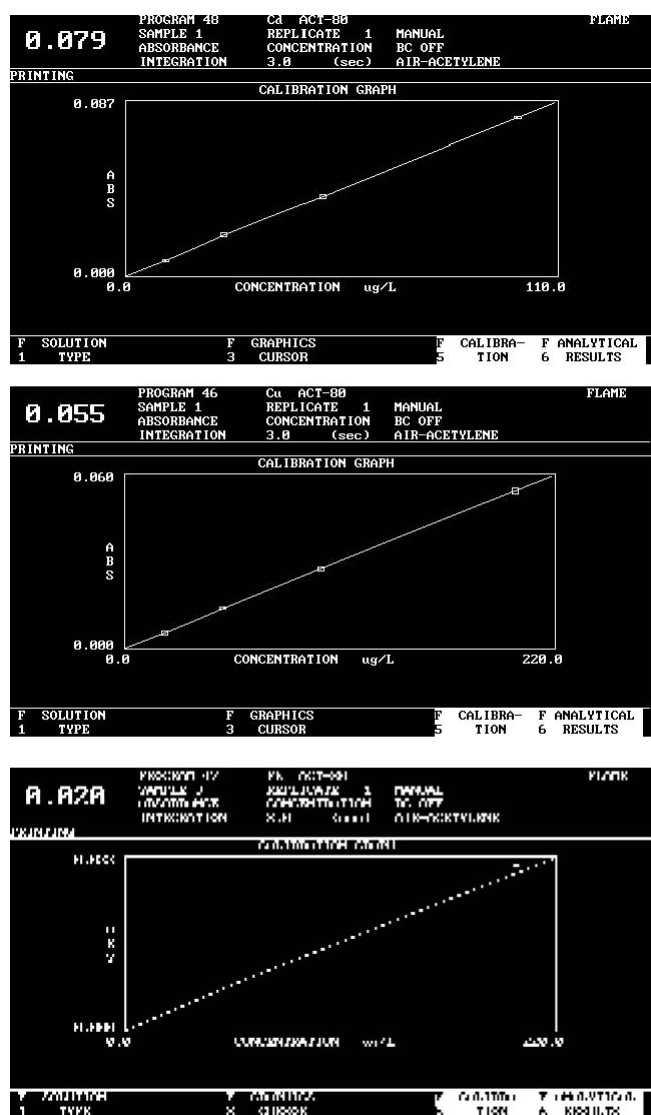


Figure 5. Calibration graphs used to measure quality control samples.

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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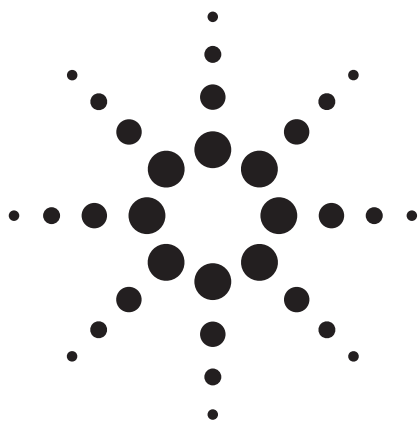
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Sensitivity Enhancement for Flame AAS Using an Atom Concentrator Tube for Elements Dissolved in Organic Solvents

Application Note

Atomic Absorption

Authors

Ragnar Bye
University of Oslo
Department of Pharmacy
P.O.Box 1068, 0316 Oslo,
Norway
and
Christopher B. Mullins

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 $20 \times (3-5) = 60 - 100$ 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 $(60 \text{ to } 100) \times (2 \text{ to } 3) = 120 \text{ to } 300$ 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.



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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 length-wise 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
<u>MIBK/ACT</u> MIBK	2.4	1.6	2.8	0.6	1.1
<u>MIBK/ACT</u> AQ/ACT	3.3	4.0	3.8	2.1	n.d.
<u>MIBK/ACT</u> aq	8.6	6.0	10.9	2.2	n.d.
<u>AQ/ACT</u> aq	2.7	1.5	2.8	1.0	n.d.
<u>MIBK</u> aq/ACT	1.3	2.5	1.3	3.5	n.d.
<u>MIBK</u> aq	3.6	3.8	3.6	3.6	n.d.

n.d. = Not determined

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