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- Increasing Sample Throughput with High-Speed Megabore Columns
- DuraGuard Columns: GC Columns with Built-In Protection
- Using Agilent ChemStation to generate summary reports for a single analysis or a sequence of analyses
- 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
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- A Column-Flow Independent Configuration for QuickSwap
- High-Pressure Injection Device for the Agilent 7890A and 6890 Series Gas Chromatographs
- Investigation of the Unique Selectivity and Stability of Agilent GS-OxyPLOT Columns
- Detection of Sulfur Compounds in Natural Gas According to ASTM D5504 with Agilent's Dual Plasma Sulfur Chemiluminescence Detector (G6603A) on the 7890A Gas Chromatograph
- Achieving Lower Detection Limits Easily with the Agilent Multimode Inlet (MMI)
- Analysis of Permanent Gases and Light Hydrocarbons Using Agilent 7820A GC With 3-Valve System
- 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
- GC Analysis of Sulfur Components in Propylene using a Pulsed Flame Photometric Detector
- Permanent Gases on a COX Module Using a Agilent 490 Micro GC
- Returning to Fixed Pathlength Infrared Spectroscopy: Gaining Detail and Removing the Obstacles
- Analysis of tert-Butyl Mercaptan in Natural Gas on a CP-Sil 13 CB Using the Agilent 490 Micro GC
- Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer
- Using a Dual LTM Series II System with Flow Modulated Comprehensive GCxGC
- Analysis of Tetrahydrothiophene (THT) in Natural Gas using the Agilent 490 Micro GC
- Analysis of Methyl Ethyl Sulfide (MES) in Natural Gas using the Agilent 490 Micro GC

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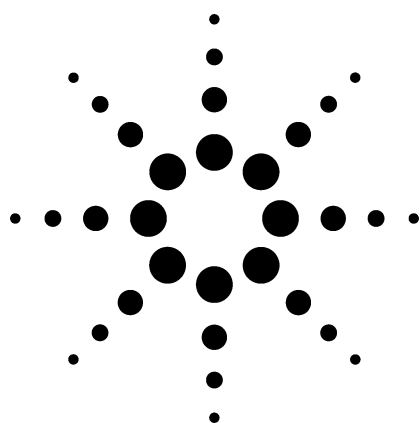


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- Guidelines for Using Non-Aqueous Solvents in Atomic Absorption Spectrometry
- Agilent Oil Analyzer: customizing analysis methods
- AA or ICP - Which Do You Choose?
- Improving Throughput for Oils Analysis by ICP-OES
- Separation of Permanent Gases on a Liquid Phase
- Detailed Separation of C1-C5 Light Hydrocarbons on CP-Al₂O₃/Na₂SO₄ PLOT GC Column
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- 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 µm	1997 (28)
	75 meters	0.540 mm	3.00 µm	1447
DB-624	75 meters	0.446 mm	2.55 µm	1402 (22)
	75 meters	0.546 mm	3.00 µm	1090
DB-502.2	75 meters	0.453 mm	2.55 µm	1526 (20)
	105 meters	0.544 mm	3.00 µm	873
DB-WAX	30 meters	0.447 mm	0.85 µm	1656 (25)
	30 meters	0.544 mm	1.00 µm	1357
DB-1	30 meters	0.455 mm	1.30 µm	1477 (27)
	30 meters	0.551 mm	1.50 µm	1357
DB-5	30 meters	0.446 mm	1.30 µm	1895 (23)
	30 meters	0.540 mm	1.50 µm	1454
DB-608	30 meters	0.450 mm	0.71 µm	1477 (23)
	30 meters	0.535 mm	0.83 µm	1134

[1] Phase ratio (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

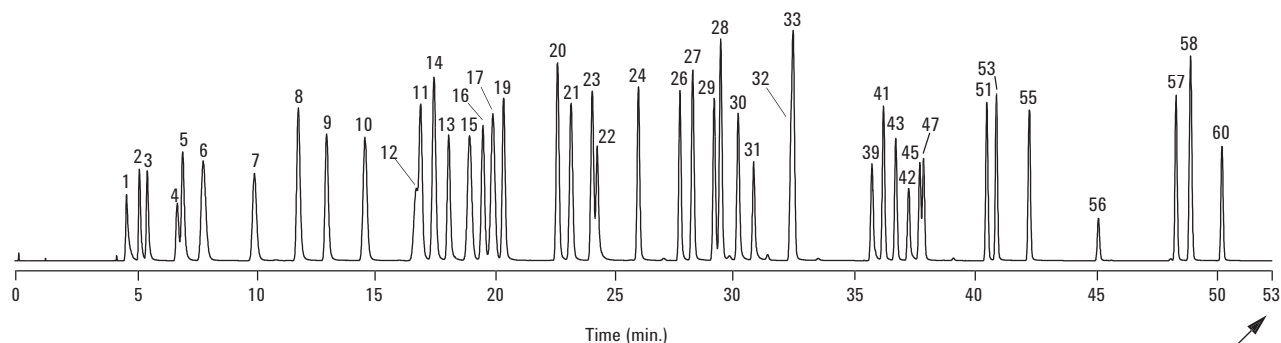
41. 1,1,2,2-Tetrachloroethane
42. Bromobenzene
43. 1,2,3-Trichloropropane
44. n-Propylbenzene
45. 2-Chlorotoluene
46. 1,2,3-Trimethylbenzene
47. 4-Chlorotoluene
48. tert-Butylbenzene
49. 1,2,4-Trimethylbenzene
50. sec-Butylbenzene
51. 1,3-Dichlorobenzene
52. para-Isopropyltoluene
53. 1,4-Dichlorobenzene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

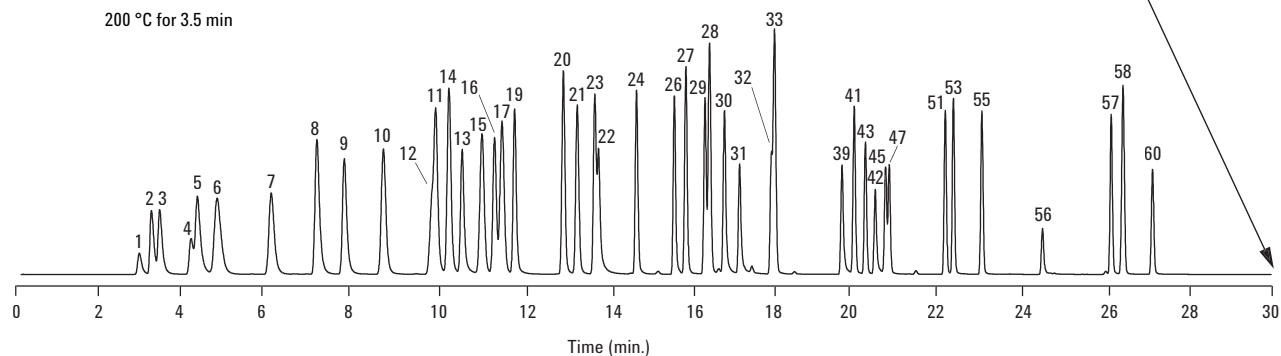


Conditions

Column: DB-502.2, 75 m x 0.45-mm ID, 2.55 μ m
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

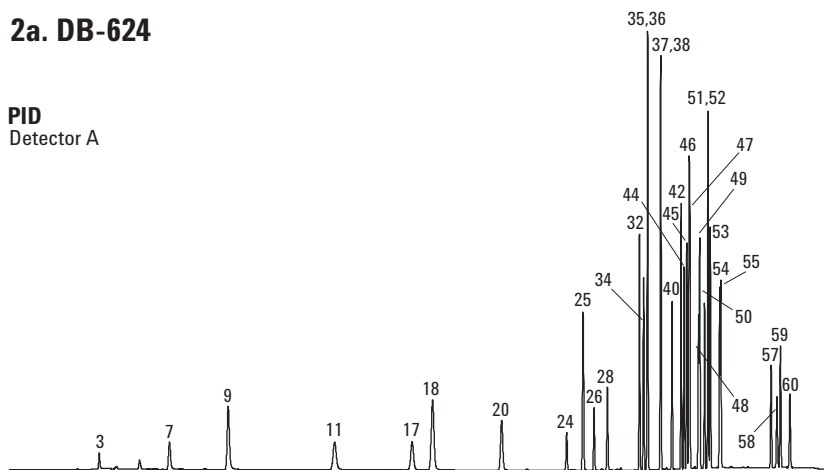
200 °C for 4 min

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

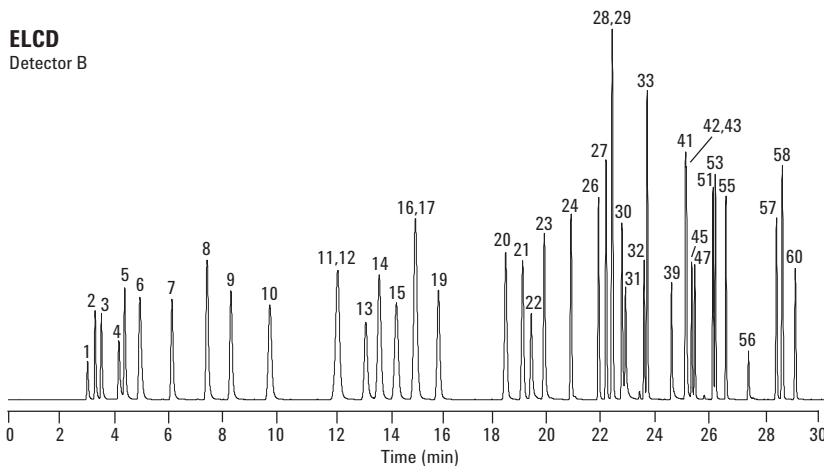
Trap: Tenax/Silica gel/Charcoal

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**

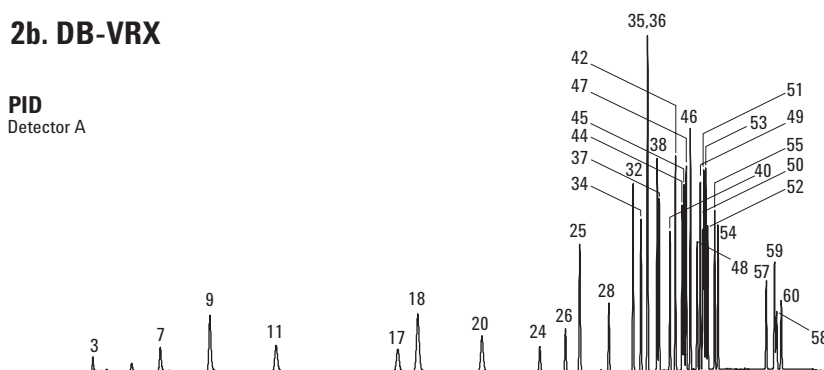
Detector A

**ELCD**

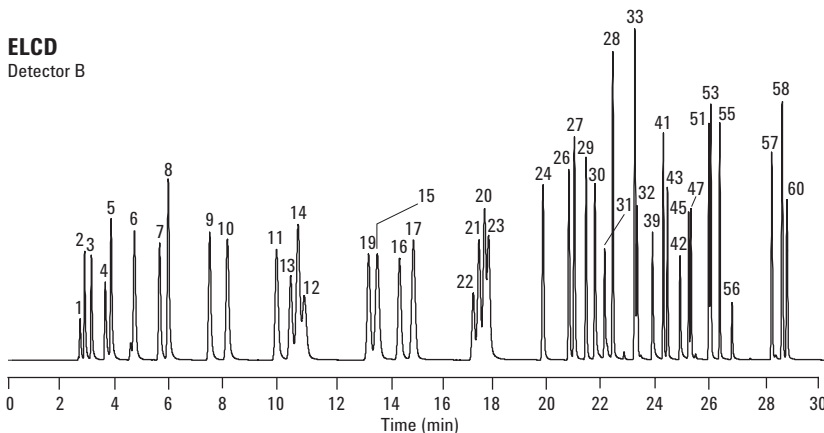
Detector B

**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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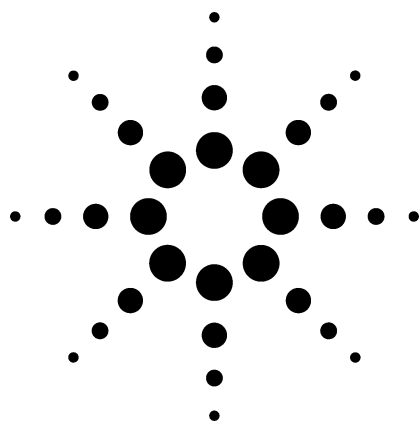
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DuraGuard Columns: GC Columns with Built-In Protection

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.

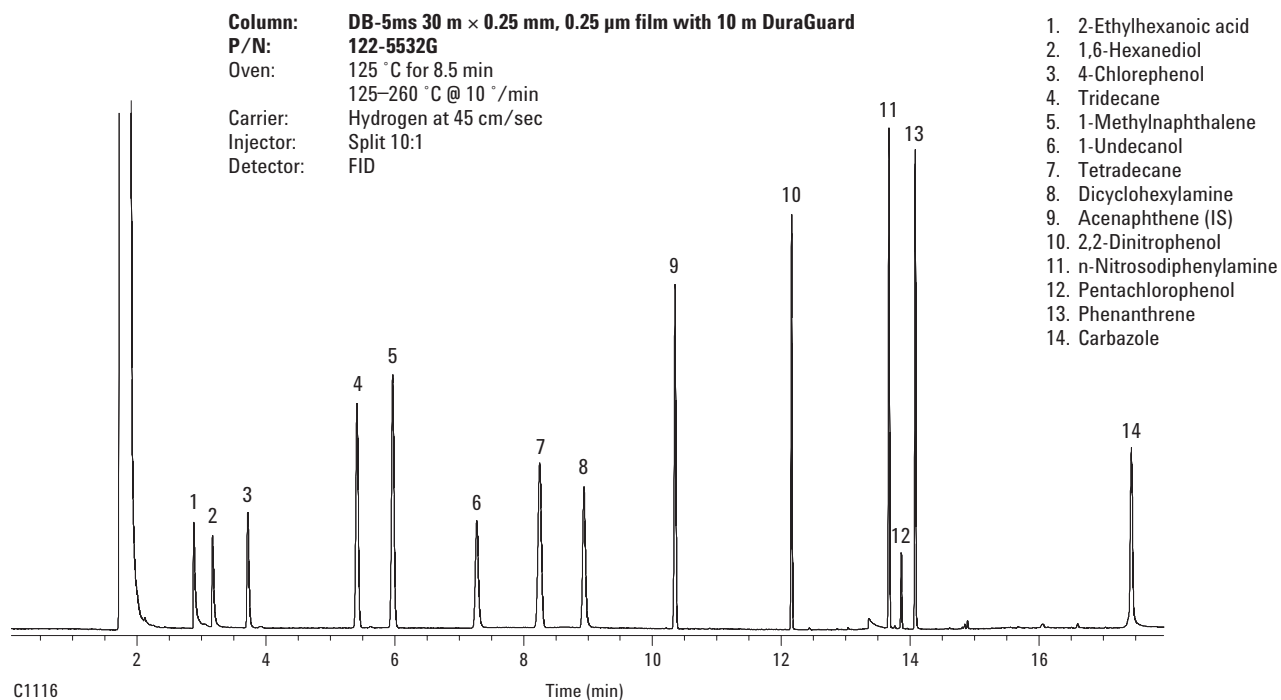


Figure 1. Chromatogram of test mixture using combination guard and analytical columns.

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.

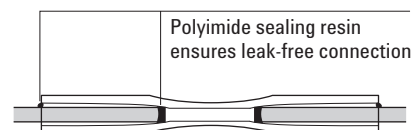


Figure 2. Detail of glass press fit union with polyimide sealing resin.

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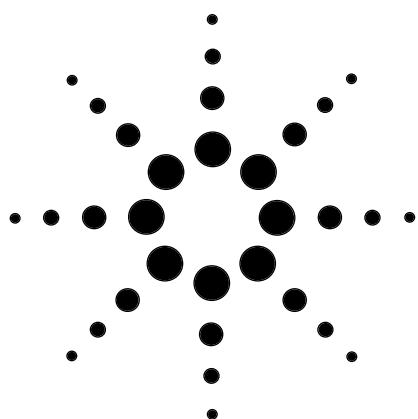
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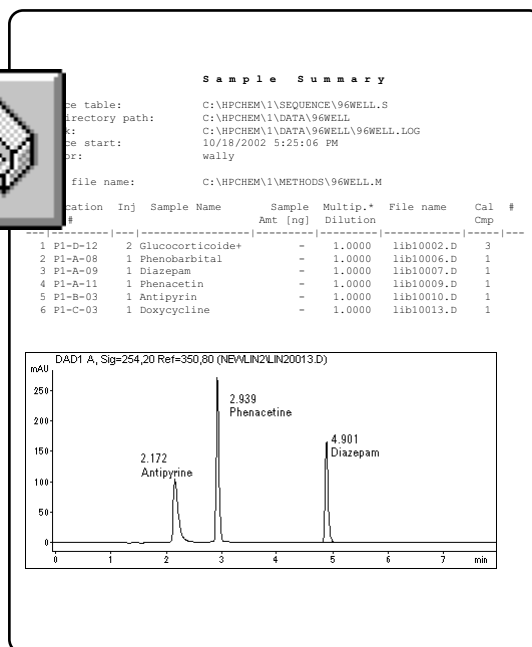
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Using Agilent ChemStation to generate summary reports for a single analysis or a sequence of analyses

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.

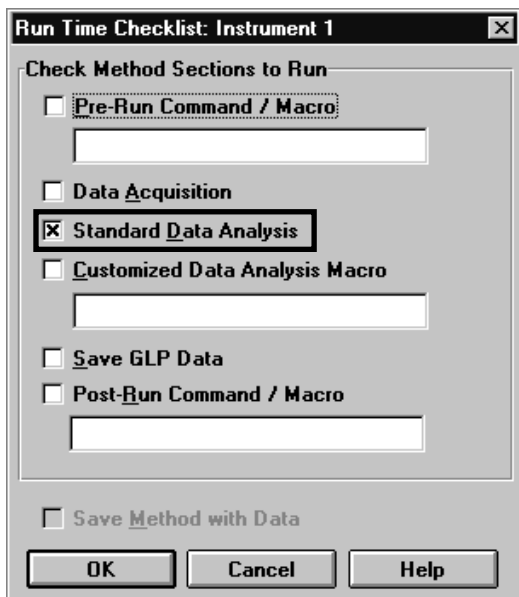


Figure 1
Activating *Standard Data Analysis*, including integration and quantification as part of the ChemStation method, is mandatory to obtain automated printouts of all report types available in the ChemStation base software

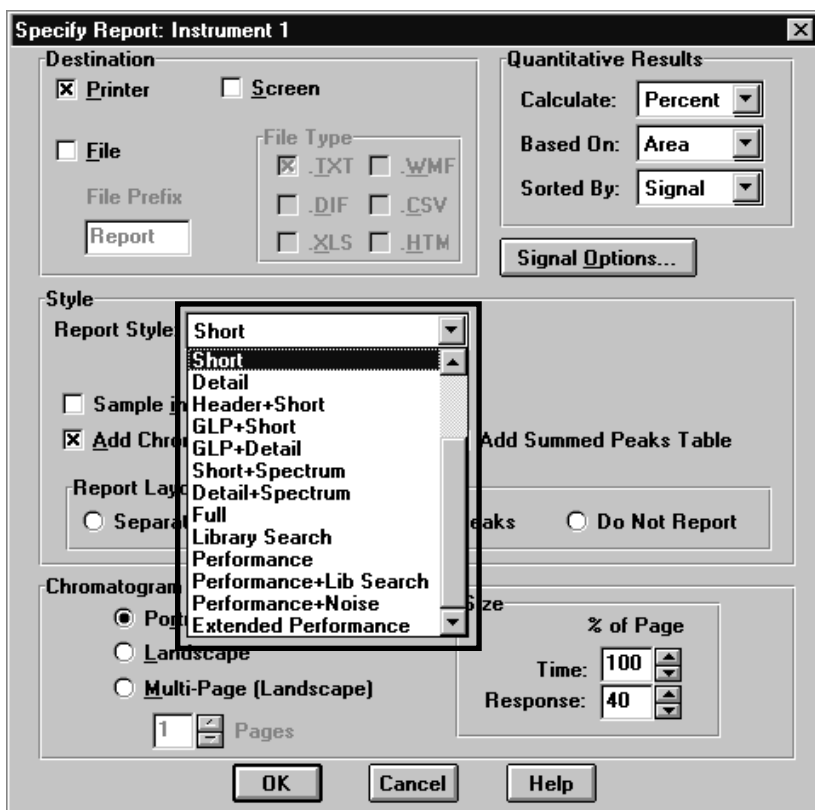


Figure 2
Specifying individual run reports

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.

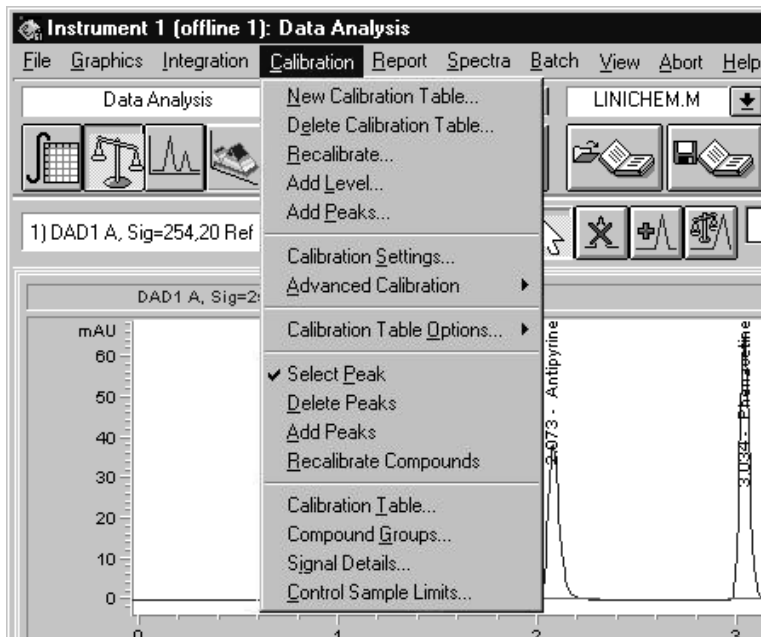


Figure 3
Calibration setup menu

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)

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.

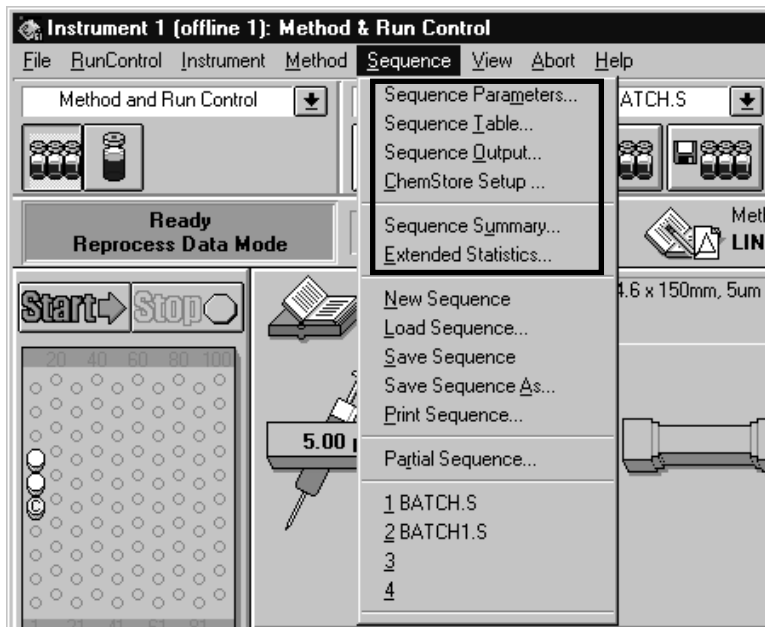


Figure 7
Entries need to be made in these sections to obtain automatically a sequence summary report at the end of a sequence

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-

Sequence Parameters: Instrument 1

Operator Name: cnickel

Data File
☒ Auto ☐ Prefix/Counter
 Prefix: SIG1 Counter: 0001
 Subdirectory: DEMO
 Path: D:\HPCHEM\1\DATA\

Bar Code Reader
☐ Use In Sequence
 On a bar code mismatch
☐ Inject anyway
☒ Don't inject

Shutdown
☐ Post-Sequence Cmd / Macro
 nRdy Timeout: 0 min

Part of methods to run
 According to Runtime Checklist
 According to Runtime Checklist
 Acquisition Only
 Reprocessing Only
 (after loading a new method)

Sequence Comment:
 Batch Review Demonstration

OK Cancel Help

Figure 8
Sequence parameters screen

Sequence Output: Instrument 1

Sequence Summary
☒ Print Sequence Summary Report
☒ Report to Printer
☐ Report to File: GLPrpt.txt
☐ Report to HTM
☒ Print individual reports for each run as well
 Destination of individual report
☒ as specified in each Method
☐ as specified here
☒ Printer
☐ Screen
☐ File
 File Prefix: report
 File Type
☒ .TXT ☐ .WMF
☐ .DIF ☐ .CSV
☐ .XLS ☐ .HTM
 Setup ...
 OK Cancel Help

Sequence Summary Parameters: Instrument 1

Activate report:
☐ 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

Style:
 Standard Statistic
 Standard Statistic
 Sample Summary
 Sample Summary
 Compound Summary
 OK Cancel Help

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.

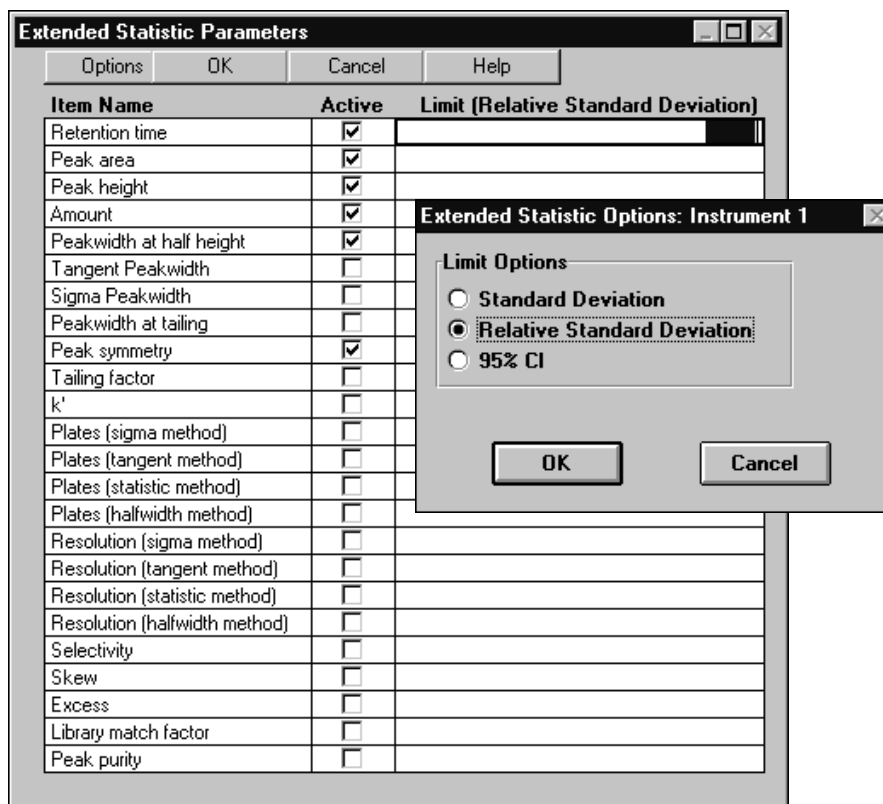


Figure 10
Setup of statistical calculations for sequence runs

Sequence Table: Instrument 1

Currently Running

Line: Method: Location: Inj:

Sample Info for P1-D-12:

Lib105

Plate 1 ID:

Plate 2 ID:

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

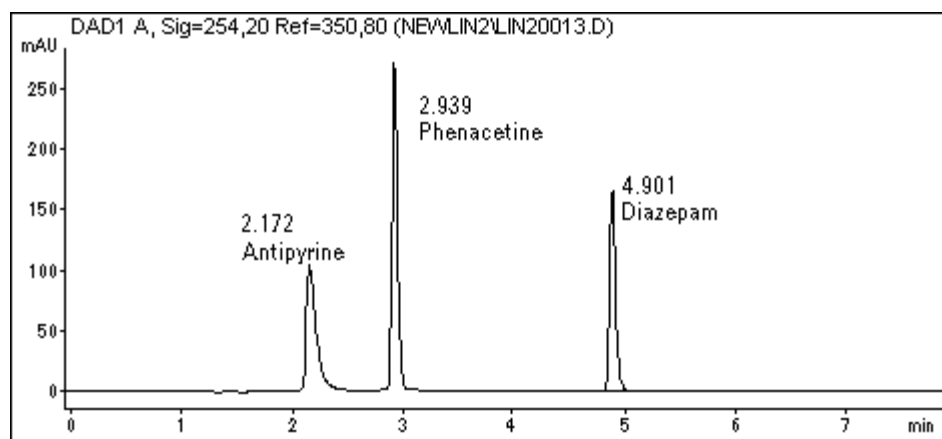
The following pages show examples of summary reports that can be generated with the ChemStation base software. The examples were generated using the print-to-file function and may have different pagination than a report printed directly from the ChemStation. Reports shown include:

- 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		

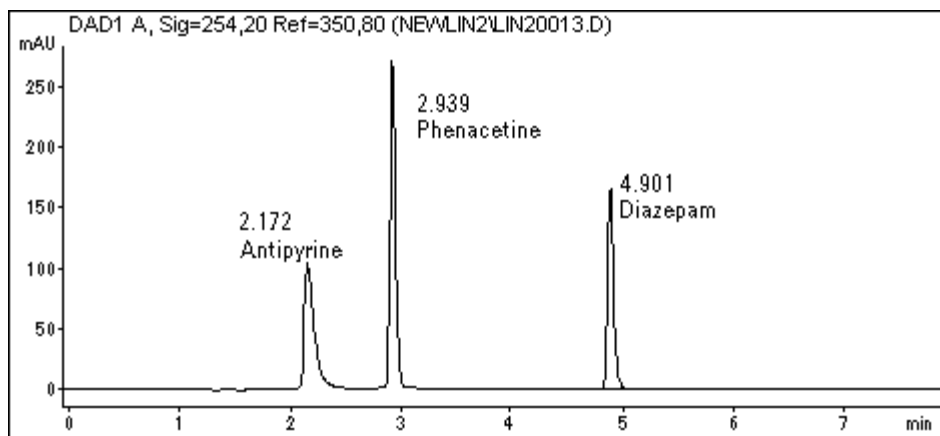
*** End of Report ***

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		

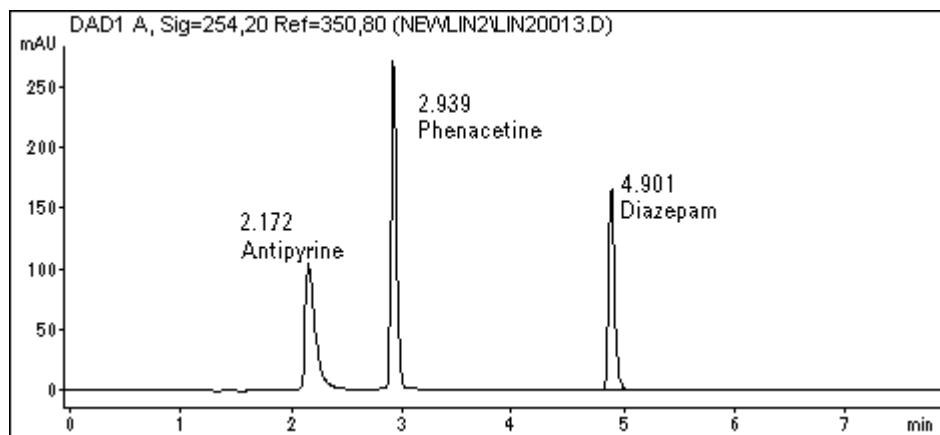
*** End of Report ***

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

```

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

```

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

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
=====
```

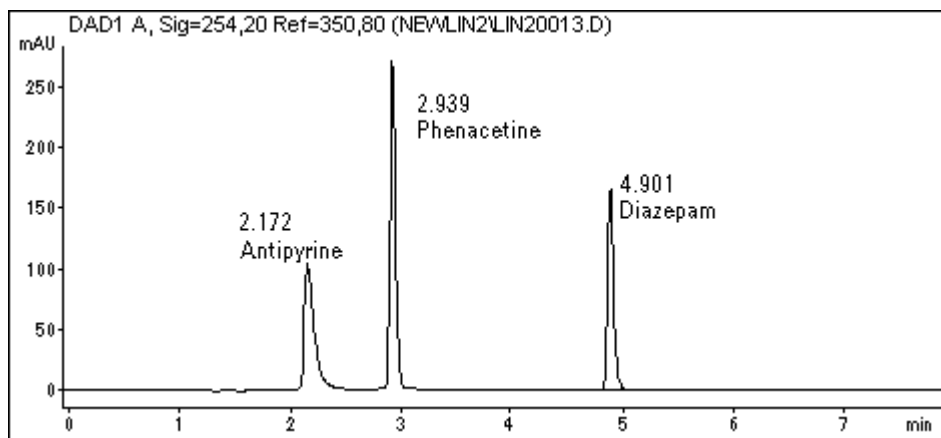
Short GLP Report (continued)

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 ***

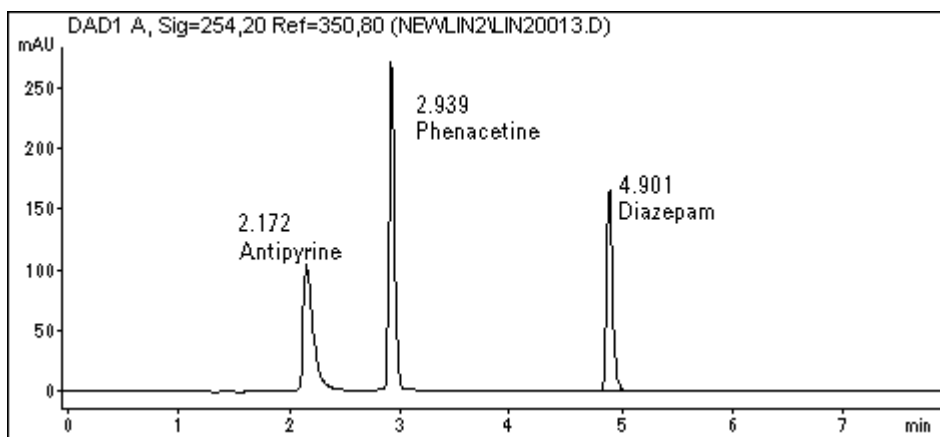
Performance report

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!

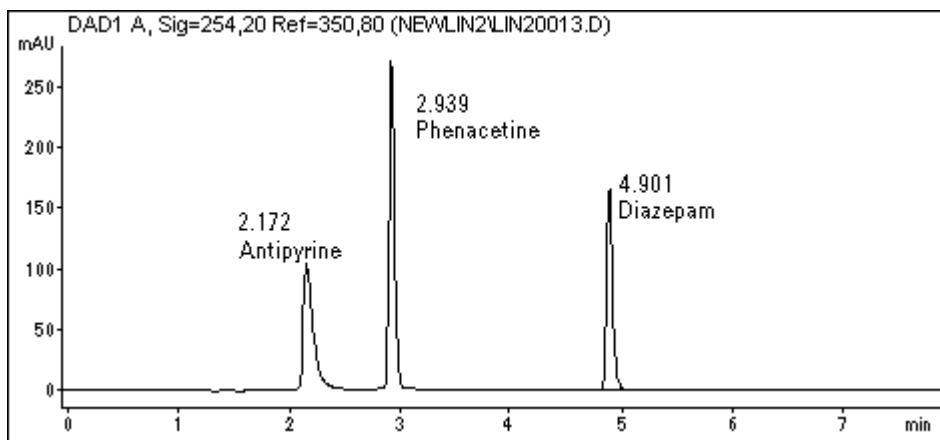
RetTime [min]	k'	Sig	Amount [ng]	Symm.	Width [min]	Plates	Resol	Name
2.172	0.81	1	438.70069	0.44	0.0883	3351	4.47	Antipyrine
2.939	1.45	1	937.28787	0.83	0.0524	17435	6.40	Phenacetine
4.901	3.08	1	599.59734	0.80	0.0550	43990	21.47	Diazepam

*** 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

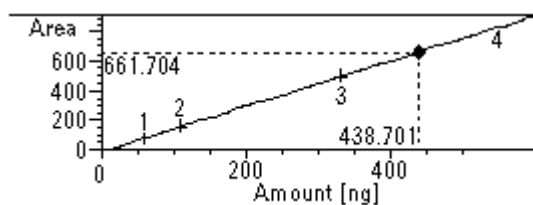
RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng]	Grp	Name
2.172	BB	661.70422	6.62986e-1	438.70069		Antipyrine
2.939	BB	934.32690	1.00317	937.28787		Phenacetine
4.901	BB	610.64050	9.81915e-1	599.59734		Diazepam
Totals :				1975.58590		

```
=====
```

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:

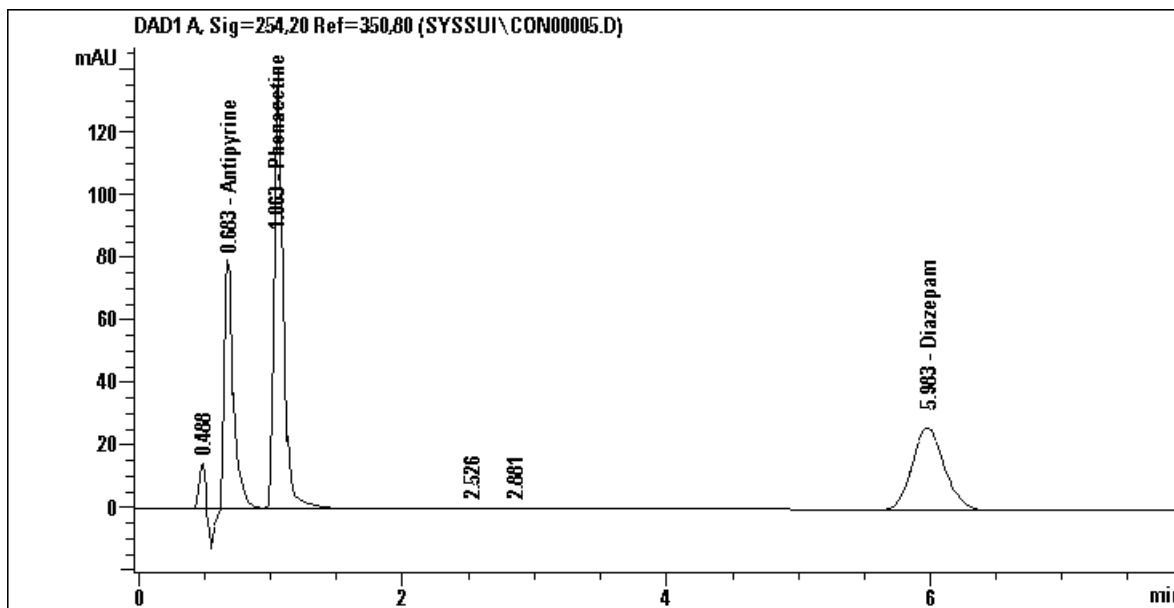
Operator:	agratz
Date/Time:	2/11/029:06:34 AM
Data file name:	D:\HPCHEM\1\DATA\SYSSUI\CON00005.D
Method file name:	D:\HPCHEM\1\METHODS\SYSSUIP.M

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

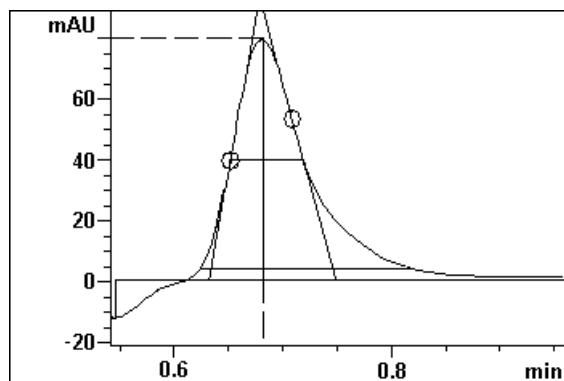
Symmetry: 0.483

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 ***

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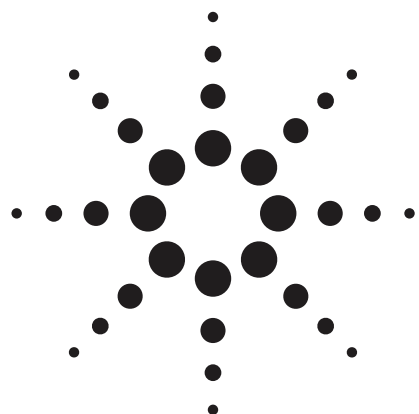
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Agilent Technologies



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

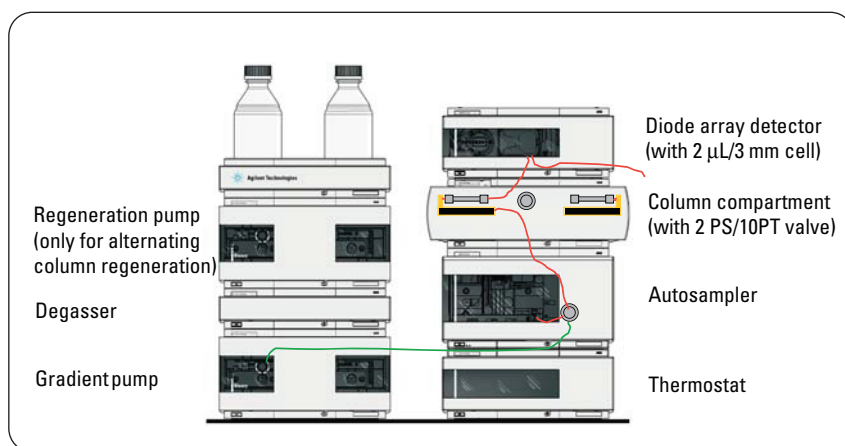


Figure 1
System setup with low delay volume for high speed applications using 2.1-mm id columns with lengths from 20 to 50 mm.

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-acetonitril 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

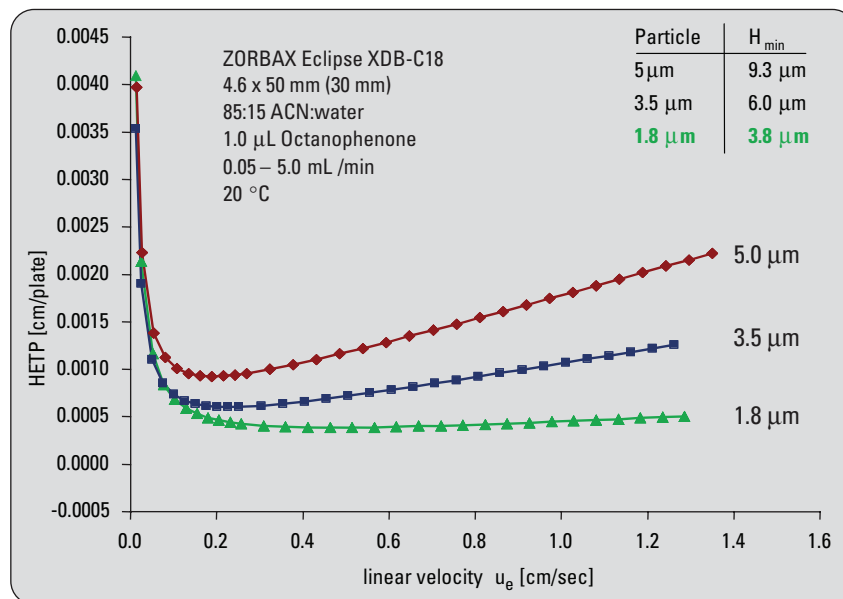


Figure 2
Van Deemter curves of columns packed with 1.8 μm , 3.5 μm and 5.0 μm particles.

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).

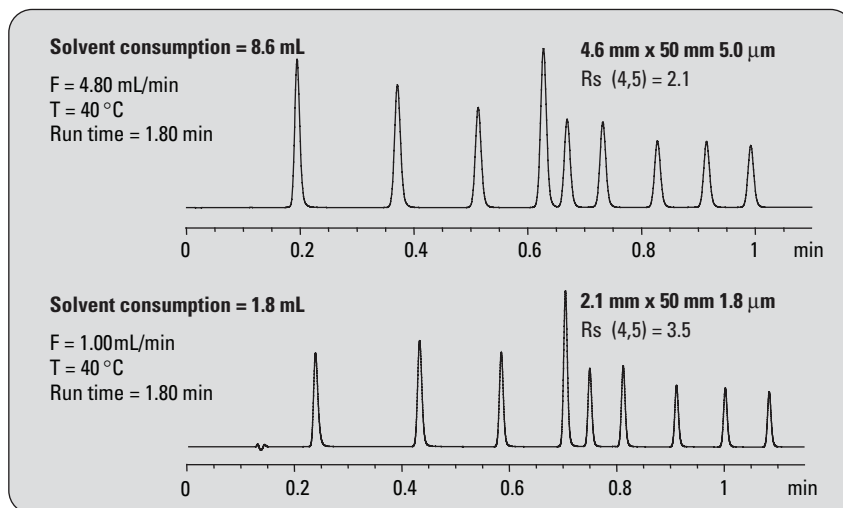


Figure 3
Analysis with 1.8-µm particle column vs. 5.0 µm particle column.

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.</i>
	<i>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

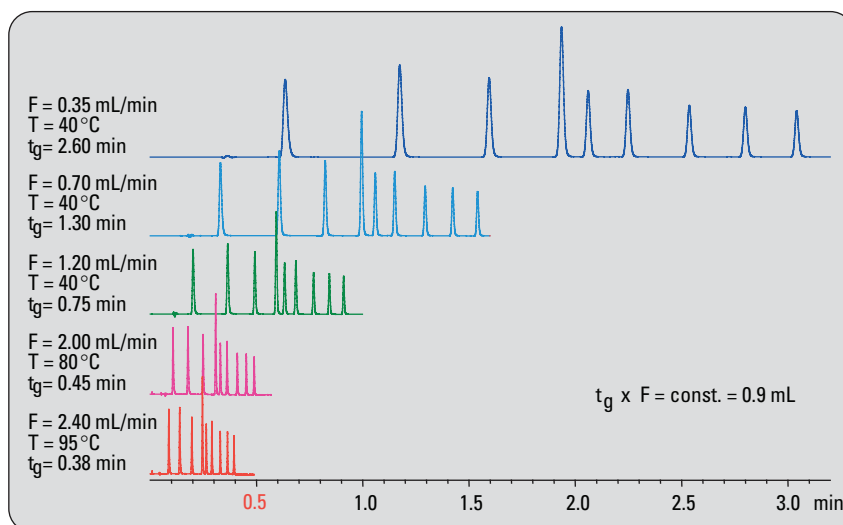


Figure 4
Increasing separation speed by increasing temperature and flow rate while decreasing gradient time.

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

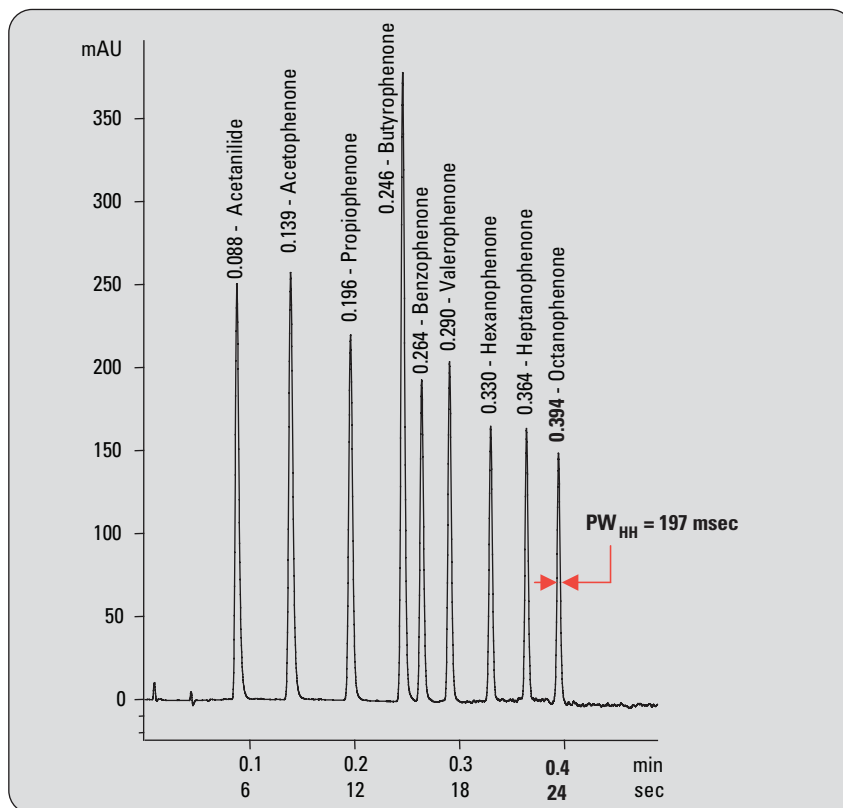


Figure 5
Separation of a nine compound mixture under ultra fast conditions.

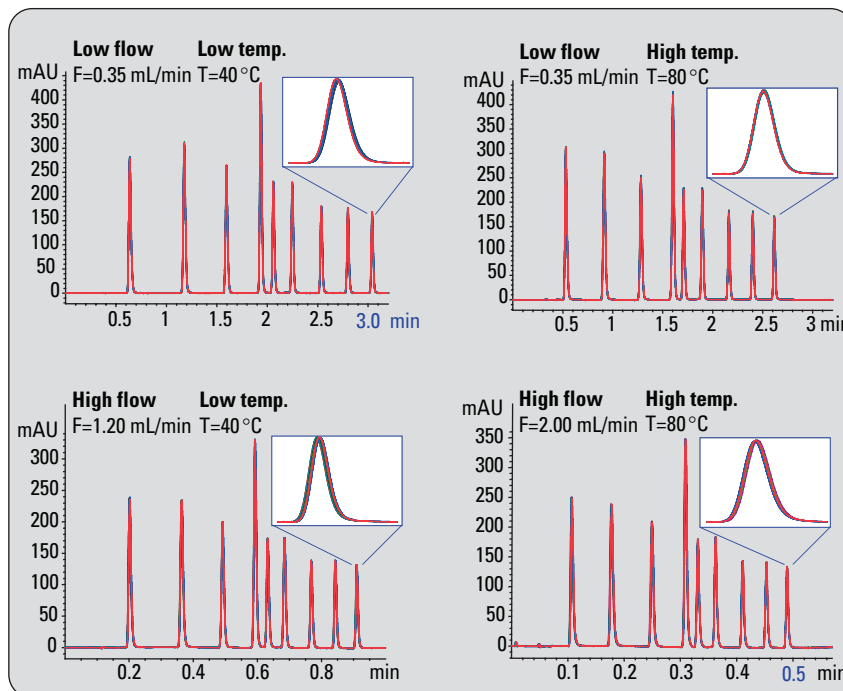


Figure 6
Overlaid chromatograms of the repeated analysis of a 9 compound mixture under various conditions.

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

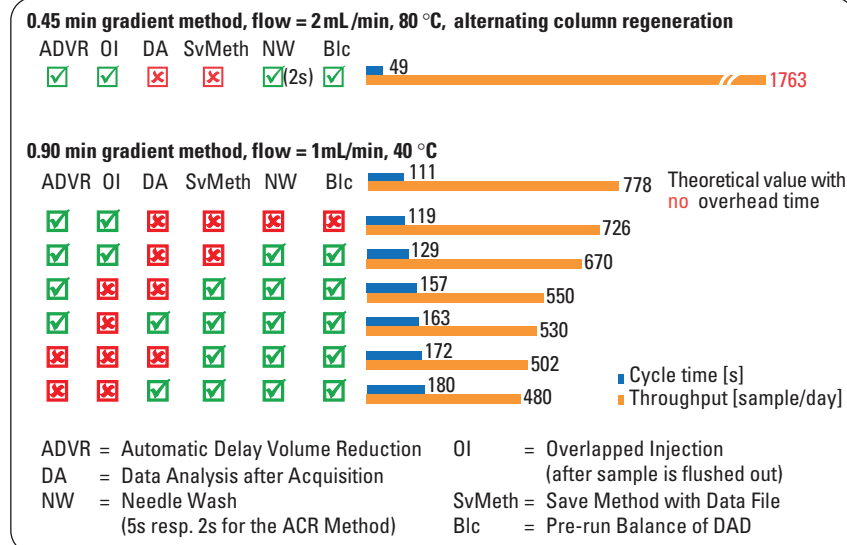


Figure 7
Cycle time and daily throughput optimization.

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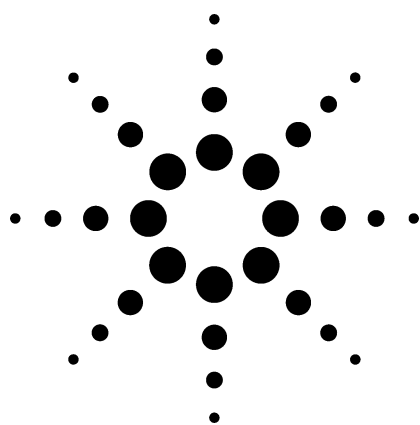
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Improving the Effectiveness of Method Translation for Fast and High Resolution Separations

Application

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Abstract

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

Introduction

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

Simplistically, a column of 250-mm length and containing 5- μm particles can be replaced by a 150-mm length column packed with 3- μm particles. If the ratio of length to particle size is equal, the two columns are considered to have equal resolving power. Solvent consumption is reduced by 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

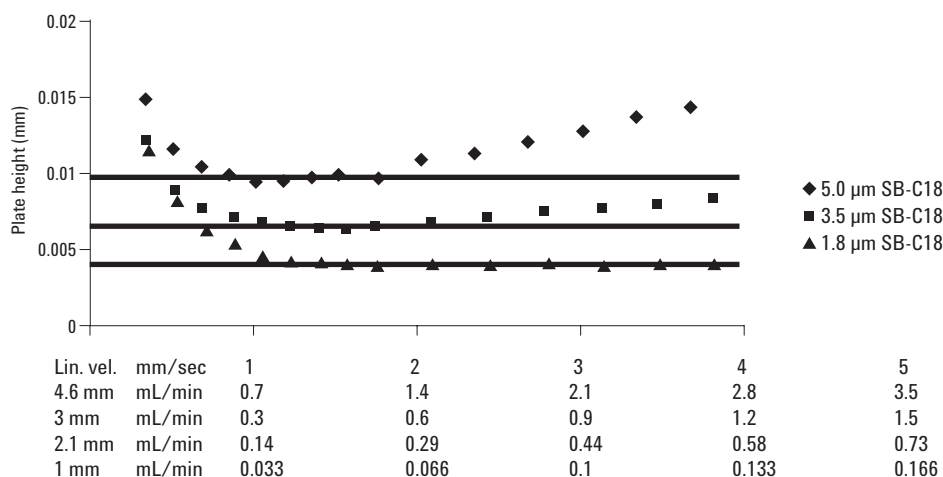


Figure 1. van Deemter plot with various flow rates and particle sizes.

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

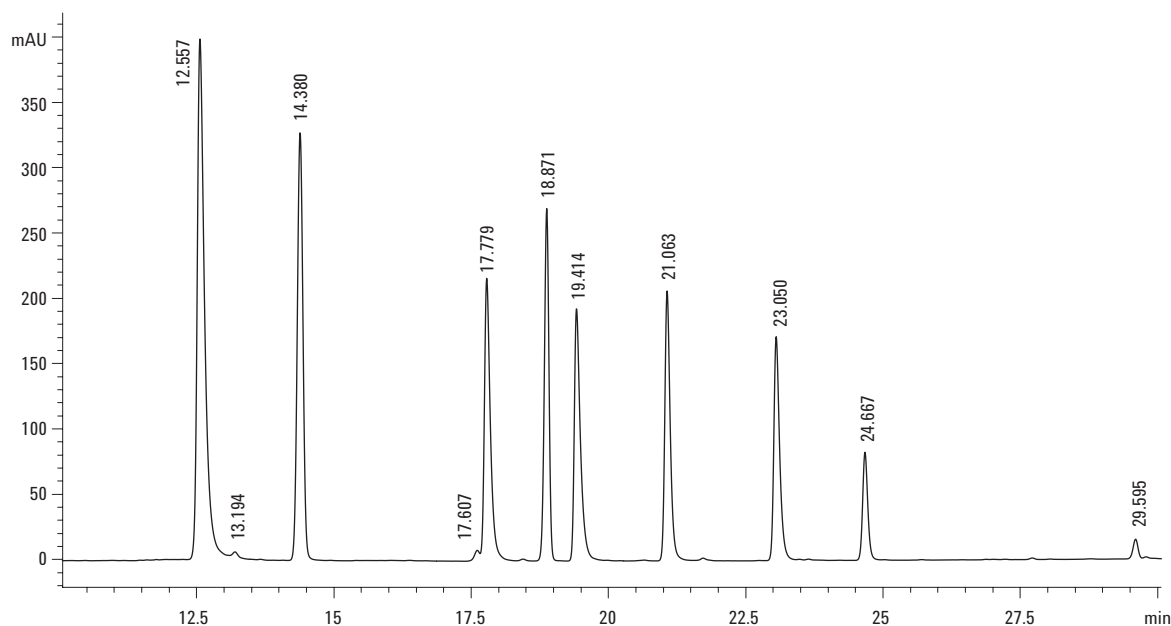
Standard mixture of chlorinated phenoxy acid herbicides,
 100 μg/mL in methanol

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

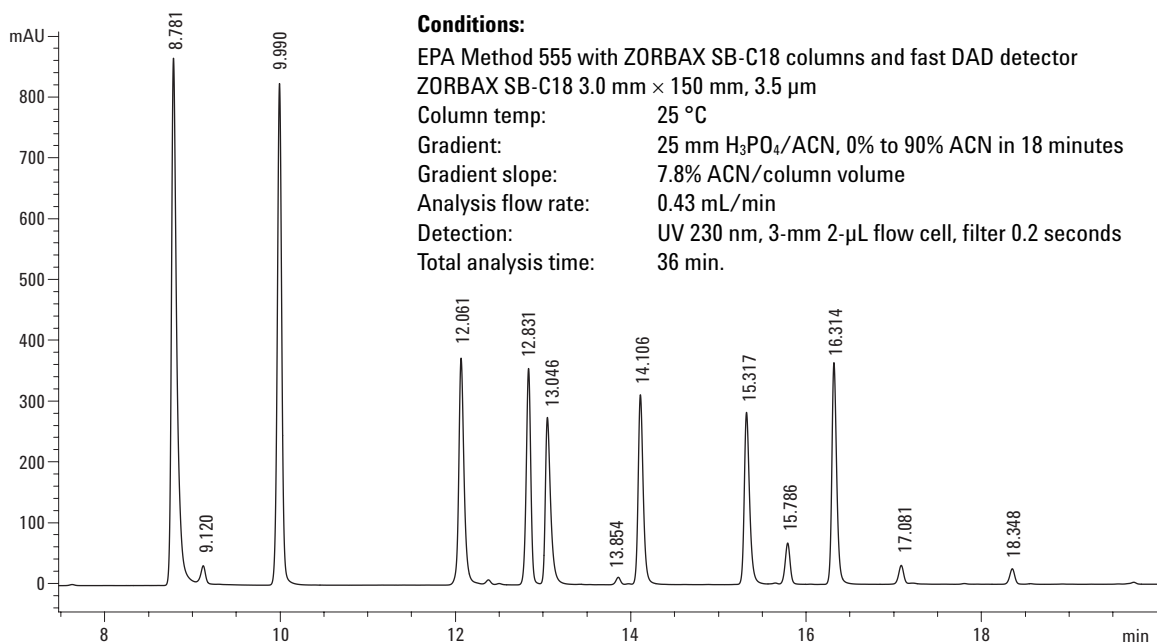
Analysis flow rate: 1 mL/min

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.

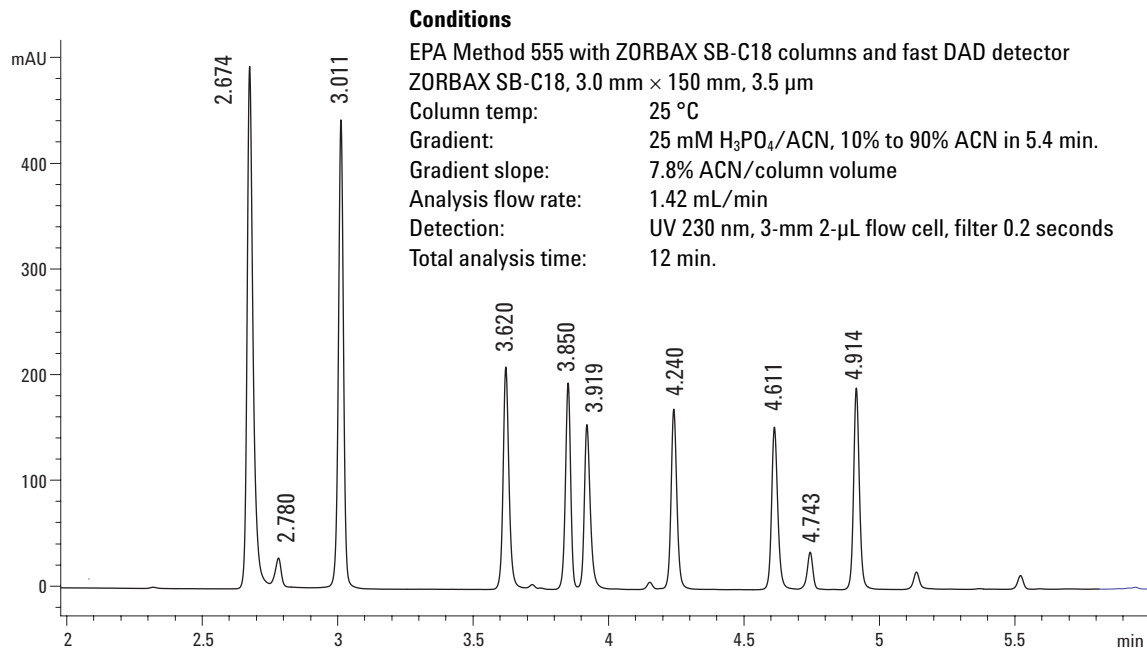


Figure 4. High speed gradient separation of herbicides on 3.0 × 150 mm, 3.5-μm ZORBAX SB-C18.

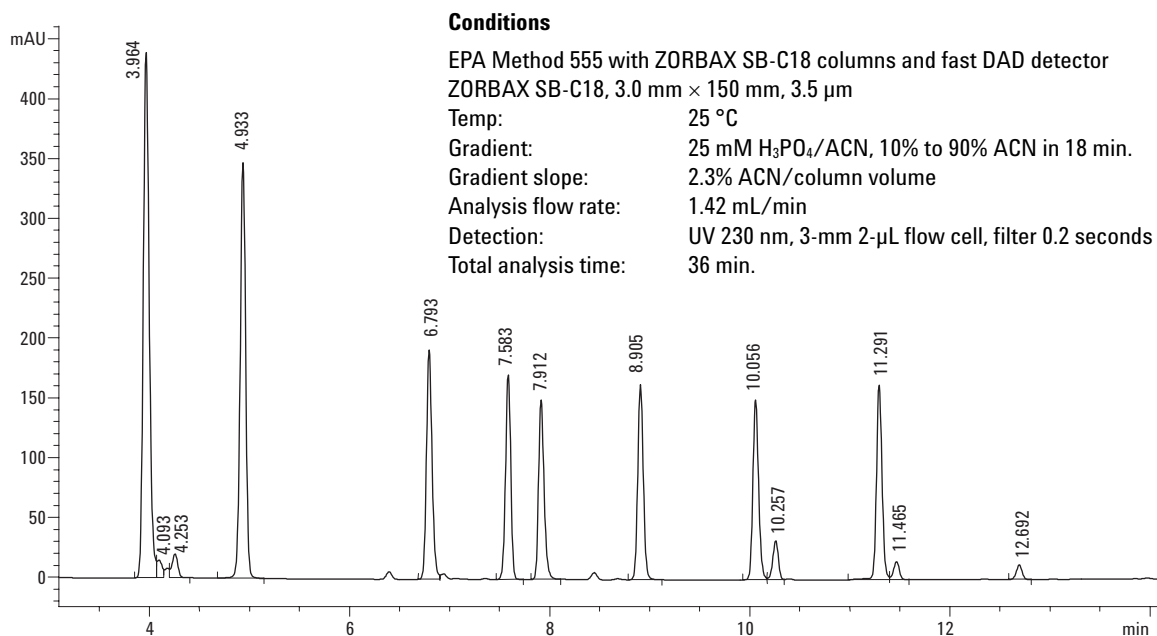


Figure 5. Reduced slope gradient separation of herbicides on 3.0 × 150 mm, 3.5-μm ZORBAX SB-C18.

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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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.

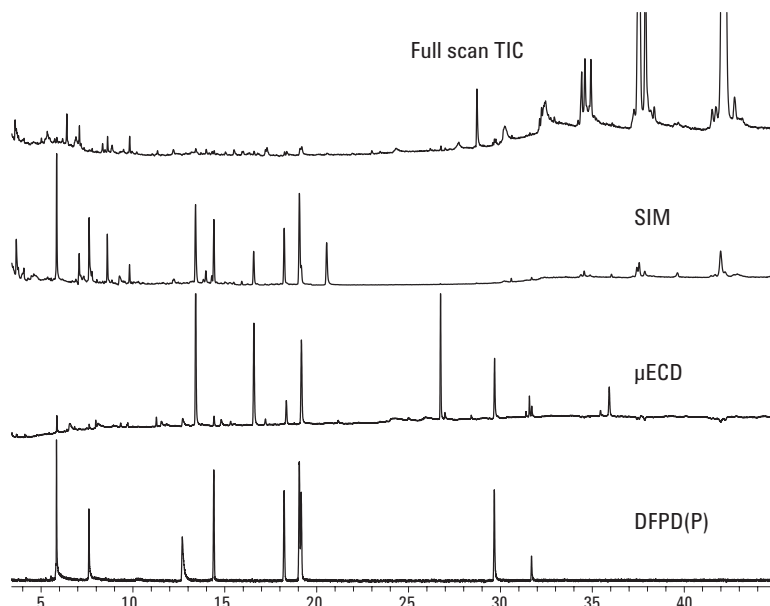


Figure 1. Four chromatograms collected simultaneously from a single injection of a milk extract.



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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

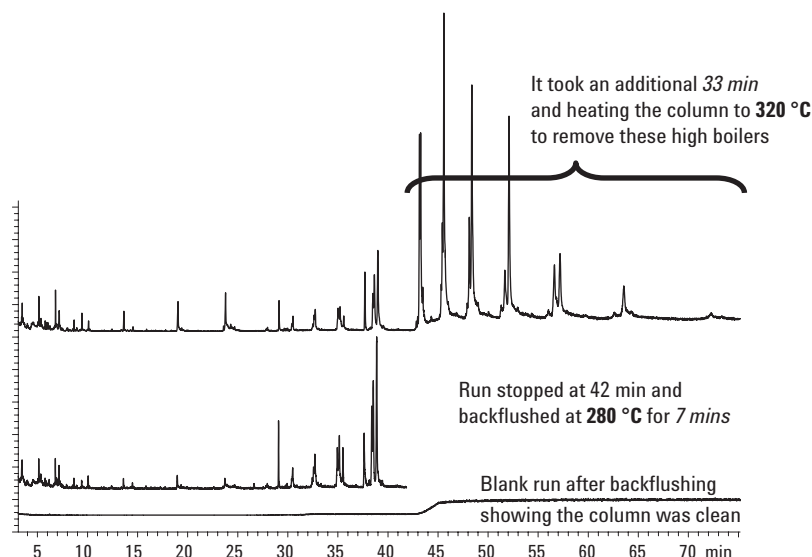


Figure 2. Three total ion chromatograms comparing the results with and without backflush.

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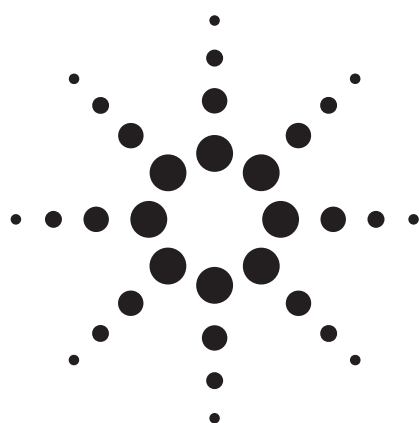
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High-Pressure Liquid Injection Device for the Agilent 7890A and 6890 Series Gas Chromatographs

Application

Hydrocarbon Processing

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Abstract

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

Introduction

There are several known techniques for injecting volatile liquefied hydrocarbons in gas chromatographs. The simplest tools are high-pressure

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

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

Experimental

Injection Device

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



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

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

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

Guideline for choosing Aux flow source

7890AGC

G3471A Pneumatic Control Module (PCM) or
G3470A Aux EPC module

6890GC

G1570A Aux EPC or
G2317A PCM module

The PCM is the preferred source for both GCs.

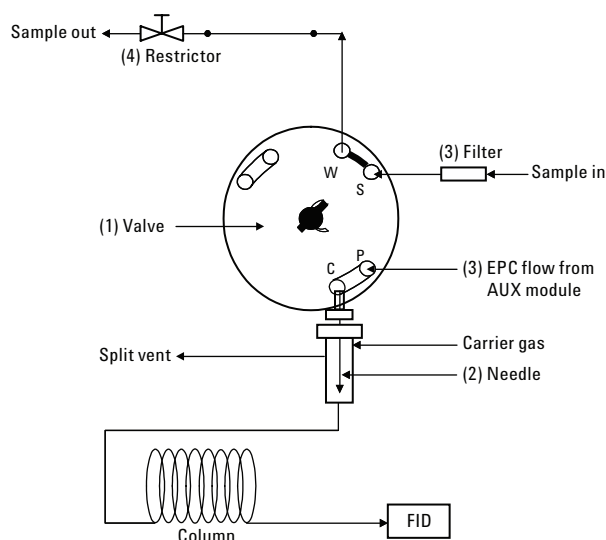


Figure 1. Flow diagram of the HPLI device.

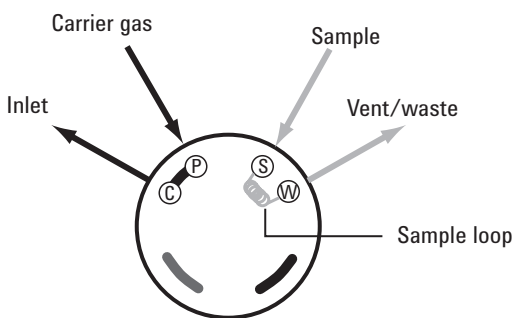
Samples for System Evaluation

- Liquefied natural gas: Calibration standard, 1,200 psi, with nC7-nC9 (0.102%–0.0503%)
- Liquefied ethylene: Purity 99.5, 1,200 psi
- Pressurized propylene: Grade C. P., purity 99.0%, 200 psi
- Pressurized propane + n-butane: 50.0%:50.0%, 200 psi
- Pressurized 1, 3-butadiene: Purity 99.5%, 180 psi
- n-Hexane + 1.0 % 2# BP standard (Agilent PN 5080-8768, nC5–nC18)
- nC5–nC40 D2887 1# BP standard (Agilent PN 5080-8716, diluted by CS₂)
- Glycols, including monoethylene glycol, diethylene glycol, and triethylene glycol
- C8 to C16 hydrocarbons at 100 ppm each

Operating Process

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

Load



Inject

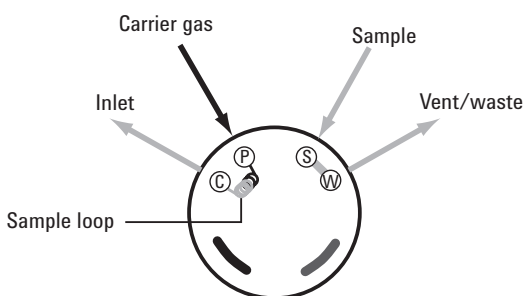


Figure 2. Pneumatic and sample paths in load and inject positions.

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

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

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



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

Table 1. Instrumental Conditions

Gas chromatograph	Agilent 7890A
Injection source	HPLI device at near ambient temperature
Injection port	Split/splitless, 250 °C (350 °C for C5–C40)
Sample size	0.5- μ L (0.2 μ L for C5–C40) device supplied with 0.06- μ L rotor
Carrier gas	Helium
Aux or PCM	150 mL/min (Helium)
FID	250 °C (350 °C for C5–C40) H ₂ , 35 mL/min Air, 400 mL/min

Table 2. Columns and Parameters

Samples	Columns	Column flow mL/min	Split ratio	Temperature program	Sample pressure psig
Natural gas	30 m $\times$ 0.53 mm $\times$ 0.5 μ m DB-1 #125-1037	8	40:1	35 °C, 1 min 20 °C/min to 180 °C, 1 min	1200
Ethylene	50 m $\times$ 0.53 mm $\times$ 15 μ m AL203 PLOT/KCL + 30 m $\times$ 0.53 mm $\times$ 5 μ m DB-1, #19095P-K25 and #125-1035	8	20:1	35 °C, 2 min 4 °C/min to 160 °C, 3.8 min	1100
Propylene	50 m $\times$ 0.53 mm HP AL203 PLOT + 30 m $\times$ 0.53 mm $\times$ 5 μ m DB-1	7	25:1	35 °C, 2 min 4 °C/min to 160 °C, 1.8 min	180
Propane + n-butane	30 m $\times$ 0.53 mm $\times$ 1.0 μ m DB-1, #125-103J	5	50:1	35 °C	150
1,3-Butadiene	50 m $\times$ 0.53 mm AL203 PLOT/KCL	10	15:1	35 °C, 2 min 10 °C/min to 195 °C, 15 min	180
n-Hexane	30 m $\times$ 0.53 mm $\times$ 1.0 μ m DB-1	5	50:1	45 °C	N/A
nC5-nC40	10 m $\times$ 0.53 mm $\times$ 0.88 μ m HP-1, #19095Z-021	10	15:1	35 °C, 1 min 15 °C/min to 350 °C, 5 min	N/A
Glycols	30 m $\times$ 0.25 mm $\times$ 1.0 μ m HP-1 ms	1.8	15:1	50 °C, 3 min 15 °C/min to 250 °C, 2 min	

Results and Discussion

Check for Carryover

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

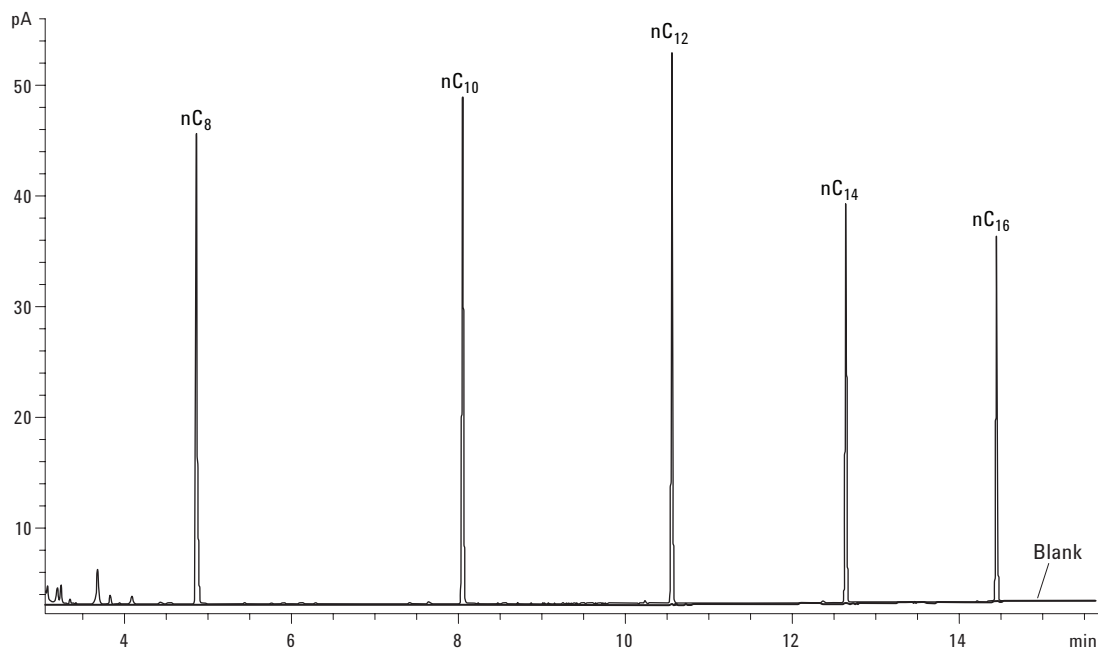


Figure 4. Overlay of standard versus blank (100 ppm each in cyclohexane).

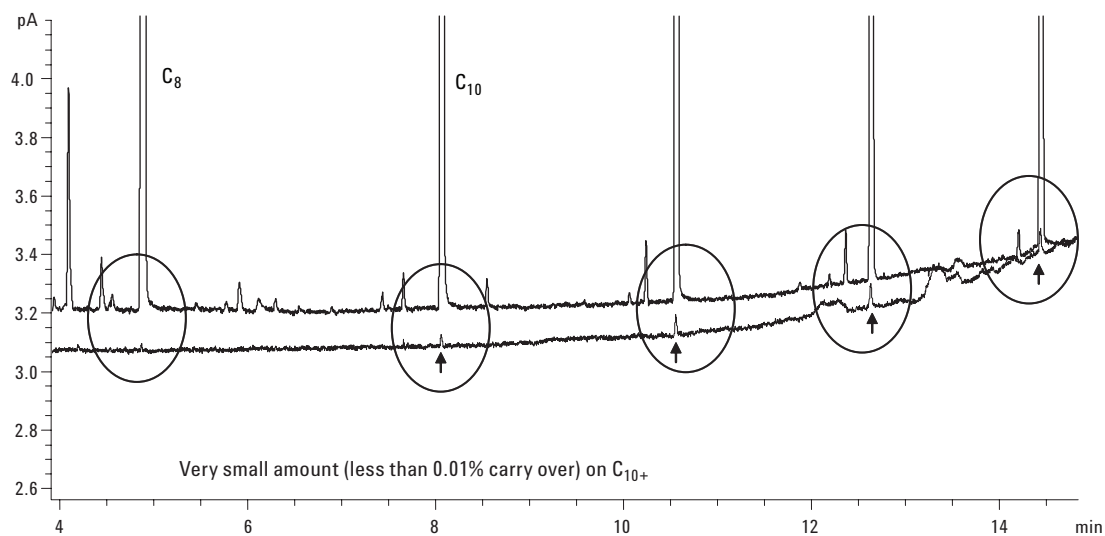


Figure 5. Carryover less than 0.01% on C₁₀₊.

Sample Analysis

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

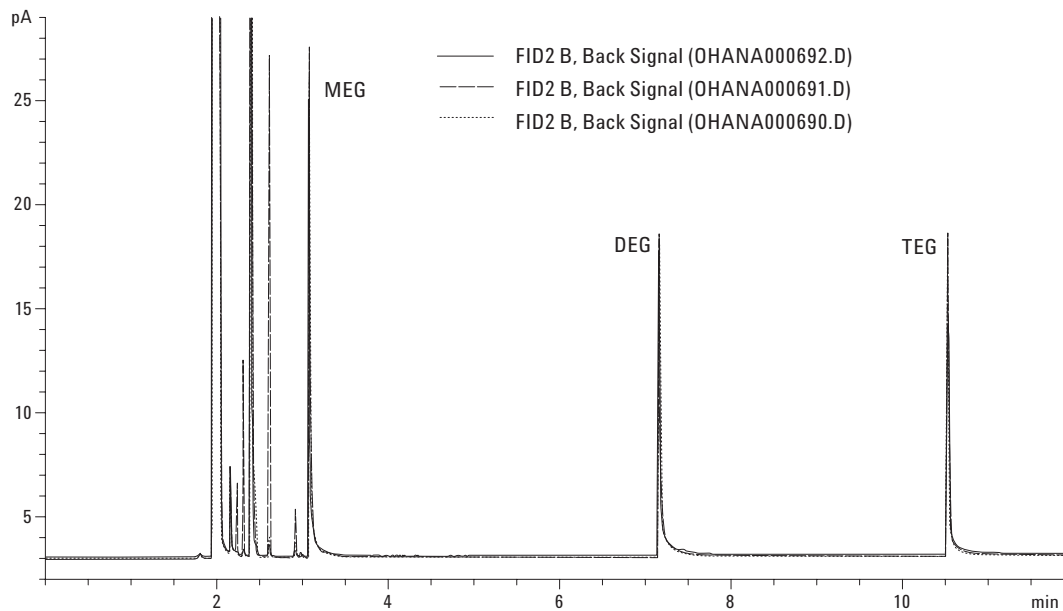


Figure 6. Triplicate run of 100 ppm each of MEG, DEG, and TEG in IPA.

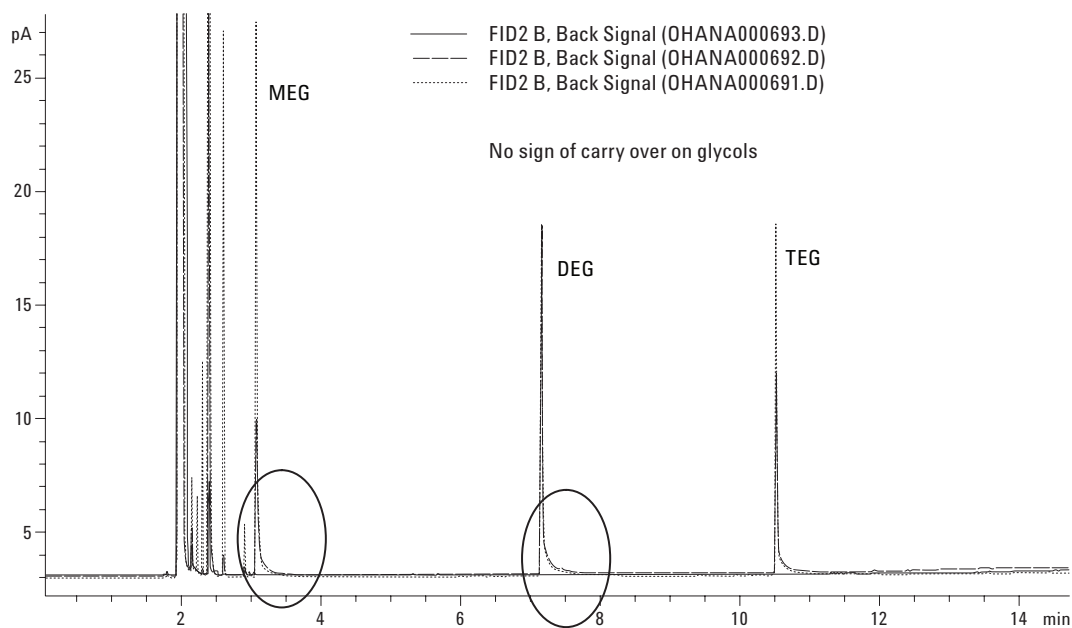


Figure 7. Glycols versus blank. Two standard duplicates, blank run immediately after injection of standard.

A. Liquefied Natural Gas

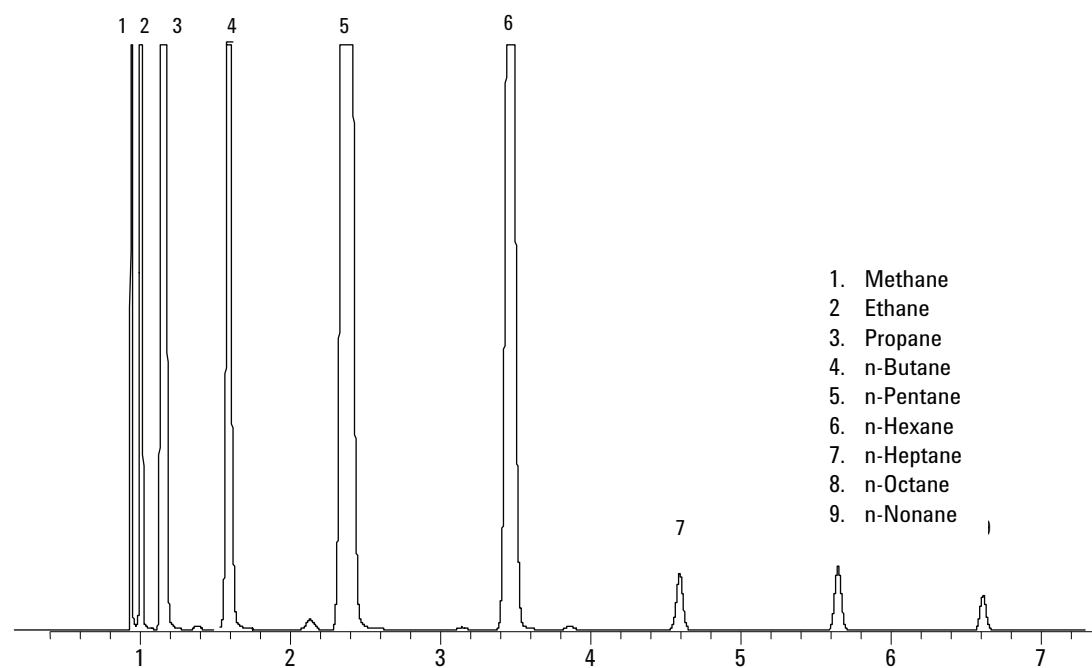


Figure 8. Chromatogram of liquefied natural gas (calibration standard).

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

B. Liquefied Ethylene

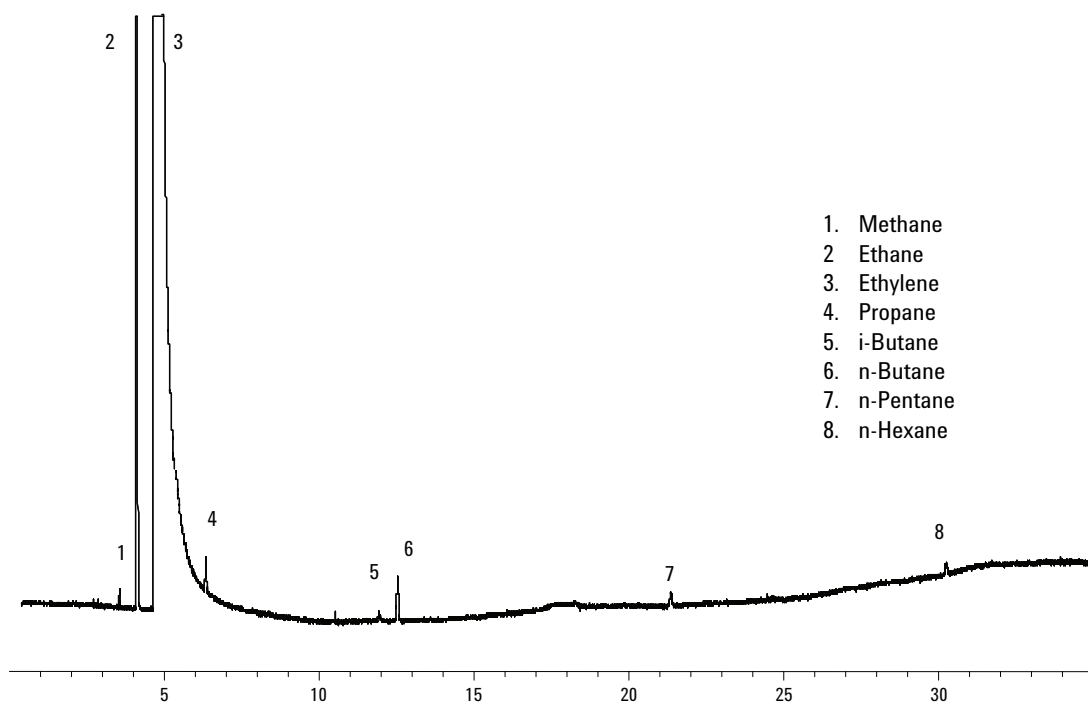


Figure 9. Chromatogram of liquefied ethylene.

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

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

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

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

C. Pressurized Propylene

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

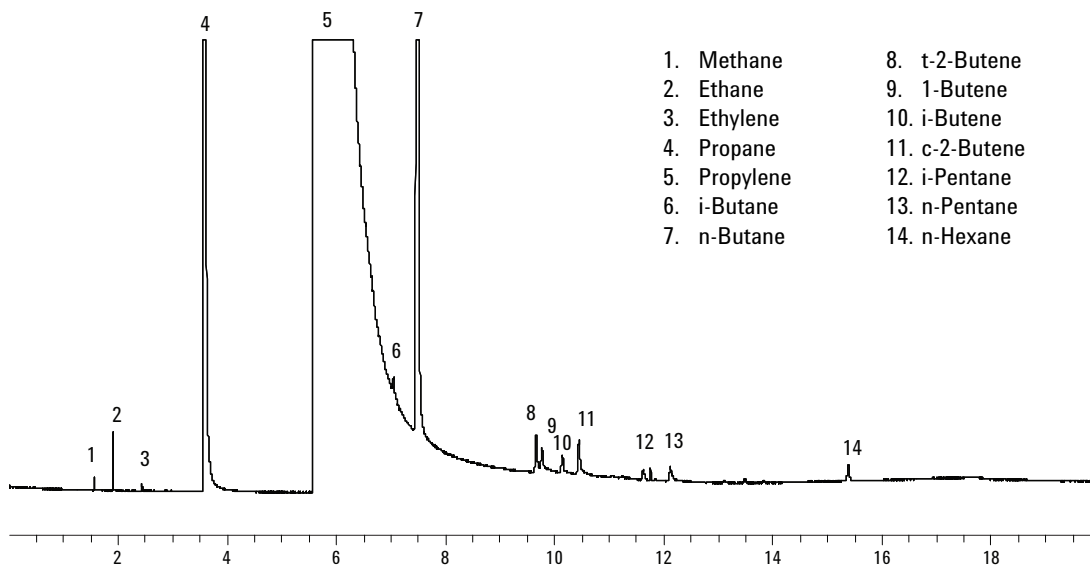


Figure 10. Chromatogram of pressurized propylene.

D. Pressurized 1,3-Butadiene

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

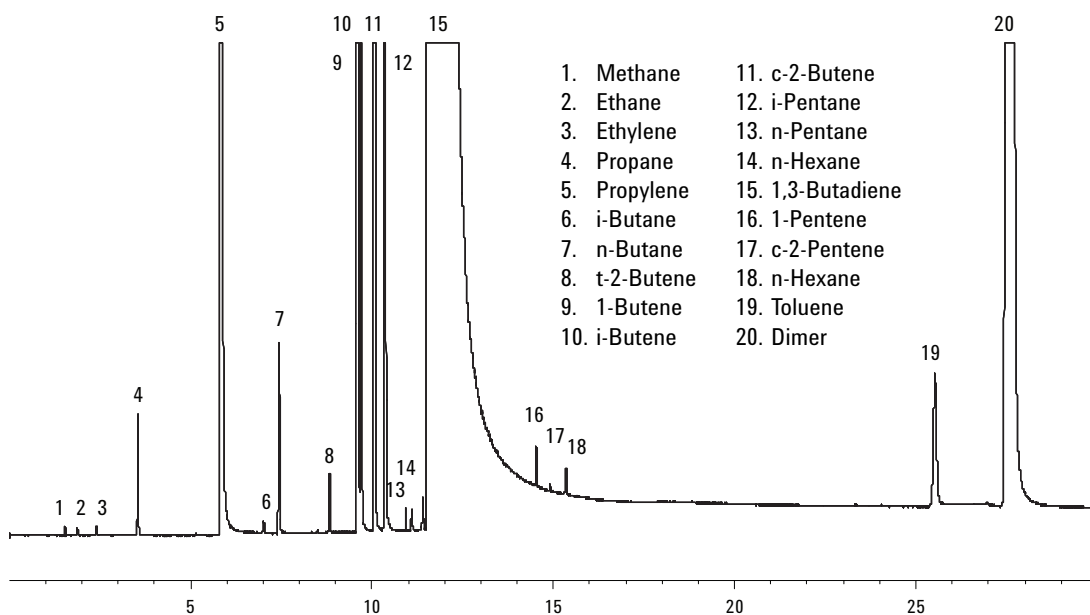


Figure 11. Chromatogram of pressurized 1,3-butadiene.

E. Pressurized Propane + n-Butane

This is a quantitative calibration sample:

Propane:n-Butane = 50%:50%.

The chromatogram is shown in Figure 12 with the results of a quantitative analysis shown in Table 4.

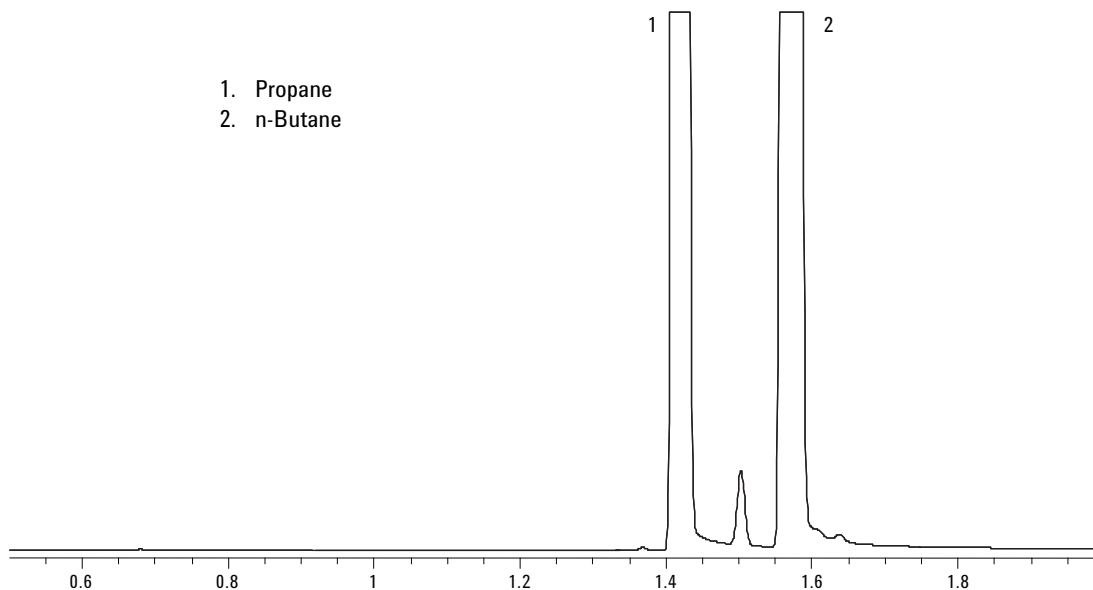


Figure 12. Chromatogram of pressurized propane + n-butane.

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

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

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

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

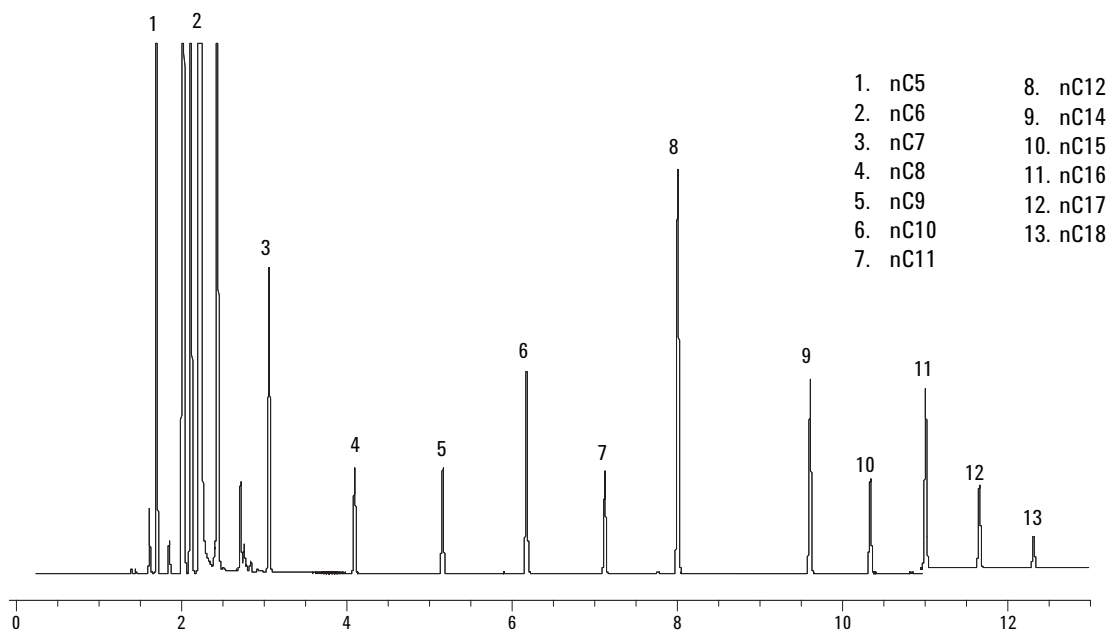


Figure 13. Chromatogram of n-hexane + 1.0% BP standard.

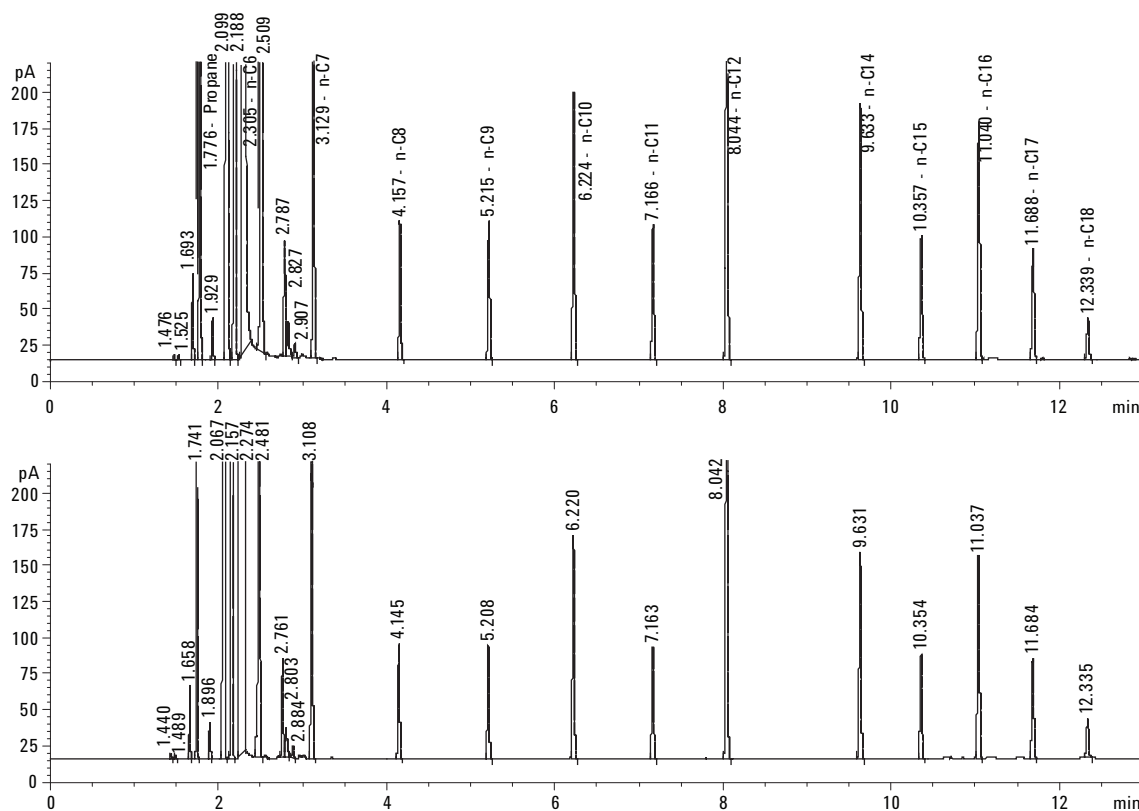


Figure 14. Chromatograms of n-hexane + 1.0% BP standard. Top: HPLI. Bottom: ALS (syringe).

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

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

The peak width of hexane at top: 0.0209 min

The peak width of hexane at bottom: 0.0195 min

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

G. nC5-nC40 (D2887 BP Standard Diluted by CS₂)

A sample with hydrocarbons (nC5-nC40 D2887 1# BP standard diluted by CS₂) is also run on HPLI. The chromatogram is shown in Figure 15.

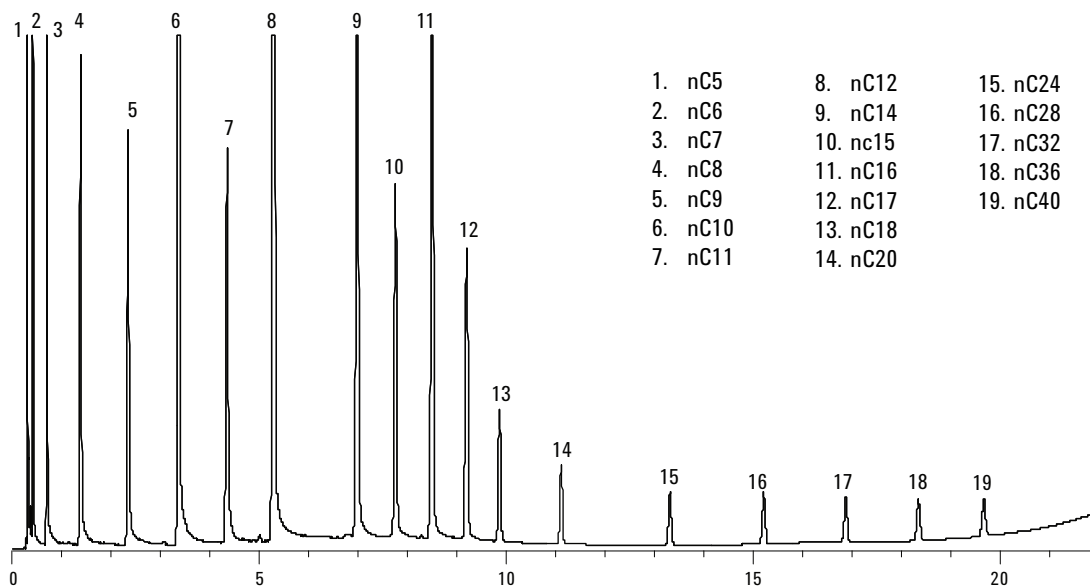


Figure 15. Chromatogram of nC5-nC40 (D2887 BP standard diluted by CS₂).

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

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

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

Conclusions

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

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1. C. J. Cowper and A. J. DeRose, "The Analysis of Gases by Chromatography" (Pergamon Series in Analytical Chemistry, Vol. 7), Pergamon Press, Oxford, 1983, Ch. 6.
2. K. J. Rygle, G. P. Feulmer, and R. F. Scheideman, *J. Chromatogr. Sci.*, 22 (1984) 514–519.
3. Jim Luong, Ronda Gras, and Richard Tymko, *J. Chromatogr. Sci.*, 41 (2003) 550–5.

Acknowledgement

Figures 1 through 4 are courtesy of Ronda Gras and Jim Luong, Dow Chemical Canada, Analytical Sciences.

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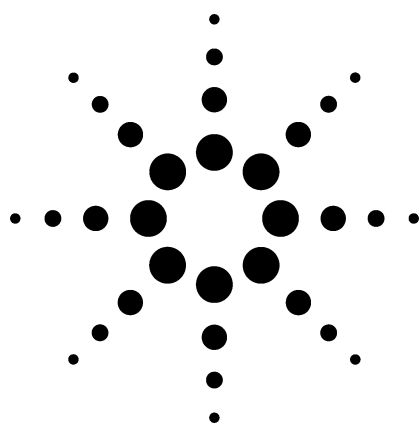
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A Column-Flow Independent Configuration for QuickSwap



Application

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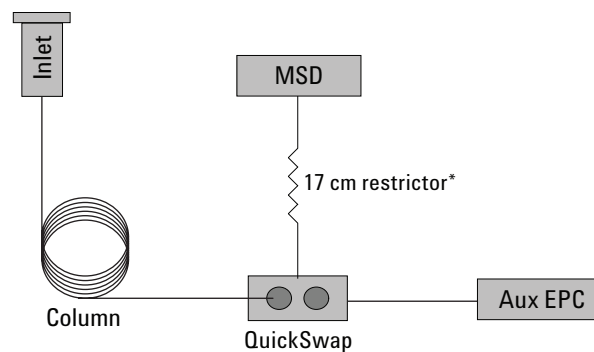
Abstract

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

Introduction

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

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



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

Figure 1. General concept of QuickSwap.



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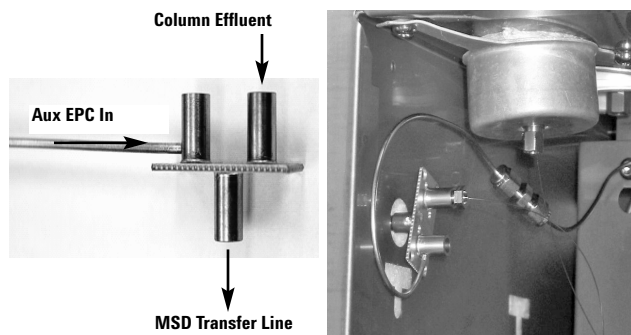


Figure 2. QuickSwap is pictured on the left showing permanent (Aux EPC In) and temporary connections. A picture of a normal QuickSwap installation is shown on the right.

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.

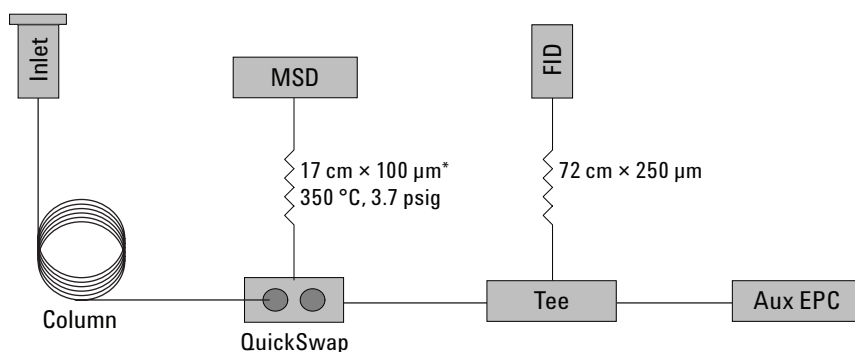
In general, when flow to the MSD changes,

- 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.

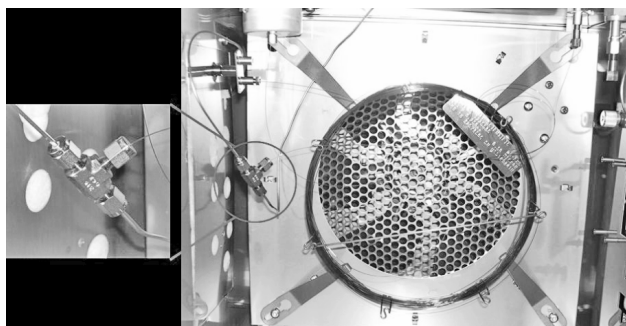
- Simplifies retention time locking applications with QS
- Allows pressure pulse injections without having to change QS restrictor
- Allows more aggressive backflush conditions than if larger restrictors were used
- Allows method translation and speed up without having to change QS restrictor
- Allows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

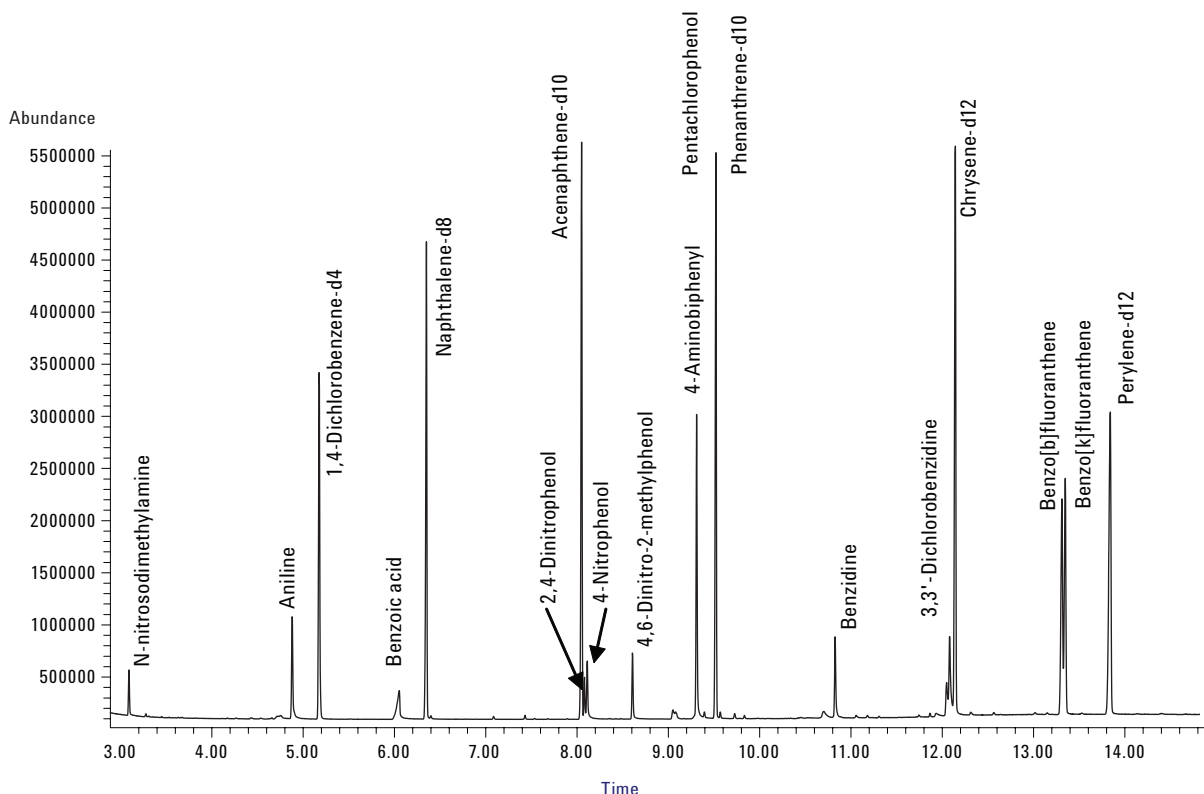


Figure 4. Reference chromatogram for Fast 8270 method.

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).

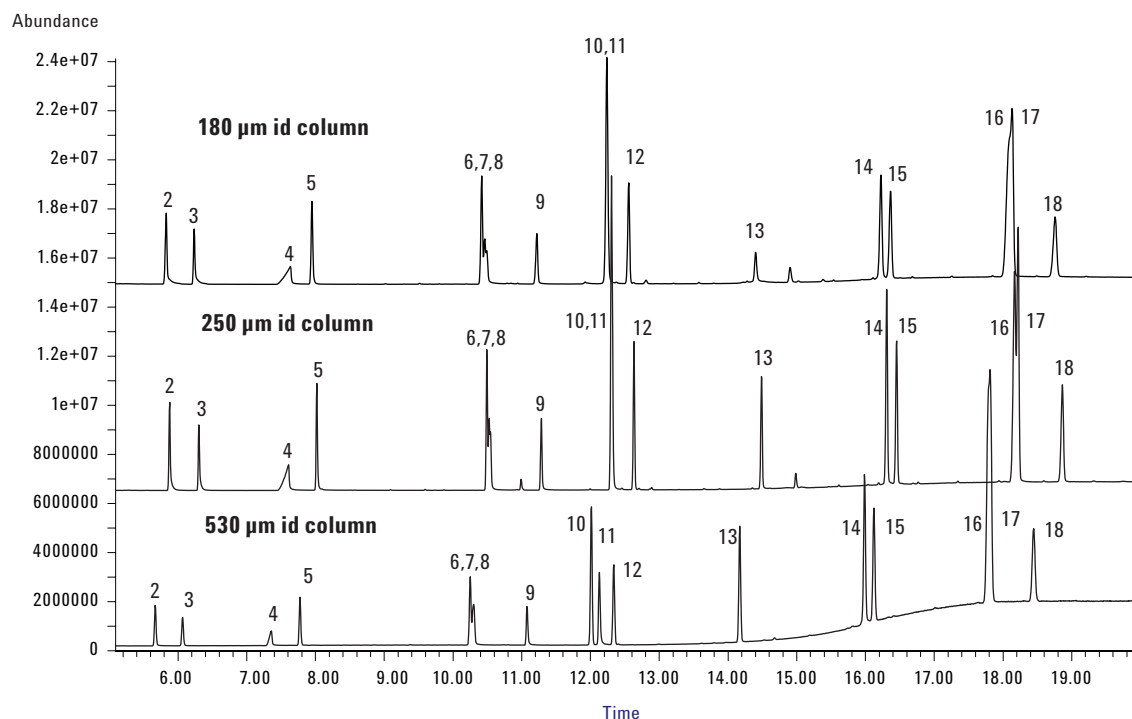


Figure 5. Constant pressure mode analysis with three different column dimensions; 0.5- μL splitless injections of 80-ppm semi-volatiles test sample, with flow conditions from Table 2.

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.

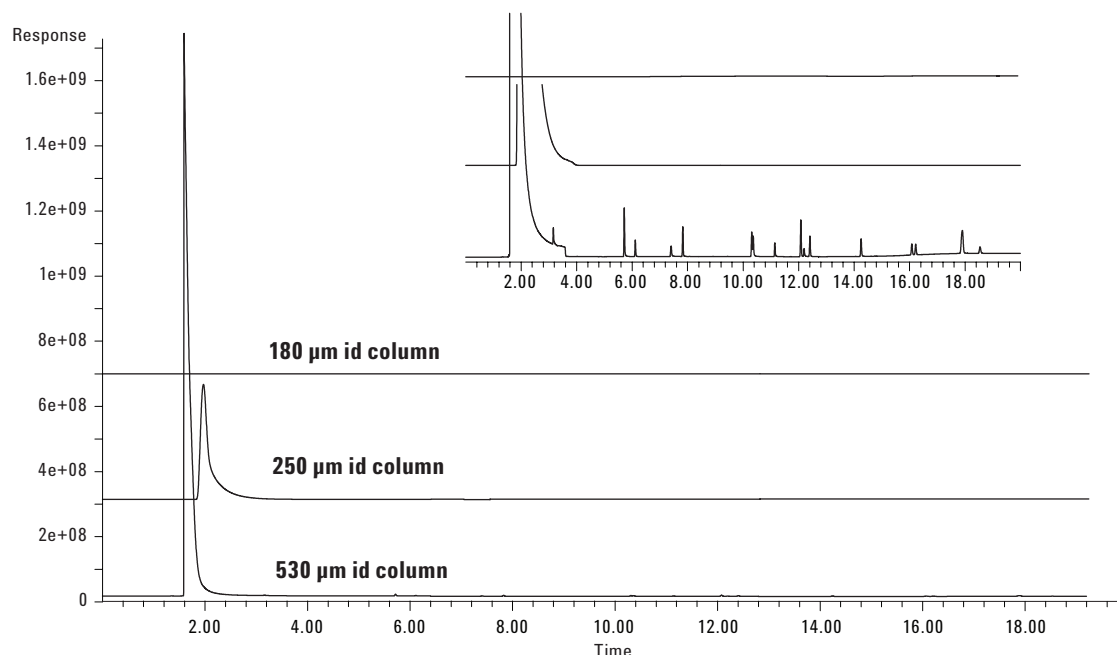


Figure 6. FID signal of vent stream shows what is vented when column flow exceeds flow to MSD.

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- μ m 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.

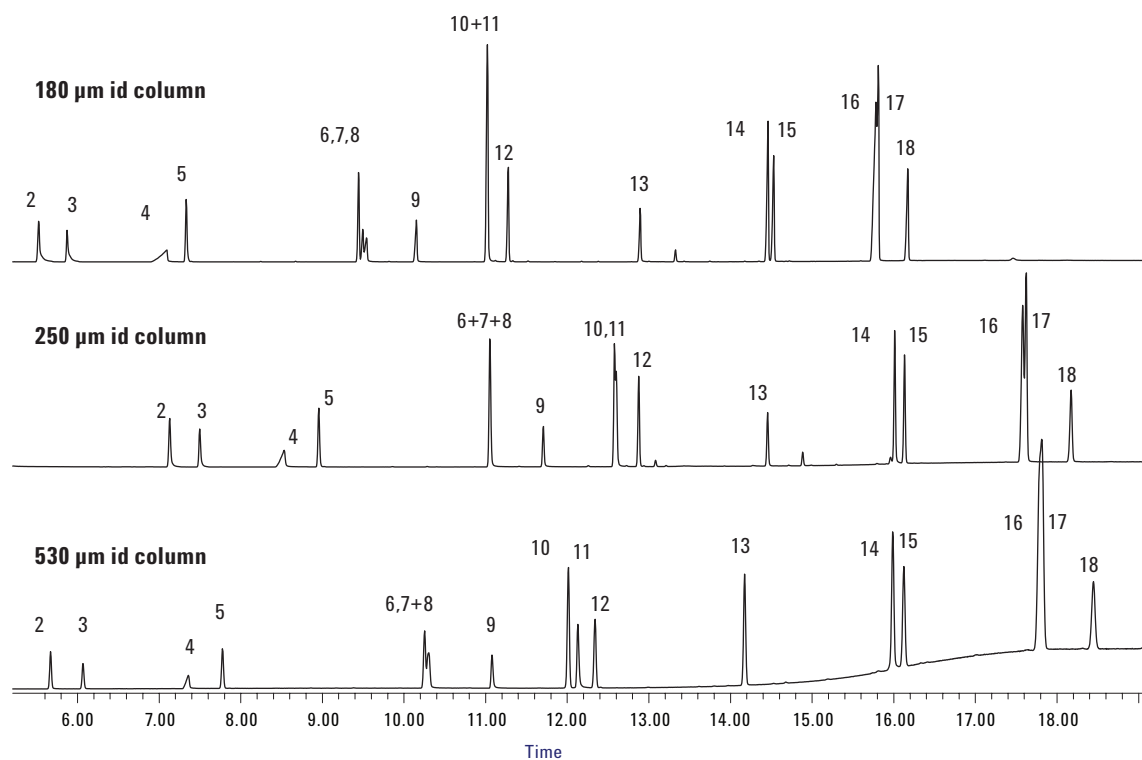


Figure 7. TIC chromatograms for the three columns under optimal constant flow mode conditions.

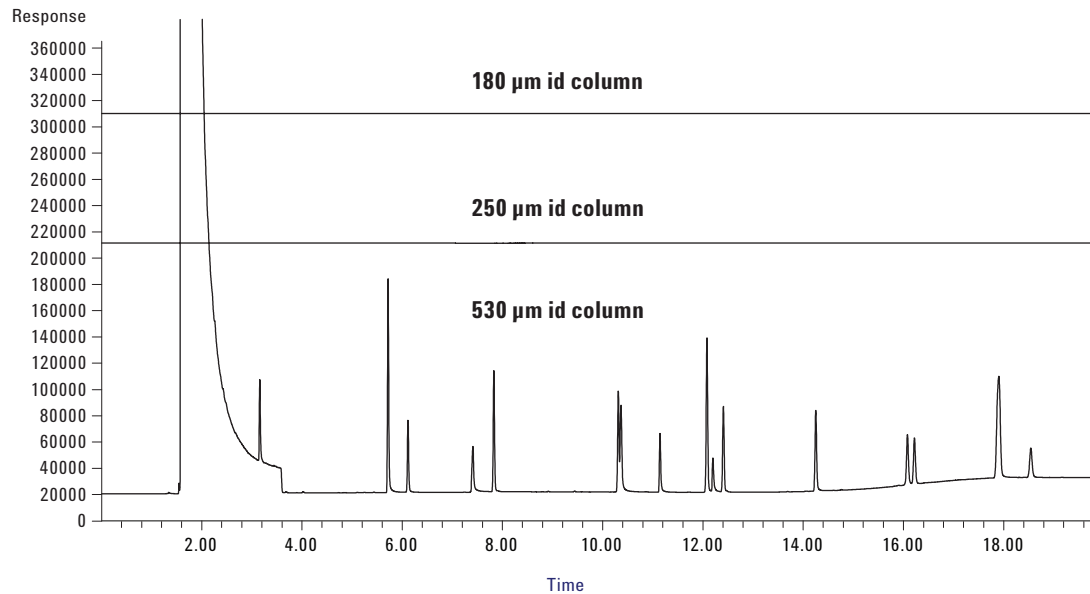


Figure 8. FID vent signal for three columns under optimal flow conditions. Only the 530-µm id column has a flow that exceeds the 1 mL/min flow to the MSD.

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.

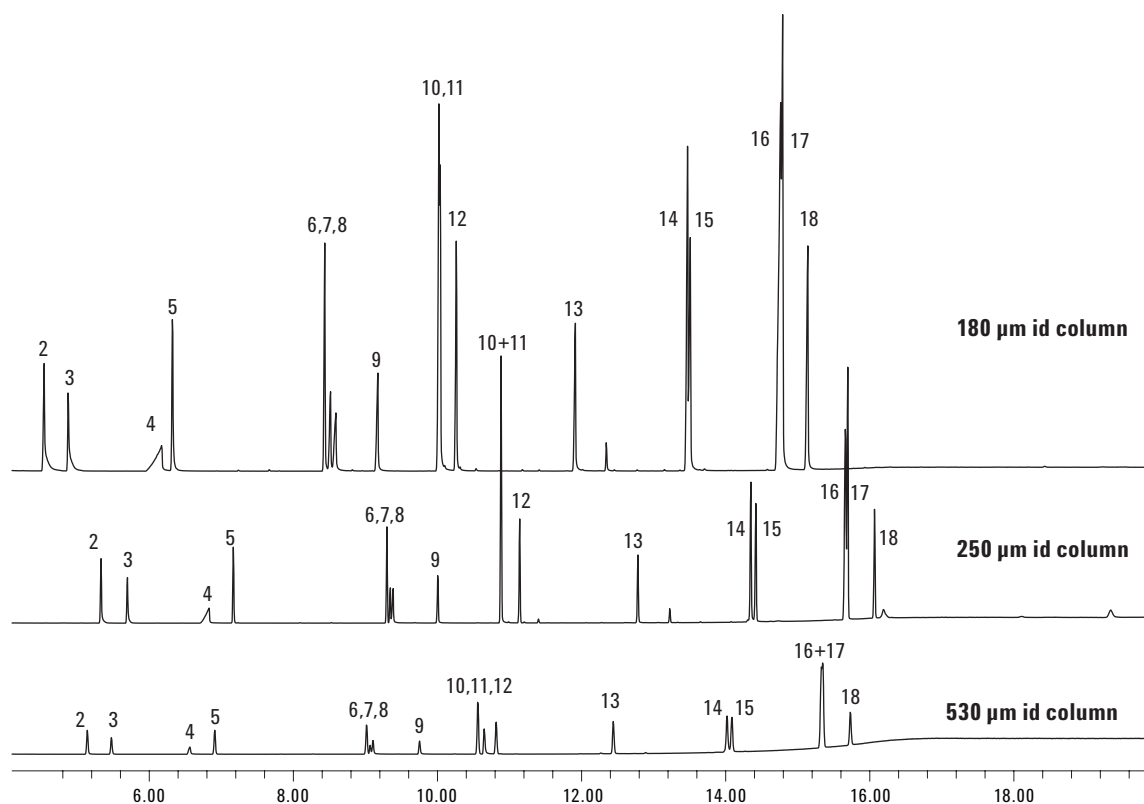


Figure 9. Comparison of MSD TIC chromatograms for three columns run at 2X optimal constant flow mode. Scale is constant for the three, showing the absolute amount of sample reaching the MSD.

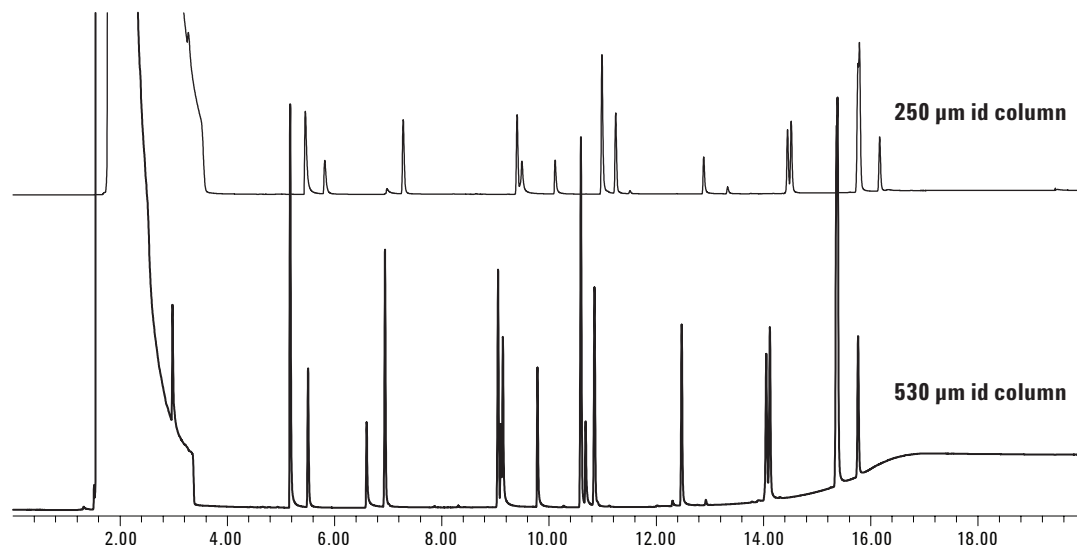


Figure 10. FID vent signals for the two largest columns operated at 2X optimal constant flow rate conditions.

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.

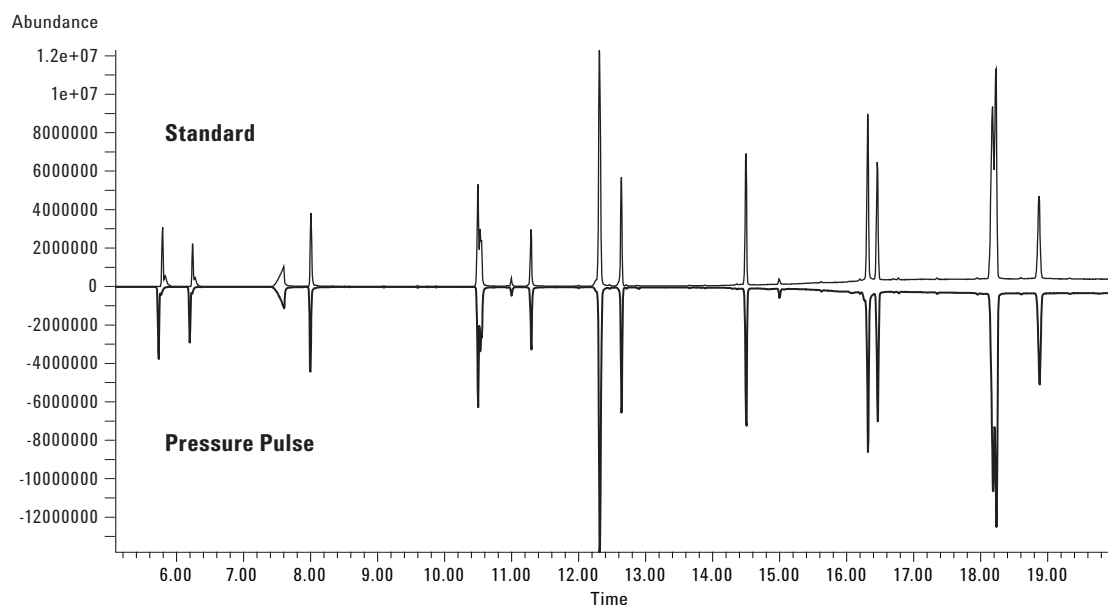


Figure 11. Comparison of standard and pressure-pulse injection modes. No adjustment of QuickSwap pressure was required for the pressure-pulse mode—a benefit of using QuickSwap split configuration.

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.

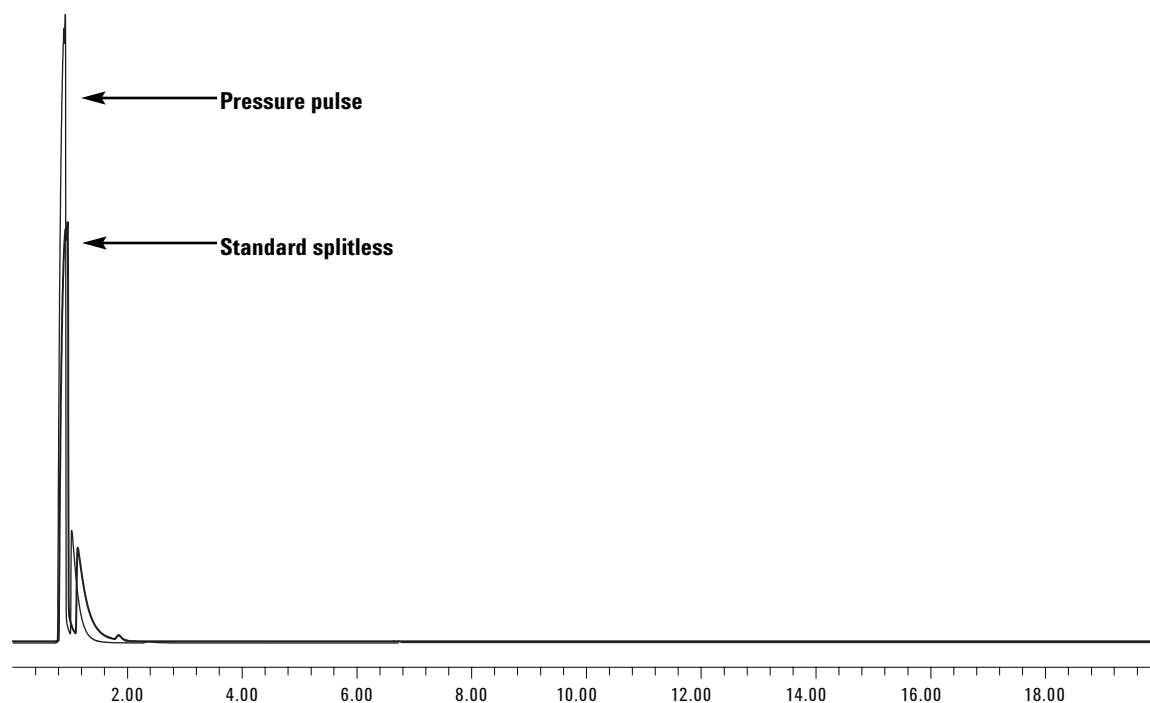


Figure 12. FID vent signal for pressure-pulse injection versus standard splitless injection.

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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3. "Agilent G3185B QuickSwap Accessory Reference Manual," Agilent publication number G3185-90101.
4. "Simplified Backflush Using Agilent 6890 GC," Agilent publication number 5989-5111EN.
5. "Fast USEPA 8270 Semivolatiles Analysis Using the 6890N/5975 Inert GC/MSD," Agilent publication number 5989-2981EN.

Parts List

Part	Description	Part number
QuickSwap	Kit	G3185B
QuickSwap restrictors	92 µm	G3185-60361
	100 µm	G3185-60362
	110 µm	G3185-60363
1/16" tee	Regular	0100-0782
	ZDV	0100-0969
SilTite 1/16" ferrules	For connecting 1/16" SS lines	G2855-2055
Deactivated FS	250-µm id FID vent restrictor	160-2255-5
Split vent trap	Kit—vent alternative to FID	G1544-0124
1/16" straight union		0100-0124
SilTite ferrules for capillary 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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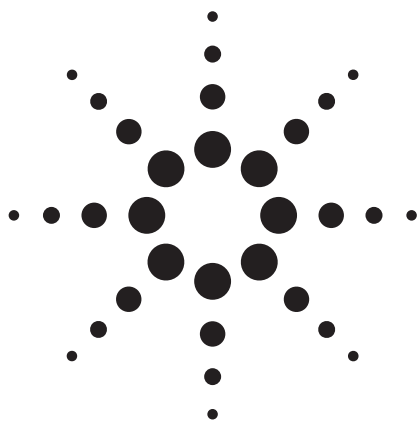
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High-Pressure Injection Device for the Agilent 7890A and 6890 Series Gas Chromatographs

Accessory G3505A

Introduction

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

Injection Device

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

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

Ordering Information

Order accessory G3505A. The accessory is compatible with both the 7890A and 6890 series GCs.

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

- **Filter:** To remove particles from samples.
- **Restrictor:** To maintain sample pressure, a metering valve (Agilent PN 101-0355) is connected to the end of the sample exit line tubing. Restrictor is not included in accessory kit.

Guideline for choosing Aux flow source

7890AGC

G3471A Pneumatic Control Module (PCM) or
G3470A Aux EPC module

6890GC

G1570A Aux EPC or
G2317A PCM module

The PCM is the preferred source for both GCs.



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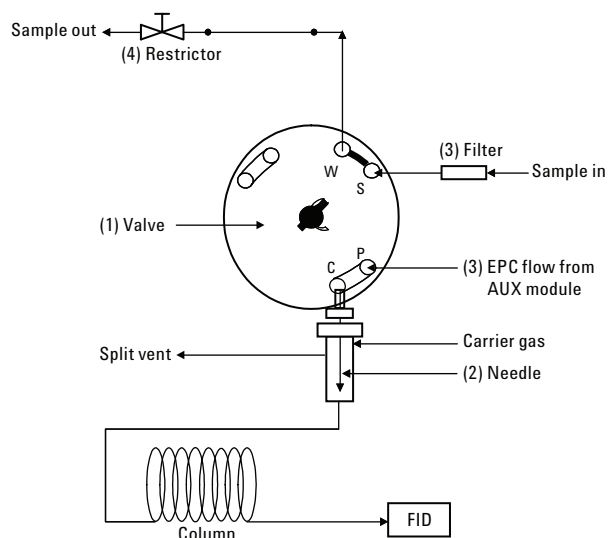


Figure 1. Flow diagram of the high-pressure injection device (HPLI).

Typical Instrumental Conditions

Gas chromatograph	Agilent 7890A
Injection source	High-pressure injection device (HPLI) at near ambient temperature
Injection port	Split/splitless, 250 °C (350 °C for C5–C40)
Sample size	0.06 µL
Carrier gas	Helium
Aux or PCM	150 mL/min (Helium)
FID	250 °C (350 °C for C5–C40) H ₂ , 35 mL/min Air, 400 mL/min



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

Sample Chromatograms

Pressurized Propylene

This sample is analyzed by the same conditions as in ASTM D6159. A typical chromatogram is shown in Figure 2.

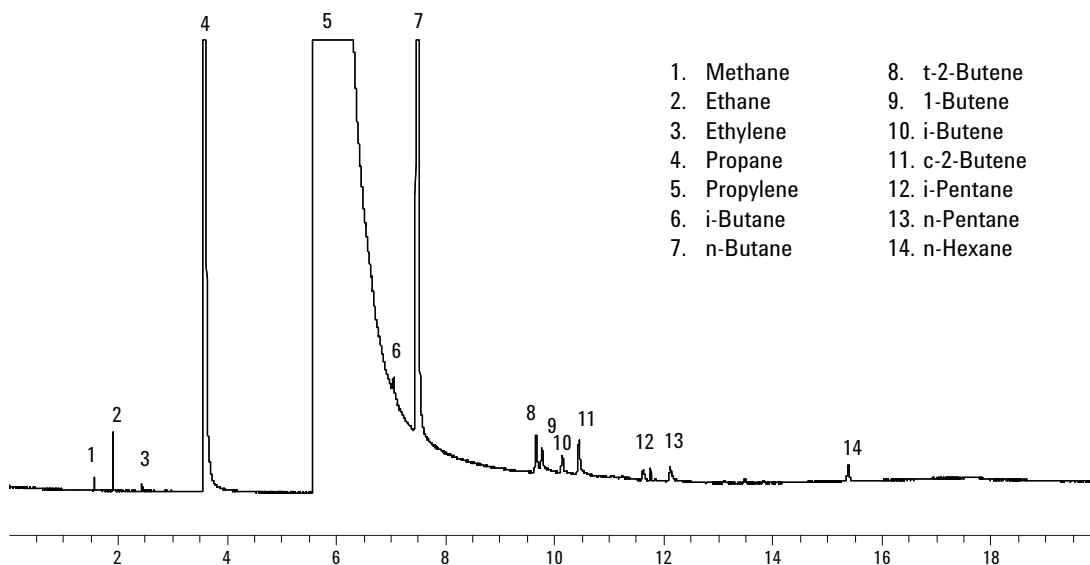


Figure 2. Chromatogram of pressurized propylene.

Pressurized 1,3-Butadiene

Figure 3 is an example of C4 hydrocarbons analysis showing 1,3-butadiene purity.

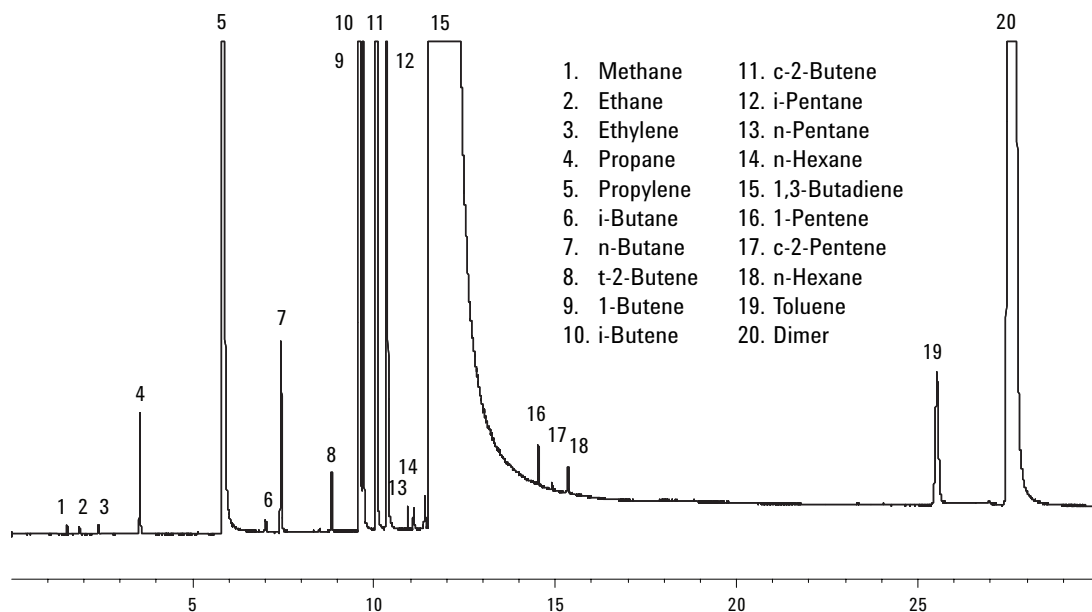


Figure 3. Chromatogram of pressurized 1,3-butadiene.

Summary

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

Competitive Advantages

The HPLI can be used with a wide variety of sample streams or pressurized vessels. Because the sampling valve is interfaced directly to the inlet with an inert needle, loss or adsorption of

analytes is minimized compared to conventional liquid sample valve systems. Compared to other gas chromatographic vaporizers for handling pressurized or nonpressurized samples, the Agilent HPLI has the following advantages:

- Better results with polar analytes such as glycols
- Superior inertness
- Low discrimination (no discrimination up to C₁₆)
- Flexibility: Install or uninstall in less than 10 minutes
- Good for trace impurity analysis with 0.5 µL rotor
- Excellent repeatability, typically RSDs below 1 %

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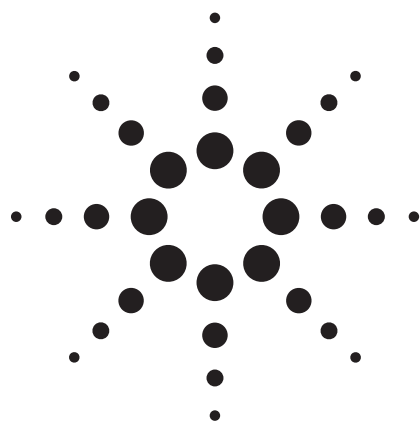
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Investigation of the Unique Selectivity and Stability of Agilent GS-OxyPLOT Columns



Application

Gas Chromatography

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Abstract

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

Introduction

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

Methanol is one of the oxygenates that often present in light hydrocarbon streams. For example, it is added to natural gas and production of crude oil to prevent hydration of hydrocarbons during transportation via pipelines. Therefore, it is important

to accurately measure the content of methanol from light hydrocarbons at different concentrations, including at trace levels.

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

Using Capillary Flow Technology, such as 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.

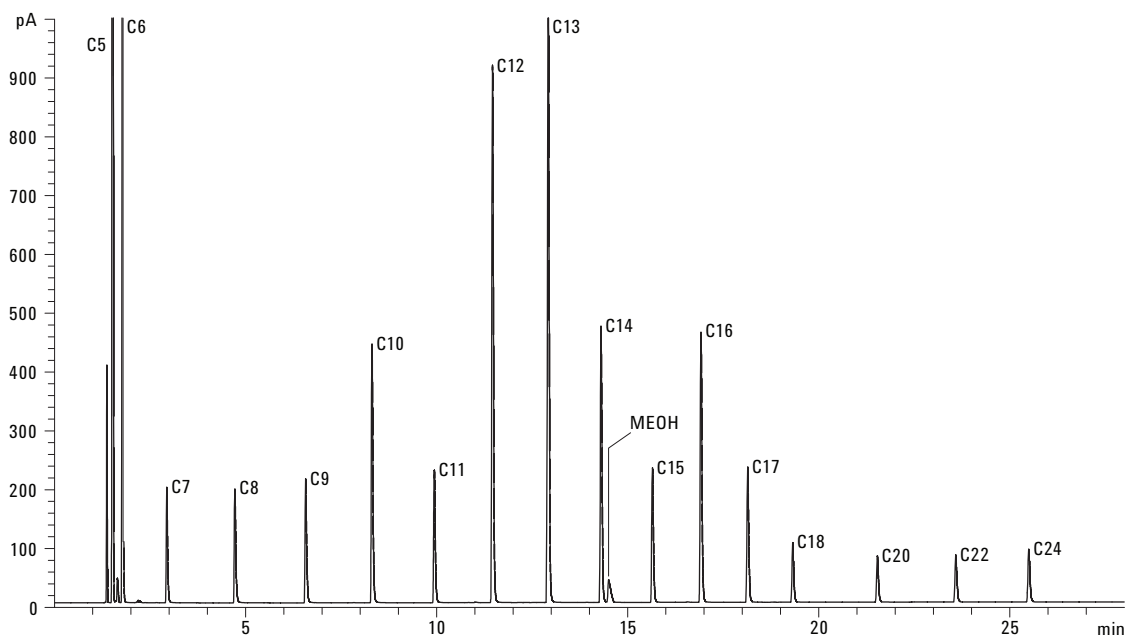


Figure 1. Analysis of methanol and normal hydrocarbons on a GS-OxyPLOT column, 10 m × 0.53 mm × 10 µm.

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.

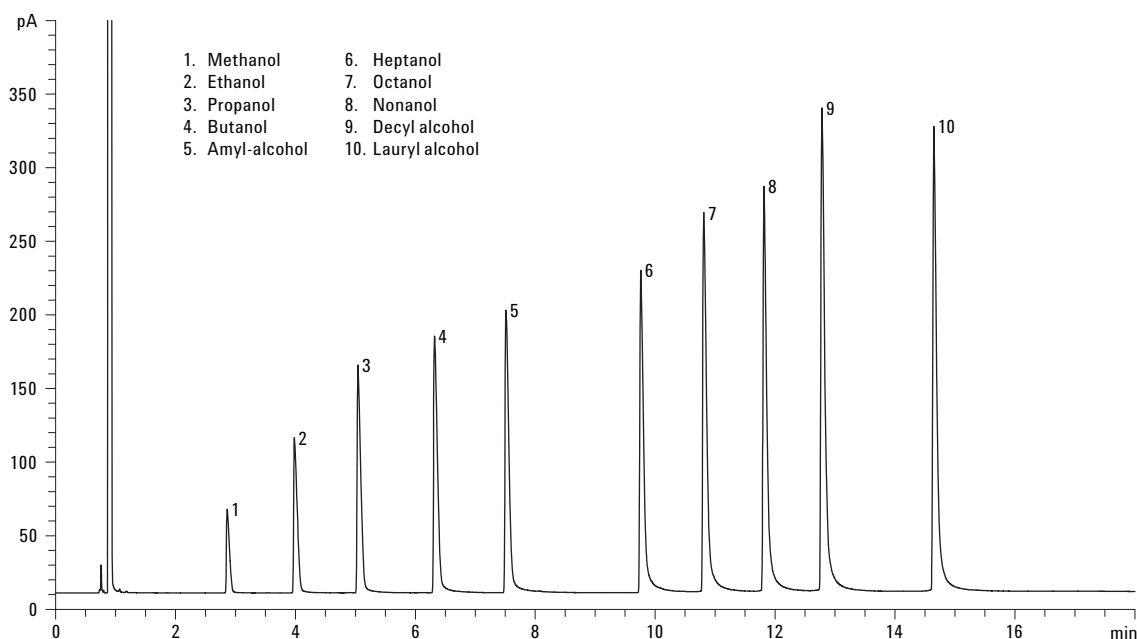


Figure 2. Separation of alcohols using GS-OxyPLOT, 10 m × 0.53 mm × 10 µm.

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.

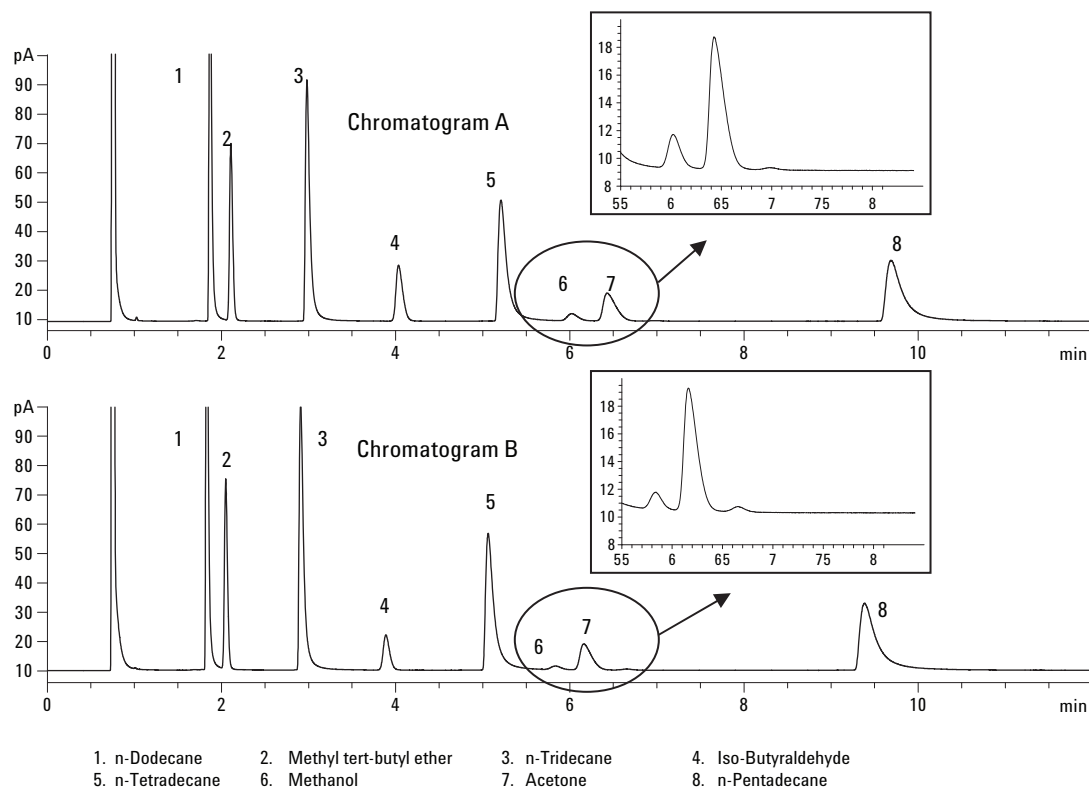


Figure 3. Comparison of test mixture separation before (A) and after (B) 100 injections of water.

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.

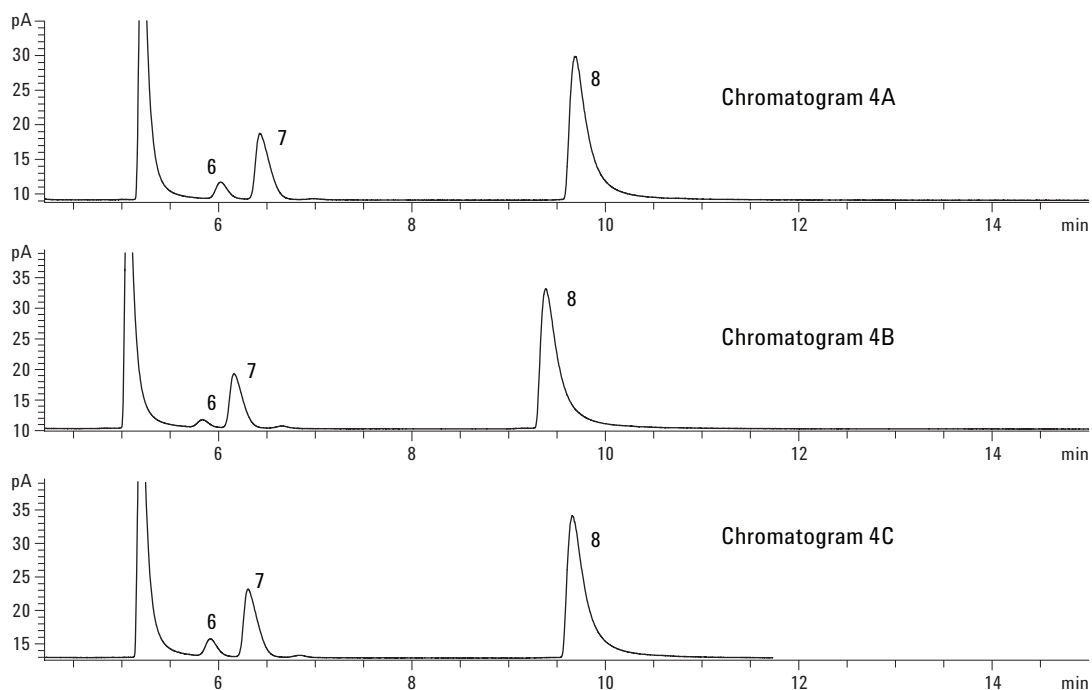


Figure 4. Expanded view shows comparison of test mixture separation on GS-OxyPLOT.
4A. Before injection of water. 4B. After 100 injections of water. 4C. After conditioning the column.

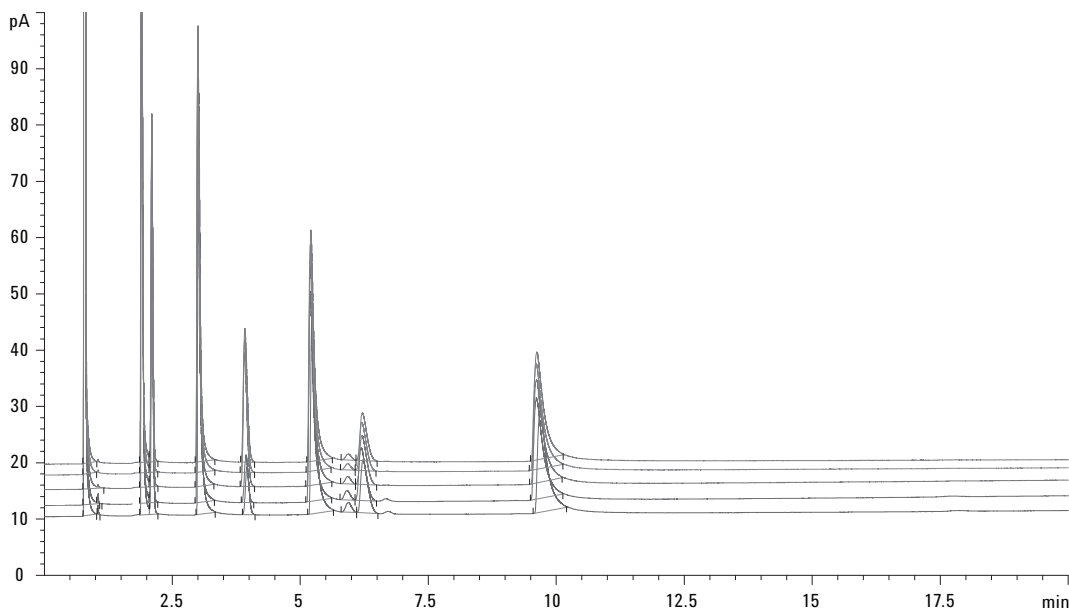
Table 6. Comparison of Test Mixture Separation

	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

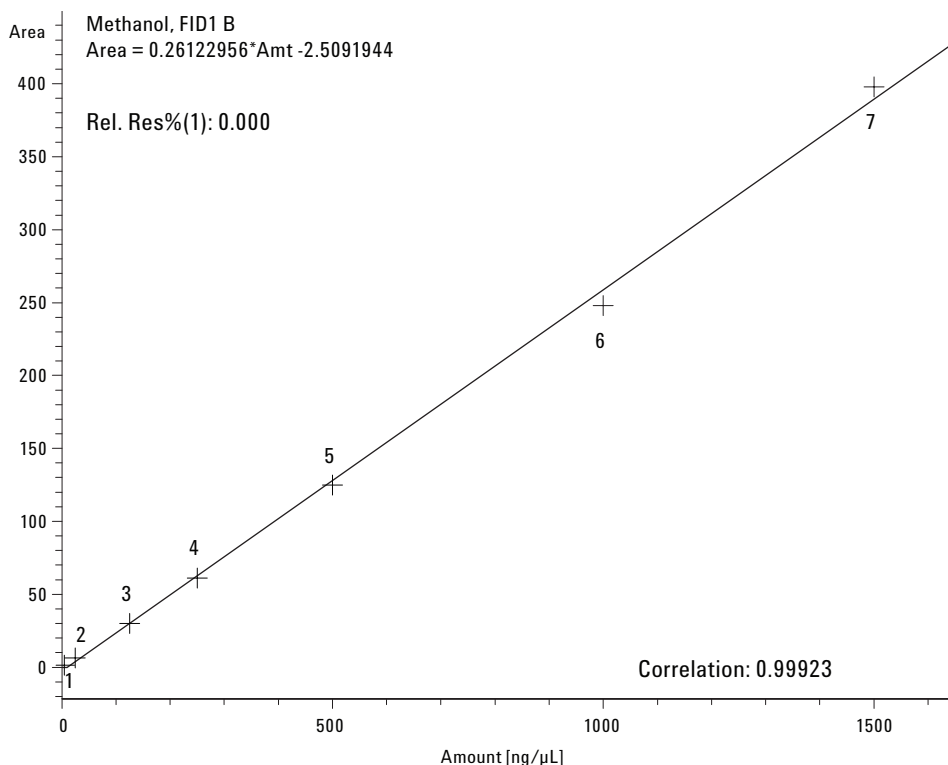


Figure 6. The calibration curve of methanol in toluene.

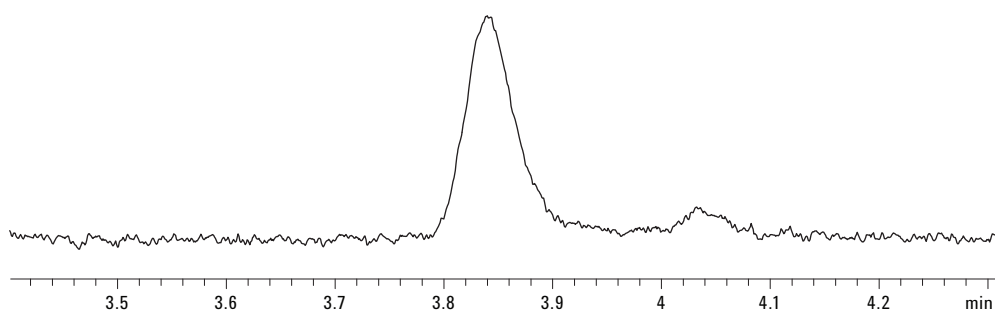


Figure 7. Test mixture of 5 ppm methanol in toluene.

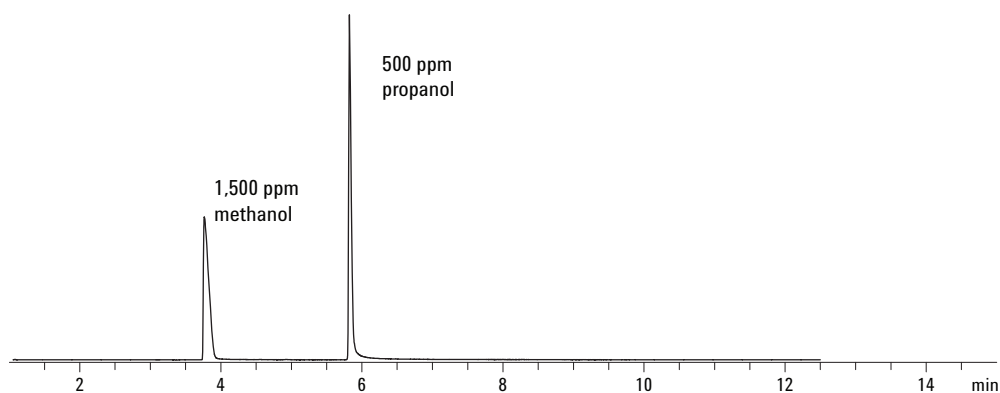


Figure 8. Test mixture of 1,500 ppm methanol in toluene.

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	

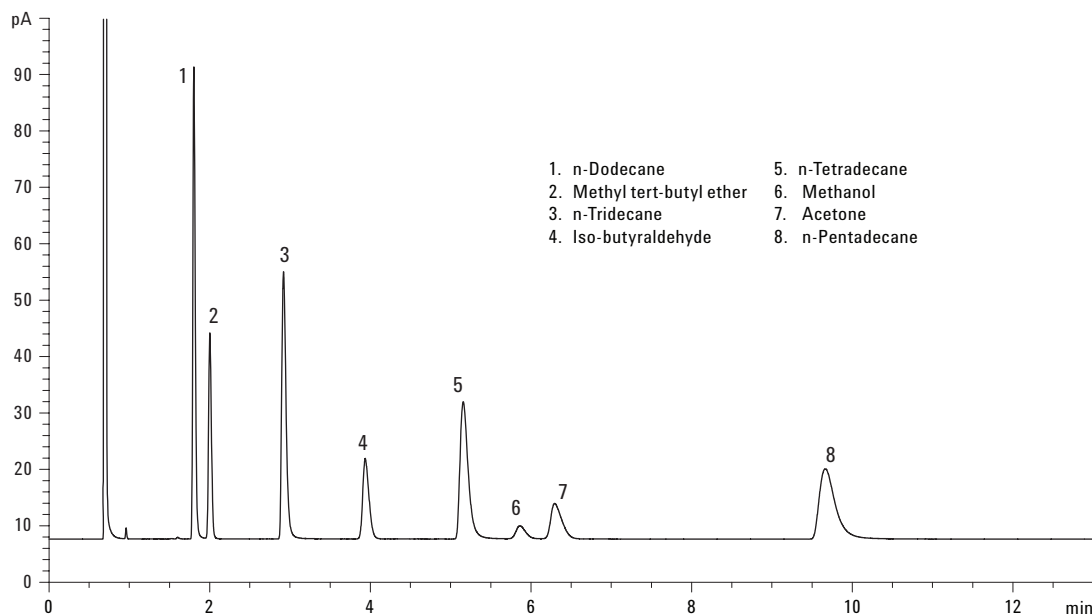


Figure 9. Chromatogram of performance mixture after 1,500 injections.

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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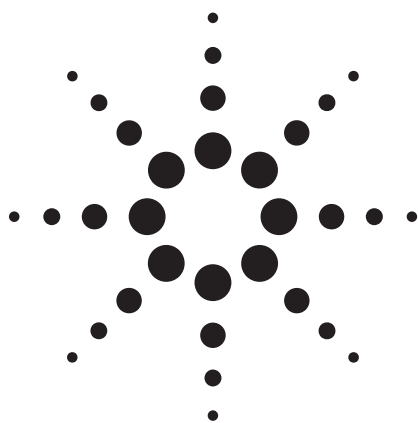
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Detection of Sulfur Compounds in Natural Gas According to ASTM D5504 with Agilent's Dual Plasma Sulfur Chemiluminescence Detector (G6603A) on the 7890A Gas Chromatograph

Application

Hydrocarbon Processing

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Abstract

An Agilent dual plasma sulfur chemiluminescence detector (DP SCD) combined with an online dilutor was used for the analysis of sulfur compounds. By using this method, the detection limits of the sulfur compounds achieved the ppb level. The stability of the DP SCD was also investigated. The long-term and short-term stability show that the performance of DP SCD is stable, and no hydrocarbon interference was found during the analysis of natural gas samples.

Introduction

Many sources of natural gas and petroleum gases contain varying amounts and types of sulfur compounds. The analysis of gaseous sulfur compounds is difficult because they are polar, reactive, and present at trace levels. Sulfur compounds pose problems both in sampling and analysis. Analysis of sulfur compounds many times requires special treatment to sample pathways to ensure inertness

to the reactive sulfur species. Sampling must be done using containers proven to be nonreactive. Laboratory equipment must also be inert and well conditioned to ensure reliable results. Frequent calibration using stable standards is required in sulfur analysis [1].

GC SCD configuration with inert plumbing is one of the best methods to detect sulfur compounds in different hydrocarbon matrices. Sulfur compounds elute from the gas chromatographic column and are combusted within the SCD burner. These combustion products are transferred to the SCD detector box via vacuum to a reaction cell for ozone mixing. This detection technique provides a highly sensitive, selective, and linear response to volatile sulfur compounds.

Agilent Technologies DP technology is the detector of choice for sulfur analysis when dealing with a hydrocarbon matrix. The burner easily mounts on the 6890 and 7890A GCs and incorporates features for easier and less frequent maintenance. In this application, the Agilent 355 DP SCD was used to analyze the gaseous sulfur compounds in natural gas. Detection limits, stability and linearity were investigated.

Experimental

An Agilent 7890A GC configured with a split/splitless inlet (Sulfinert-treated), and an Agilent 355 DP SCD were used. Sample introduction was through a six-port Hastelloy C gas sample valve (GSV) interfaced directly to the sulfur-treated inlet with Sulfinert tubing. An online dilutor was used for preparation of ppb-level sulfur compounds in



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different matrices. Two four-port valves were used – one for sample introduction and one for static sample injection. The valves were installed sequentially prior to the GSV. Figure 1 illustrates the configuration of the gas blending system and GC SCD.

The sulfur standards were blended in helium at 1 ppm (V/V) and were purchased from Praxair, Inc. (Geismar, LA). See Table 1 for component details.

Table 1. Sulfur Standards in Helium

1.	Hydrogen sulfide	H ₂ S
2.	Carbonyl sulfide	COS
3.	Methyl mercaptan	CH ₃ SH
4.	Ethyl mercaptan	CH ₄ CH ₃ SH
5.	Dimethyl sulfide	CH ₃ SCH ₃
6.	Carbon disulfide	CS ₂
7.	2-propanethiol	CH ₃ SHC ₂ H ₅
8.	Tert-butyl mercaptan	(CH ₃) ₃ CSH
9.	1-propanethiol	CH ₃ (CH ₂) ₂ SH
10.	Thiophene	C ₄ H ₄ S
11.	n-butanethiol	CH ₃ (CH ₂) ₃ SH
12.	Diethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₃
13.	Methyl ethyl sulfide	CH ₃ SCH ₂ CH ₃
14.	2-methyl-1-propanethiol	(CH ₃) ₂ CHCH ₂ SH
15.	1-methyl-1-propanethiol	CH ₃ CH ₂ CHSHCH ₃

Experimental Conditions

GC Conditions

Front Inlet Split/splitless (Sulfinert-treated capillary inlet system)

Heater	150 °C
Pressure	14.5 psi
Septum purge flow	3 mL/min
Mode	Splitless
Gas saver	20 mL/min after 2 min
Sample loop	1 mL
Oven	30 °C (1.5 min), 15 °C/min 200 °C (3 min)
Column	HP-1 60 m × 0.53 mm × 5 µm
Injection mode	Static flow and dynamic flow modes

SCD Conditions

Burner temperature	800 °C
Vacuum of burner	372 torr
Vacuum of reaction cell	5 torr
H ₂	40 mL/min
Air	53 mL/min

Results and Discussion

From the comparative results of the sulfur detectors' sensitivity, it could be seen that SCD is the best detector for sulfur components, especially at low levels [3]. The Agilent DP technology is the most sensitive and selective detector for sulfur-containing gaseous hydrocarbon samples.

Figure 2 is the chromatogram of low-level sulfur compounds at 1.35 ppb (H₂S), which is prepared by the point-of-use gas blending system. Table 2 is the calculated signal to noise (S/N) of each compound, from the achieved data. It can be seen that DP SCD can detect low-level sulfur compounds.

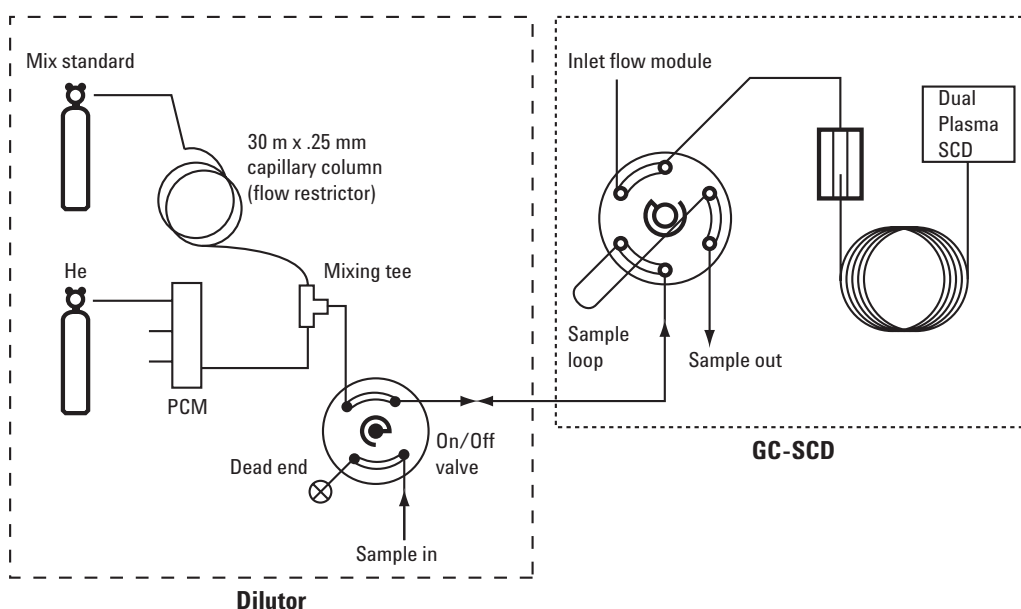
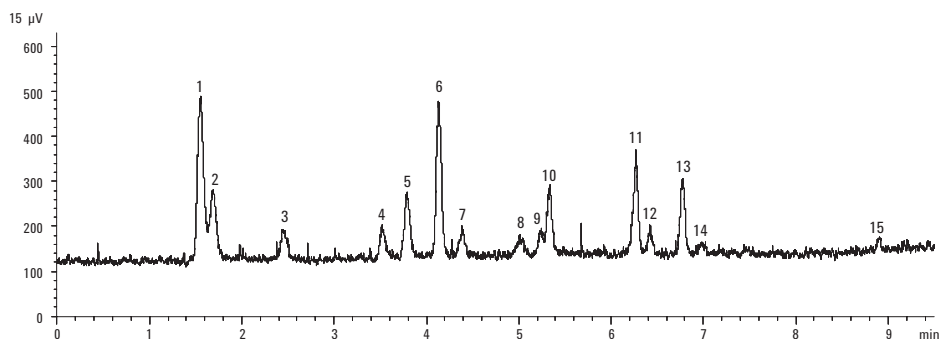


Figure 1. Diagram of online dilutor GC-DP SCD.

Table 2. S/N of Each Sulfur Component at 1.35 ppb (Refer to Table 1 for peak identification.)

Peak No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
S/N	12.0	5.0	2.1	2.6	4.9	11.5	4.0	2.7	3.7	9.1	7.6	2.3	5.7	1.0	1.1

**Figure 2. Chromatogram of sulfur compounds in helium at 1.35 ppb. (Refer to Table 1 for peak identification.)**

Because the low-level sulfur components were prepared by the online dilutor system, which was prepared by adjusting the aux EPC to get appropriate diluent flow, high diluent flow could have the potential to cause high pressure in the sample loop, which results in the amount of the sample in the loop being different when the diluent flow changes from low to high. In this application, two sample injection modes, static and dynamic, were investigated. The mode is actuated by the on/off valve installed prior to GSV. When using static

injection mode, the valve is switched to the off position, the pressure in the sample loop balances to ambient pressure, and then the sample is injected into the GC.

Table 3 shows the linear ranges of the two injection modes. The two injection modes have no difference from a linearity perspective, which means that the two injection modes are both suitable when using the 1-mL sample loop. The 1-mL sample loop's resistance is not high enough to cause variation in the sample injection amount.

Table 3. Linear Ranges of Two Injection Modes (Refer to Table 1 for peak identification.)

	1	2	3	4	5	6	7	8
Linear range (ppb)	6.24-544.5							
Static mode	1	0.99996	0.99995	0.99999	0.99996	0.99999	0.99996	0.99999
Dynamic mode	1	0.99996	0.99997	0.99997	0.99996	0.99999	0.99998	0.99998
	9	10	11	12	13	14	15	
Linear range (ppb)	6.24-544.5							
Static mode	0.99995	0.99994	0.99996	0.99996	0.99996	0.99998	0.99998	
Dynamic mode	0.99998	0.99997	0.99998	0.99998	0.99998	1	0.99998	

Table 4 shows the long-term (72 hours) and short-term (8 hours) stability of the SCD at different concentration levels.

In an effort to investigate the coelution of hydrocarbon and sulfur, the same sulfur standards in natural gas were analyzed on the SCD. Figure 3 shows the chromatogram; no quenching was found.

Table 4. The Long-Term and Short-Term Stability of SCD (Refer to Table 1 for peak identification.)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
20.79 ppb	2.7	2.6	2.9	3.0	0.9	1.4	2.8	4.0	2.6	1.7	1.7	3.3	3.2	8.6	7.9
S.T. RSD (%)															
L.T. RSD (%)	3.0	2.7	2.4	2.5	1.4	1.5	2.6	4.3	3.8	2.7	2.0	4.9	3.2	7.9	6.9
1.38 ppb	6.6	10.1	11.7	22.8	30.4	4.1	6.9	18.7	10.7	25.1	5.1	11.1	5.8	29.6	24.1
S.T. RSD (%)															
L.T. RSD (%)	14.4	7.5	16.3	20.8	21.7	4.6	6.1	27.7	23.7	25.3	12.2	24.6	6.1	35.7	38.4

ST: Short term (8 hours); LT: Long term (72 hours)

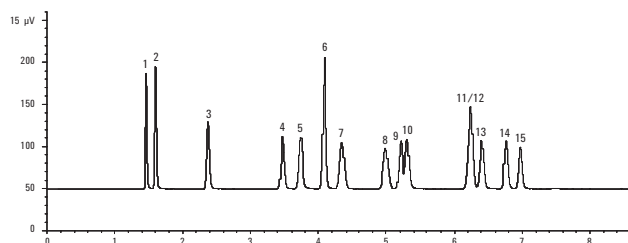


Figure 3. Chromatogram of sulfurs in natural gas. (Refer to Table 1 for peak identification.)

Natural Gas Sample Analysis

Three natural gas samples were analyzed by using the GC DP SCD system. Because the concentration of the target compounds is at ppm level, split mode was used and the method was recalibrated at ppm level. Table 5 shows the result of the three gas samples.

Table 5. Result of the Three Real Samples

Samples		H ₂ S	COS	Methyl Mercaptan
BLEND AL	Conc. (ppm, v/v)	2.3	2.0	2.0
	RSD (% , n = 5)	2.3	0.3	1.4
BLEND 6	Conc. (ppm, v/v)	27.1	21.9	17.3
	RSD (% , n = 5)	1.2	0.4	2.3
BLEND 12	Conc. (ppm, v/v)	15.0	9.2	10.1
	RSD (% , n = 5)	0.7	0.6	0.6
Standard natural gas	Conc. (ppm, v/v)	2.0	0.8	0.9
	RSD (% , n = 5)	1.7	2.5	1.7

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Conclusions

An online dilutor combined with a GC DP SCD is suitable for gaseous sulfur components analysis, especially for the low-level components. The online dilutor offers an automatable means of system calibration and the detection limits for the trace sulfur detection are down to ppb level. By using an on/off valve prior to the GSV, both the static and dynamic injection modes of the sample gas blending system can be used. The static injection mode is important when a small sample loop with a large resistance is used. The diluter system with GC/SCD is available as an Agilent SP1, please refer to SP1 7890-0375 for order information.

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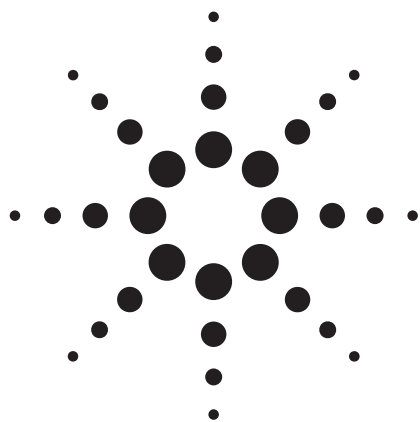
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Achieving Lower Detection Limits Easily with the Agilent Multimode Inlet (MMI)

Application Note

All Industries

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Abstract

This application note discusses three injection techniques: hot splitless, cold splitless, and solvent vent mode available on the Multimode Inlet. The cold splitless and solvent vent mode injections allow analysts to achieve a lower detection limit by making large volume injections (LVI). A total ion chromatogram overlay of 40-ppb pesticide standards from 2- 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.

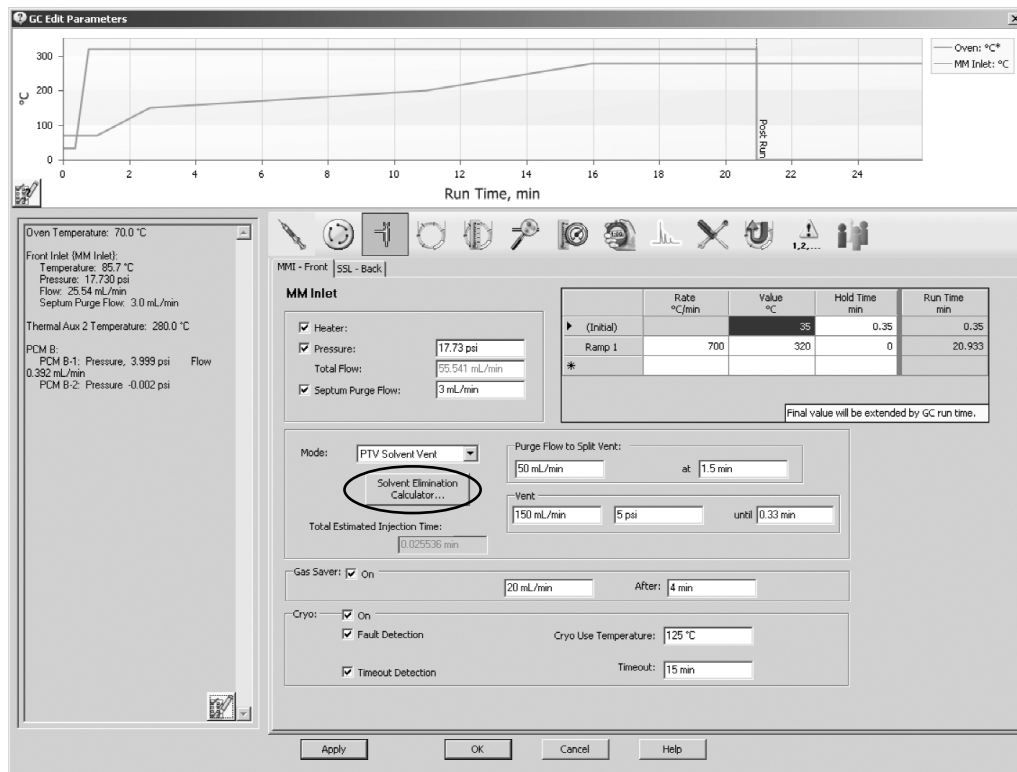


Figure 1. Multimode Inlet "Solvent Elimination Calculator" imbedded in ChemStation for easy method development.

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 (µL)
 25 µL

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).

Solvent Elimination Calculator

Agilent Solvent Elimination Calculation Wizard

Confirm Copy values to Method Editor.
(Check parameters to change.)

☒ Inlet temperature	35 °C
☒ Initial hold time	0.33 min
☒ First ramp rate	600 °C/min
☒ First temperature	325 °C
☒ First hold time	5 min
☒ Vent time	0.33 min
☒ Vent pressure	5 psi
☒ Vent flow rate	150 mL/min
☒ Purge time	2.83 min
☒ Purge flow rate	60 mL/min
☒ Injection rate	75 µL/min
☐ Oven initial temperature	50 °C
☐ Oven initial hold time	2.83 min

Figure 4. Confirm values suggested by the Calculator and download to ChemStation.

Results and Discussion

Figure 5 compares the responses of a 40-ppb standard solution from three injection modes.

The bottom total ion chromatogram (TIC) is a typical 2- 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.

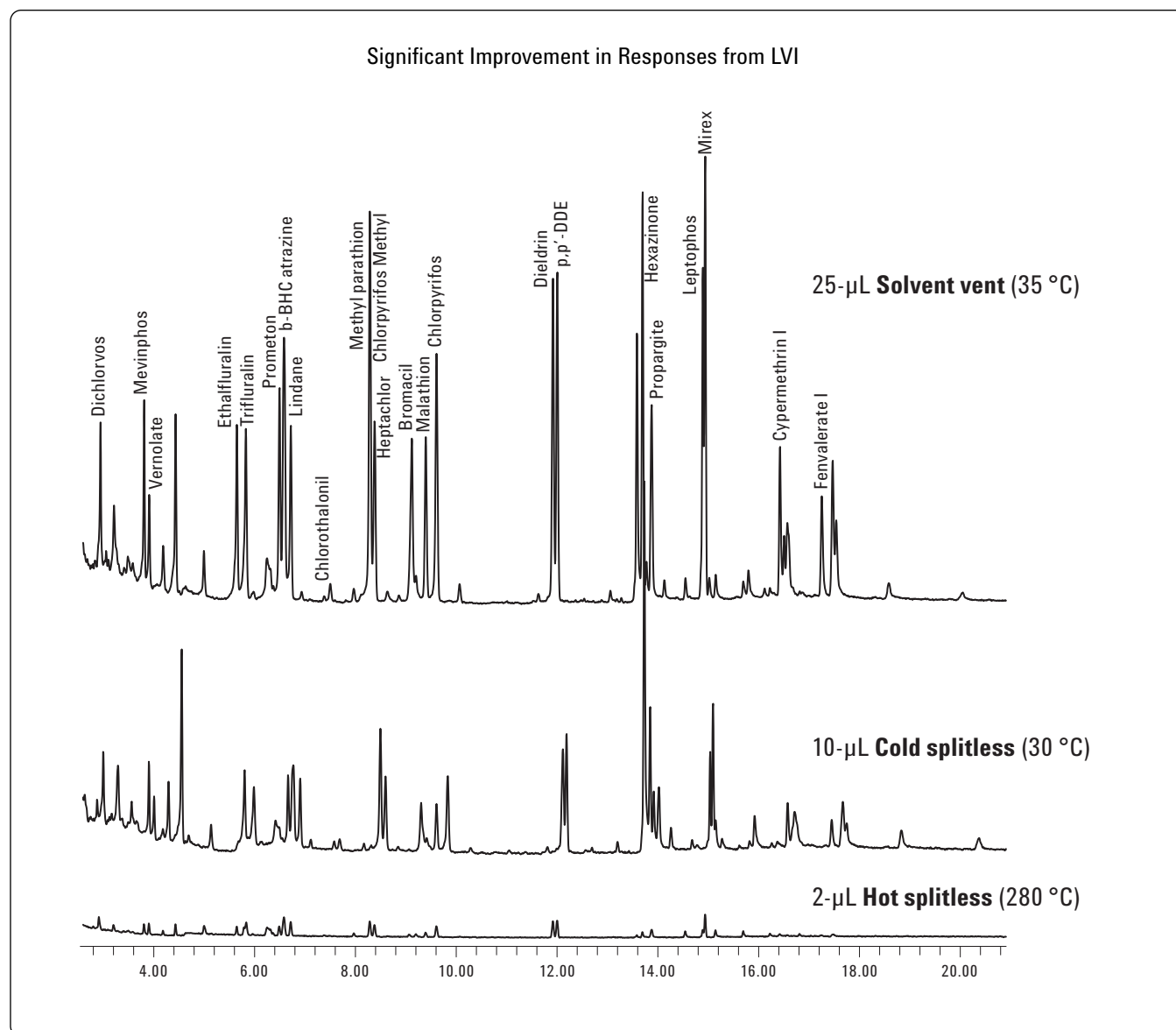


Figure 5. Overlay of total ion chromatograms (TICs) from three injection modes, plotted on the same scale.

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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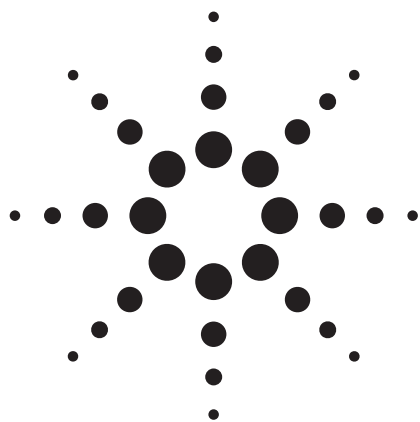
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Agilent Technologies



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

Application Note

HPI

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Highlights

- Agilent 7820A GC 3-valve system provides a low-cost but powerful platform for analysis of permanent gases and light hydrocarbons.
- Full electronic pneumatics control (EPC) provides an easy-to-use operation for the end user and ensures excellent repeatability for both retention time and peak area.
- This application work can also be used as a reference in the analysis of natural gas, petroleum gas, synthesis gas, purified gas, water gas, blast furnace gas, stack gas, and so on.

Abstract

A new economical solution is provided to test permanent gases and light hydrocarbons. An Agilent 7820A Gas Chromatograph equipped with three valves, a flame ionization detector (FID), and a thermal conductivity detector (TCD), is configured for analysis of permanent gases and light hydrocarbons. The TCD channel with packed columns is used to measure H_2 , CO_2 , O_2 , N_2 , CH_4 and CO . A capillary column (Al_2O_3 PLOT: 50 m $\times$ 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.

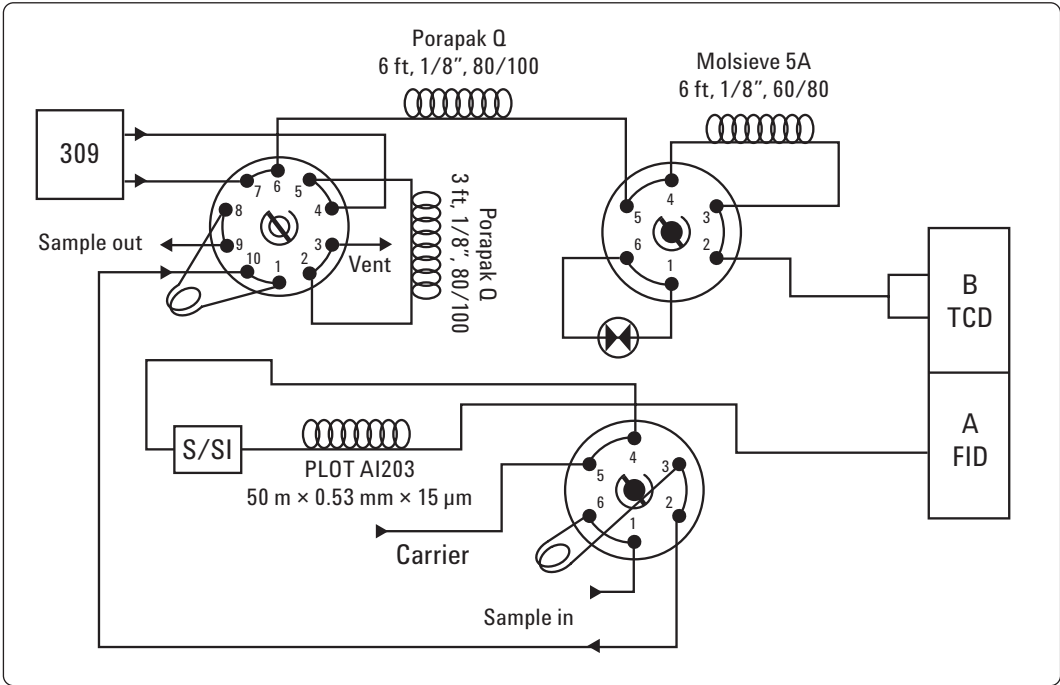


Figure 1. Valve diagram for dual-channel natural gas analysis.

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.

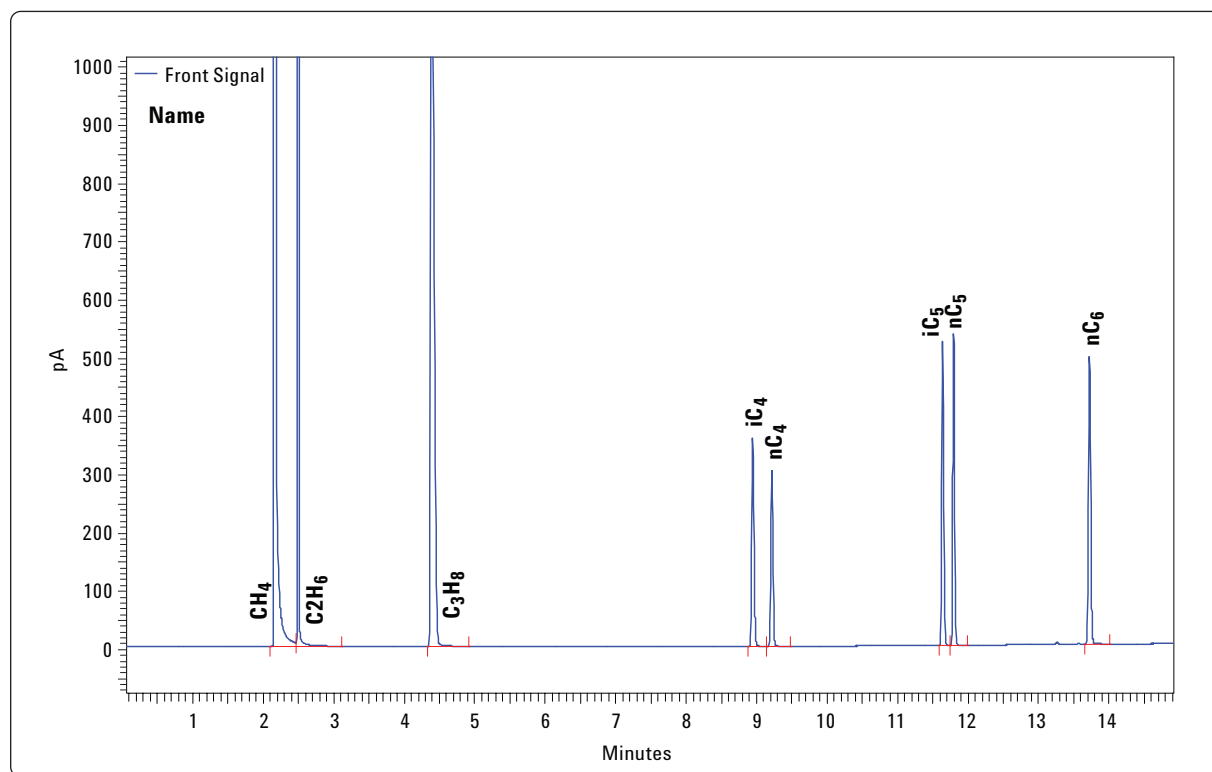


Figure 2. FID Channel chromatogram of CH₄, C₂H₆, C₃H₈, iC₄, nC₄, iC₅, nC₅, and nC₆.

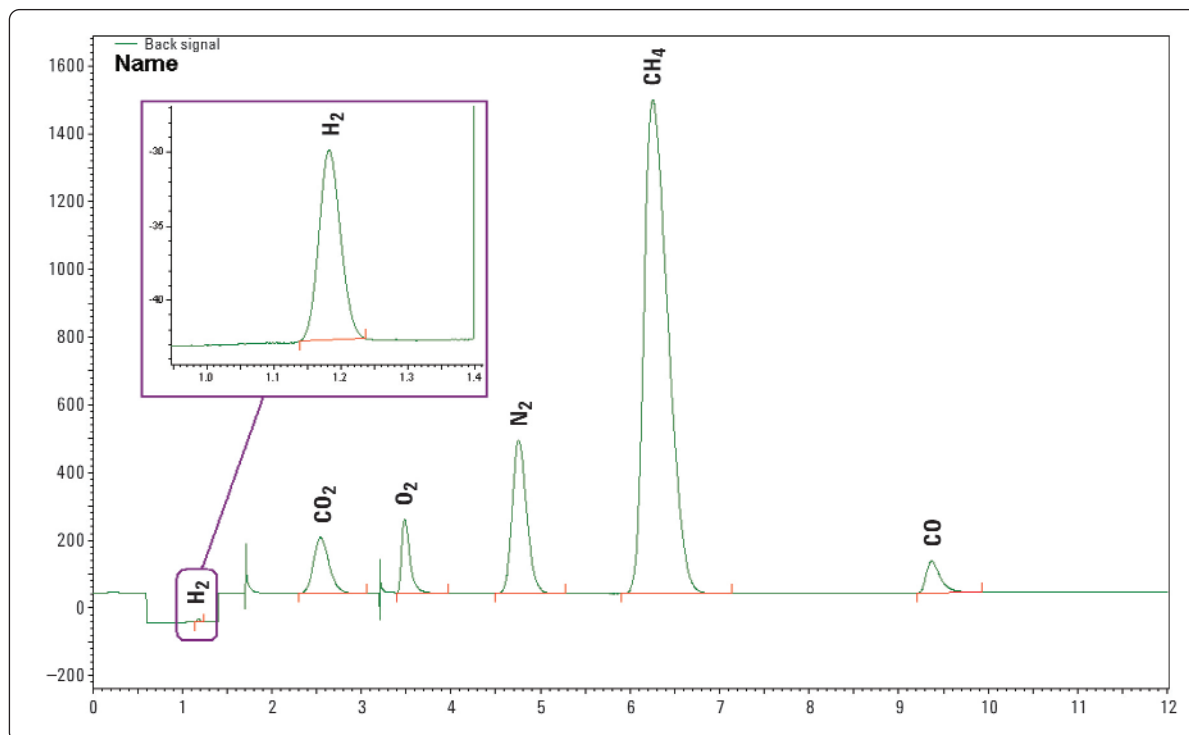


Figure 3. TCD Channel chromatogram of H₂, O₂, CO₂, N₂, CH₄, CO.

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

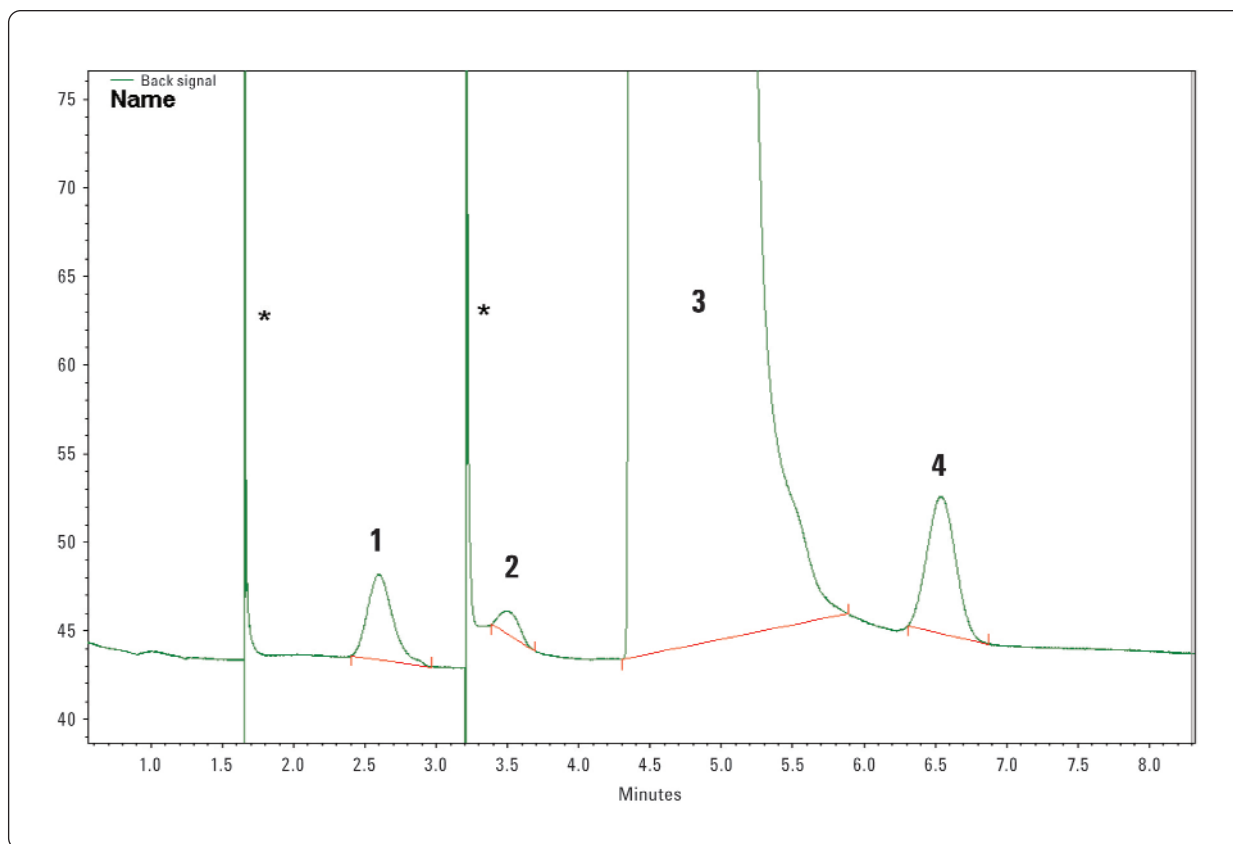


Figure 4. Chromatogram of low level permanent gas standard mix.

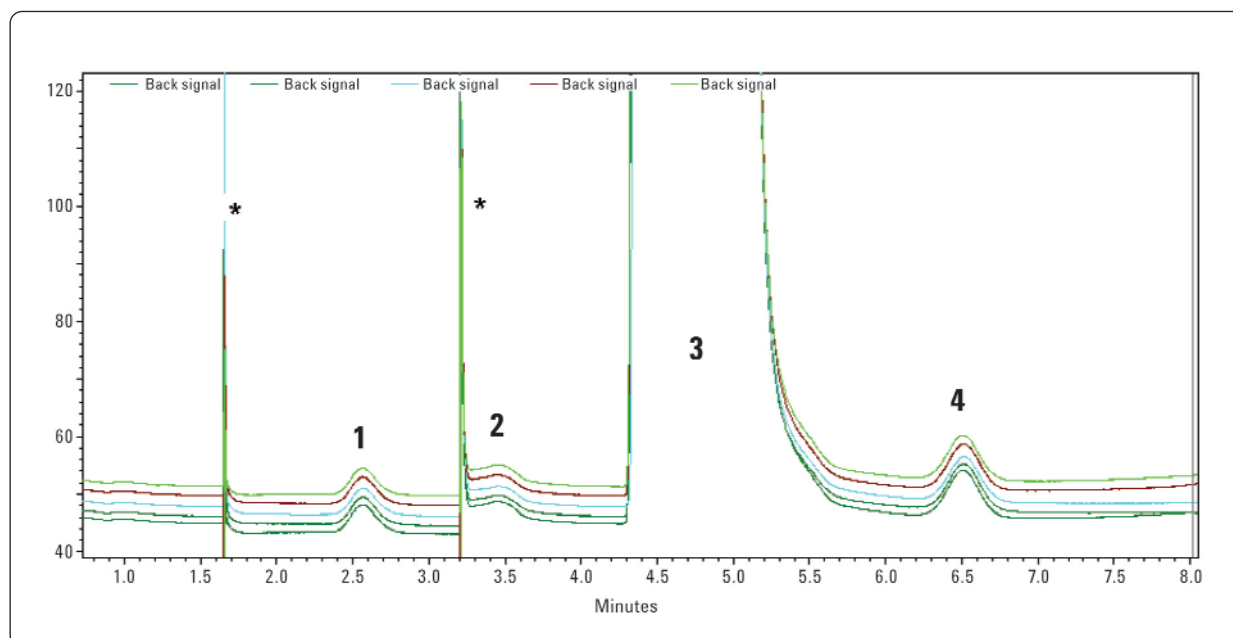


Figure 5. Overlapped chromatograms of five runs.

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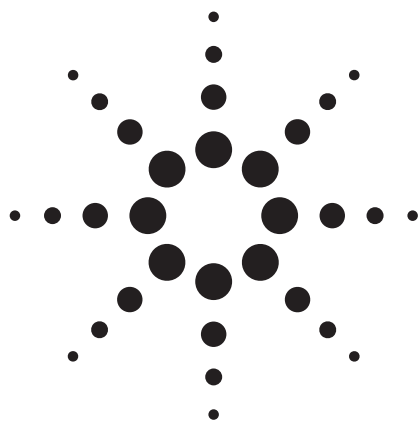
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Evaporation from 2-mL Vials on the Agilent 7696A Sample Prep WorkBench: Septa Unpierced, Septa Pierced with a Syringe Needle, Septa with an Open Hole

Application Note

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Introduction

In the course of sample analysis by gas chromatography, the vial septum may be pierced multiple times before each injection, often with multiple injections. Once the septum is pierced, solvent evaporation from the vial occurs. This usually does not create a reproducibility problem for GC analysis, even with multiple injections, unless the time between runs is an hour or longer. With the Agilent 7696A Sample Prep WorkBench, the number of times a septum is pierced may be greater, and the time before the final sample is analyzed may be much longer than is typical in GC.

Another problem that arises with the Agilent 7696A Sample Prep WorkBench is the need to withdraw large volumes from 2 mL vials. For example, transferring 0.5 mL solvent or sample from one vial to another can create a partial vacuum in the source vial. This results in poor reproducibility because the degree of vacuum varies from vial to vial and the amount of liquid actually transferred also varies. One way to eliminate this problem is to prepierce the septum with a small off-center hole so that no vacuum is created and the syringe needle is still wiped by the septum when withdrawn from the vial.

The evaporation rates of hexane (bp = 70 °C) and isooctane (bp = 100 °C) were measured at ambient temperature for three different septum scenarios to determine the magnitude of the problem. The three scenarios are as follows: a new unpierced septum, a septum prepierced approximately nine times, and a septum cored to prevent vacuum formation. Evaporation from the new, unpierced screw cap vial septa was considered negligible. Evaporation was greater with the septa pierced with a syringe needle and much greater with the cored septa.



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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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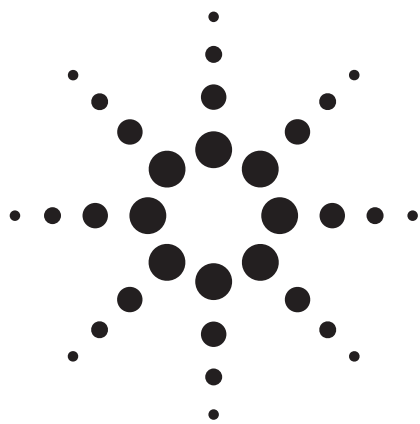
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GC Analysis of Sulfur Components in Propylene using a Pulsed Flame Photometric Detector

Application Note

Hydrocarbon Processing

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Abstract

The Agilent J&W Select Low Sulfur column measures trace levels of target components in C3 hydrocarbon streams without any matrix interference.

Introduction

Hydrogen sulfide (H_2S), carbonyl sulfide (COS) and methyl mercaptan (CH_3SH) are common components in light hydrocarbon streams. They have corrosive and toxic properties, causing damage to pipes and equipment. The emission of undesired odors caused by volatile sulfur compounds in intermediates and final products have serious economic and environmental impact. In addition, the presence of sulfur can affect the performance of industrial processes, causing chemical reactions, loss of catalyst activity (catalyst poisoning), and ultimately lower yield.

These sulfur components must be quantified at low ppb levels. They can be measured with sulfur specific detection devices like the Pulsed Flame Photometric Detector (PFPD) but large sample volumes are needed to reach the desired low parts per billion (ppb) detection limits. This creates matrix overload and quenching effects (decreased signal/sensitivity due to background interferences) on most sulfur specific detectors, limiting the detector's sensitivity and linearity and raising quantification limits. The capillary PLOT column, Agilent J&W Select Low Sulfur column, with a novel stationary phase was developed for the analysis of sulfur species such as H_2S , COS and CH_3SH in light hydrocarbon C3 matrices, with high loadability properties and unique selectivity giving baseline resolution for sulfur components and matrix components.



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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.

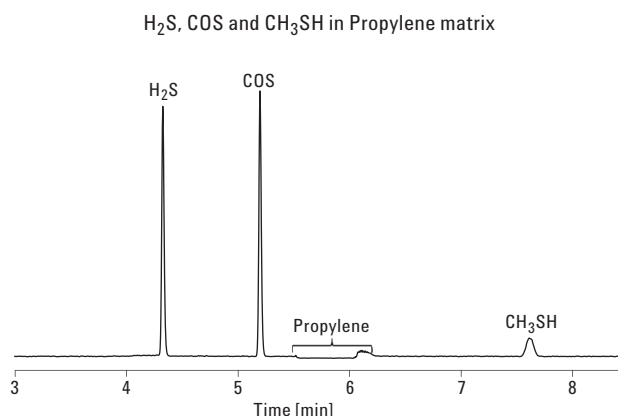


Figure 1. Chromatogram of sulfur compounds H₂S, COS and CH₃SH in a propylene matrix, using the Agilent J&W Select Low Sulfur with GC-PFPD.

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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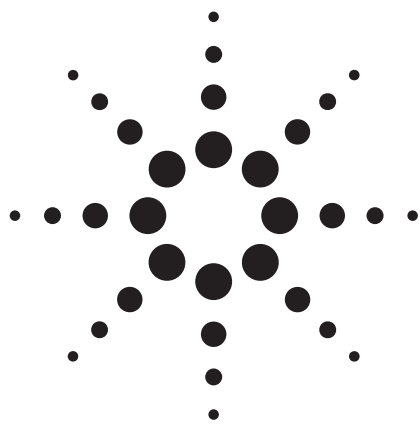
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Agilent Technologies



Permanent Gases on a COX Module Using a Agilent 490 Micro GC

Application Note

Micro Gas Chromatography

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Abstract

This application note demonstrates the capabilities of the COX column with the Agilent 490 Micro GC, including separation of permanent gases and backflush possibilities to ensure extended column lifetimes.

Introduction

Separation of permanent gases is usually performed on a Molsieve column. This column offers the best separation for all permanent gases but also has some severe drawbacks. Water and carbon dioxide do not elute from a Molsieve column under regular GC conditions. A bake out at high temperatures (250 – 300 °C) is needed to fully regenerate the column. Regeneration is very time consuming in a Micro GC usually taking overnight or longer because the maximum temperature is 180 °C. In addition, it is likely that regeneration from moisture does not occur at this temperature.

If there is no need to separate oxygen and nitrogen, the COX column is a better alternative. It delivers good separation of permanent gases, and carbon dioxide elutes from the column. COX is an ideal alternative for a Molsieve column, offering prolonged lifetime and instrument uptime.



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Experimental

Instrumentation

An Agilent 490 Micro GC system with a COX column module was used for these experiments. The COX column module was equipped with a heated injector and an optional precolumn with backflush.

Conditions

Column temperature	100 °C
Carrier gas	Argon, 100 kPa
Backflush to vent time	13 s
Injection time	80 ms
Injection temperature	110 °C
Sample line temperature	100 °C
Sampling time	30 s
Stabilization time	5 s
Run time	200 s

Sample Information

Standard gas samples were used. Concentrations were in % levels.

Table 1. Repeatability Figures Per Component on Peak Area

Run	He	H ₂	N ₂	CO	CH ₄	CO ₂
1	943213	16024030	20593423	1439534	1535598	1064007
2	947355	16092042	20685887	1444814	1538714	1062243
3	949818	16142635	20749728	1446996	1544418	1070193
4	949808	16167426	20781405	1449939	1542239	1066091
5	952725	16194789	20815739	1453498	1539162	1066940
6	952107	16206479	20826967	1456289	1543749	1063772
7	954648	16228802	20856620	1455219	1548126	1074325
8	954635	16249294	20879589	1456795	1547760	1079645
9	955454	16251565	20883920	1456611	1552320	1064839
10	955872	16250493	20901246	1473831	1547242	1065483
Average	951563.5	16180756	20797452	1453353	1543933	1067754
St. Dev	4053	75870	97930	9249	5122	5456
RSD%	0.43	0.47	0.47	0.64	0.33	0.51

Results and Discussion

The above settings produce the chromatogram shown in Figure 1, with repeatability data in Table 1.

The chromatogram shows a baseline separation of helium and hydrogen. Oxygen and nitrogen eluted as a single peak but separate from carbon monoxide and methane. Carbon dioxide eluted perfectly.

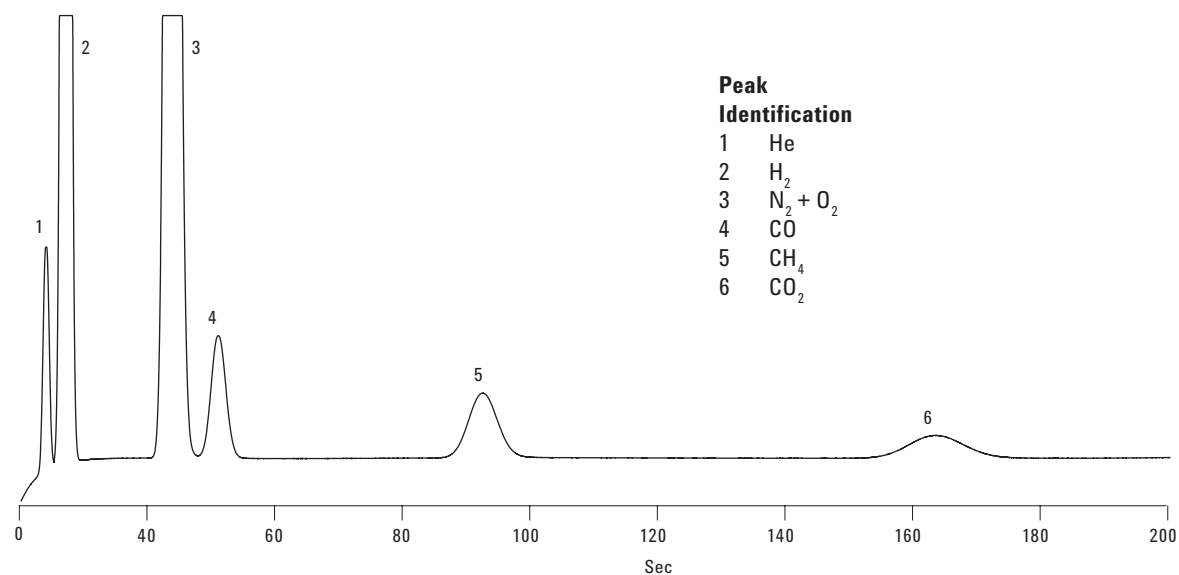


Figure 1. Excellent baseline separation of a gas sample on a COX column.

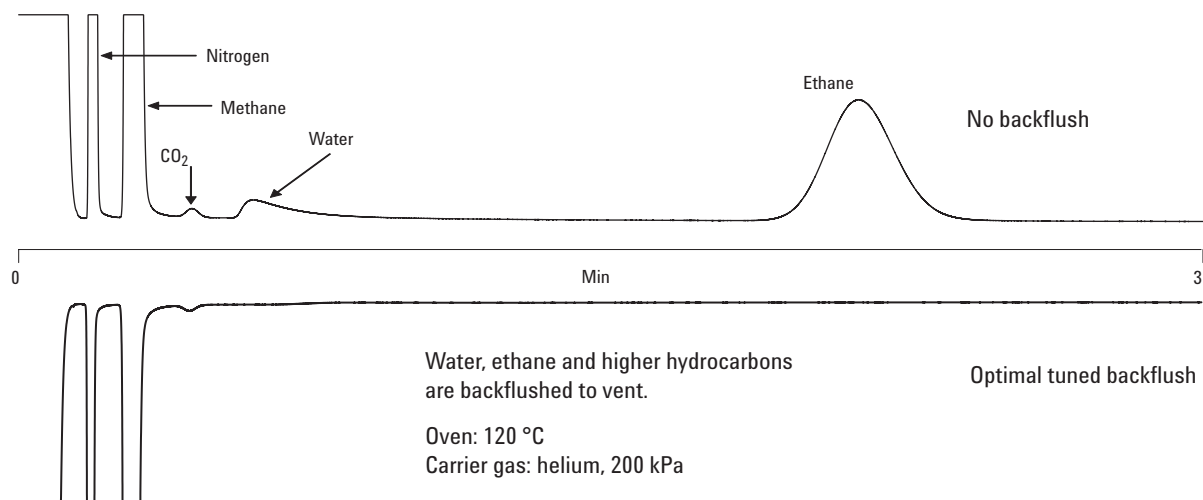


Figure 2. Backflush of water and ethane.

Other components such as water and higher hydrocarbons were backflushed to vent.

If the backflush time is set at a high value then virtually all the sample components enter the analytical column and eventually elute. However, if higher hydrocarbons are present the COX column is polluted because these components elute late and can influence the succeeding analysis.

Figure 2 shows the elution of water and ethane if no backflush is applied. If the backflush time is optimally tuned, water, ethane and higher hydrocarbons are backflushed to vent and does not enter the analytical column.

Conclusion

For the analysis of permanent gases the COX column is a good alternative to the commonly used Molsieve column.

Although the COX column does not separate oxygen and nitrogen, it does separate hydrogen and helium. In addition, carbon dioxide is analyzed and water elutes from the COX column. Repeatability figures are good, ensuring reliable analysis results.

The COX module can be equipped with a precolumn. This allows backflush of higher components and prolongs column lifetime.

The Agilent 490 Micro GC is a rugged, compact and portable “lab-quality” gas analysis platform. When the composition of gas mixtures is critical, this fifth generation Micro Gas Chromatograph generates more data in less time for faster and better performance.

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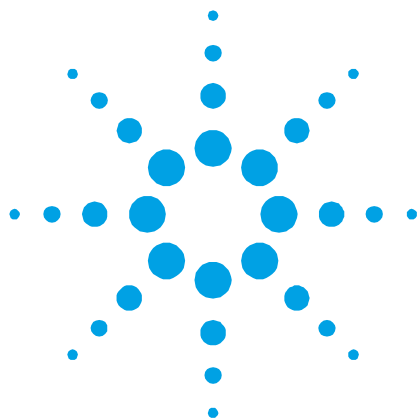
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Returning to Fixed Pathlength Infrared Spectroscopy: Gaining Detail and Removing the Obstacles

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Introduction

This article discusses the benefits of making infrared (IR) transmission measurements from liquids with a fixed pathlength. The pros and cons, mainly cons, of traditional fixed pathlength cells are reviewed first, with the main “cons” being difficulties with filling and cleaning, and the need to protect the IR windows from moisture. ATR has become a practical alternative method for a liquid, however, the technique, by nature, is a surface-based measurement and there are significant limitations in regard to physical pathlength, which is very short.

A new system that provides a fixed pathlength IR transmission measurement for liquid sample handling and analysis is reviewed. The system features 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.

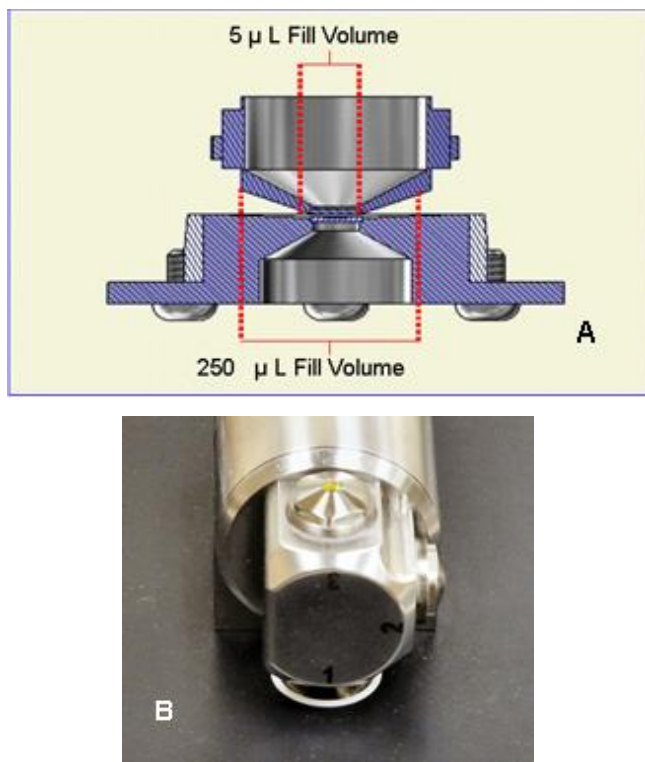


Figure 1. The 5500 DialPath FTIR sampling point concept (A); provides a user selectable pathlength, with one of three fixed/calibrated optical paths, designated 1, 2 and 3 (B)

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} .

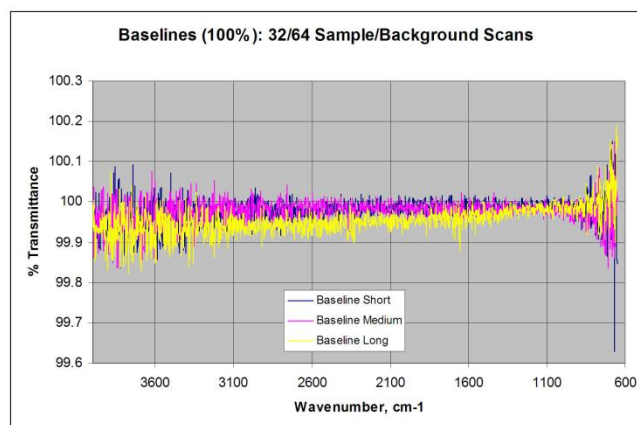


Figure 2. 100% Baseline performance; spectra from long, medium and short pathlengths presented with an average SNR of 8000:1 (2100 cm^{-1} to 1100 cm^{-1})

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.

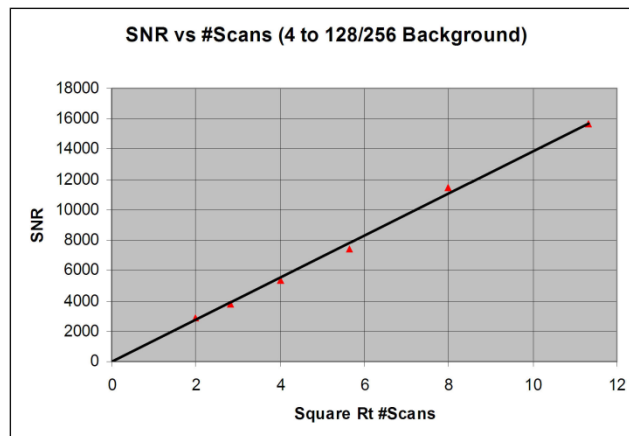


Figure 3. The adherence of the measurement system to the square root law of measured SNR

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

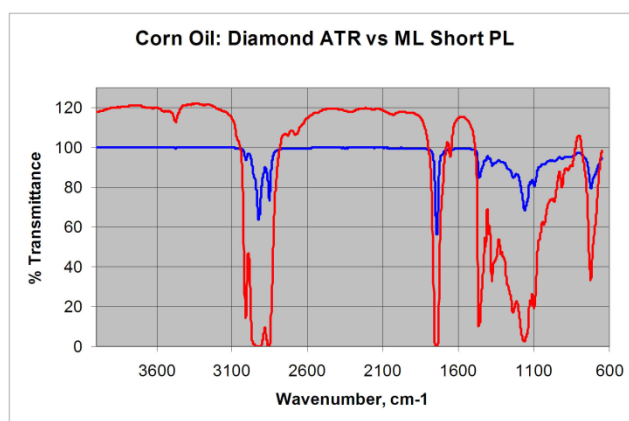


Figure 4. Comparison of the effective pathlength of a diamond ATR integrated system with the short fixed pathlength ($\sim 30 \mu\text{m}$) transmission spectrum for corn oil

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 (30µm, 50µm and 100µm). The results (Figure 5) indicate a high level of correlation between the two different sets of fixed pathlength spectra, providing calibration equations for the three 5500a system pathlengths; short = 31.9 µm, medium = 52.6 µm, and long = 114.7 µm.

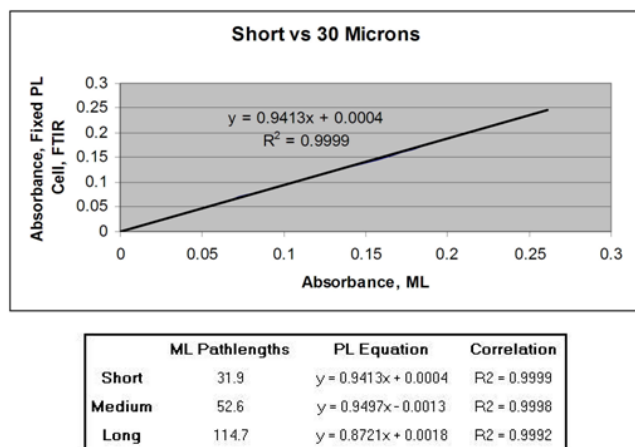


Figure 5. Example calibration for the short pathlength (No 1) of the Agilent 5500 DialPath FTIR system based on comparisons with a calibrated fixed pathlength cell for a series of xylene solutions

These experiments have demonstrated that the fixed pathlengths of the 5500 DialPath system are highly reproducible, and once calibrated provide an accurate duplication of the fixed pathlength performance of the standard, calibrated fixed pathlength cells.

Practical applications of a fixed pathlength measurement system

The ability to measure with known fixed pathlengths is important for a wide range of applications. An obvious application is for the analysis of very dilute solutions where a pathlength of 100 µm or more is required. The application shown in Figure 6, are spectra of dilute solutions (<1% solute) of methanol are measured in a non-polar solvent (carbon tetrachloride).

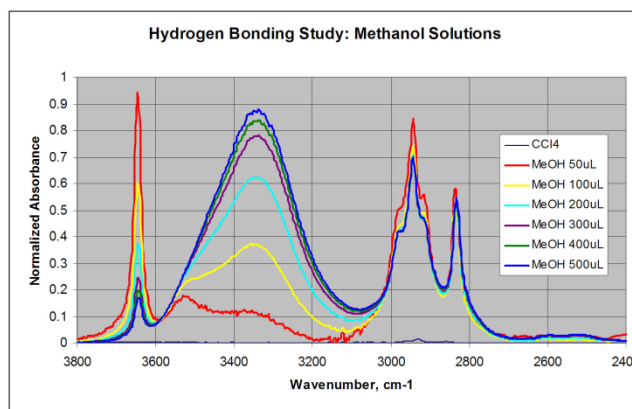


Figure 6: Dilute solutions of methanol in carbon tetrachloride; a study of the effects of hydrogen bonding in non-polar solvents

This is a classical measurement where changes in intermolecular hydrogen bonding are demonstrated. The normal condensed phase spectrum of methanol exhibits a broad absorption centered at 3450 cm⁻¹ assigned to polymeric hydrogen bonding. Upon dilution with the non-polar solvent, this hydrogen bond profile changes as indicated in the red and yellow band profiles of Figure 6. These spectra correspond to the transition, through oligomeric forms to the non-bonded form with the narrow absorption at 3630 cm⁻¹. This experiment is only practical with a long path measurement (100+ µm in this case). The ATR method is impractical for this type of application.

The largest benefit of the open architecture of the 5500 DialPath system is the ability to handle medium to high viscosity liquids. Typical applications that are constrained by viscosity are measurements on vegetable oils (including cooking and edible oils), dairy products (such as milk, cream and butter products) and automotive products, including fuels, lubricating oils

and greases. While an ATR liquid measurement system might be used for some of these applications, the increased spectral detail of a longer pathlength is preferred for product quality and performance-related measurements. Figure 7 is important for both edible and cooking oils and products derived from these materials, such as biodiesel fuels. Recent regulations on food quality and safety have focused on the need to eliminate trans unsaturated fats from food preparation. The total level of unsaturates and the type of unsaturates, including the trans configuration can be determined from the spectral region from 1000 cm^{-1} to 650 cm^{-1} . In the case of biodiesel, many quality parameters are linked to components formed in the esterification process. These components, such as free acid, free glycerol and glyceride fragments can be determined from the spectrum. These include the OH stretching region featured in Figure 7A where residual water (from esterification) and free glyceride components can be detected and measured. These measurements require the extended pathlengths used in the spectra shown in Figure 7A/B ($100+\text{ }\mu\text{m}$ pathlength).

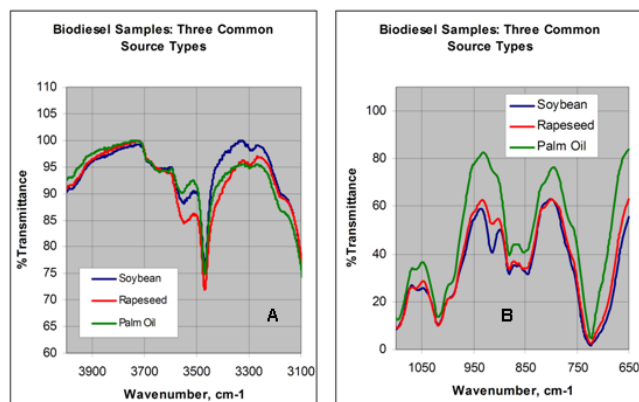


Figure 7. Detailed information from the base ester components used in the production of biodiesel methyl esters; hydroxyl (A) and unsaturation (B) functionalities

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.

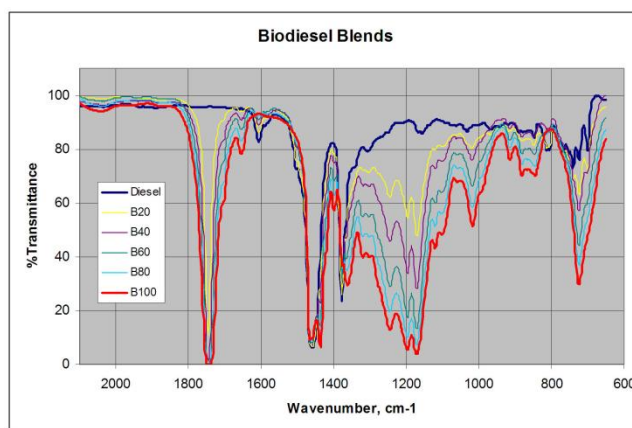


Figure 8. Measurement of biodiesel blends, experimental data from B0 (diesel fuel) to B100 (biodiesel) and intermediate biodiesel/diesel blends

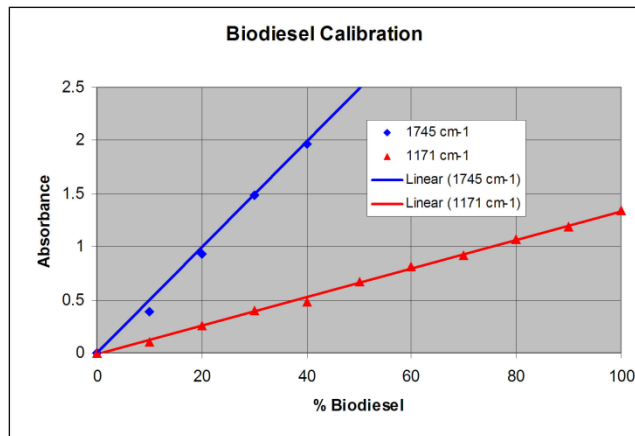


Figure 9. Quantitative measurement of biodiesel blends, B0, B10 to B90 and B100

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.

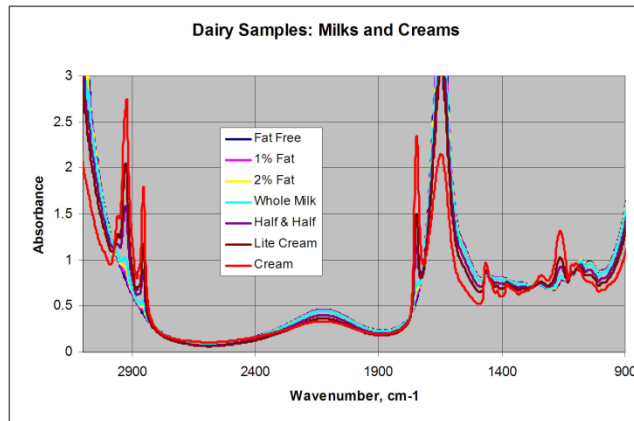


Figure 10. Dairy product spectra; short fixed pathlength (~30 mm), from fat free skim milk to standard heavy cream

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

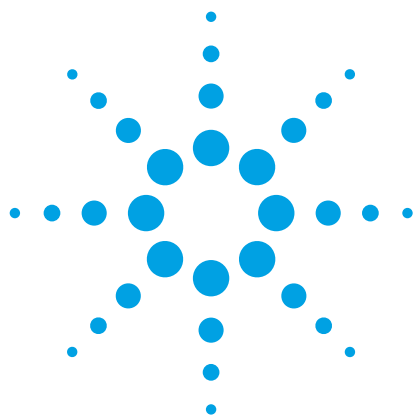
This article has reintroduced the concept of making fixed pathlength mid-infrared transmission measurements without the complexity or the difficulties of the traditional sample handling method. A two-step approach summarized as “drop it on” and “wipe it off” is proposed, where the sample is put in place 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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Analysis of tert-Butyl Mercaptan in Natural Gas on a CP-Sil 13 CB Using the Agilent 490 Micro GC

Application Note

Micro Gas Chromatography, Hydrocarbon processing, Natural Gas Analysis

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Introduction

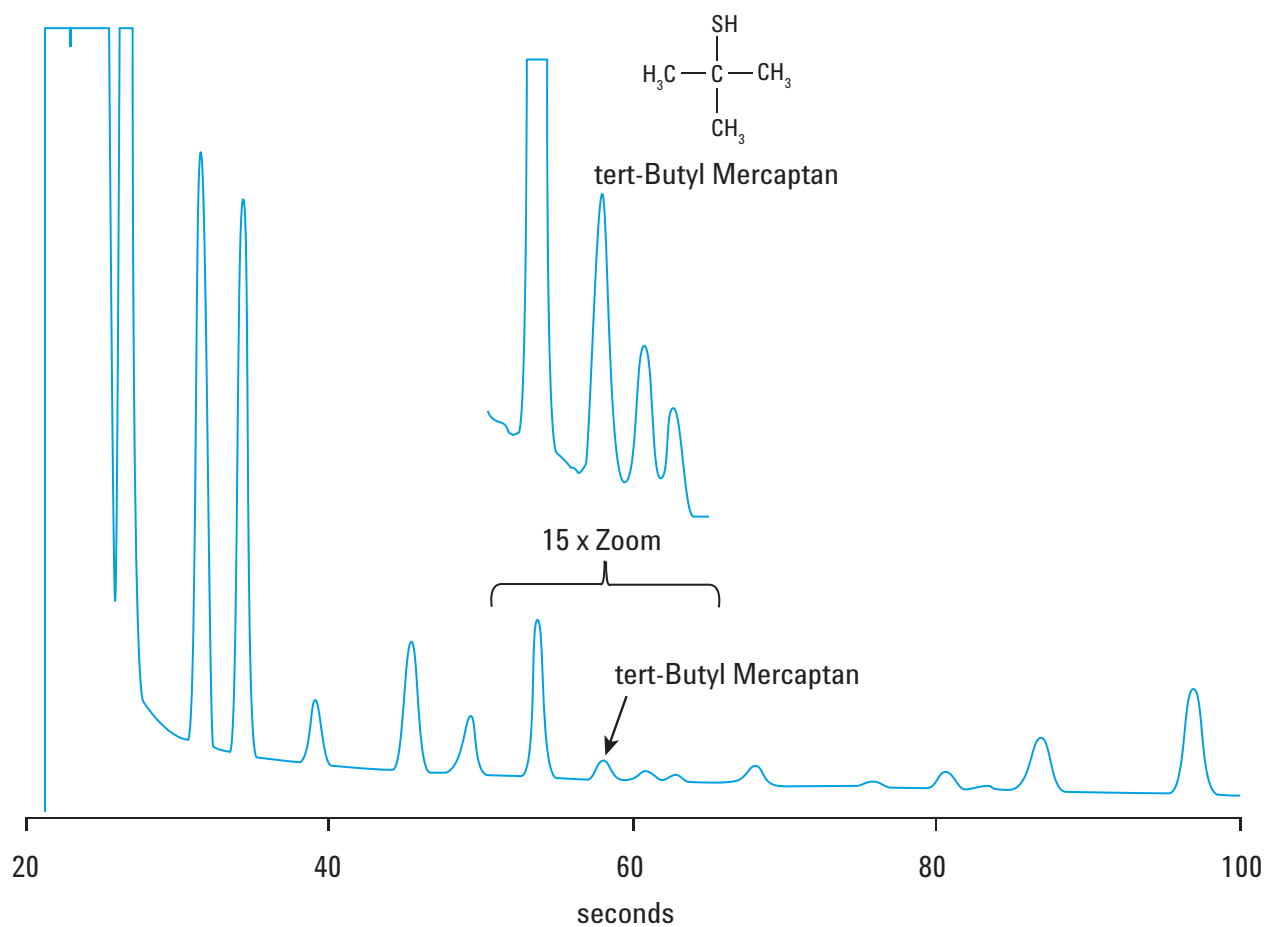
This application note shows the analysis of tertiary-butyl mercaptan (TBM) in a natural gas matrix using the Agilent 490 Micro GC. The dimensions and instrument conditions for the column channel used in this application note, a CP-Sil 13 CB, clearly shows the separation of TBM from the other compounds in the natural gas sample.

The advantage of the Agilent 490 Micro GC, in combination with the CP-Sil 13 CB column channel, is the ease of use and the speed of analysis. Tertiary-butyl mercaptan elutes just before 60 seconds and the total analysis time is only 100 seconds.

The Agilent 490 Micro GC is a rugged, compact and portable lab-quality gas analysis platform. When the composition of gas mixtures is critical, count on this fifth generation micro gas chromatography.



Agilent Technologies



Instrumentation

Instrument	Agilent 490 Micro GC (G3581A)
Column channel	CP-Sil 13 CB for TBM
Column temperature	40°C
Carrier gas	Helium, 250 kPa
Injection time	255 msec

Sample information

Natural gas	Matrix
Tert-butyl mercaptan (TBM)	4 ppm

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com.

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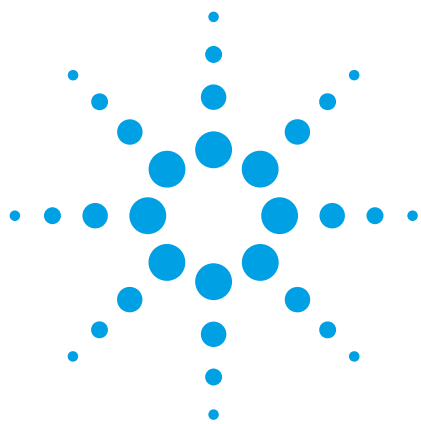
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Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer

Application note

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Abstract

The OneNeb nebulizer for inductively coupled plasma optical emission spectrometry (ICP-OES) features unique Flow Blurring technology. Compared to previous nebulizers, this universal nebulizer provides improved sensitivity, greater tolerance to dissolved salts and strong acids such as HF, resistance to most common organic solvents and efficient operation over a much wider flow rate range.

This application note demonstrates the superior performance of the OneNeb nebulizer compared to commercially available glass concentric nebulizers usually provided with ICP-OES instruments. Detection limits and reproducibility were better in a range of analytes and liquids.



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.

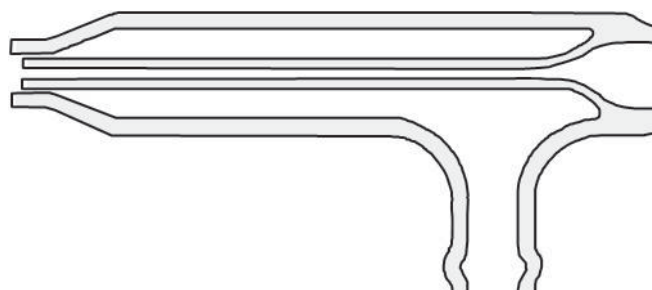


Figure 2. Concentric glass nebulizer

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.

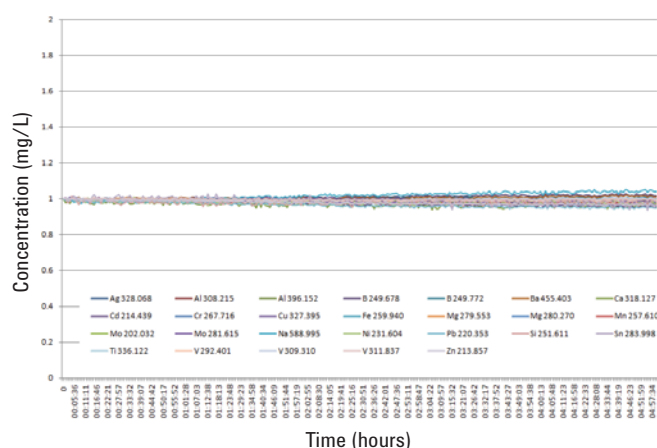


Figure 3. Long-term stability of the OneNeb nebulizer with diisobutyl ketone

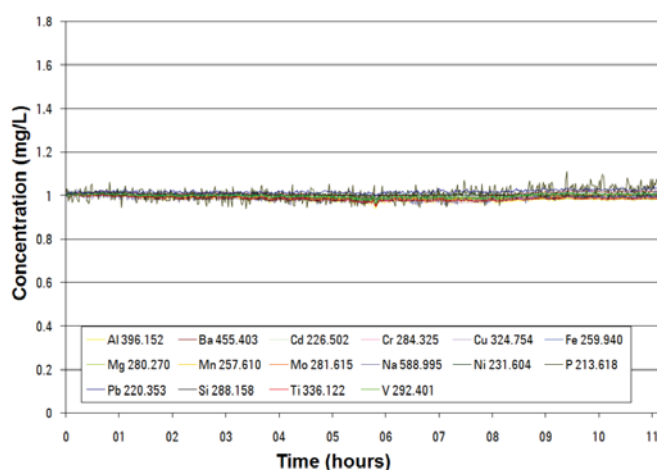


Figure 4. Long-term stability of the OneNeb nebulizer with ShellSol

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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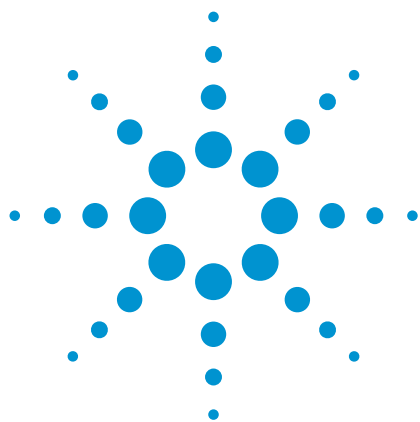
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Agilent Technologies



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

Application Note

Application Area Identifier

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Abstract

A comprehensive GCxGC system based on differential flow modulation is described that uses three independent programmable ovens. The first dimension separation occurs in the 7890A air bath oven while two simultaneous second dimension separations occur on 5 inch LTM Series II modules. All columns operate in constant flow mode. Oven temperature programs can be customized independently for each column. Typically the two LTM columns will be of different polarities and phase ratios to maximize the information that can be gathered from the sample. A typical column configuration consists of a 20 m $\times$ 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.

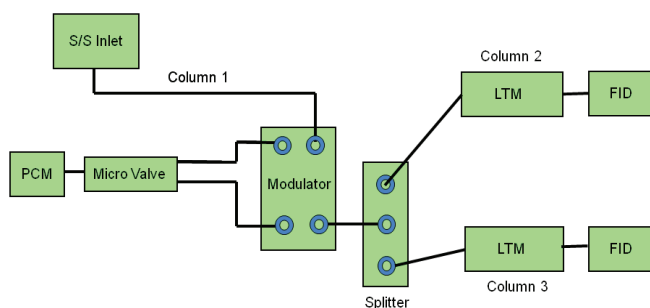


Figure 1. Diagram of the dual LTM GCxGC system.

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.

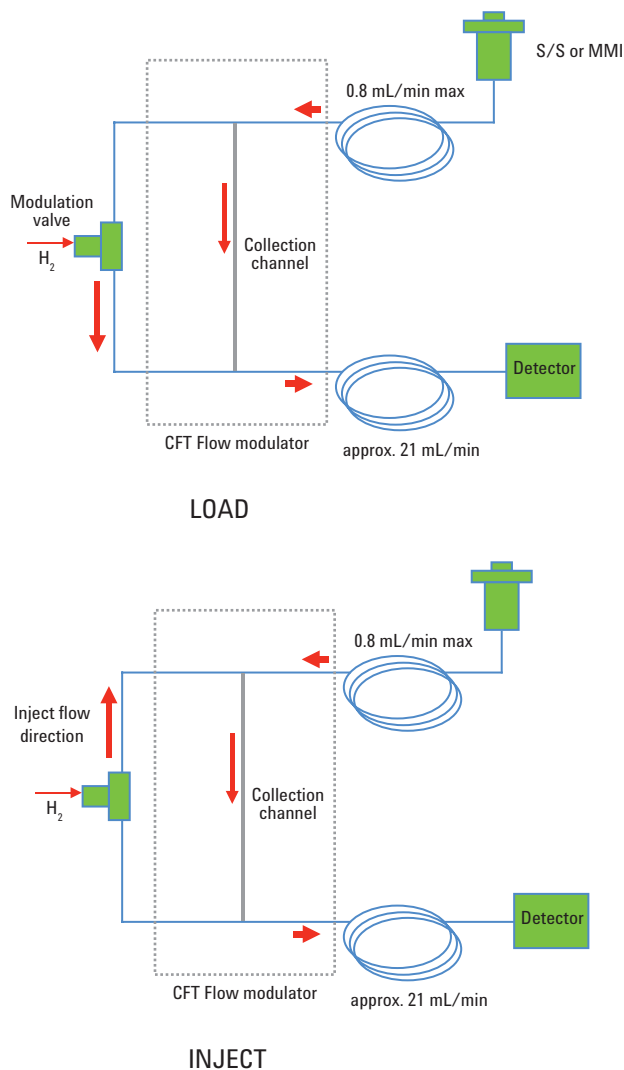


Figure 2. Operational detail of the flow modulator showing load and inject states.

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.

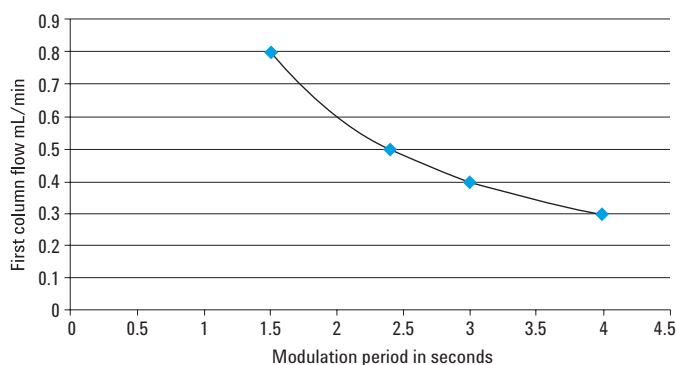


Figure 3. Relationship between modulation period and first dimension column flow rate.

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.

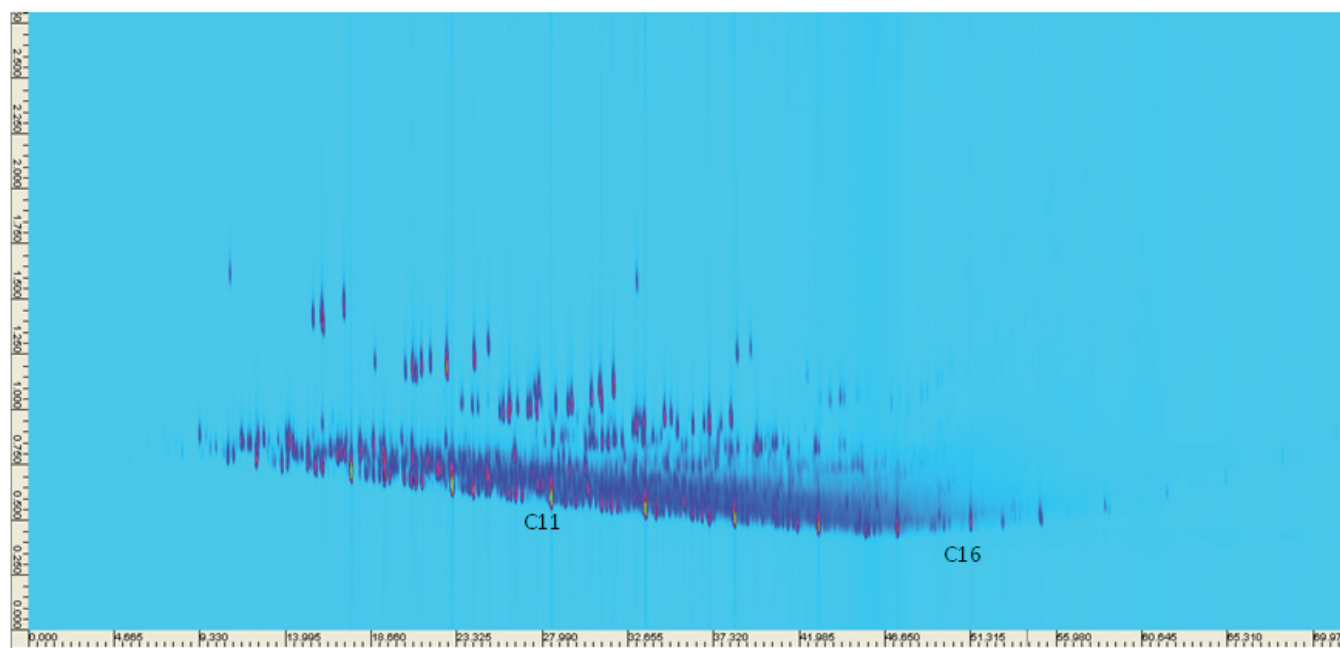


Figure 5a. Jet fuel 2D image. 7 m $\times$ 0.25 mm $\times$ 0.24 μ m HP-INNOWax, LTM program: 55 $^{\circ}$ C (3 min) to 270 $^{\circ}$ C @ 5 $^{\circ}$ C/min. 7890A program: 35 $^{\circ}$ C (2 min) to 280 $^{\circ}$ C @ 3 $^{\circ}$ C/min.

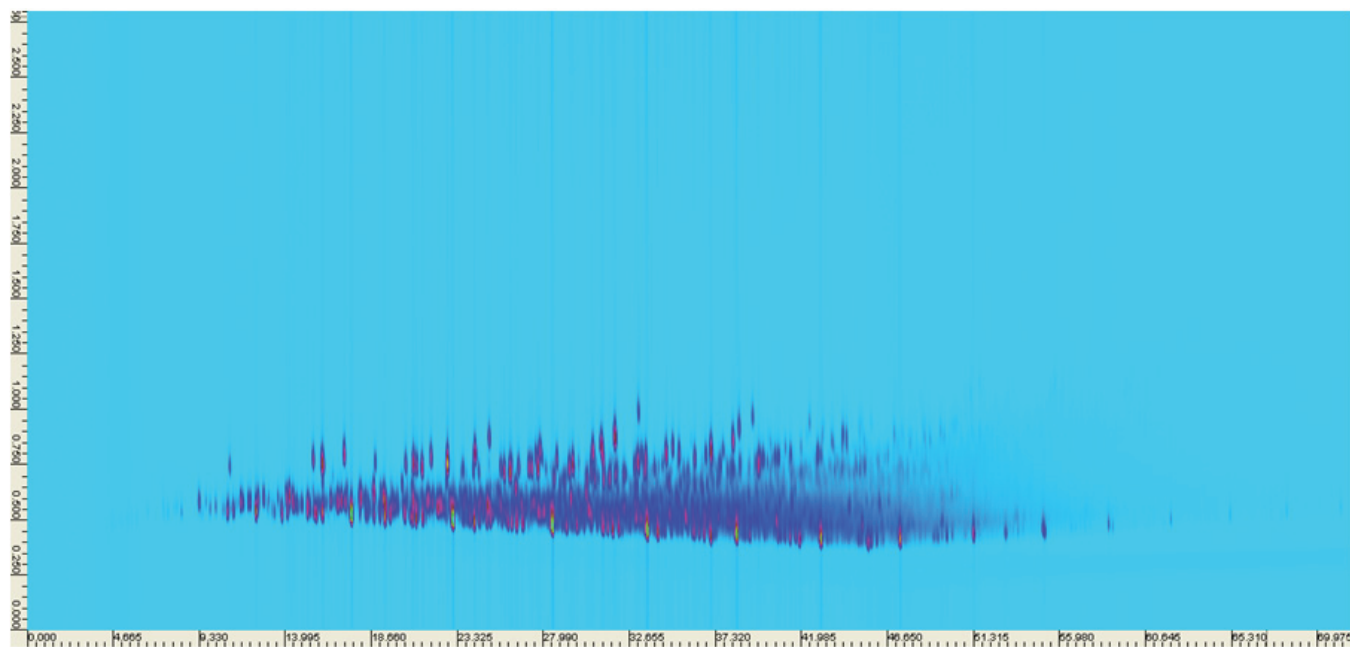


Figure 5b. Jet fuel on 5 m $\times$ 0.25 mm $\times$ 0.15 μ m DB17HT, LTM program: 60 $^{\circ}$ C (5 min) to 300 $^{\circ}$ C @ 3 $^{\circ}$ C/min. 7890A program: 35 $^{\circ}$ C (2 min) to 280 $^{\circ}$ C @ 3 $^{\circ}$ C/min.

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.

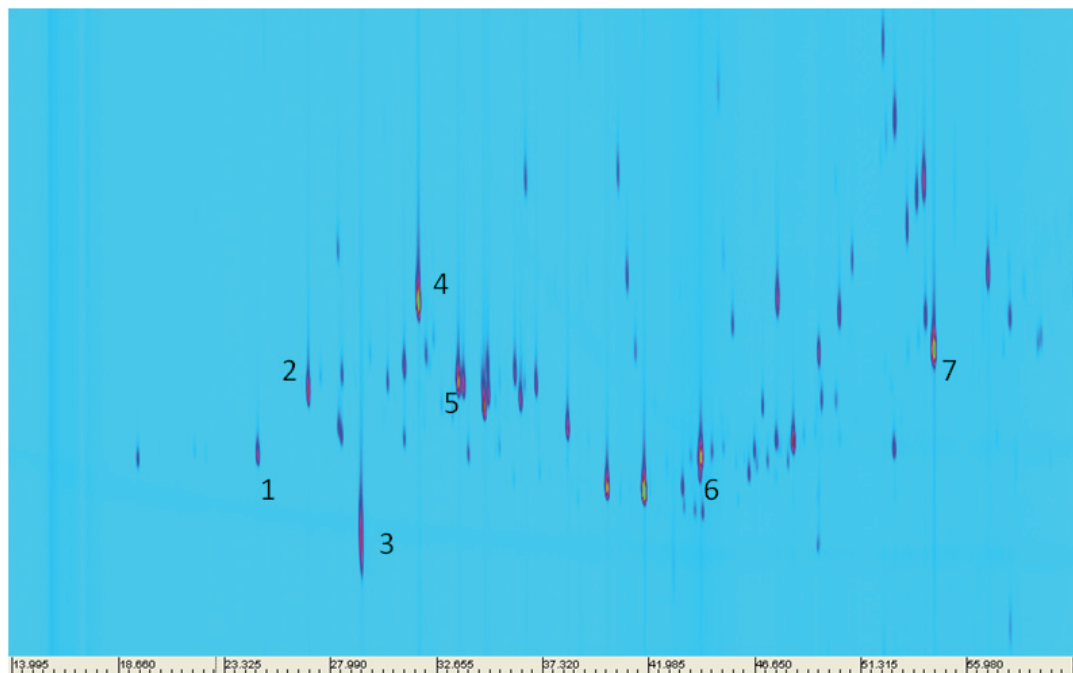


Figure 6a. Fragrance additive using 7 m INNOWax for 2nd dimension, LTM program: 55 °C (3 min) to 270 °C @ 5 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min. 1. Alpha Pinene, 2. Limonene, 3. 2,6 dimethyl 7-octen-2-ol, 4. Phenethyl acetate, 5. Terpenol, 6. Bicyclopentadiene, 7. 4-tert-butylcyclohexyl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

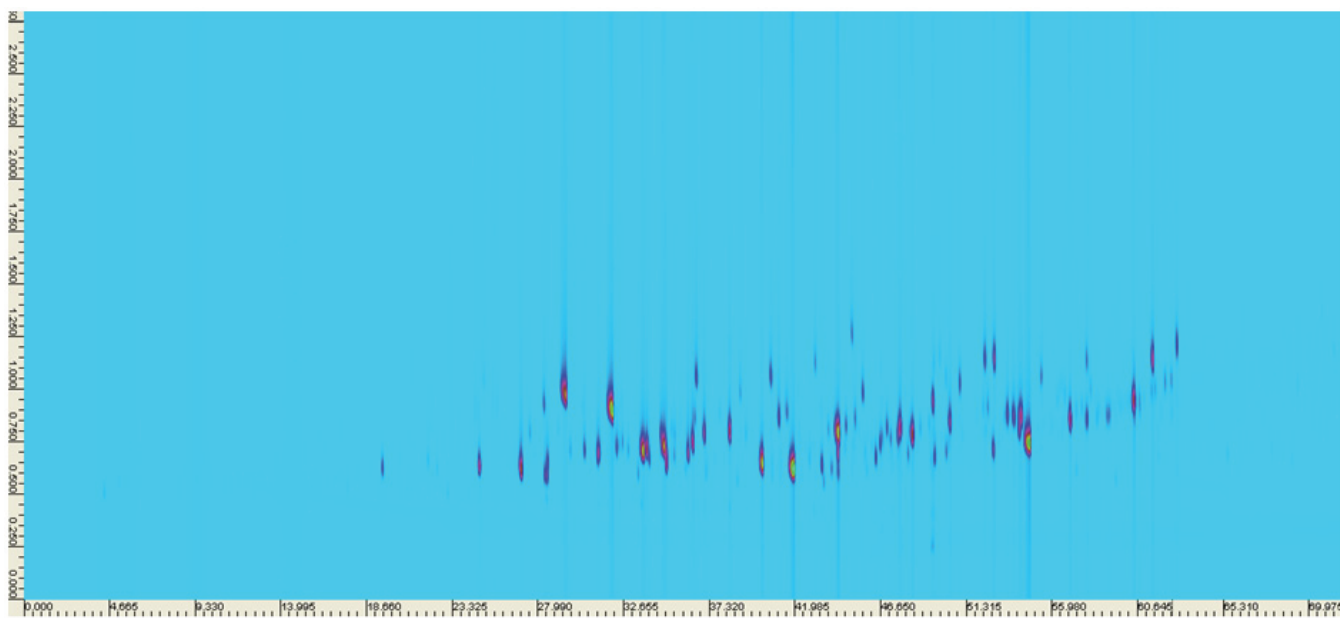


Figure 6b. Fragrance additive using 5m DB17HT for 2nd dimension separation. LTM program: 60 °C (5 min) to 300 °C @ 3 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min.

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.

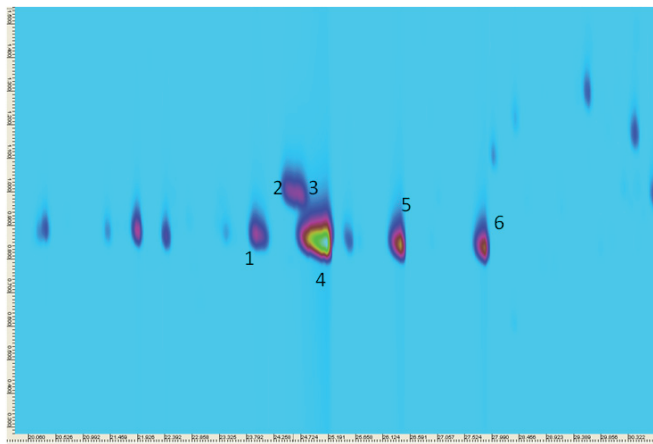


Figure 7a. Lime oil on the 7 m INNOWax. LTM program: 55 °C (3 min) to 270 °C @ 5 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min. 1. Alpha Pinene, 2. Limonene, 3. 2,6 dimethyl 7-octen-2-ol, 4. Phenethyl acetate, 5. Terpenol, 6. Bicyclopentadiene, 7. 4-tert-butylcyclohexyl acetate 1.beta pinene,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

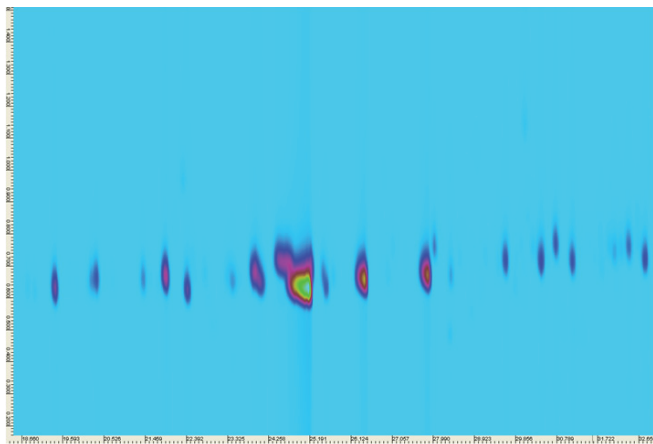


Figure 7b. Lime oil on the 5 m DB17HT. LTM program: 60 °C (5 min) to 300 °C @ 3 °C/min. 7890A program: 35 °C (2 min) to 280 °C @ 3 °C/min.

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.

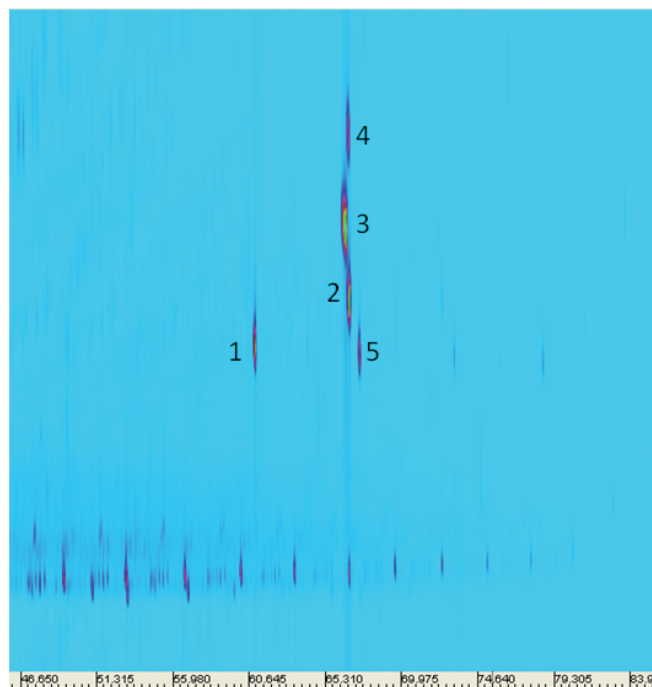


Figure 8. Separation of C16 and C18 fatty acid methyl esters in B20 biodiesel on a 5 m × 0.25 mm × 0.15 μm LTM INNOWax column in the 2nd dimension. LTM program: 30 °C (0 min) to 270 °C (5 min) @ 3 °C/min. 1. C16:0, 2. C18:1, 3. C18:3, 4. C18:3, 5. C18:0.

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.

References

1. Comprehensive Flow Modulated Two-Dimensional Gas Chromatography, Roger L. Firor, Application Note 5989-6078EN, 2008
2. Comprehensive GC System Based on Flow Modulation for the 7890 GC, Roger L. Firor, Application Note 5989-8060EN, 2009

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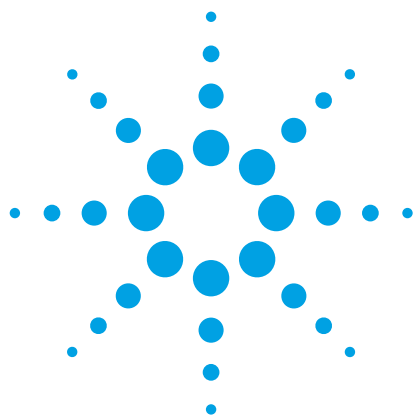
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Agilent Technologies



Analysis of Tetrahydrothiophene (THT) in Natural Gas using the Agilent 490 Micro GC

Application Note

Micro Gas Chromatography, Natural Gas Analysis, Sulfur Compound Analysis

Author

Remko van Loon
Agilent Technologies
Middelburg
The Netherlands



Introduction

This application note shows the analysis of Tetrahydrothiophene (THT) in a Natural Gas matrix using the Agilent 490 Micro GC. THT consists of a five-membered ring containing a sulfur atom and four carbon atoms. THT is used as an odorant in Natural Gas, because of its smell.

The chromatogram clearly shows the separation of THT from the other compounds in the Natural Gas sample. The dimensions for the column channel used, a CP-Sil 19 CB for THT, are optimized for this application. Moreover, this column channel is factory tested to ensure the separation between THT and Nonane.

The advantage of the Agilent 490 Micro GC, in combination with the CP-Sil 19 CB column channel, is the ease-of-use and the speed of analysis. Tetrahydrothiophene elutes around 40 sec and the total analysis time is less than 90 sec.

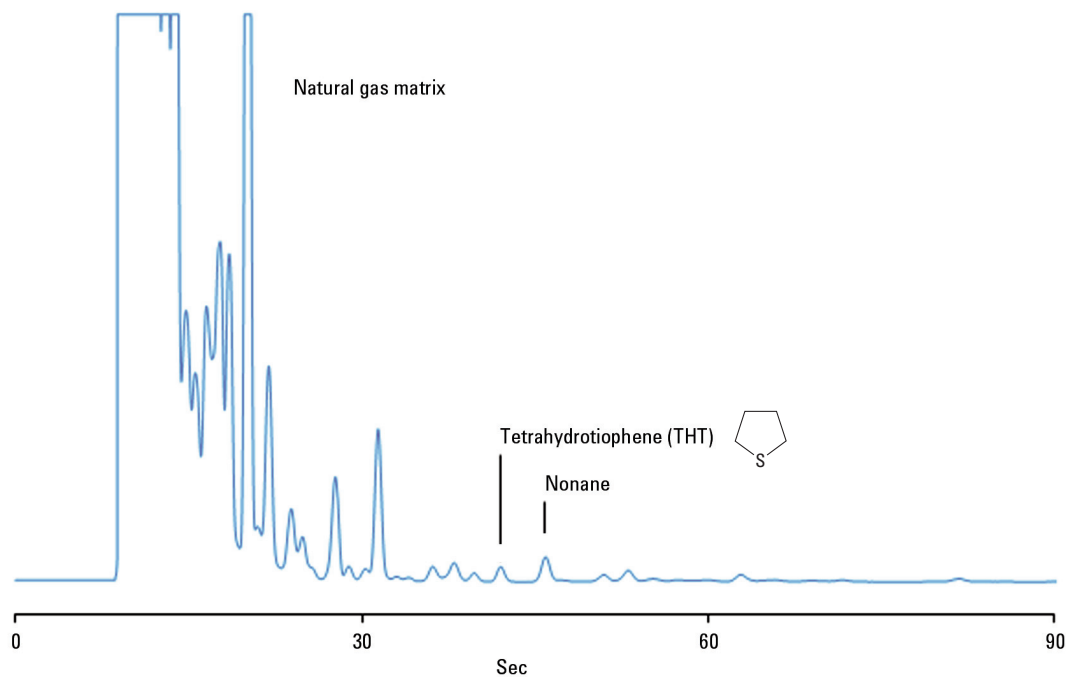
The Agilent 490 Micro GC is a rugged, compact, and portable lab-quality gas analysis platform. When the composition of gas mixtures is critical, count on this fifth generation micro gas chromatography.



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Instrumentation

Instrument	Agilent 490 Micro GC (G3581A)
Column channel	CP-Sil 19 CB for THT
Column temperature	90 °C
Carrier gas	Helium, 200 kPa
Injection time	255 msec
Injector temperature	110 °C
Sampling time	30 sec



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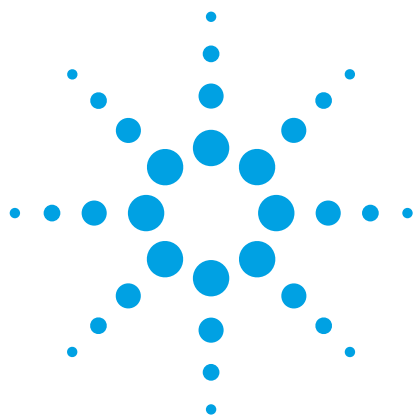
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Agilent Technologies



Analysis of Methyl Ethyl Sulfide (MES) in Natural Gas using the Agilent 490 Micro GC

Authors

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Application Note

Micro Gas Chromatography, Natural Gas Analysis, Sulphur Compound Analysis



Introduction

This application note shows the analysis of Methyl Ethyl Sulfide (MES) in natural gas using the Agilent 490 Micro GC. Methyl Ethyl Sulfide is an organosulfur compound with a characteristic odor, and therefore used in some countries as an odorant for natural gas.

This Micro GC column channel is equipped with a special dedicated column, MES in natural gas, for the separation of MES from the other compounds in natural gas. Moreover, this column channel is factory tested to ensure the separation between n-Decane and MES.

If you want the ability to measure anywhere and get the results you need in seconds, the Agilent 490 Micro GC is the ideal solution. With its rugged, compact, laboratory quality gas analysis platform, the 490 Micro GC generates more data in less time for faster, and better, business decisions.



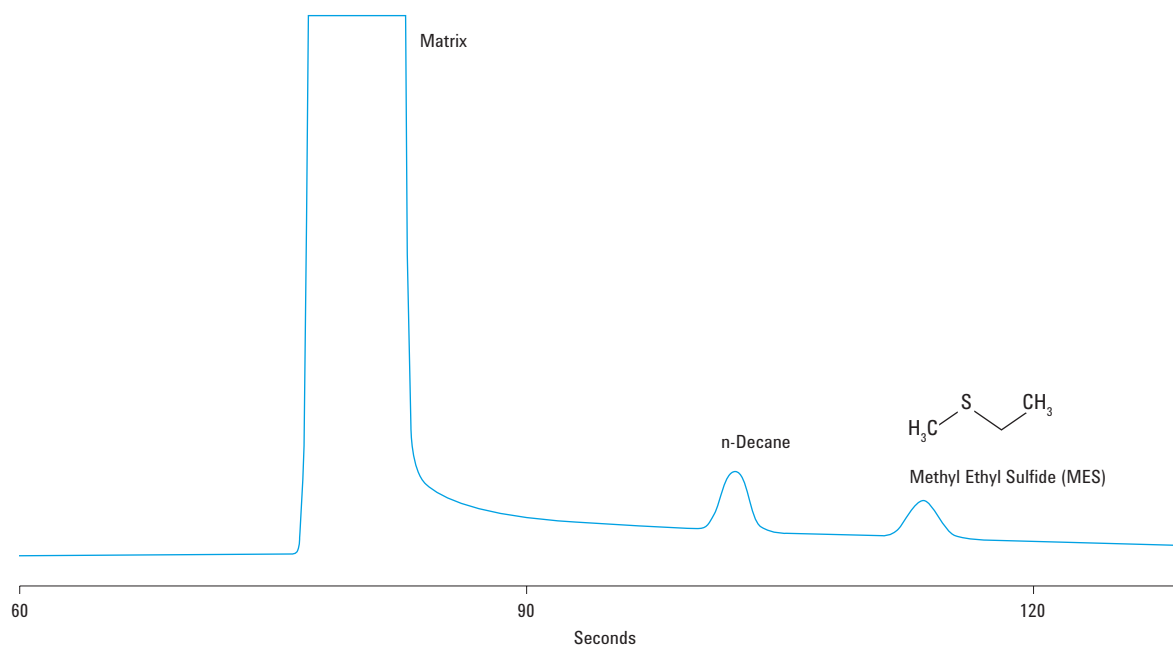
Agilent Technologies

Instrumentation

Instrument	Agilent 490 Micro GC (G3581A)
Column channel	MES in natural gas
Column temperature	90 °C
Carrier gas	Helium, 70 kPa
Injection time	255 msec
Injector temperature	110 °C
Sampling time	30 sec

Sample information

n-Decane	11 ppm
Methyl Ethyl Sulfide (MES)	14 ppm



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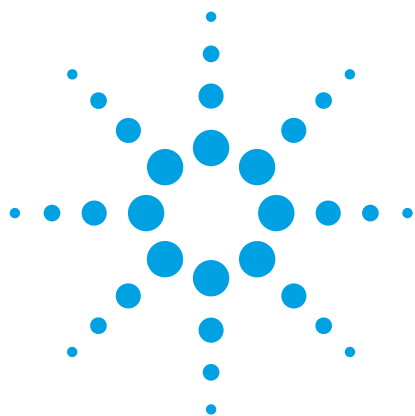
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Agilent Technologies



C1 – C3 Hydrocarbon Analysis Using the Agilent 490 Micro GC – Separation Characteristics for PoraPLOT U and PoraPLOT Q Column Channels

Application Note

Micro Gas Chromatography, Hydrocarbon analysis

Author

Remko van Loon
Agilent Technologies, Inc.
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The Netherlands



Introduction

This application note shows the possibilities and limitations in fast analysis of saturated and unsaturated C1 to C3 hydrocarbons using an Agilent 490 Micro GC. The chromatograms and results outline the similarities and differences when using a PoraPLOT U and a PoraPLOT Q column channels. Both the PoraPLOT U and the PoraPLOT Q are capable of resolving methane from the composite air peak and separate CO₂ from methane and the C2 hydrocarbons.

The PoraPLOT U column channel will have the following separation characteristics:

- Baseline separation for ethane, ethylene and acetylene
- Coelution of propane and propylene

The separation characteristics for the PoraPLOT Q column channel are:

- Coelution of ethylene and acetylene
- Baseline separation for propane and propylene



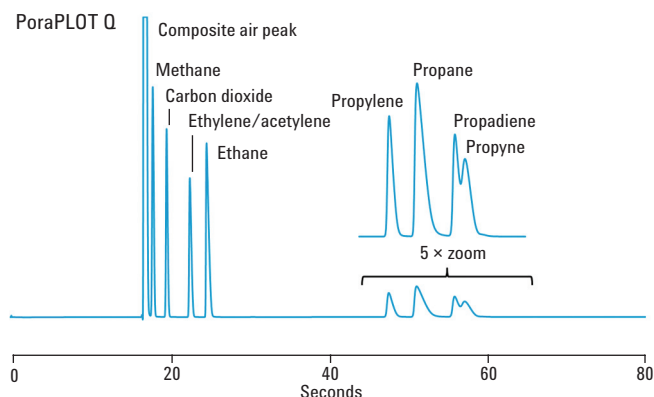
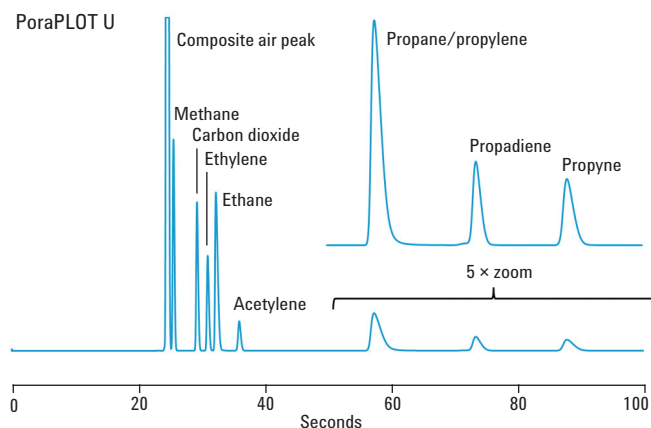
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If you want the ability to measure anywhere and get the results you need in seconds, the Agilent 490 Micro GC is the ideal solution. With its rugged, compact, laboratory quality gas analysis platform, the 490 Micro GC generates more data in less time for faster, and better, business decisions.

Instrumentation

For this application an Agilent 490 Micro GC (G3581A) equipped with a PoraPLOT U and a PoraPLOT Q was used. The setup parameters for the column is found in the table below.

	PoraPLOT U, 10 m	PoraPLOT Q, 10 m
Column temperature	80 °C	80 °C
Carrier gas	Helium, 200 kpa	Helium, 200 kpa
Injector temperature	110 °C	110 °C
Injection time	20 ms	20 ms



Sample information

Nitrogen	Balance
Methane	5.0 %
Carbon dioxide	3.0 %
Ethylene	2.0 %
Ethane	4.0 %
Acetylene	1.0 %
Propylene	1.0 %
Propane	2.0 %
1,2-Propadiene	0.97 %
Propyne	0.99 %

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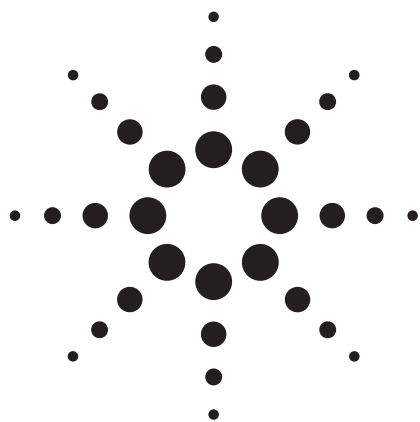
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Agilent Technologies



Obtaining Optimum Performance When Using the SIPS Accessory

Application Note

Atomic Absorption

Introduction

The SIPS accessory, which was introduced in December 1994, was the first practical dilution system for flame AA to provide calibration from a single standard and fast, on-line dilution of over range samples. A few simple procedures, outlined in this information sheet, ensure reliable and productive operation of this accessory.

The Agilent SIPS pump tubing is manufactured from a composite material known as Santoprene. The pump tubing commonly used on VGA and ICP pumps is a single-mix polymer. All types of pump tubing, but especially composite tube materials, can sometimes show signs of "spalling" under normal operation. This is a variable effect in which very small particles of the tubing material break away. If severe spalling occurs, these particles can stick together and cause blockage of the nebulizer.

Spalling occurs in various degrees with all peristaltic pump tubing manufactured from composite materials. It is not unique to SIPS.



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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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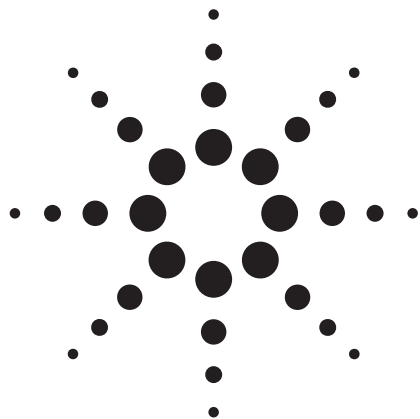
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Routine Maintenance for Atomic Absorption Spectrophotometers

Application Note

Atomic Absorption

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Introduction

Instruments in good operating condition are a necessity in any analytical laboratory. This level of integrity can be achieved by a regular maintenance schedule with minimal work. The four main areas of such a program for atomic absorption spectrophotometers include:

- General instrument maintenance
- Gas supply maintenance
- Flame component maintenance
- Furnace component maintenance

The benefits of routine maintenance include:

- Increased instrument lifetime
- Reduced downtime
- Overall improvement in instrument performance; giving the operator greater confidence in the validity of his analytical results



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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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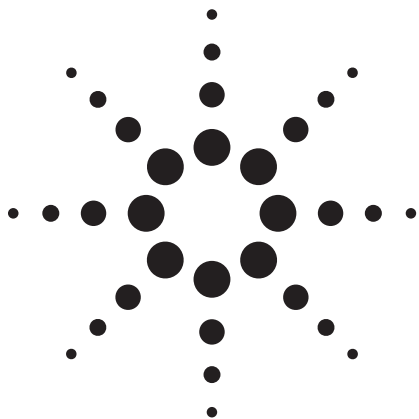
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Guidelines for Using Non-Aqueous Solvents in Atomic Absorption Spectrometry

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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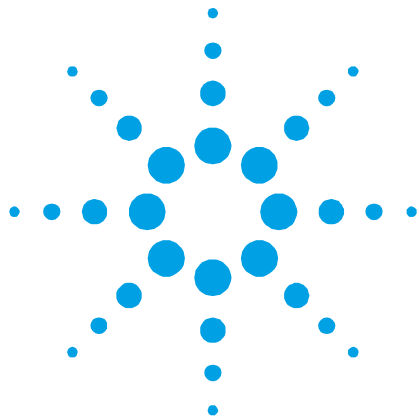
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Agilent Oil Analyzer: customizing analysis methods

Application Note

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Introduction

Traditionally, the analysis of used oils has been conducted by physical and wet chemical methods. FTIR spectroscopy has become a routinely used technique to analyze used oils, providing the following major 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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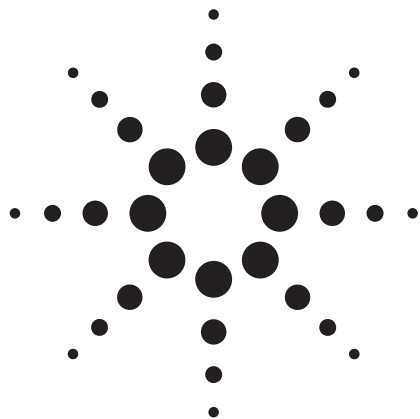
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AA or ICP – Which Do You Choose?

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

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Introduction

For many analysts Atomic Absorption Spectrometry (AAS) is a well established and understood technique. However, even though Inductively Coupled Plasma Emission Spectrometry (ICP-ES) instrumentation has been commercially available for over a decade, the technique has proven to be more complex. This article discusses the main differences between the two techniques.

AAS Versus ICP

The basic difference between the two techniques is that one relies upon an atomic absorption process while the other is an atomic/ionic emission spectroscopic technique. The next essential difference is the means by which the atomic or ionic species are generated. A combustion flame or graphite furnace is typically used for AA while ICP-ES uses a plasma.



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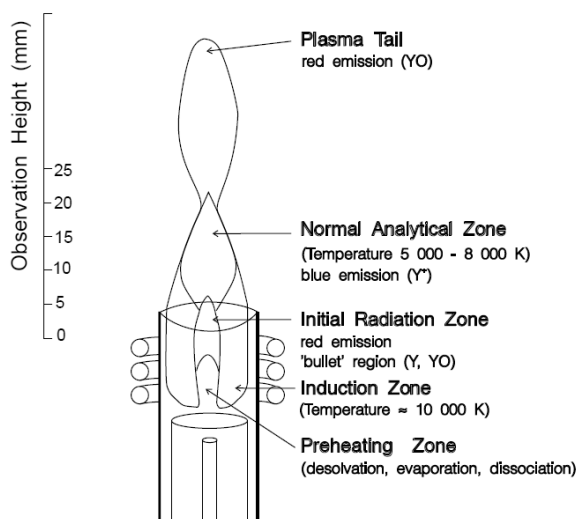


Figure 1. A plasma used for emission spectrometry. The regions refer to those seen when a Yttrium solution is introduced.

The typical maximum temperature for an air/acetylene flame is 2300 °C while for nitrous oxide acetylene, it is 2900 °C. Temperatures as high as 10,000 K can be reached in an argon plasma.

Detection Limits

The comparison of detection limits in Table 1 highlights the following differences:

- Furnace AA detection limits are generally better in all cases where the element can be atomized.
- Detection limits for Group I elements (for example, Na, K) are generally better by flame AAS than by ICP.
- Detection limits for refractory elements (for example, B, Ti, V, Al) are better by ICP than by flame AAS.
- Non metals such as sulfur, nitrogen, carbon, and the halogens (for example, I, Cl, Br) can only be determined by ICP.

While it is possible to determine phosphorous by AAS, its detection limit by ICP is more than three orders of magnitude better.

Optimum detection of non metals such as S, N and halogens by ICP-ES can only be achieved if a vacuum monochromator, with purged transfer optics, is used. The optics must be purged to exclude atmospheric oxygen and eliminating its absorption.

Sulfur can be measured at 180.73 nm by purging the monochromator. To detect the primary aluminium wavelength at 167.08 nm, the monochromator must first be evacuated, then purged with the inert plasma gas.

Note that a continuous flow vapor generation accessory can be used with either ICP-ES or AAS for improved detection limits for As, Se, Hg, Sb, Bi and Ge.

Sample Throughput

In ICP-ES, the rate at which samples may be determined depends on the type of instrument: both simultaneous and sequential ICP spectrometers are available. Most ICP spectrometers purchased are the sequential type, providing maximum flexibility of choice of element and analytical wavelength. Surveys have shown that most analysts are interested in 6–15 elements per sample and choose to pump the sample (which increases washout times) to improve precision and accuracy by minimizing viscosity effects. Simultaneous ICP spectrometers demonstrate an advantage in analytical speed over sequential ICP spectrometers when more than 6 elements/sample are measured.

If a "one off" sample is presented for a few elements, flame AAS is faster. However, with flame equilibration time, program recall and monochromator condition changes, the cross over point where sequential ICP becomes faster than AAS is approximately 6 elements/sample for routine analysis.

Unattended Operation

Flame AAS cannot be left completely unattended for safety reasons. An ICP-ES instrument or graphite furnace AA can be left to run overnight as no combustible gases are involved, effectively increasing the working day from 8 hours to 24 hours.

Linear Dynamic Range

The inductively coupled plasma is doughnut shaped (with a "hollow" center). The sample aerosol enters the base of the plasma via the injector tube. The "optical thinness" of the ICP results in little self absorption and is the main reason for the large linear dynamic range of about 10^5 . For example, copper can be measured at the 324.75 nm wavelength from its detection limit of about 0.002 ppm to over 200 ppm. In ICP, extrapolation of two point calibrations can be accurately used to achieve orders of magnitude above the top standard. This compares to a linear dynamic range of typically 10^3 for AAS.

Interferences

Chemical

Chemical interferences are relatively common in AA, especially with graphite furnace AA, but may be minimized with chemical modifiers.

ICP-ES is almost free from chemical interferences. The chemical bonds that still exist at below 3000 °C are completely ruptured at above 6000 °C. The high temperatures reached in a plasma eliminate chemical interferences, which accounts (for the most part) for the better detection limits achieved for refractory elements.

Ionization

The ICP contains a large number of free electrons, so ionization interferences for most applications are virtually nonexistent. Ionization interferences can be encountered when determining elements in matrices that contain very high concentrations of Group I elements (for example, Na & K). However, these effects can be minimized by optimizing the plasma viewing height.

Ionization interferences may also be found in AAS, such as, when measuring certain Group II elements in a nitrous oxide flame. An ionization buffer such as Cs, Li or K can be added to both samples and standards to minimize this effect.

Spectral

The optical requirements of AAS are fairly simple. The monochromator only needs to distinguish a spectral line emitted from the hollow cathode lamp from other nearby lines. The lamp itself only emits a few spectral lines. Most elements require 0.5 nm resolution with only iron, nickel and cobalt of the common elements requiring 0.2 nm or better.

In ICP-ES, the rich spectra present in the plasma means that there is a greater possibility of spectral interference. Spectral resolutions of 0.010 nm or better are required to resolve nearby interfering lines from the atomic and ionic analytical emission signals of interest.

Spectral interference in sequential ICP spectrometers can, in most cases, be overcome by selecting a different elemental wavelength with similar detection limits. With simultaneous ICP spectrometers, the elements and the wavelengths which may be determined are fixed at the time of purchase, and an alternative line may not be available. In this case, inter-element correction may be used to minimize the spectral interference.

Physical

These interferences relate to the different properties of various samples and can affect sample transport and droplet formation. ICP tends to be more susceptible to such interference because of the smaller droplet size required and lower transport efficiency.

Precision

Precision can be termed short term (or within-run) and long term (over a period of one day). For AAS a precision of 0.1–1% is typical for the short term, but recalibration is required over a longer period. With ICP-ES the short term precision is typically 0.3–2%, but precisions of 2–5% are not uncommon over an 8 hour period without recalibration.

One technique used to eliminate backlash in the grating drive mechanism of ICP spectrometers is by scanning and measuring at the same time. This method of measurement can be termed as “measurement on the move” and effectively results in poor short term precision. A more recent method drives the grating to a wavelength near the analytical peak. A refractor scan is then performed over a smaller wavelength region in order to identify and locate the peak position. Finally the refractor plate is repositioned “at the peak” where the replicate measurements are then performed. This method offers better precision.

AAS v ICP – A quick guide

	ICP-OES	Flame AAS	Furnace AAS
Detection limits	Best for : Refractories Non metals P, S, B, Al V, Ba, Ti	Best for : Group I metals Na, K Volatile elements Pb, Zn Rare Earths	Best for : All elements except : B,W,U, Refractories, for example P, S Halogens
Sample throughput	Best if more than 6 elements/sample	Best if less than 6 elements/sample	Slow (typically 4 mins/element)
Linear dynamic range	10 ⁵	10 ³	10 ²
Precision	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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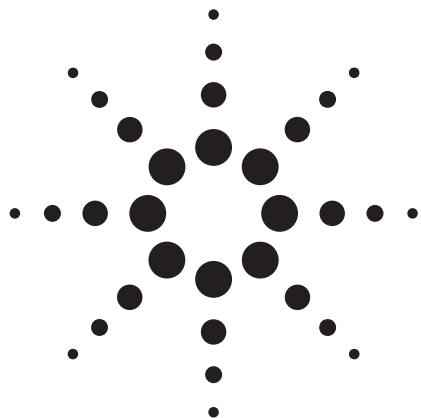
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Improving Throughput for Oils Analysis by ICP-OES

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

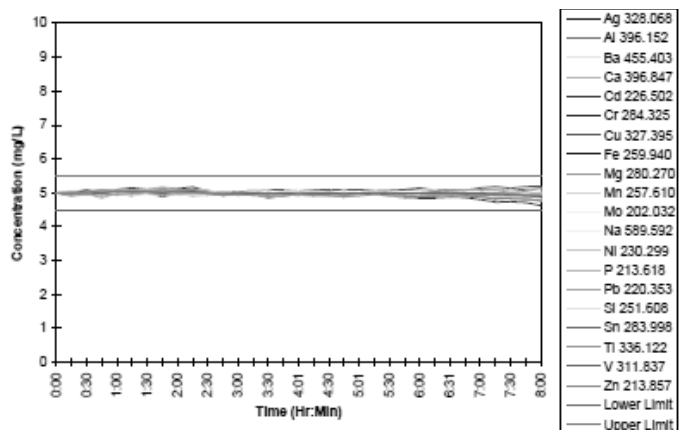


Figure 1. Stability of the Vista-PRO radial instrument over 8 hours. Results remained within $\pm 10\%$ for all elements in the 5 mg/L S21 kerosene solution without internal standardization or recalibration.

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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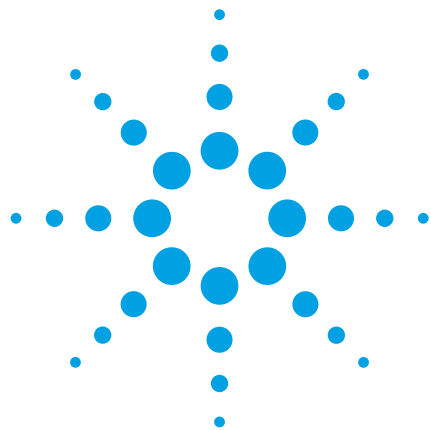
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Separation of Permanent Gases on a Liquid Phase

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

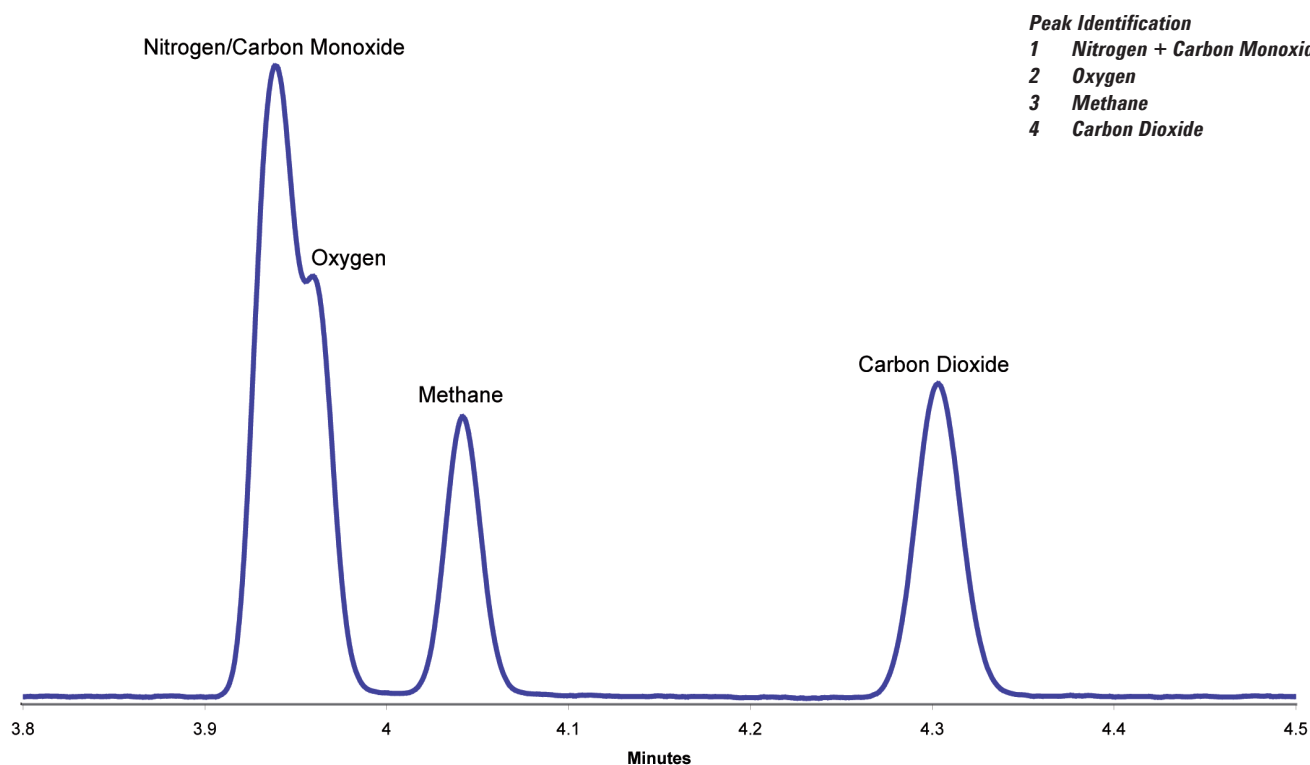
Normally permanent gases are separated by PLOT (porous layer open tubular) columns with their high retentive phases. With WCOT (wall coated open tubular) columns sub-ambient temperatures are normally necessary. Thick films, like the 8 μm film thickness of the Agilent J&W Select CP-Sil 5CB for Formaldehyde, 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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Detailed Separation of C_1 - C_5 Light Hydrocarbons on CP- Al_2O_3 / Na_2SO_4 PLOT GC Column

Application Note

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Agilent Technologies, Inc.

Introduction

Aluminum oxide PLOT columns are specifically designed for detailed C_1 - C_{10} hydrocarbon analysis in chemical and petrochemical industries. Due to the high selectivity of CP- Al_2O_3 PLOT columns, it is possible to analyze ppm to percent levels of any C_1 - C_5 impurities, including isomers, in main stream C_1 - C_5 products. CP- Al_2O_3 PLOT columns offer a higher level of analytical selectivity and efficiency compared to super-thick film non-polar liquid stationary phase columns.



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The aluminum oxide column carries a sodium sulfate (Na_2SO_4) deactivation layer. The deactivation provides a reproducible and stable selectivity up to 200 °C. Sodium sulfate deactivation results in a more polar surface than potassium chloride (KCl)-treated alumina, retaining unsaturated compounds such as ethylene, acetylene (ethyne) and methyl acetylene (propyne) more strongly than their unsaturated peers.

The analysis of light hydrocarbons is performed in refinery gas, liquefied petroleum gas (LPG) and natural gas. Refinery gas is a mixture of gases generated during refinery processes used to process crude oil into various petroleum products as intermediate products or high grade end-products. The composition of refinery gas may vary. Common components include butanes, butenes (butylenes), methane, ethane and ethene (ethylene). The aluminum PLOT column offers added value in separating all of the components.

Natural gas consists of methane, light hydrocarbons such as ethane, propane and butane, and small quantities of derivatives such as carbon dioxide and nitrogen. The precise composition of natural gas may differ from region to region. LPG is a mixture of light hydrocarbons. It occurs naturally in crude oil and natural gas production fields and is also produced in the oil refining process. The main component gases of LPG are propane and butane.

The $\text{CP-Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ GC column provides separation of the main components and gives detailed quantitative data on the impurities.

This application note shows the analysis of 18 light hydrocarbons on a $\text{CP-Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ GC column.

Materials and Methods

Technique: GC-FID
 Column: $\text{CP-Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$, 50 m x 0.32 mm, df=5 µm (part number CP7565)
 Temperature: 70 °C, 3 °C/min, 170 °C
 Carrier Gas: Hydrogen, constant pressure, 100 kPa (1.0 bar, 14.5 psi)
 Injection: 250 °C, split 1:50
 Detection: FID, 275 °C
 Sample: Gas mixture, for concentrations see Table 1
 Injection Volume: 5 µL

Results and Discussion

Figure 1 shows the chromatogram of the detailed analysis of 18 hydrocarbons within 20 minutes. The $\text{CP-Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ column provided very good peak shape and baseline separation. The alkynes, acetylene and propyne, show some tailing. This tailing is typical for Na_2SO_4 deactivated Al_2O_3 PLOT and is caused by the higher interaction of the polar alkynes with the polar Na_2SO_4 deactivation layer.

Table 1. Peak Identification

Peak	Compound	Concentration % (moles in He)
1	Methane	24.9
2	Ethane	5.0
3	Ethene (ethylene)	24.9
4	Propane	5.0
5	Cyclopropane	0.50
6	Propene (propylene)	5.1
7	Isobutane	0.50
8	n-Butane	1.00
9	Propadiene	0.60
10	Ethyne (acetylene)	1.01
11	<i>trans</i> -2-Butene	0.50
12	1-Butene	0.50
13	Isobutene	1.00
14	<i>cis</i> -2-Butene	0.50
15	Isopentane	0.50
16	n-Pentane	0.199
17	1,3-Butadiene	1.00
18	Propyne (methyl acetylene)	1.01

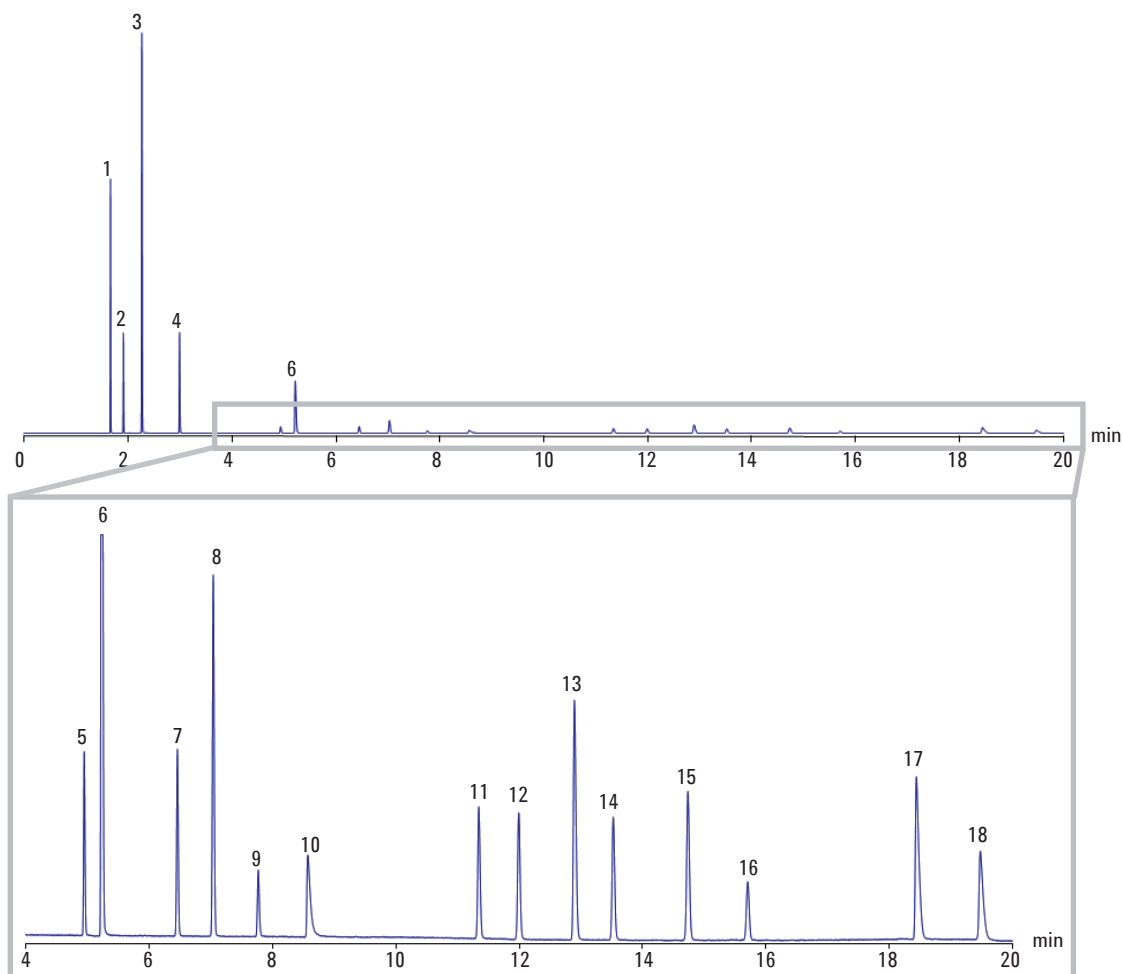


Figure 1. C_1 - C_5 hydrocarbons analyzed on a $CP-Al_2O_3/Na_2SO_4$ column

Conclusion

The $CP-Al_2O_3/Na_2SO_4$ column is very suitable for the analysis of light hydrocarbons. The sodium sulfate deactivation provides additional resolution for separating all C_4 isomers.

The robustness of the column allows temperatures up to 200 °C to be used, enabling bake-out of the column at the end of the analysis without changes in selectivity.

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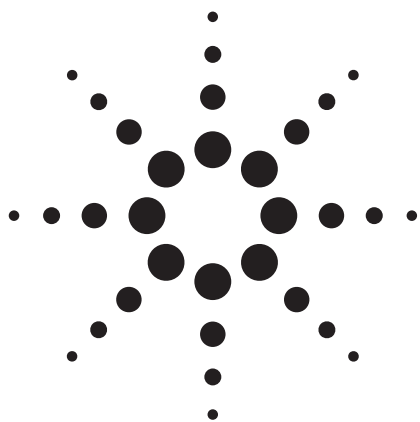
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Sensitivity Enhancement for Flame Atomic Absorption Spectrometry Using an Atom Concentrator Tube, the ACT 80

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.

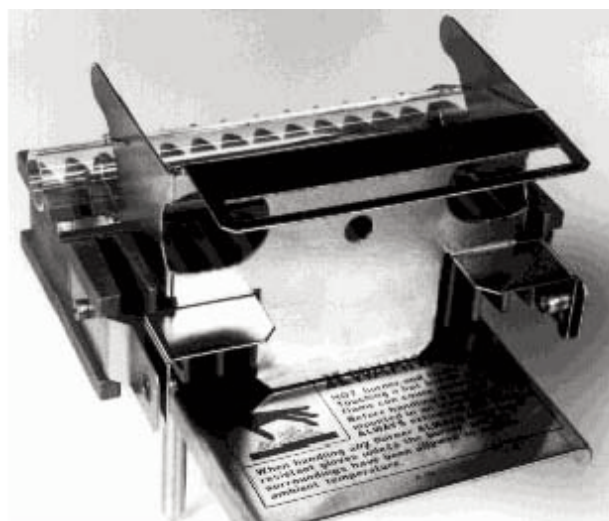


Figure 2. The ACT 80 Atom Concentrator Tube.

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.

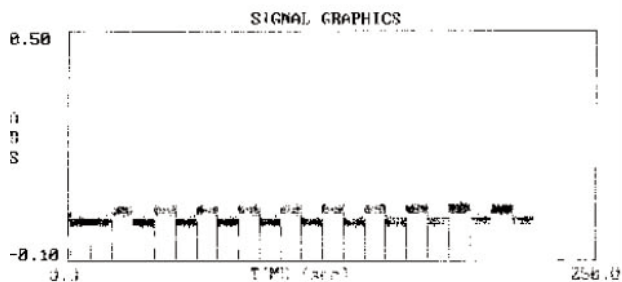


Figure 3(a). Pb signal compared to blank without ACT-80 tube.

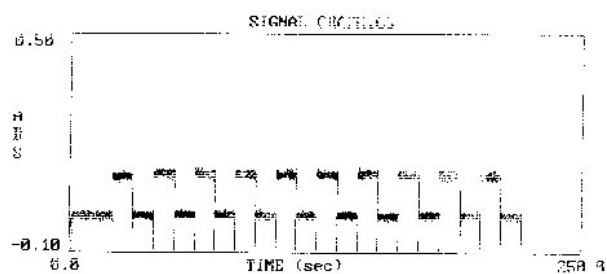


Figure 3(b). Pb signal compared to blank with ACT-80 tube.

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.

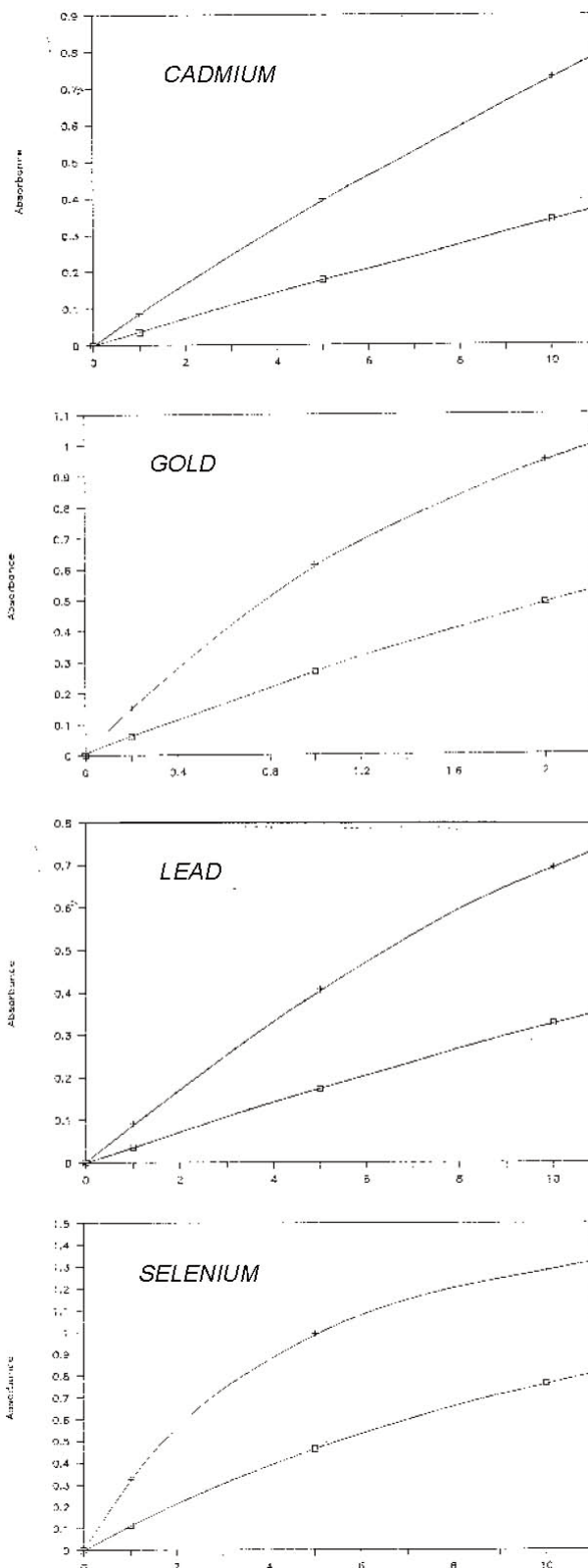


Figure 4. Calibration graphs of selected elements showing improvement in sensitivity. (+ = ACT-80, □ = normal FAAS)

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.

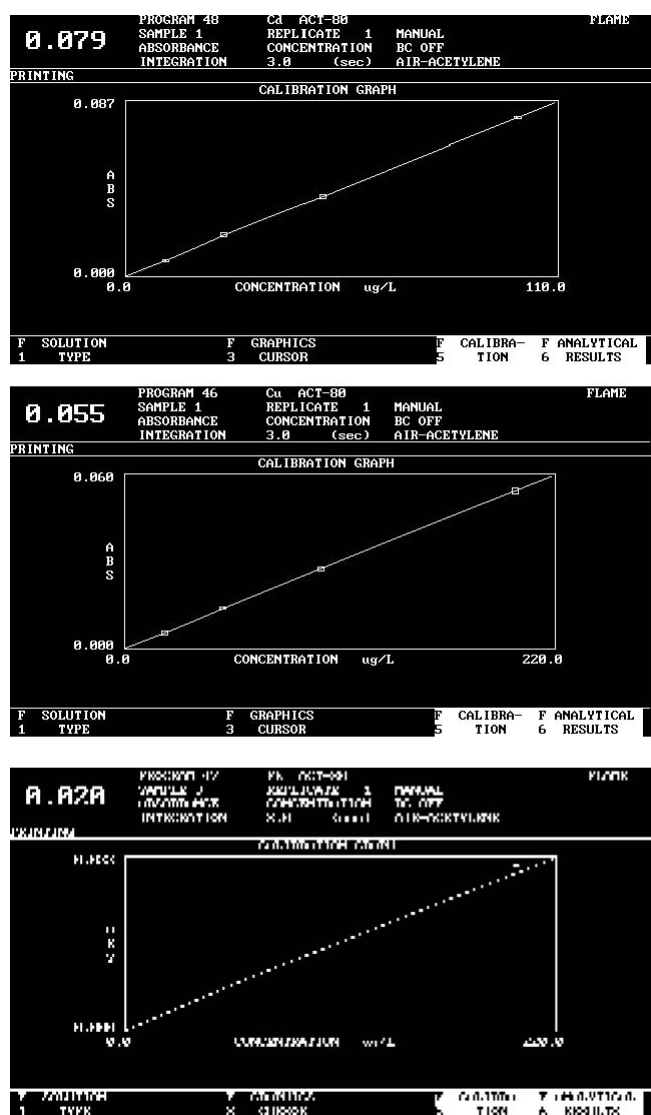


Figure 5. Calibration graphs used to measure quality control samples.

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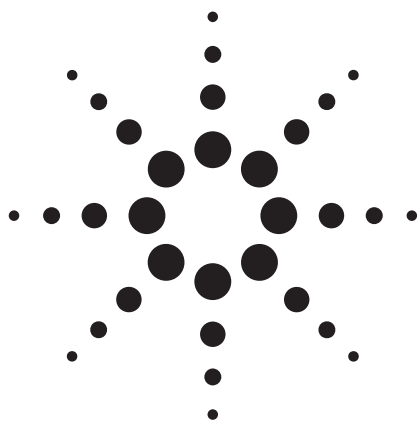
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Sensitivity Enhancement for Flame AAS Using an Atom Concentrator Tube for Elements Dissolved in Organic Solvents

Application Note

Atomic Absorption

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Introduction

The application of a slotted tube placed on an ordinary atomic absorption burner head in order to increase the sensitivity and detection limit for a number of elements in flame-atomic absorption spectrometry (FAAS) was first demonstrated by Watling [1,2]. A very similar technique had been used before in combination with either a nickel “cup” [3] or a tantalum “boat” [4] for the same purpose. The enhancement effect using the combination of a slotted tube and an ordinary acetylene/air flame was later confirmed by several authors who demonstrated that the sensitivity and the detection limit could typically be improved by a factor of 2–5 for easily atomized elements [5–11].

Extraction of aqueous samples into a small volume of an organic solvent after addition of a complexing agent in order to enhance the detection limit is a well established method [12–14]. A concentration factor of at least 20 times can easily be achieved.

Moreover, it is also well known that atomizing organic solutions (especially those rich in oxygen, for example, ketones) can result in 3–5 times better sensitivity for many elements [15] and references therein. Thus the improvement in sensitivity for flame-AAS after extraction should be about $20 \times (3-5) = 60 - 100$ 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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