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# Trace Level Hydrocarbon Impurities in Ethylene and Propylene

Application

Gas Chromatography

March 1997


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## Abstract

**An Agilent 6890 Series gas chromatography system was used to determine trace (low ppm) levels of hydrocarbon impurities in high-purity ethylene and propylene. The gas chromatograph (GC) was equipped with a heated gas sample valve, split/splitless inlet, and flame ionization detector (FID). An Agilent HP-PLOT $Al_2O_3$ column was used for separation of the trace hydrocarbons. Impurity levels below 10 ppm (mole) were easily detected in both ethylene and propylene.**


## Introduction

High-purity ethylene and propylene are commonly used as feedstocks for production of polyethylene, polypropylene, and other chemicals. Typically, these low molecular weight monomers are of very high purity (99.9+ percent). However, hydrocarbons, sulfur compounds, and other impurities in feed streams can cause such problems as reduced catalyst lifetime and changes to product quality. Process yields can also be adversely affected. Many impurities have been identified as potential contaminants (1,2).

Recently, ASTM has proposed several procedures to determine trace hydrocarbon impurities in both ethylene and propylene (3). These methods, currently in the investigation stage, use alumina porous layer open tubular (PLOT) columns. This application note describes the suggested Agilent configuration for such methods and illustrates resulting separations of both quantitative calibration blends and actual process samples. These proposed methods should be valuable in meeting commercial specifications.

## Experimental

All experiments were performed on an 6890 Series gas chromatograph (GC) equipped with a split/splitless inlet and capillary optimized flame ionization detector (FID). All gas flows and pressures within the GC were controlled electronically. Gas sample injections were made using an automated sample valve placed in the 6890 valve oven (80 °C). The gas sample valve was interfaced to the capillary inlet using an aluminum tube (1/8-in.) that jacketed the stainless steel transfer line (option 860). The inlet was fitted with a split/splitless liner (part no. 19241-60540). All injections were made in the split mode.

A 50-m × 0.53-mm, HP-PLOT $Al_2O_3$ "M" column was used for separation. For ethylene analysis only, a 30-m × 0.53-mm, 5-µm HP-1 column was placed directly behind the HP-PLOT column. The two columns were joined using a glass press-fit connector.

The Agilent ChemStation was used to control the 6890 Series GC and to provide data acquisition and peak integration. The ChemStation was operated at a data acquisition rate of 10 Hz.

Standards for retention time and response factor calculation were obtained from DCG Partnership (Houston, Texas, USA 77061). Samples used for this work were obtained from commercial sources.

Table 1 lists the entire set of equipment and conditions.

## Results and Discussion

### Ethylene

The configuration used for ethylene analysis is found in figure 1.

The HP-PLOT $Al_2O_3$ column was used for hydrocarbon separation. The use of HP-PLOT $Al_2O_3$ columns for light hydrocarbon analyses has been previously described (4). These columns exhibit excellent separation characteristics for the $C_1$ through $C_5$ isomers.

The proposed method for ethylene specifies the use of a second nonpolar column placed after the HP-PLOT alumina column to improve the separation of impurity peaks eluting on the tail of ethylene. This nonpolar column gains importance for trace level analysis, where higher concentrations of ethylene (99.9 percent and higher) exhibit increased tailing. No attempt was made to compare separations without the nonpolar Agilent HP-1 column.

**Table 1. Instrument Configuration and Operating Conditions**

| Item | Description |
|---|---|
| ***Gas Chromatograph*** | |
| G1540A | 6890 Series GC |
| Option 112 | Split/splitless inlet |
| Option 211 | Capillary optimized FID |
| Option 701 | 6-port gas sample valve and automation |
| Option 751 | Valve oven |
| Option 860 | Valve to inlet interface |
| Column | • 50-m x 0.53-mm HP-PLOT $Al_2O_3$ "M" (part no. 19095P-M25)<br>• 30-m x 0.53-mm, 5-µm HP-1 (part no. 19091Z-236), used for ethylene analysis only |
| ***Data Acquisition*** | |
| G2070AA | Agilent ChemStation |
| ***Operating Parameters*** | |
| Injection port temperature | 200 °C |
| Detector temperature | 250 °C |
| Split ratio | 10/1 to 50/1 depending on sample |
| FID conditions | 30 mL/min hydrogen, 350 mL/min air, nitrogen make-up (25 mL/min column + makeup) |
| Temperature program | • Ethylene: 35 °C (2 min), 4 °C/min to 190 °C<br>• Propylene: 40 °C (2 min), 4 °C/min to 190 °C |
| Injection volume | • Ethylene: 0.5 mL<br>• Propylene: 0.25 mL |
| Column flow | • Ethylene: 6 mL/min constant flow (10 psi)<br>• Propylene: 3.5 mL/min constant flow (4 psi) |
| Valve temperature | 80 °C |

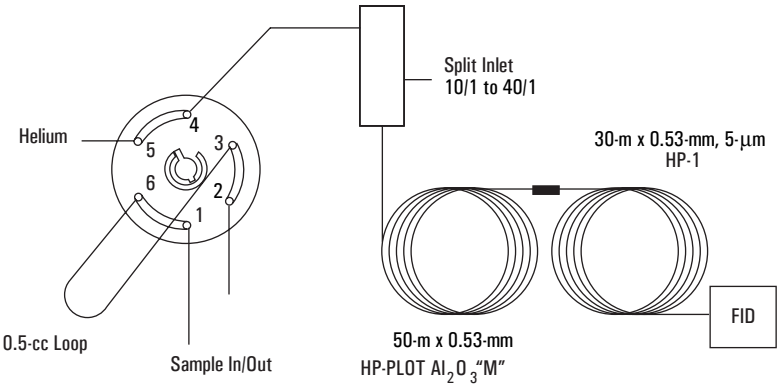


**Figure 1. Valve drawing for impurities in ethylene.**

Figure 2 shows the chromatogram of an ethylene calibration blend containing most of the major hydrocarbon impurities. This sample was analyzed at a split ratio of 10/1. The concentration of most components (except for ethane) ranges from 8 to 12 ppm (mole). For this analysis, baseline separation is achieved for all the impurities except for propane. Total analysis time is approximately 30 minutes. Because this separation is more than adequate, analysis time can be reduced by increasing the temperature program rate. Based upon conditions used for this analysis, most components can be detected at the 1-ppm level.

Chromatographic results for two process ethylene samples are given in figures 3 and 4. The sample presented in figure 3 contains only methane, ethane, and propylene as impurities. Less than 1-ppm methane was detected. The ethylene sample in figure 4 shows a high concentration of methane, with trace amounts of ethane, propane, and propylene.

1. Methane (10 ppm)
2. Ethane (219 ppm)
3. Ethylene
4. Propane (12 ppm)
5. Propylene (9 ppm),
6. Isobutane (10 ppm)
7. n-Butane (10 ppm)
8. Propadiene (10 ppm)
9. Acetylene (10 ppm)
10. t-2-Butene (8 ppm)
11. 1-Butene (8 ppm)
12. Isobutylene (9 ppm)
13. c-2-Butene (9 ppm)
14. 1,3-Butadiene (10 ppm)
15. Methylacetylene (9 ppm)

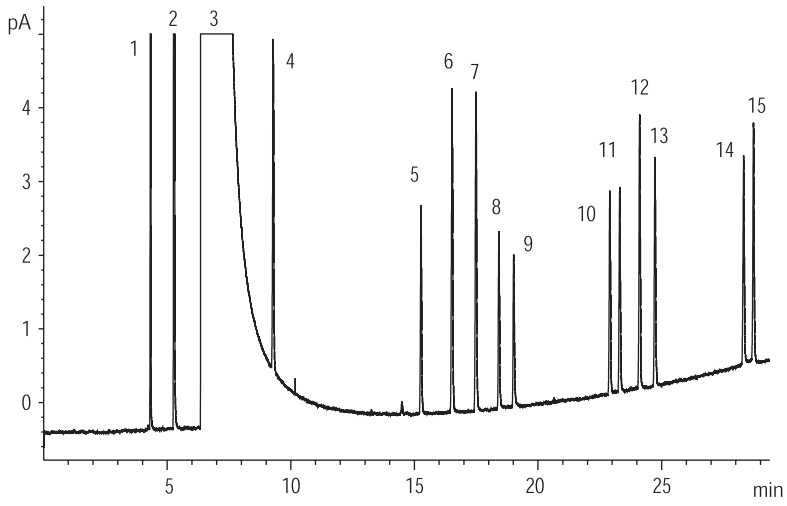


**Figure 2. Chromatogram of ethylene calibration blend, split ratio 10/1.**

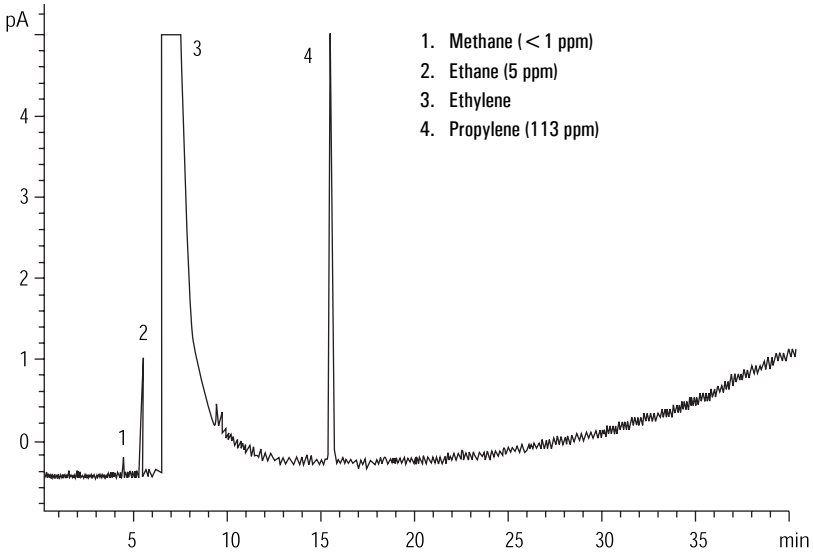


**Figure 3. Chromatogram of process ethylene sample, split ratio 20/1.**

### Propylene

The configuration used for propylene analysis is illustrated in figure 5. This configuration is essentially the same as for ethylene, but without the HP-1 column. The sample volume was reduced to 0.25 mL. Propylene was sampled in the gas state.

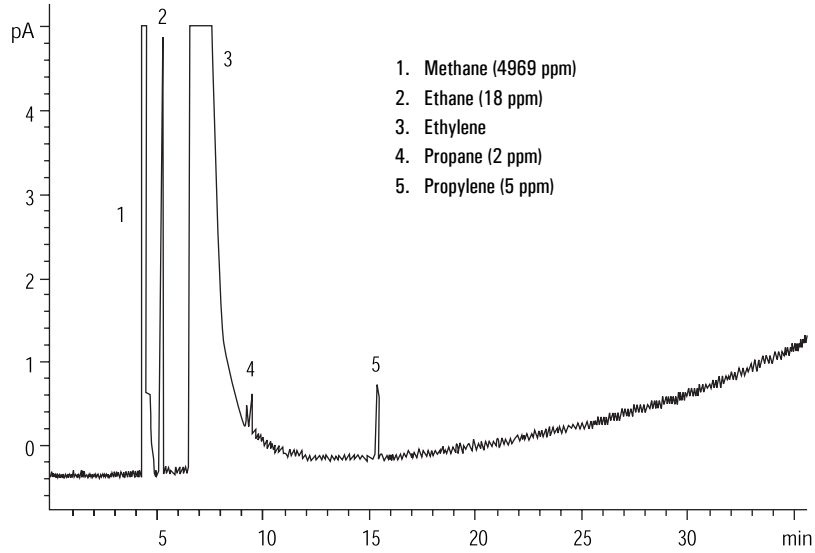


**Figure 4. Chromatogram of process ethylene sample.**

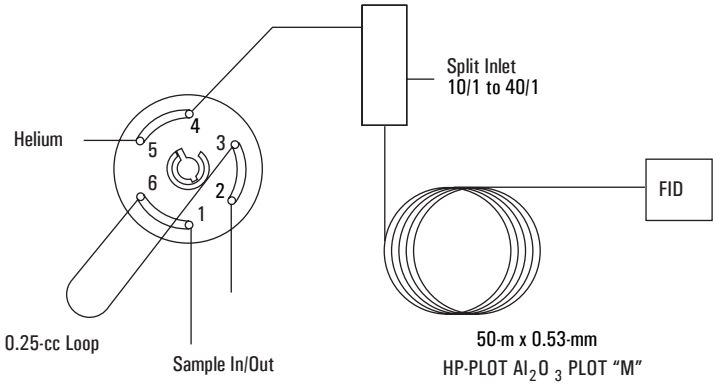


**Figure 5. Valve drawing for impurities in propylene.**

A chromatogram representing the trace hydrocarbon impurities in propylene is shown in figure 6. This sample was analyzed at a split ratio of 20/1. The concentration of most impurities range from 8 to 20 ppm. Ethylene is present at a higher concentration level. Most of the impurities in the sample are well separated using the conditions described in table 1. Cyclopropane elutes just before propylene and is baseline separated under these conditions. Several of the $C_4$ hydrocarbons elute on the tail of the high-purity propylene. This affects the lower limit of detection for these peaks, compared to those components that are baseline separated. The remainder of the $C_4$ and $C_5$ impurities are well separated.

1. Methane
2. Ethane (10 ppm)
3. Ethylene (50 ppm)
4. Propane
5. Cyclopropane (10 ppm)
6. Propylene
7. Isobutane (10 ppm)
8. n-Butane (7 ppm)
9. Propadiene
10. Acetylene
11. t-2-Butene (10 ppm)
12. 1-Butene
13. neo-Pentane
14. Isobutylene (9 ppm)
15. Isopentane
16. c-2-Butene (9 ppm)
17. n-Pentane (10 ppm)
18. 1,3-Butadiene (9 ppm)

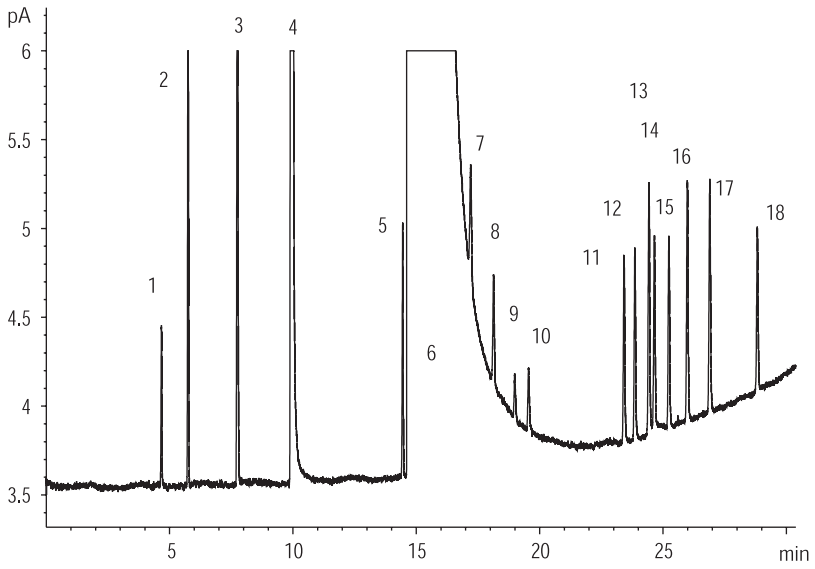


**Figure 6. Chromatogram of propylene calibration standard.**

For comparison, figure 7 shows the analysis of a second calibration blend containing a higher level of impurities (50 to 1000 ppm).

Figure 8 presents the chromatographic results for a high-purity propylene process sample. This sample contains only ethane and propane impurities.

## Summary

This application note describes two methods for analyzing trace hydrocarbon impurities in ethylene and propylene. These methods use a gas sample valve with split injection, an Agilent HP-PLOT $Al_2O_3$ and HP-1 (for ethylene only) column, and an FID. Impurities below the 10-ppm mole level can be easily quantitated using these methods. For some impurities, especially those that are well separated from the large ethylene or propylene peaks, detection limits were estimated to be about 1 ppm.

1. Methane
2. Ethane
3. Ethylene
4. Propane (988 ppm)
5. Cyclopropane (100 ppm)
6. Propylene
7. Isobutane (129 ppm)
8. n-Butane
9. Propadiene (62 ppm)
10. Acetylene (48 ppm)
11. t-2-Butene
12. 1-Butene
13. Isobutylene
15. Isopentane
16. c-2-Butene
17. 1,3-Butadiene
18. Methylacetylene (100 ppm)

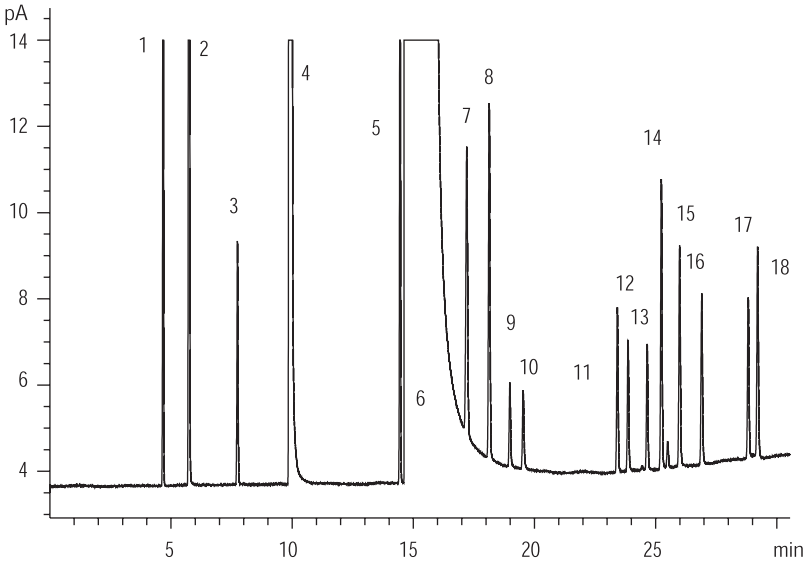


**Figure 7. Chromatogram of propylene calibration blend containing higher levels of impurities.**

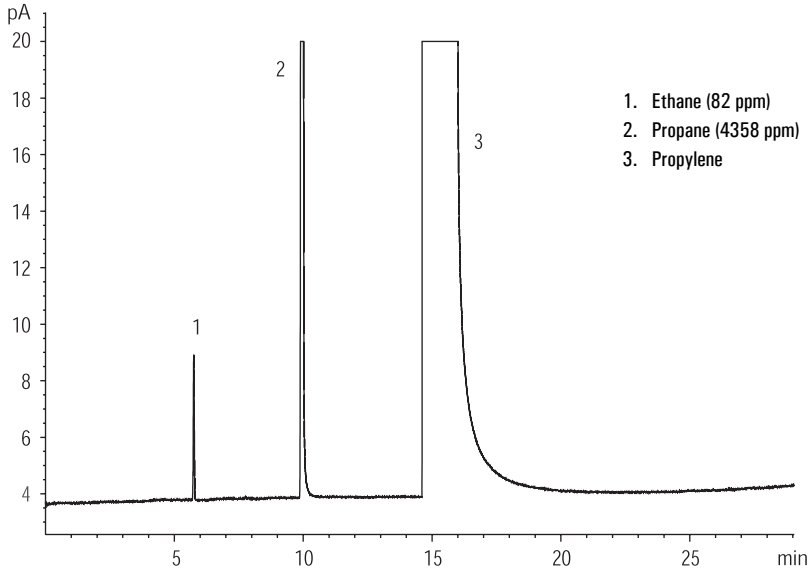


**Figure 8. Chromatogram of process propylene sample.**

## References


1. ASTM Method D 5325, “Standard Guide for the Analysis of Ethylene Product,” Annual Book of Standards, Volume 5, ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
2. ASTM Method D 5273, “Standard Guide for the Analysis of Propylene Concentrates,” Annual Book of Standards, Volume 5, ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
3. Proposed methods for hydrocarbon impurities in ethylene and propylene by gas chromatography are being investigated under ASTM committee D-2, subcommittee D.
4. “Optimized Determination of $C_1$–$C_6$ Impurities in Propylene and Ethylene Using HP-PLOT/$Al_2O_3$ Columns,” Agilent Technologies, Inc. Publication (43) 5062-8417E, March 1994.

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# The Analysis of Trace Contaminants in High Purity Ethylene and Propylene Using GC/MS

## Agilent Technologies/Wasson ECE Monomer Analyzer

Application


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## Abstract

**A new product (Application 460B-00) from Agilent Technologies/Wasson-ECE uses a 5973N GC/MSD (gas chromatograph/mass selective detector) for the determination of trace levels of impurities that are moderate-to-low carbon-content such as oxygenates, mercaptans, sulfides, arsine, and phosphine in ethylene and propylene. This work describes the performance of Application 460B-00 with respect to linearity, repeatability, and limits of detection (for most compounds, low parts-per-billion). Compared to determinations with GC/FID (flame ionization detection) or GC/TCD (thermal conductivity detection), the use of GC/MSD demonstrates comparable performance with respect to linearity and repeatability: for example, for mercaptans and sulfides (40–100 ppb) in the ethylene assay, correlation coefficients for calibration curves range from 0.992 to 1.000 and relative standard deviations range from 1.95% to 9.31% RSD. Compared to GC/FID for the range of contaminant analytes studied here, the sensitivity is increased 50-fold; compared to GC/TCD, the sensitivity is increased 5000-fold. While the sensitivity of MS detection is comparable to that of sulfur chemiluminescence detection for sulfur-containing compounds, MS has the same sensitivity for a broader range of compound types. Moreover, the use of MS detection provides specificity for positive identification of analytes. In Application 460B-00 the multipart assays are automated via "composite methods" [1]. The result is a tool that provides higher productivity and more key information about feedstock materials-both of which aid the polymer industry.**


## Introduction

For the polymer industry, the purity of ethylene and propylene monomer feedstocks is a high priority. Trace contaminants at the part-per-billion (ppb) concentration levels can affect yields dramatically by altering subsequent polymer properties and characteristics. Additionally, some trace impurities can irreversibly poison reactor catalysts. The competitive marketing strategies of monomer manufacturers include using new analytical technologies to guarantee lower and lower trace impurity levels.

Agilent Technologies/Wasson-ECE has focused on supplying integrated application products for the analysis of impurities in polymer feedstocks. One of the most recent products, Application 262-00, effectively combined the separate analyses for ethylene and propylene into a single analytical system [2].

Application 262-00 employs a gas chromatograph (GC) with two separate flame ionization detectors (FIDs), two capillary columns, appropriate valving, and analytical methods to quantitate very low levels of carbon monoxide and carbon dioxide by a methanizer FID and paraffins and olefins up to n-pentane by direct FID. Recently Agilent Technologies/ Wasson-ECE has expanded the capabilities of Application 262-00 by adding mass spectrometric (MS) detection in another product, Application 460B-00. This note describes applying GC/MS instrumentation and methods to analyze trace contaminants in polymer grade ethylene and propylene feedstocks.

## Using GC/MS for Trace Contaminant Analyses

### Mass Spectrometric Detection

Utilizing a mass spectrometer as the chromatographic detector provides significant benefits:

- Increased sensitivity
- Detection of analytes that do not produce a response with a FID
- Selectivity
- Positive identification through mass spectra

As the impact of trace levels of impurities becomes better understood, the need for increasing sensitivity in an analytical technique becomes more important. With flame ionization detection in Application 262-00, detection levels for carbon monoxide and carbon dioxide are on the order of 50 ppb while those for the paraffins and olefins up to n-pentane are about 1 ppm (parts-per-million). MS detection is equivalently sensitive for these compounds. However, MS detection offers gains in sensitivity for those compounds with little or no FID response factors, for example, oxygenates, sulfur-containing compounds, and compounds with no carbon-hydrogen bonds (hydrogen sulfide, carbonyl sulfide, arsine, phosphine). Moreover, the selectivity afforded by MS detection is important because it provides confirmation that an analyte in question is indeed present by examining its mass spectrum (scan mode) or monitoring of multiple, specific ions (selected ion monitoring - SIM mode).

The GC/MS methods described here address a range of analytes beyond the scope of Application 262-00.

### Gas Chromatographic Separation

Even with the inherent strengths of a mass spectrometer, some chromatography must still be employed. The detector's selectivity is not absolute, especially when simultaneously detecting components at vastly different concentrations (ppb) versus bulk or percent levels). This means that the ppb contaminants must be reasonably separated from their ethylene or propylene matrix since coelution of a trace contaminant with the major matrix component yields a false positive with respect to the contaminant. Additionally, some of the analytes may interfere with each other by having the same molecular weight and/or fragment ions. Therefore, both chromatography and mass spectrometry are needed to provide identification.

For such a complex sample, no single gas chromatographic column provides adequate separation of the whole range of analytes and matrix components. Different selectivities of the capillary column stationary phases must be invoked to separate the various groups of very similar analytes. For this reason, Agilent Technologies/Wasson-ECE employs a multivalve, multicolumn approach to the chromatograph configuration.

### Agilent Technologies/Wasson-ECE Application 460B-00

A new application product was developed to merge the advantages of MS detection with the necessary resolution afforded by appropriate chromatographic columns and automatic control of valved GC injections. The application includes multiple special inert capillary columns that do not irreversibly bind the analytes, addition of multiple valves, passivation of all components along the sample path (for example, valves, transfer lines), analytical methods for the GC/MS, and control software that coordinates the entire application.

In the multivalve, multicolumn approach, the sample (a gas or vaporized liquid) is purged through the injection valve. In this manner, the injection valve contains an aliquot of original sample, sized appropriately for the column to be used. The flexibility of programming both valve operation and chromatographic system pressures results in the sequential injection of the aliquot onto one of the multiple columns, the appropriate one being selected with a portion of the total analysis in mind. Each injection process defines a

method, resulting in a total of three sequential methods that comprise a full “composite method” to perform the selected assay. In executing a “composite method,” Agilent Technologies/ Wasson-ECE's Composite Analysis Control Software (CACS) automatically sequences the sampling of the three separate aliquots of a feedstock sample, applying the appropriate GC/MS methods to each, and produces a combined, final report.

### A Modular Approach to the Analysis of Trace Contaminants: Building on Application 460B-00

Application 460B-00 is a building block in a modular approach to providing the degree of automation appropriate to the users' needs. As described just above, Application 460B-00 is suitable for use in the laboratory where an analyst connects one pressurized sample container at a time to the system. However, a sampling system that automatically and sequentially samples pressurized sample containers is available from Agilent Technologies/ Wasson-ECE; once the samples are installed, no user intervention is required.

Moreover, other products from Agilent Technologies/Wasson-ECE move Application 460B-00 from the laboratory to the process stream. In this configuration, there is a single sample source that is repetitively sampled. Since a “composite method” for Application 460B-00 takes about 1 hour per sample, knowledge of the bulk ethylene or propylene streams is available in a timely manner. This makes it possible to improve the quality of the product and reduce manufacturing costs associated with rework or waste disposal of large amounts of product that are out-of-specification due to contaminants in the bulk reactant.

## Experimental

The instrumentation is outlined in Table 1. For the results presented here, an HP 5972 MSD was used. Table 2 outlines the impurities that were characterized for the evaluation of Application 460B-00. Note that the ethylene and propylene analyses each require three separate GC/MS methods; these methods are not the same.

**Table 1. The Instrumentation and Control Software for the Ethylene and Propylene Analyses in the Agilent Technologies/Wasson-ECE Product, Application 460B-00**

| | |
|---|---|
| Mass spectrometer | 5973 MSD and later models |
| Gas chromatograph | 6890 GC |
| GC Valve configuration | Provided by Agilent Technologies /Wasson-ECE. Sample loops of 100 µL and 500 µL |
| Columns | Provided by Agilent Technologies/Wasson-ECE: Wasson Part No. KZA and Wasson Part No. KZB |
| Software | · G1701 DA<br>· Composite Analysis Control Software from Agilent Technologies/Wasson-ECE |
| GC/MSD Methods | Provided by Agilent Technologies/Wasson-ECE |

**Table 2. Analytes Used to Characterize the Performance of Agilent Technologies/ Wasson-ECE Application 460B-00 for Impurities found in Ethylene**

| Component | Quant ion | Prepared analyte levels (ppb) |
|---|---|---|
| Methyl mercaptan | 47 | 25, 35, 70, 115, 410 |
| Ethyl mercaptan | 62 | 15, 25, 55, 105, 315 |
| Methyl-t-Butyl ether | 73 | 10, 20, 38, 75, 223 |
| Methanol | 31 | 28, 55, 110, 205, 625 |
| t-Butanol | 59 | 12, 25, 45, 85, 265 |
| Ethanol | 31 | 18, 38, 75, 140, 433 |
| isopropanol | 45 | 15, 30, 78, 107, 335 |
| *sec*-Butanol | 45 | 15, 25, 45, 88, 270 |
| 1-Propanol | 31 | 15, 30, 45, 110, 333 |
| 1-Butanol | 56 | 12, 23, 58, 87, 270 |
| Hydrogen sulfide | 34 | 25, 100, 190, 575 |
| Carbonyl sulfide* | 60 | 15, 25, 75, 100, 310 |
| Arsine | 76 | 55, 115, 215, 440 |
| Phosphine | 34 | 50, 110, 205, 420 |

* For carbonyl sulfide in propylene, prepared analyte levels spanned 1–300 ppb

Standard mixtures of analytes in the bulk material were prepared by using permeation tubes from Agilent Technologies/Wasson-ECE; in this approach, concentration levels are determined by the flow rate of the bulk material. Mixtures of multiple trace analytes in the bulk material were prepared by plumbing multiple permeation tubes in series. The bulk ethylene was obtained from Alphagaz ("primary standard" grade). The analytes came from Chem Service.

Linearity for each analyte was determined in the usual manner (construction of calibration curves with the HP G1701 BA software) for the concentration levels noted in Table 2. For the repeatability studies, a single concentration level near the low end of the calibration range for each analyte was injected seven to eight times.

In general, detection limits (DLs) were determined in two ways. The first was to use the linearity and repeatability data to target the lowest concentrations at which the repeatability for five replicates would give 1% to 10% RSD (relative standard deviation). Samples at these concentrations were run in SIM mode (including automated peak detection and integration, and automated reporting) to provide actual minimum DLs.

The second was to run samples in SIM mode at concentrations estimated to yield responses having S/N (signal-to-noise) ratios of about 2.5. Integration was done manually, using the SIM mass chromatogram for each analyte.

## Results

Figures 1 through 3 are examples taken from propylene and ethylene assays to show the type of output using the Agilent Technologies/Wasson-ECE product.

Tables 3 through 6 present the results of the experiments to characterize the performance of Application 460B-00 with respect to linearity, repeatability, and limits of detection (LOD).

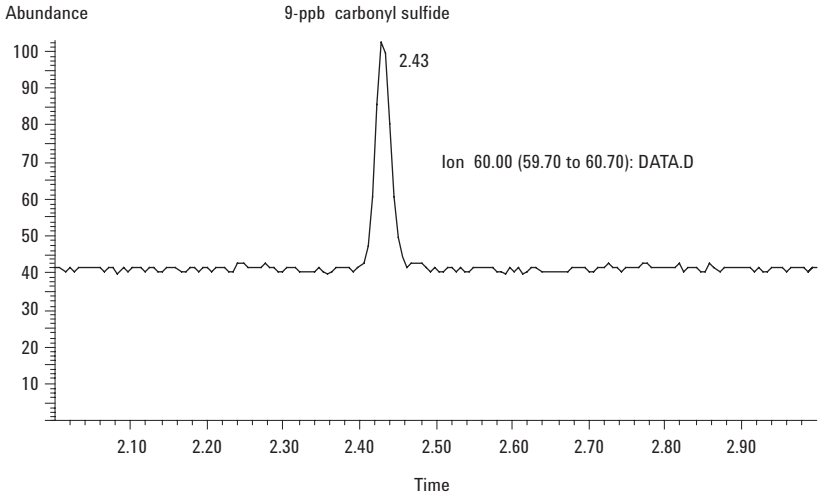


**Figure 1. A section of chromatogram showing SIM detection for the determination of 9-ppb carbonyl sulfide in propylene at a customer's facility.**

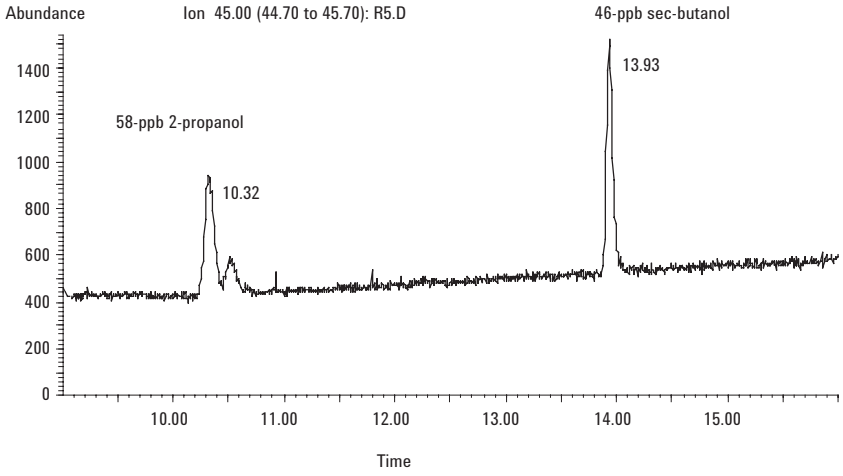


**Figure 2. A section of chromatogram showing SIM detection for the determination of 58-ppb isopropanol and 46-ppb *sec*-Butanol in ethylene.**

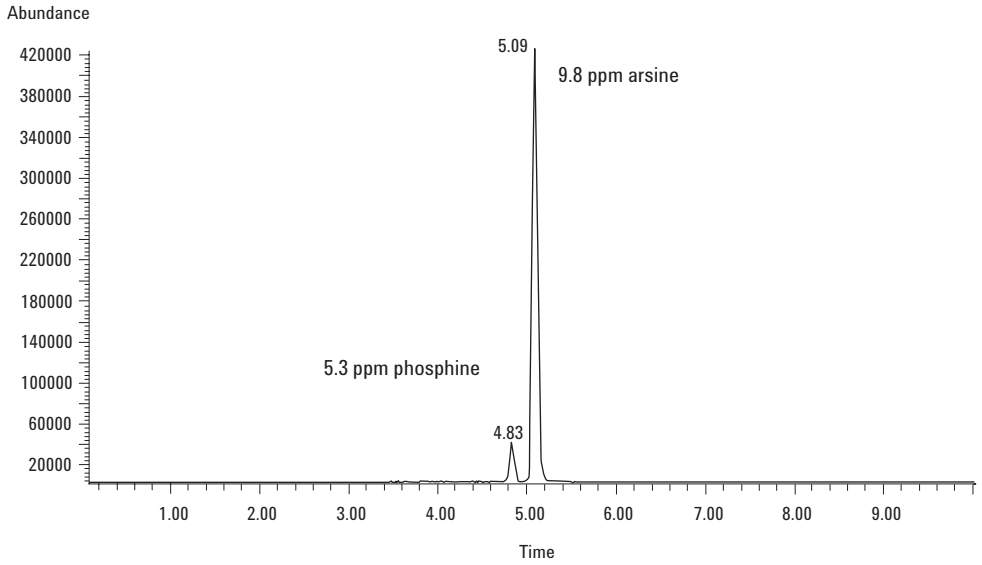


**Figure 3. A section of chromatogram showing SIM detection for the determination of 240-ppb arsine in ethylene.**

**Table 3. Measures of Linearity for the Ethylene Impurity Analysis**

| | Concentration range | Number of calibration points | Correlation coefficient |
|---|---|---|---|
| Methyl mercaptan | 25–410 ppb | 5 | 0.999 |
| Ethyl mercaptan | 15–315 ppb | 5 | 1.000 |
| Methyl-t-Butyl-ether | 10–223 ppb | 5 | 1.000 |
| Methanol | 28–625 ppb | 5 | 0.999 |
| t-Butanol | 12–265 ppb | 5 | 1.000 |
| Ethanol | 18–433 ppb | 5 | 0.999 |
| isopropanol | 15–335 ppb | 5 | 1.000 |
| *sec*-Butanol | 15–270 ppb | 5 | 1.000 |
| 1-Propanol | 15–333 ppb | 5 | 0.999 |
| 1-Butanol | 12–270 ppb | 5 | 0.998 |
| Hydrogen sulfide | 25–575 ppb | 4 | 0.992 |
| Carbonyl sulfide | 15–310 ppb | 5 | 1.000 |
| Arsine | 55–440 ppb | 4 | 1.000 |
| Phosphine | 50–420 ppb | 4 | 0.995 |

**Table 4. Repeatability for Sulfur-Containing Compounds at ppb Concentrations Using the Agilent Technologies/Wasson-ECE Method for Determination of Ethylene Impurities**

| Sample number | Hydrogen sulfide | Carbonyl sulfide | Methyl mercaptan | Ethyl mercaptan |
|---|---|---|---|---|
| 1 | 106.42 | 41.70 | 77.96 | 60.29 |
| 2 | 90.05 | 41.74 | 79.23 | 57.96 |
| 3 | 98.50 | 50.61 | 79.90 | 61.36 |
| 4 | 107.15 | 40.77 | 80.18 | 59.30 |
| 5 | 111.59 | 39.97 | 76.96 | 57.27 |
| 6 | 95.75 | 40.30 | 81.74 | 61.33 |
| 7 | 102.48 | 39.00 | 79.31 | 63.32 |
| **Average** | 101.71 | 42.01 | 79.33 | 60.12 |
| **Standard Deviation** | 7.44 | 3.91 | 1.55 | 2.11 |
| **% RSD** | 7.31 | 9.31 | 1.95 | 3.51 |

**Table 5. Repeatability for Oxygenates at ppb Concentrations Using the Agilent Technologies/Wasson-ECE Method for Determination of Ethylene Impurities**

| Sample number | Methyl-t-Butyl ether | Methanol | t-Butanol | Isopropanol |
|---|---|---|---|---|
| 1 | 48.25 | 160.91 | 54.62 | 73.03 |
| 2 | 46.33 | 141.46 | 51.91 | 65.61 |
| 3 | 48.58 | 79.02 | 49.19 | 61.98 |
| 4 | 48.38 | 122.15 | 48.99 | 62.01 |
| 5 | 44.91 | 98.72 | 51.29 | 70.76 |
| 6 | 46.52 | 126.15 | 53.50 | 67.15 |
| 7 | 48.92 | 127.03 | 54.32 | 66.80 |
| 8 | 45.35 | 127.09 | 52.54 | 64.90 |
| **Average** | 47.16 | 122.82 | 52.05 | 66.53 |
| **Standard Deviation** | 1.57 | 24.91 | 2.15 | 3.88 |
| **% RSD** | 3.33 | 20.29 | 4.12 | 5.83 |

**Table 5 (continued). Repeatability for Oxygenates at ppb Concentrations Using the Agilent Technologies/Wasson-ECE Method for Determination of Ethylene Impurities**

| Sample number | Ethanol | *sec*-Butanol | 1-Propanol | 1-Butanol |
|---|---|---|---|---|
| 1 | 86.10 | 52.38 | 63.47 | 58.22 |
| 2 | 81.44 | 54.94 | 67.02 | 60.33 |
| 3 | 82.82 | 53.65 | 62.64 | 59.24 |
| 4 | 75.90 | 52.05 | 67.34 | 54.88 |
| 5 | 95.45 | 51.00 | 68.12 | 59.47 |
| 6 | 80.51 | 54.19 | 66.98 | 59.89 |
| 7 | 85.32 | 54.20 | 65.37 | 58.13 |
| 8 | 84.86 | 53.50 | 71.87 | 55.85 |
| **Average** | 84.05 | 53.24 | 66.60 | 58.25 |
| **Standard Deviation** | 5.65 | 1.32 | 2.88 | 1.95 |
| **% RSD** | 6.73 | 2.47 | 4.32 | 3.35 |

**Table 6. DLs for the Ethylene Impurity Analysis***

| | Approach A** (ppb) | Approach B*** (ppb) |
|---|---|---|
| Methyl mercaptan | 18 | 2 |
| Ethyl mercaptan | 14 | 3.5 |
| Methyl-t-Butyl-ether | 10 | 4 |
| Methanol | 28 | 20 |
| t-Butanol | 12 | 4 |
| Ethanol | 19 | 9 |
| isopropanol | 15 | 4 |
| *sec*-Butanol | 12 | 3 |
| 1-Propanol | 15 | 4 |
| 1-Butanol | 12 | 4 |
| Hydrogen sulfide | 26 | 10 |
| Carbonyl sulfide | 14† | 10 |
| Arsine | 10 | 7 |
| Phosphine | 50 | 30 |

* All values are in mole ppb or mole ppm.

** The lower DL was determined by the ability of the established integration parameters to detect the peak and integrate the peak properly.

*** Peak height at 2.5 times the noise. This peak will typically be integrated manually. This value was extrapolated from lowest concentration analyzed for each component.

† The DL for carbonyl sulfide in propylene using Approach A was found to be 5 ppb.

## Summary

The performance of Agilent Technologies/Wasson-ECE's Application 460B-00 was evaluated for linearity, repeatability, and LOD for trace contaminants in ethylene. The results show that impurities in ethylene can be precisely determined to the low ppb levels for compounds that are not amenable to either trace analysis by GC/FID (where the typical LOD for the cited compounds range from 50 ppb for carbon dioxide and carbon monoxide to ppm for paraffins and olefins) or by GC/TCD (where the sensitivity is 5000-fold lower).

Application 460B-00 can also be used to determine trace contaminants in propylene as demonstrated by the carbonyl sulfide in propylene results (Figure 1). Additionally, it should be applicable to other analytes that were not studied in this work: acetone, 4-methylcyclohexene, 4-ethyl-cyclohexane, and aromatics.

By having "composite methods" that automatically perform the appropriate sequences of sampling plus methods, manual intervention is minimized for each sample. In the laboratory, the operator needs only to install each pressurized sample source from one sample to another and start the composite method. A greater degree of automation with less intervention per sample is possible by adding an automatic sampler product.

The analysis times for the “composite method” are wellmatched to the needs of polymer manufacturers for feedstock assays. For example, the full composite method for the ethylene assay takes about 1 hour. Typically in an off-line analysis approach, manufacturing facilities obtain samples of the feedstock and submit them to the laboratory for analysis. The 1-hour analysis time is a fairly small part of the total turn-around-time (several hours) to get analytical information back to the production line.

By moving the Application 460B-00 online using other products from Agilent Technologies/ Wasson-ECE, the polymer manufacturer could analyze feedstock materials about once per hour to maintain maximum productivity and quality while minimizing loss of product and/or rework.

The Agilent Technologies/ Wasson-ECE product, Application 460B-00, provides reliable results in a timely manner for bulk ethylene and propylene feedstock fluids with a minimum of manual intervention for the determination of impurities that have minimal carbon content and/or are highly oxygenated.

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1. 460B-00
2. 262-00

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Agilent Technologies

# Dual-Channel Gas Chromatographic System for the Determination of Low-Level Sulfur in Hydrocarbon Gases

Application

**Hydrocarbon Processing**


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## Abstract

**A 6890N equipped with dual flame photometric detectors is described for the analysis of ppb level volatile sulfur compounds in a variety of hydrocarbons using thick film DB-1 and GS-GasPro columns. Enhanced performance flame photometric detectors are employed that can achieve detection of sulfur compounds below 20 ppb. Examples of arsine and phosphine analysis with the same hardware are also discussed.**


## Introduction

Gas chromatography with sulfur selective detection is finding widespread application in many segments of the petroleum, petrochemical, and specialty chemical industries. Demand for low-level sulfur detection will increase in the future in response to more stringent regulations and tighter quality control.

Sulfur compounds can be significant poisons for various catalytic processes involved in hydrocarbon conversion. Monitoring these low-level poisons can lead to considerable saving in terms of improved yields, increased catalyst lifetime, and higher quality products. In looking at the future of fuel cells, fuel contaminants can adversely affect performance of fuel cell systems and fuel processors that are powered by natural gas or other fossil fuels. Finally, environmental regulatory issues in certain regions will continue, necessitating the need to monitor fuel impurities.

A common problem with many gas chromatographic sulfur selective detectors is hydrocarbon interference, especially from co-elution. The measurement challenge is acute when the interfering hydrocarbon comprises the majority of the sample, as in the analysis of impurities in ethylene and propylene, or sulfur in natural gas [1, 2]. In most cases, an accurate determination of the sulfur compound is difficult or not possible even with highly selective sulfur detectors. However, the use of a dual-channel system employing two very different separation columns (in terms of selectivity) largely avoids the interference problem. The configuration is shown in Figure 1. Sulfur compounds that have a severe interference on one column are likely to be separated from that interference on the other column. By assuring that a given sulfur compound will be separated on at least one of the columns, the system can use a reliable, stable, and relatively inexpensive flame photometric detector (FPD) for detection. If the hydrocarbons can be chromatographically separated from the sulfur compounds of interest, enhanced FPDs can quantitate sulfur to less than 20 ppb.

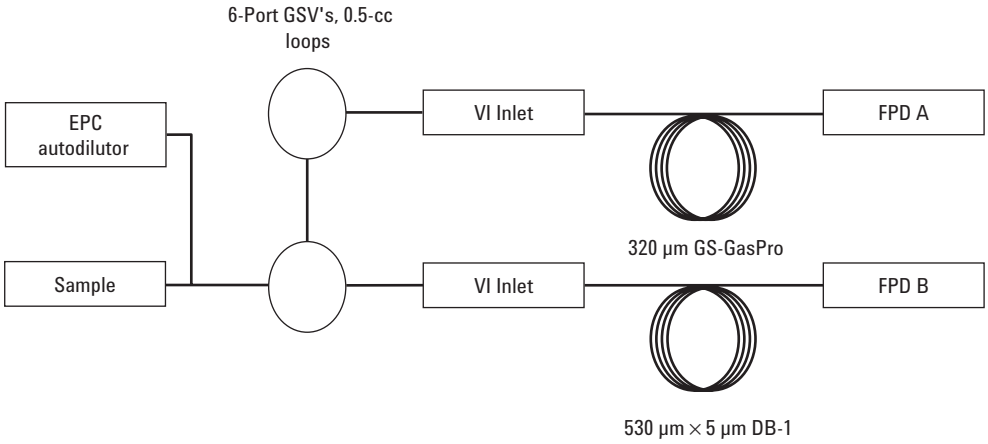


**Figure 1. System configuration on the Agilent 6890N. Valves (plumbed in series) are Hastelloy C and all plumbing is Silcosteel® or Sulfinert™ treated.**

## Experimental

Selection of the appropriate capillary column is often key to the solution of a particular analysis problem, and this is especially true for this system. Four columns are employed (two for any given analysis) as described in Table 1.

**Table 1. Recommended Column Combinations by Application**

| Applications | Column set |
|---|---|
| Natural gas, fuel cell gases | 60 m × 530 µm × 5.0 µm DB-1 |
| | 30 m × 320 µm GS-GasPro |
| Ethylene, propylene, C4 streams | 105 m × 530 µm × 5.0 µm DB-1 |
| | 60 m × 320 µm GS-GasPro |

Recommended GC oven programs are 40 °C (5 min) to 290 °C (5 min) at 25 °C/min for natural gas, fuel cell gases and ethylene, and 35 °C (7 min) to 290 °C (5 min) at 20 °C/min for propylene. Somewhat lower detection limits can be achieved for sulfur in a propylene stream by employing cryo oven programs such as: –35 °C (7 min) to 290 °C (5 min) at 20 °C/min. Split ratios, as set in the GC method, vary from 0.5:1 to 2:1.

Each valve was interfaced to a specialized inert (Silcosteel treated) volatiles interface for accurate sample introduction at low split ratios into a capillary column. Due to the tendency for organosulfur compounds (especially $H_2S$) to adsorb to metal surfaces, great care must be used in selecting and constructing the chromatographic sample introduction system. The sample loop, tubing, and inlet are either Sulfinert or Silcosteel treated for inertness.

A factory modified FPD, with enhanced sensitivity, was used for each channel. The FPD is optimized for the analysis of trace sulfur gases, arsine, and phosphine in gaseous samples. See Table 2 for appropriate gas flow settings. These detectors achieve detection limits that are roughly four times better than standard. The sensitivity advantage is illustrated in Figure 2, where standard and modified FPDs are compared using a standard calibration blend. Minimum detection level (MDL) calculated on methyl mercaptan using linearized data and the 60 m DB-1 column is better than 15 ppb.

**Table 2. FPD Gas Flow Settings**

| Analysis | Gas | Flow rate (mL/min) |
|---|---|---|
| Sulfur | Air | 60 |
| | Hydrogen | 50 |
| | Makeup | 58 |
| Arsine | Air | 150 |
| | Hydrogen | 50 |
| | Makeup | 100 |
| Phosphine | Air | 110 |
| | Hydrogen | 150 |
| | Makeup | 58 |

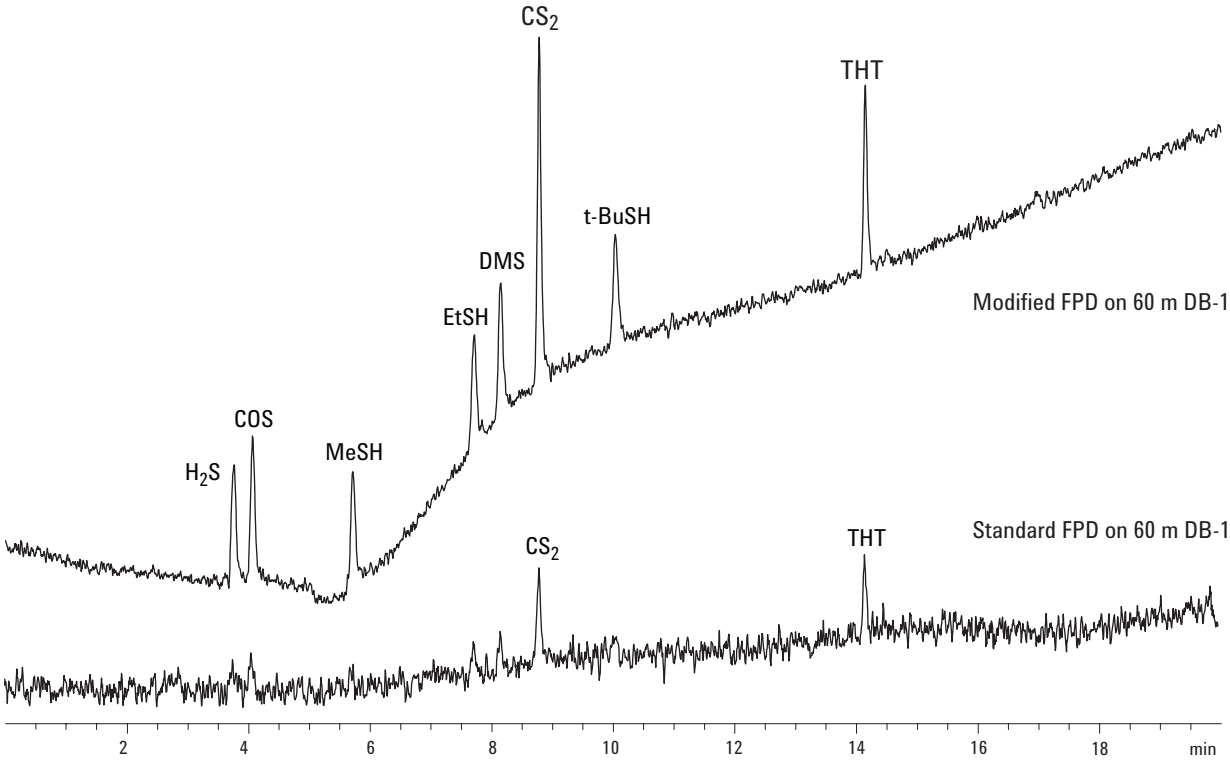


**Figure 2. Sensitivity comparison of standard and enhanced FPDs. Concentrations are 33 ppb per component (v/v) in helium.**

Due to the use of all available heated zones on the 6890N GC for either inlet or detector heating, the 6-port sample valves are not actively heated. This does not pose a problem for the light gaseous streams studied in this work. However, if desired, the valves can be heated by an auxiliary stand-alone temperature controller (Agilent model 19265B). The system is designed only for gaseous samples containing significant concentrations of hydrocarbons of $C_6$ or below.

## Discussion

Channel 1 employs the GS-GasPro column, using a unique bonded PLOT technology, where COS is separated from $C_2$ and $C_3$ hydrocarbons, allowing measurement at trace levels. However, $H_2S$ and the $C_3$s coelute. Channel 2 uses a thick film DB-1 column where $H_2S$ is well separated from $C_2$s and $C_3$s, making low-level measurements of this sulfur impurity possible. COS and $C_3$s will coelute on this column. In summary, using a dual-column approach with the unique separation capabilities of GS-GasPro and thick film DB-1, both COS and $H_2S$ can be measured in one chromatographic analysis at low ppb levels regardless of the concentrations of light hydrocarbons present in the sample. The elution order difference between the two columns is illustrated in Figure 3.

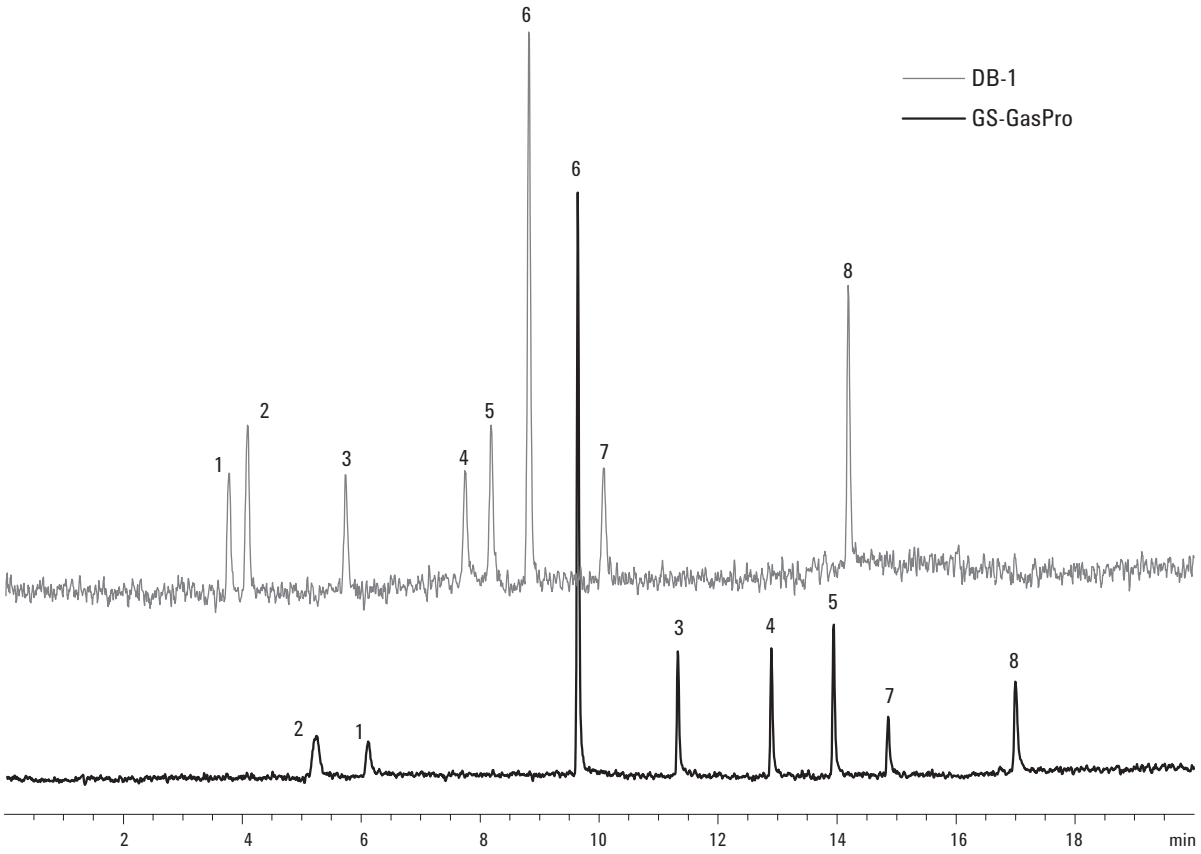


**Figure 3. The dual-column advantage. Sulfur mix at 90 ppb per component in helium. 1. $H_2S$, 2. COS, 3. MeSH, 4. EtSH, 5. DMS, 6. $CS_2$, 7. t-BuSH, 8. THT.**

Other potential interferences or coelutions between light sulfur compounds and hydrocarbons are avoided with this approach. A coeluting pair on one column will likely be separated on the other. Split ratios were set depending on the application from 0.5:1 to 2:1 in order to achieve the reported detection limits.

The sulfur calibration mix consisted of the following components at 5 ppm each: Hydrogen sulfide ($H_2S$), carbonyl sulfide (COS), methyl mercaptan (MeSH), ethyl mercaptan (EtSH), dimethyl sulfide, carbonyl sulfide (DMS), t-butyl mercaptan (t-BuSH), and tetrahydrothiophene (THT). The blend in helium was purchased from DCG Partnership, Pearland, TX. These compounds are representative of the most common light sulfur species encountered in gaseous fuels or petrochemical feedstocks.

Some adsorption of $H_2S$ on the GS-GasPro column is possible. Priming the system a few times with a low ppm sulfur stream such as the calibration mix described here can largely eliminate the loss in sensitivity that can result from adsorption. This priming is usually only necessary for low ppb analyses where the active sites in the column could adsorb most of the sulfur present in the sample during an initial run.

Gaseous blends of the sulfur standard in helium or other matrices such as natural gas, propane, liquidfied petroleum gas (LPG), propylene, and refinery gas were prepared using dynamic blending at the point and time of use. Diluent (matrix) gases were mixed with the sulfur calibration standard using an Aux EPC module on the 6890N GC. Accurate concentrations from low ppb to ppm levels can be easily prepared by knowing the flow rates of the two streams as they mix in a Tee fitting prior to the gas sampling valves on the GC. This system and the hardware employed were described previously in detail [3].

### Sulfur in Fuel Cell Gases, Natural Gas, and Proypylene

Figure 4 shows the chromatograms from the eight-component sulfur standard diluted with a fuel cell mix to 45 ppb (v/v) each component. The fuel cell

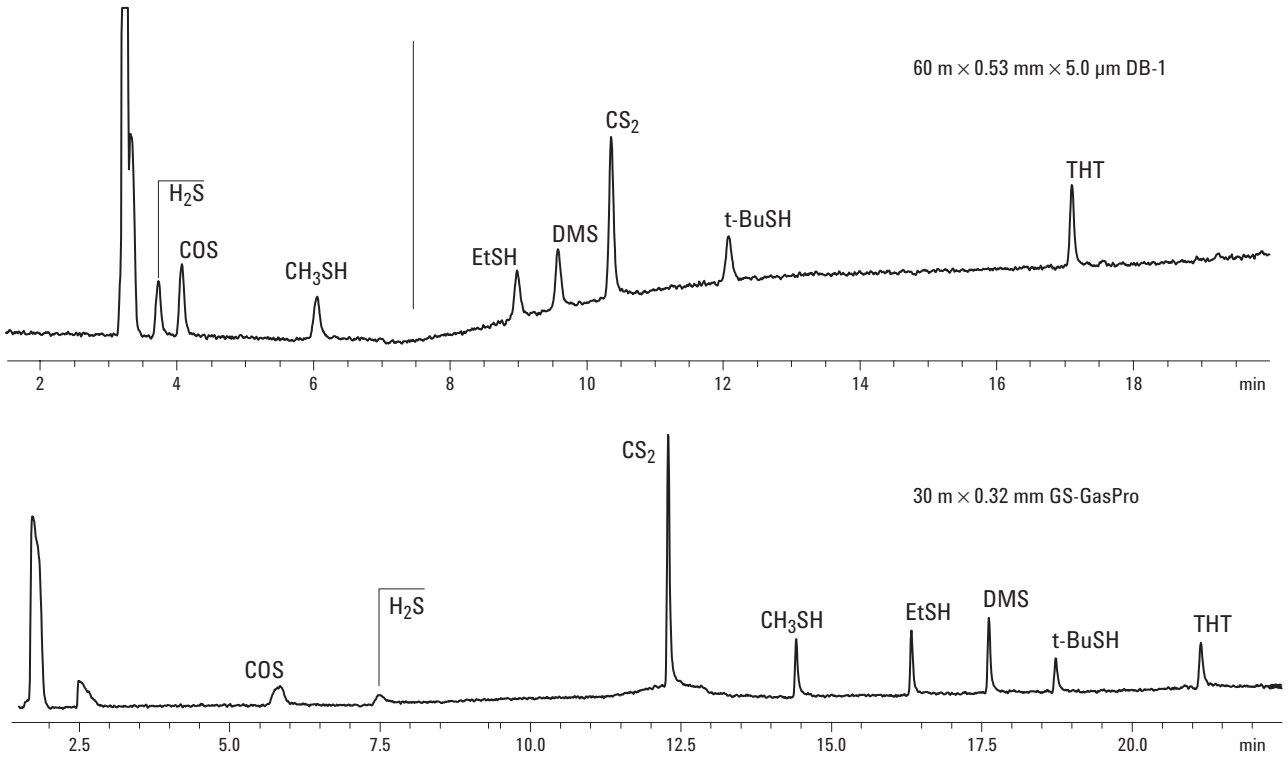


**Figure 4. Simultaneous dual column analysis of fuel cell mix containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 0.5:1.**

mix is 50% hydrogen, 10% carbon dioxide, and 5% methane. This mix is often used to simulate the output stream of a natural gas reformer used as the feed to a fuel cell. This matrix is one of the easier ones because the large hydrocarbon (methane) elutes before all of the sulfurs on both columns. Note that elution order of the sulfurs is significantly different on the GS-GasPro column compared to the DB-1 (see Figure 3). All eight compounds are clearly detectable at 45 ppb.

Natural gas is a much more challenging matrix because of the high concentrations of several hydrocarbons. These interferences extend out into the retention time range of the sulfur compounds.

Figure 5 shows the chromatograms from the eight-component sulfur standard diluted with sulfur free natural gas to 45 ppb (v/v) each component. There are more peaks evident in these chromatograms than just the eight sulfur compounds. The additional peaks are interference responses from the large hydrocarbons in the natural gas.

In the DB-1 chromatogram, $H_2S$ is clear but COS is lost to a severe overlap with a large $C_3$ peak. Ethyl mercaptan is also overlapped with n-pentane. On the GS-GasPro column, however, only the $H_2S$ is occluded by interference. The COS and EtSH are free from interferences. With the dual-column approach, all eight compounds can be measured down to 45 ppb.

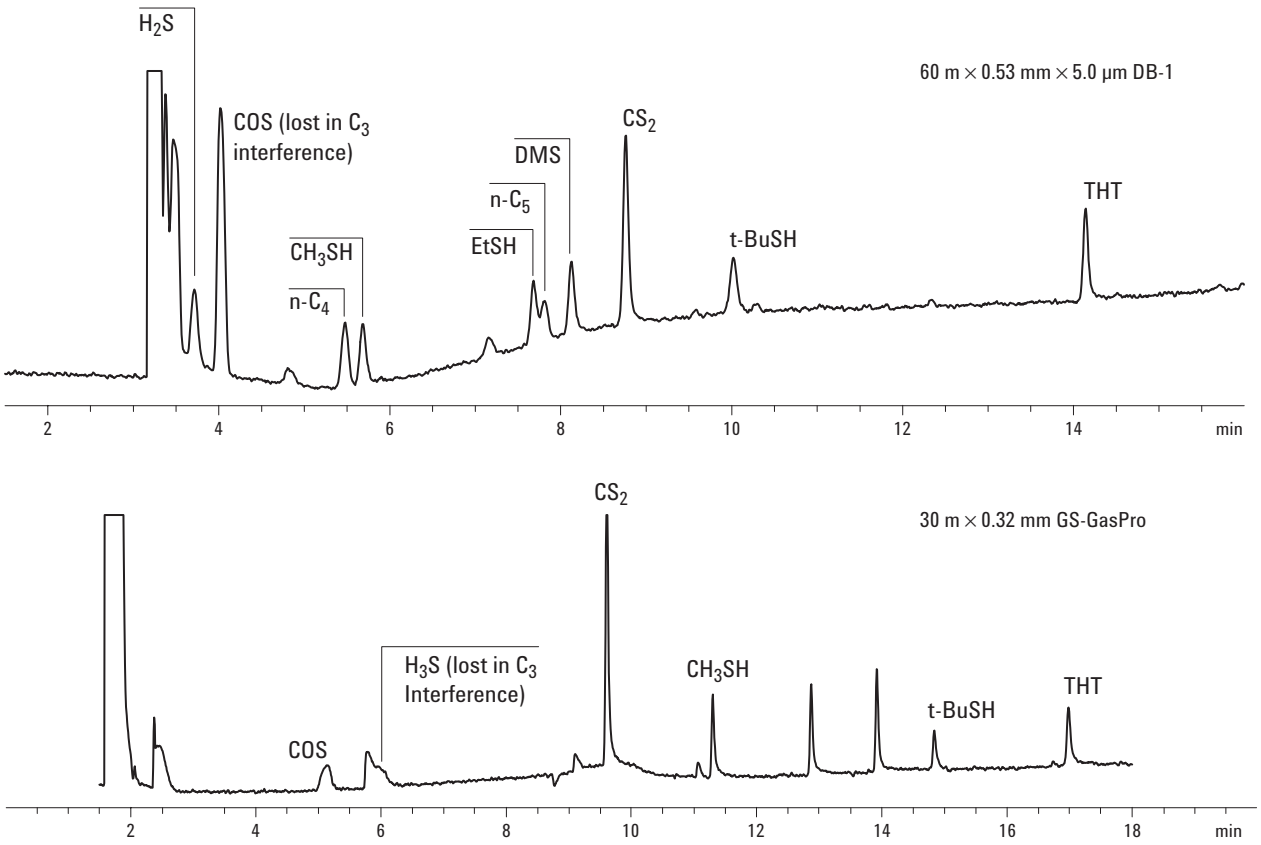


**Figure 5. Natural gas blend containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 0.5:1.**

Propylene monomer offers another interesting challenge. The huge $C_3$ peaks interfere with both the $H_2S$ and COS on both columns used above. To address this, longer versions of the same columns were used (Table 1). The oven temperature and split ratio are also modified (see Experimental on page 2) to improve resolution of the $H_2S$ and COS from the $C_3$s.

Figure 6 shows the chromatograms from the eight-component sulfur standard diluted with polymer-grade propylene to 45 ppb (v/v) each component. By using longer DB-1 and GS-GasPro columns, lower oven temperature, and a higher split ratio, the $H_2S$ and COS can be measured with somewhat poorer detection limits.

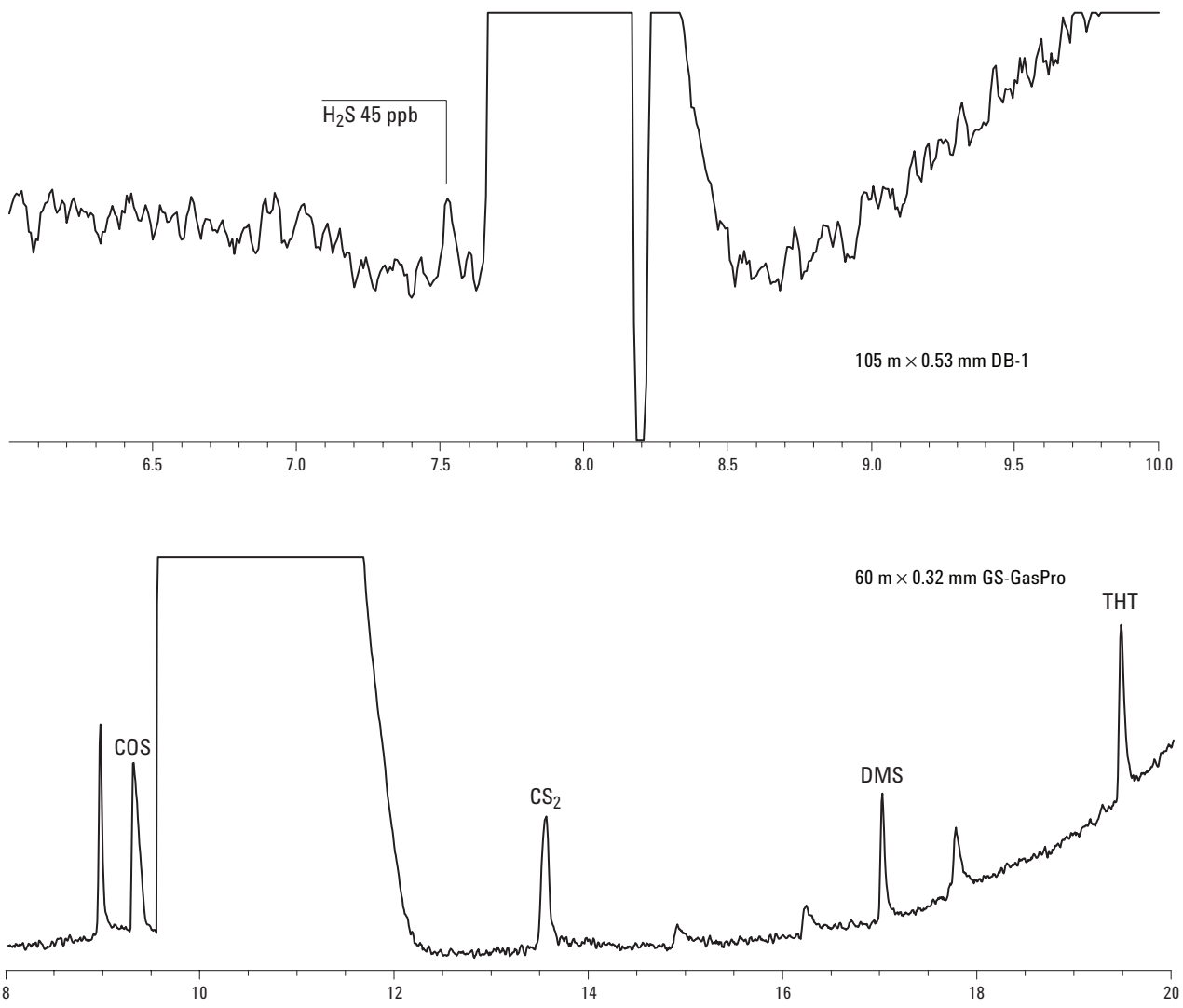


**Figure 6. Polymer-grade propylene blend containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 2:1. Top chromatogram: 105 m × 530 µm DB-1 showing only $H_2S$, bottom: 60 m GS-GasPro.**

Cryogenic oven temperatures were evaluated to see if the separation of $H_2S$ and COS could be improved enough to allow use of the more sensitive 0.5:1 split ratio. The oven program tested was: -35 °C for 7 min, 20 °C/min to 300 °C, hold for 5 min. The separation was improved enough to allow the analysis of $H_2S$ on the DB-1 column with the 0.5:1 split ratio, but COS was still occluded by the $C_3$s on the GS-GasPro. A DB-1 chromatogram illustrating the increased separation between $H_2S$ and propylene is given in Figure 7.

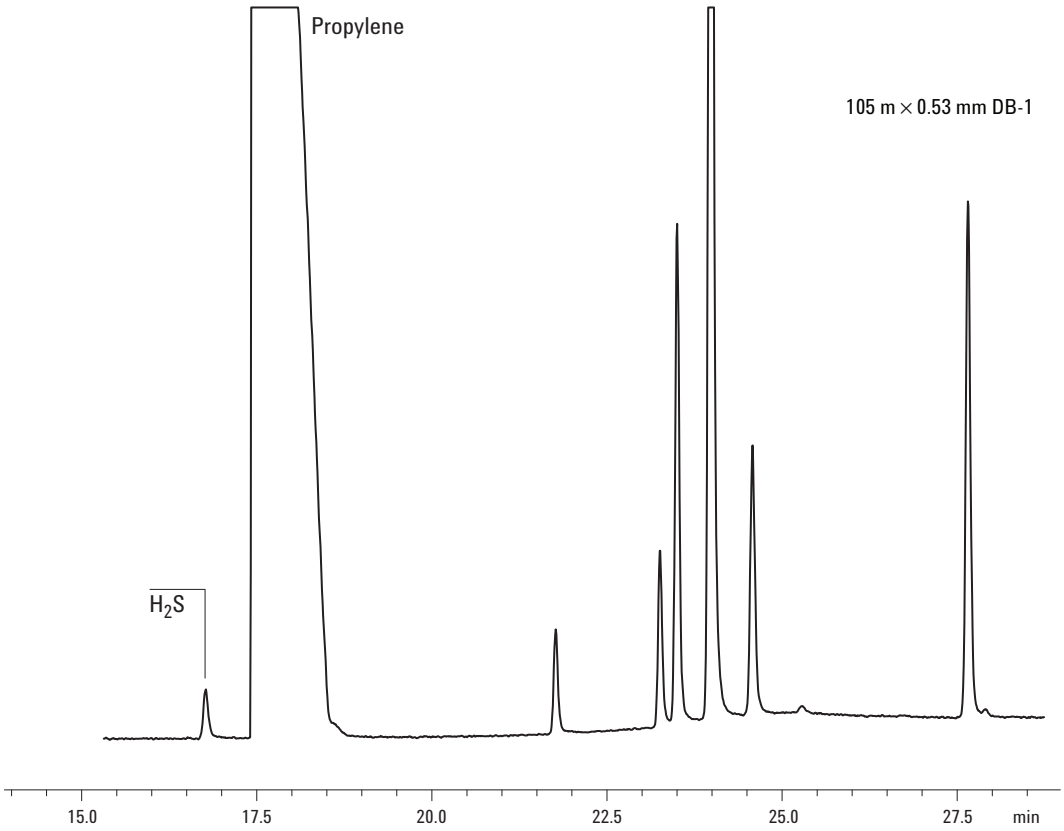


**Figure 7. Use of cryogenic oven temperatures for analysis of $H_2S$ (400 ppb) in propylene at 0.5:1 split.**

### Phosphorus and Arsenic on the Same System

One interesting characteristic of the modified FPD is that the filter used also passes the emissions for phosphorus and arsenic. This means that the same detectors can also be used to measure arsine and phosphine in polymer grade ethylene and propylene. A change of detector gas flows to that optimum for each element, followed by a rerun of the sample is all that is required. Since the 6890N detector flows are controlled by EPC, these reruns can be automated.

Figure 8 shows the chromatograms from an arsine and phosphine standard (DCG Partnership) diluted with polymer grade propylene to 36 ppb (v/v) each component. These are run under the same chromatographic conditions as in Figure 6, except that the FPD detector flows are set to those listed for phosphorus detection and the split ratio is back to 0.5:1. The detection limit under these conditions for phosphine in helium is under 5 ppb. If the detector flows are set to those listed for arsenic detection, the detection limit for arsine is about 60 ppb measured in helium. This system is well suited for gas analysis, however it is not really applicable to pesticide analysis due to the lack of selectivity between sulfur, phosphorus, and arsenic.

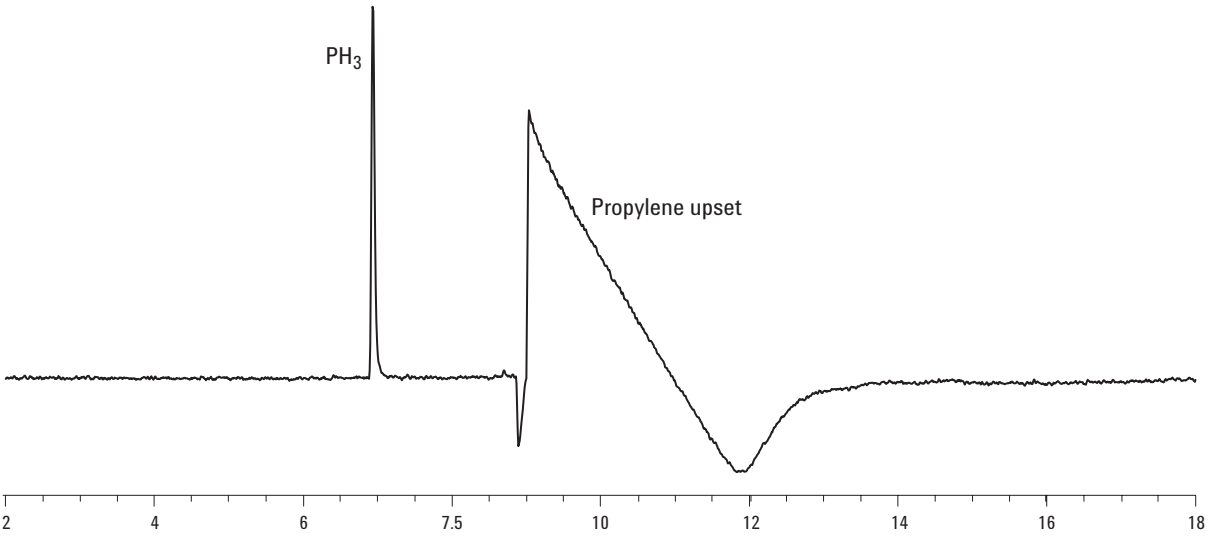


**Figure 8. Polymer-grade propylene blend containing 36 ppb (v/v) each of arsine and phosphine. Split ratio is 0.5:1. Note longer 105 m DB-1 columns are used.**

An example of arsine detection in propylene is shown in Figure 9.

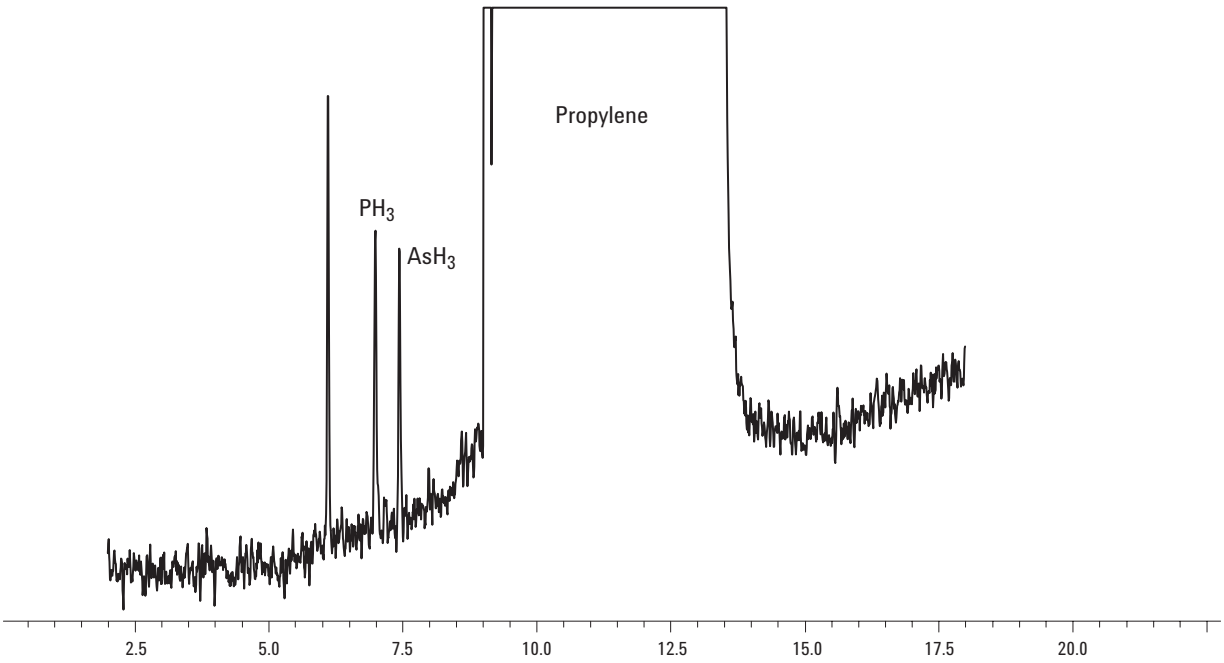


**Figure 9. Arsine optimized FPD flows. $H_2$: 50 mL/min, air: 150 mL/min. 60 m × 0.32 mm GS-GasPro, 0.5 to 1 split. 90 ppb each of $AsH_3$ and $PH_3$.**

## How to Order and Configure a Dual-Channel FPD System

The Dual-Channel FPD System, including columns and valves, can be ordered as a special (SP-1) option on any new Agilent 6890N GC. This special also includes the enhanced performance FPD. Contact your local Agilent representative for more information.

Learn more about low-level sulfur detection from these application notes available from any Agilent sales office or Agilent's Web site at www.agilent.com/chem. Just click "Library" in the menu listing, and type "sulfur" in the keyword field.

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Agilent Technologies

# Determination of Low Level Hydrocarbon Impurities in Propylene Using the Agilent 6820 Gas Chromatograph

Application

**Petrochemical**


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## Abstract

**A method for analyzing trace hydrocarbon impurities in propylene is described. The method employs an Agilent 6820 gas chromatography (GC) system configured with a gas sampling valve, split/splitless inlet, and flame ionization detector. The Agilent Cerity Networked Data System for Chemical QA/QC was used to control the 6820 GC and to provide data acquisition and data analysis. An Agilent HP-$Al_2O_3$ column was used for separation of the trace hydrocarbons. Impurity levels at 1 ppm were easily detected in propylene. This method does not determine all possible impurities such as CO, $CO_2$, $H_2O$, alcohols, nitrogen oxides, and carbonyl sulfide, or hydrocarbons larger than decane.**


## Introduction

High purity propylene is commonly used as the feedstock for production of polypropylene, and the quality of this monomer is critical to successful polymerization. The presence of trace amounts of certain hydrocarbon impurities can have deleterious effects on the catalyst. For example, acetylene can be adsorbed at the active center of the catalyst, resulting in catalyst deactivation. Dienes may reduce the rate of polymerization and adversely affect product quality. To maintain catalytic efficiency, most propylene processes require that alkyne and diene contaminants in the monomer be less than 10 ppm. The availability of a suitable method for the determination of impurities in propylene is critical to setting specifications, controlling internal quality, and doing development or research work.

Some propylene producers use their own standard method in which packed columns are used. It is difficult to detect trace level impurities by packed column. Presently, the American Society of Testing and Materials (ASTM) has published Method D2712 for the determination of trace hydrocarbon impurities in propylene streams [1]. In this method, an alumina porous layer open tubular (PLOT) column is used. The improved efficiency of the PLOT column provides better resolution and increases effective sensitivity.

## Experimental

An Agilent 6820 GC system was used for this work. It was configured with a split/splitless capillary inlet and a flame ionization detector (FID). Gas samples were injected using an automatic gas sample valve that was heated to 80 °C. The sample loop volume was 0.25 mL. The gas sample valve was connected to the inlet using an aluminum-jacketed stainless steel tube that maintains the sample temperature during transfer from the sample loop. The configuration used for propylene analysis is shown in Figure 1 and the instrument conditions are given in Table 1.

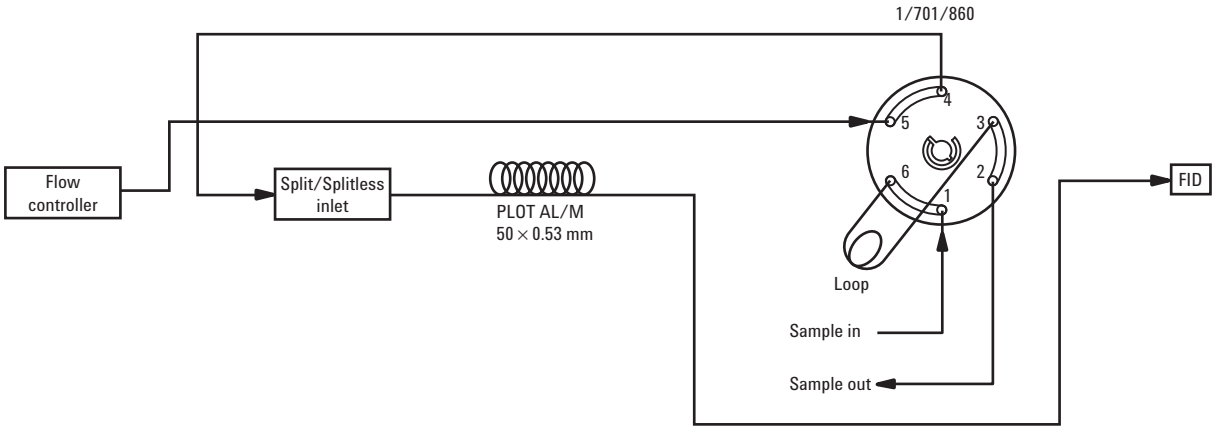


**Figure 1. Configuration diagram.**

An Agilent 50 m × 0.53 mm PLOT $Al_2O_3$ "M" deactivated column was used. The sample was run in the split mode using an Agilent split liner (Agilent part number 19251-60540).

The Agilent Cerity NDS for Chemical QA/QC was used for instrument control, data acquisition, and data analysis. Data was acquired at 20 Hz.

**Table 1. Instrument Conditions**

| | |
|---|---|
| Split/Splitless inlet | 175 °C, Split mode, with 15:1 and ~4:1 Split ratio |
| Valve | Gas sample valve, 6-Port, option 701 |
| Valve temperature | 80 °C |
| Sample loop | 0.25 mL |
| Column flow (He) | 4 mL/min |
| Column | PLOT $Al_2O_3$ "M" 50 m × 0.53 mm × 0.25 µm (p/n: 19095P-M25) |
| | |
| Oven | 40 °C for 2 min, 4 °C/min to 190 °C for 5 min |
| Detector | FID, 300 °C |
| $H_2$ | 35 mL/min |
| Air | 350 mL/min |
| Makeup gas ($N_2$) | 22 mL/min |

A propylene standard mix (DCG Partnership I, LTD., Pearland, TX 77581) consisting of the components listed in Table 2 at the certified concentrations shown (mole fraction) was used.

**Table 2. Propylene Sample Mix Component Concentrations**

| Compound | Concentrations (ppm) | Compound | Concentrations (ppm) |
|---|---|---|---|
| 1. Methane | 10 | 10 Acetylene | 9.8 |
| 2. Ethane | 27 | 11. *trans*-2-Butene | 9.92 |
| 3. Ethylene | 10 | 12. 1-Butene | 9.89 |
| 4. Propane | 3526 | 13. neo-Pentane | 9.86 |
| 5. Cyclopropane | 10 | 14. *iso*-Butylene | 9.87 |
| 6. Propylene | Balance gas | 15. *iso*-Pentane | 9.83 |
| 7. *iso*-Butane | 9.94 | 16. *cis*-2-Butene | 9.91 |
| 8. n-Butane | 9.85 | 17. n-Pentane | 9.86 |
| 9. Propadiene | 9.84 | 18. 1,3-Butadiene | 9.96 |

A dynamic blending system (Figure 2) was used to quantitatively dilute the sample with helium.

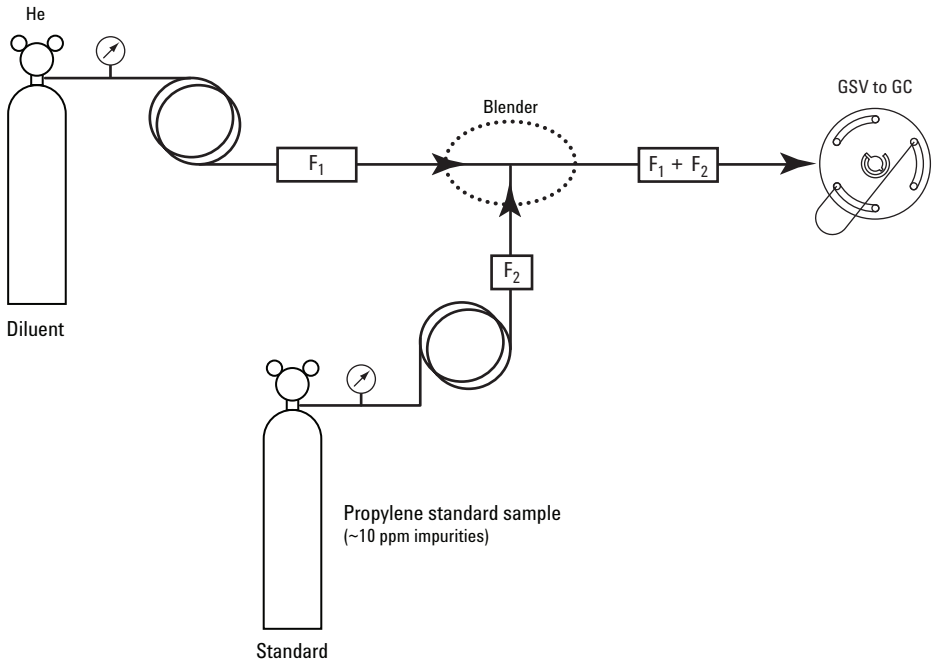


**Figure 2. Dynamic blending scheme.**

Diluted standard blend concentration is calculated by the following formula:

$C = C_o * F_2/(F_1+F_2)$

Where:
C: is diluted component concentration in ppm
$C_o$: original component concentration in standard blend in ppm
$F_1$: helium flow (mL/min)
$F_2$: propylene standard blend flow (mL/min)

## Results and Discussion

### Repeatability of 10 ppm Level Impurities in Propylene Analyses

Figure 3 shows the chromatogram from the undiluted sample. The PLOT $AL_2O_3$ column provides excellent separation for the C1 through C5 isomers [2]. The concentrations of most components are about 10 ppm. These trace level hydrocarbon impurities have a good FID response and are easily detected with baseline separation for most. Because the concentration of propylene is very high, some of the impurities such as *iso*-butane, n-butane, propadiene, and acetylene appear on the tail of the propylene peak. Even so, the Agilent 6820 GC system demonstrated very good repeatability, as shown in Table 3.

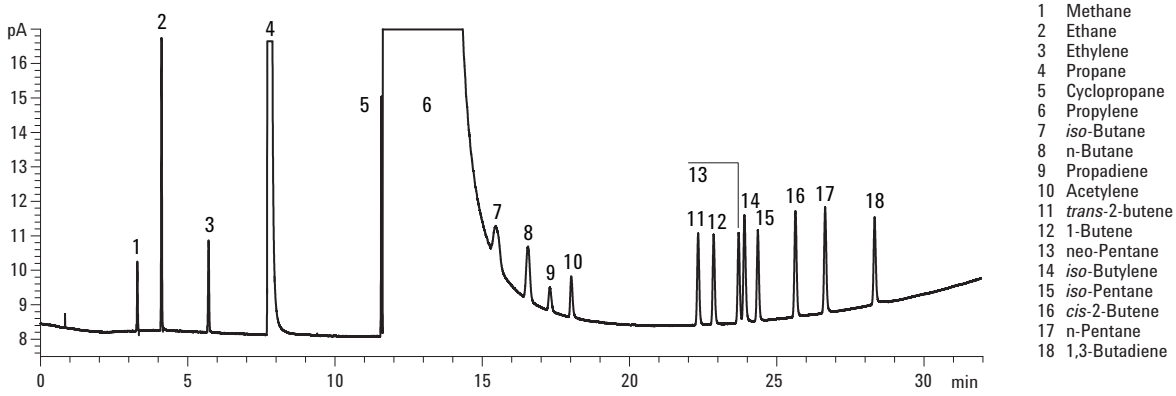


**Figure 3. Propylene standard mix. Concentrations are given in Table 2. Split ratio: 15:1.**

**Table 3. System Repeatability of Three Propylene Standard Runs**

| Component | Amt1 (ppm) | Amt2 (ppm) | Amt3 (ppm) | Avg. (ppm) | RSD (%) |
|---|---|---|---|---|---|
| Methane | 9.96 | 9.91 | 10.13 | 10.00 | 1.17 |
| Ethane | 26.95 | 26.78 | 27.27 | 27.00 | 0.92 |
| Ethylene | 10.21 | 9.90 | 9.90 | 10.00 | 1.76 |
| Propane | 3522 | 3503 | 3553 | 3526 | 0.73 |
| Cyclopropane | 9.99 | 9.95 | 10.07 | 10.00 | 0.61 |
| Propylene | 995642 | 988398 | 1004994 | 996344 | 0.84 |
| *iso*-Butane | 10.02 | 9.77 | 10.04 | 9.94 | 1.54 |
| n-Butane | 9.75 | 9.69 | 10.12 | 9.85 | 2.40 |
| Propadiene | 9.71 | 9.91 | 9.91 | 9.84 | 1.19 |
| Acetylene | 9.71 | 9.88 | 9.82 | 9.80 | 0.90 |
| t-2-Butane | 9.91 | 9.84 | 10.01 | 9.92 | 0.89 |
| 1-Butene | 9.89 | 9.80 | 9.98 | 9.89 | 0.95 |
| neo-Pentane | 9.86 | 9.76 | 9.96 | 9.86 | 1.03 |
| *iso*-Butylene | 9.88 | 9.76 | 9.98 | 9.87 | 1.12 |
| *iso*-Pentane | 9.80 | 9.76 | 9.94 | 9.83 | 0.95 |
| c-2-Butane | 9.90 | 9.84 | 9.99 | 9.91 | 0.72 |
| n-Pentane | 9.84 | 9.76 | 9.98 | 9.86 | 1.16 |
| 1,3-Butadiene | 9.97 | 9.87 | 10.04 | 9.96 | 0.85 |

### Full Dynamic Range Data

One of the advantages of the Agilent 6820 GC system is its ability to obtain full dynamic range data. The signal "range" setting is not required because the Cerity/ChemStation uses digital data that goes from the noise level all the way to 100% samples. Without this feature, the propylene peak would be flat at the top as soon as the range was exceeded, making accurate integration impossible. In many cases without digital signal processing, users would have to run the sample at two different ranges in order to quantitate both large and small peaks. The Agilent GC system with Cerity/ChemStation can simultaneously acquire both large and small peaks in one run without setting different ranges. This feature helps quantitate 100% and ppm compounds at the same time. Figures 4 and 5 separately illustrate scaling the small peaks and one large peak to demonstrate acquisition of ppm level peaks and high percent level peaks.

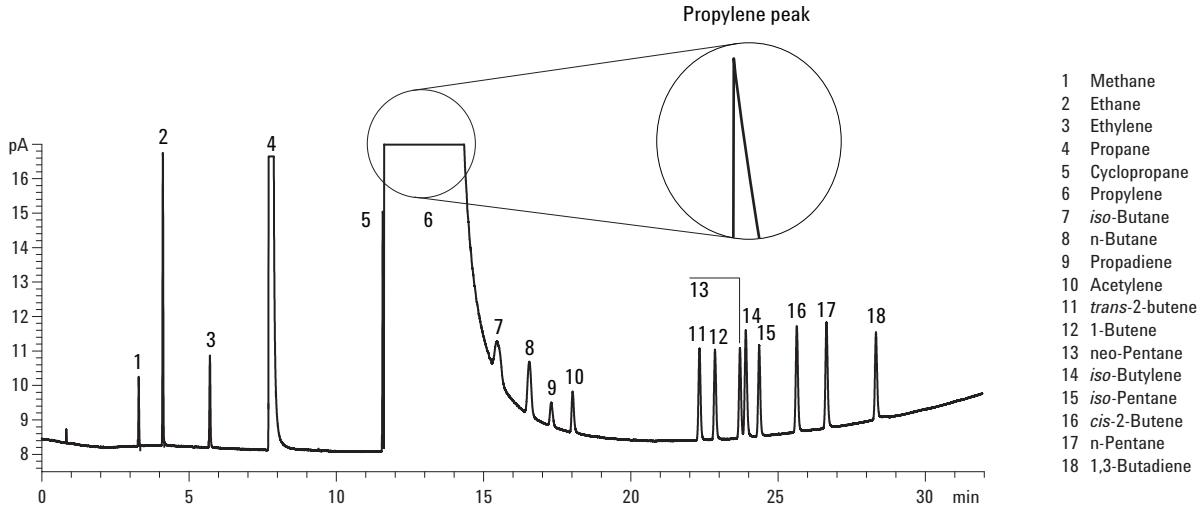


**Figure 4. Propylene standard mix shown on small scale. Propylene peak looks flat due to graphic scaling.**

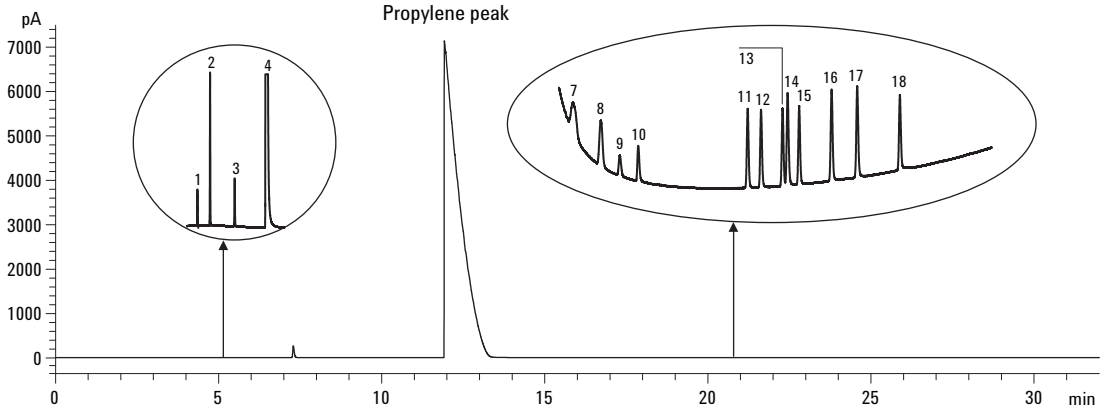


**Figure 5. Propylene standard mix shown on high scale. Zooming in shows good resolution, identification, and integration.**

### Sensitive to 1 ppm Impurities

Figure 6 illustrates the chromatogram of less than 1 ppm impurities in propylene. The injected sample was prepared by a 10X dilution of the standard mix sample using helium; the impurities level decreased to 1 ppm as well as the 10:1 dilution of the propylene peak. In this analysis, the method was modified to use a split ratio of 4:1 instead of 15:1 in order to achieve the 1 ppm impurities detection. The sample presented in Figure 6 shows *iso*-butane, n-butane, propadiene, and acetylene clearly detected on the tail of the propylene peak. Other impurities show baseline separation with excellent signal to noise as well. This demonstrates the performance of the Agilent 6820 GC for sensitive and quantitative detection of 1 ppm hydrocarbon impurities in propylene.

## Conclusions

The Agilent 6820 configured with a 6-port gas sampling valve interfaced directly to a split/splitless inlet was used to analyze trace hydrocarbon impurities in propylene with FID. Impurities below the 10 ppm mole % level can be easily quantitated. This system was able to detect 1 ppm level hydrocarbon impurities with excellent signal to noise. The Agilent 6820 system with Cerity can simultaneously acquire and quantitate both large concentrations (99 + mole %) and trace (low ppm) levels in a single run due to the use of a full dynamic range digital signal path. Manual range changes are not required. The feature of full dynamic range allows for accurate quantitation of near 100% propylene and ppm level compounds in one analysis. The system is simple and convenient to set up and use for routine QA/QC labs in the petrochemical and chemical industries.

## References


1. ASTM Method D2712, “Standard Test Method for Hydrocarbon Traces in Propylene Concentrates By Gas Chromatography”.
2. Roger Firor, “Trace Level Hydrocarbon Impurities in Ethylene and Propylene,” Agilent Technologies, publication 5965-7824E www.agilent.com/chem


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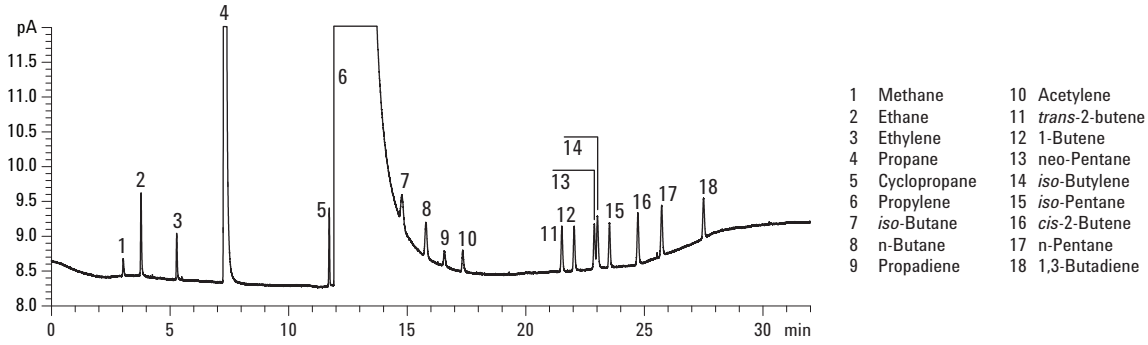


**Figure 6. One ppm level impurities in the propylene standard mix.**




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Agilent Technologies

# Determination of Low Level Hydrocarbon Impurities in Ethylene Using the Agilent 6820 Gas Chromatograph

Application

**Petrochemical**


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## Abstract

**A method for analyzing trace hydrocarbon impurities in ethylene is described. The method employs an Agilent 6820 gas chromatography (GC) system configured with a gas sampling valve, split/splitless inlet, and flame ionization detector. The Agilent Cerity Networked Data System for Chemical QA/QC was used to control the 6820 GC and to provide data acquisition and data analysis. An Agilent PLOT $Al_2O_3$ megabore column was used for separation of the trace hydrocarbons. Impurity levels at about 15 ppm were easily detected in ethylene. This method does not determine all possible impurities such as CO, $CO_2$, $H_2O$, alcohols, nitrogen oxides and carbonyl sulfide, nor hydrocarbons larger than decane.**


## Introduction

High purity ethylene is required as a feedstock for several manufacturing processes. The presence of trace amounts of certain hydrocarbon impurities can have deleterious effects on the catalysts used for conversion. For example, acetylene can be adsorbed at the active sites of the catalyst, resulting in catalyst deactivation. Dienes may reduce the rate of polymerization and adversely affect product quality. The availability of a suitable method for the determination of impurities in ethylene is critical to setting specifications, controlling internal quality, and performing development or research work.

It is difficult to detect trace level impurities by packed column. Presently, the American Society of Testing and Materials (ASTM) has published Method D6159 for the determination of trace hydrocarbon impurities in ethylene streams [1]. In this method, both an alumina porous layer open tubular (PLOT) column and a methyl silicone megabore column are used to improve the separation of methyl acetylene, *iso*-pentane, and n-pentane. In this application, an Agilent 50 m × 0.53 mm PLOT $Al_2O_3$ "M" deactivated column is used to provide resolution and effective sensitivity.

## Experimental

An Agilent 6820 GC system was used for this work. Configured with a split/splitless capillary inlet and a flame ionization detector (FID), gas samples were injected using an automatic gas sample valve heated to 80 °C. The sample loop volume was 0.25 mL. The gas sample valve was connected to the inlet using an aluminum-jacketed stainless steel tube that maintains the sample temperature during transfer from the sample loop. The configuration used for ethylene analysis is shown in Figure 1.

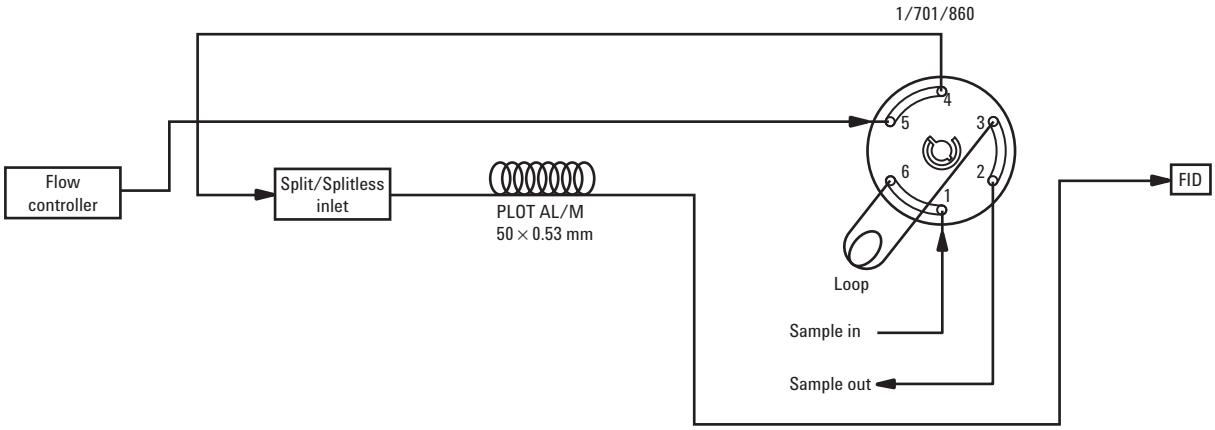


**Figure 1. Configuration diagram.**

An Agilent 50 m × 0.53 mm PLOT $Al_2O_3$ "M" deactivated column was used. The sample was run in the split mode using an Agilent split liner (Agilent part number 19251-60540) and an Agilent advanced green septum (Agilent part number 5183-4759).

The Agilent Cerity NDS for Chemical QA/QC was used for instrument control, data acquisition, and data analysis. Data was acquired at 20 Hz.

**Table 1. Instrument Conditions**

| | |
|---|---|
| Split/Splitless inlet | 175 °C, split mode, with 10:1 Split ratio |
| Valve | Gas sample valve, 6-Port, option 701 |
| Valve temperature | 80 °C |
| Sample loop | 0.25 mL |
| Column flow (He) | 6 mL/min |
| Column | PLOT $Al_2O_3$ "M" 50 m × 0.53 mm × 0.25 µm (p/n: 19095P-M25) |
| | |
| Oven | 35 °C (2 min) with 4 °C/min to 140 °C (5 min) |
| Detector | FID, 300 °C |
| $H_2$ | 35 mL/min |
| Air | 350 mL/min |
| Makeup gas ($N_2$) | 19 mL/min |

An ethylene standard mix (DCG Partnership I, LTD., Pearland, TX 77581) was used, consisting of the components listed in Table 2 at the certified concentrations shown (mole fraction).

**Table 2. Ethylene Sample Mix Components**

| Compound | Concentrations (ppm) | Compound | Concentrations (ppm) |
|---|---|---|---|
| 1. Methane | 998 | 9. *trans*-2-butene | 997 |
| 2. Ethane | 981 | 10. Butene-1 | 1000 |
| 3. Propane | 999 | 11. *iso*-Butylene | 983 |
| 4. Propylene | 1001 | 12. c*is*-2-Butene | 986 |
| 5. Acetylene | 981 | 13. Propyne | 1006 |
| 6. *iso*-Butane | 978 | 14. 1,3-Butadiene | 1003 |
| 7. Allene | 1001 | Ethylene | Balance |
| 8. n-Butane | 1000 | | |

A dynamic blending system (Figure 2) was used to quantitatively dilute the sample with helium.

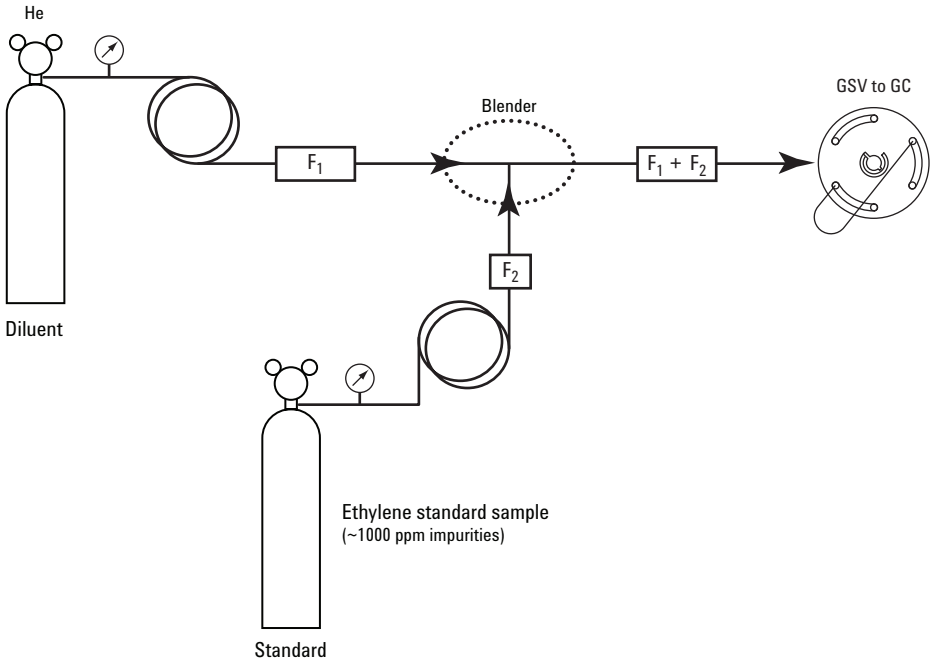


**Figure 2. Dynamic blending scheme.**

Diluted standard blend concentration is calculated by the following formula:

$C = C_o * F_2/(F_1+F_2)$

Where:
C: is diluted component concentration in ppm
$C_o$: original component concentration in standard blend in ppm
$F_1$: helium flow (mL/min)
$F_2$: propylene standard blend flow (mL/min)

## Results and Discussion

### Repeatability of Trace Level Impurities in Ethylene Analyses

Figure 3 shows the chromatogram from the blended sample. The PLOT $Al_2O_3$ column exhibits excellent separation for the C1 through C4 isomers [2]. The concentrations of most components are about 16 ppm. These trace level hydrocarbon impurities have a good FID response and are easily detected with baseline separation for most. In this method, the hydrocarbon impurities are determined and the total impurities are used to determine the ethylene content. Even in the trace level impurities, the Agilent 6820 GC system demonstrated good repeatability, as shown in Table 3.

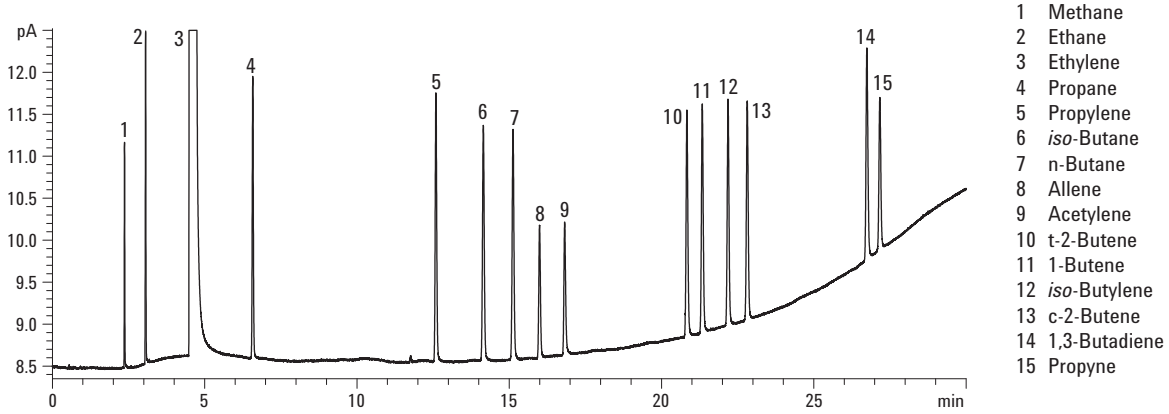


**Figure 3. Sixteen ppm level impurities in the ethylene standard mix.**

**Table 3. System Repeatability of Three Runs for Diluted Ethylene Standard Mix**

| Component | Amt1 | Amt2 | Amt3 | Avg.(ppmV) | RSD(%) | Repeatability criteria[1] (ASTM) |
|---|---|---|---|---|---|---|
| Methane | 16.28 | 16.19 | 16.03 | 16.17 | 0.80 | $0.02277 \times (ppmV^{0.6})$ |
| Ethane | 15.98 | 15.94 | 15.75 | 15.89 | 0.76 | $0.03811 \times ppmV$ |
| Propane | 16.26 | 16.22 | 16.07 | 16.18 | 0.63 | $0.03273 \times (ppmV + 21.23)$ |
| Propylene | 16.45 | 15.98 | 16.22 | 16.22 | 1.46 | $0.04780 \times ppmV^{1.15}$ |
| Isobutane | 15.97 | 16.02 | 15.69 | 15.89 | 1.10 | $0.04370 \times ppmV^{1.07}$ |
| n-Butane | 15.98 | 15.96 | 15.59 | 15.84 | 1.37 | $0.1156 \times ppmV^{0.85}$ |
| Allene | 16.38 | 16.32 | 15.95 | 16.22 | 1.42 | $0.05091 \times (ppmV + 0.7831)$ |
| Acetylene | 15.92 | 16.31 | 16.37 | 16.20 | 1.49 | $0.1189 \times ppmV \times 0.8$ |
| t-2-Butene | 16.27 | 16.30 | 15.88 | 16.15 | 1.45 | $0.063960 \times ppmV^{0.95}$ |
| 1-Butene | 16.36 | 16.34 | 15.90 | 16.20 | 1.62 | $0.03992 \times (ppmV + 17.14)$ |
| *iso*-Butylene | 16.12 | 16.05 | 15.60 | 15.92 | 1.77 | $0.1229 \times ppmV^{0.85}$ |
| c-2-Butene | 16.17 | 16.07 | 15.68 | 15.97 | 1.62 | $0.08350 \times ppmV^{0.93}$ |
| 1,3-Butadiene | 16.51 | 16.43 | 15.95 | 16.30 | 1.85 | $0.07518 \times ppmV^{0.9}$ |
| Propyne | 16.34 | 16.22 | 16.18 | 16.25 | 0.52 | $0.05205 \times ppmV^{1.1}$ |

[1]Ethylene repeatability (ASTM)-The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run and in the normal and correct operation of the test method, exceed the values in only 1 case in 20, where ppmV is the concentration of the component..

## Conclusions

The Agilent 6820 gas chromatograph configured with a 6-port gas sampling valve interfaced directly to a split/splitless inlet was used to analyze trace hydrocarbon impurities in ethylene with FID. Impurities, about 15 ppm mole % level, can be easily quantitated and show good repeatability. The Agilent 6820 system with Cerity can simultaneously acquire and quantitate both large concentrations (99 + mole %) and trace (low ppm) levels in a single run due to the use of a full dynamic range digital signal path. Manual range changes are not required. The system is simple and convenient to set up and use for routine QA/QC lab in the petrochemical and chemical industries.

## References


1. ASTM Method D6159, “Standard Test Method for Determination of Hydrocarbon Impurities in Ethylene By Gas Chromatography”
2. Roger Firor, “Trace Level Hydrocarbon Impurities in Ethylene and Propylene,” Agilent Technologies, publication 5965-7824E www.agilent.com/chem


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**Agilent Technologies**

# Use of the New 5973 inert for Determination of Low-Level Volatile Sulfur in Gaseous Streams

Application

**Gas Chromatography**


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## Abstract

**The enhanced inertness of the new 5973 inert MSD improves analysis of trace level volatile sulfur compounds. When operated in scan or selected ion monitoring mode, excellent sensitivity, selectivity, and peak symmetry are obtained for active compounds. Eight volatile sulfur species are used to demonstrate these attributes in a variety of hydrocarbon matrices. The system is well suited for the characterization of fuel feedstocks and basic petrochemicals, where impurities can poison critical catalytic processes or affect product quality.**


## Introduction

Sulfur detectors find widespread use in a broad range of applications that span across many industries. Demand for low-level sulfur detection will only increase in the future in response to more stringent quality control and regulation. The significance and need for low-level sulfur measurements are detailed in previous Agilent application literature [1, 2, 3, 4].

The mass selective detector (MSD) is usually not considered first when the need for low-level volatile sulfur quantitation and speciation arises in the analytical laboratory. Selective detectors such as the flame photometric detector (FPD), pulsed flame photometric detector (PFPD), and sulfur chemilumiscence detector (SCD) have traditionally dominated these applications [1]. The 6890N/5973 inert GC/MSD system is a very capable alternative to these detectors, providing optimized inertness and the benefit of positive compound identification. This applicaton note details how to set up the system for optimum sensitivity and selectivity. The specific hardware configuration is applicable to a wide range of applications where ppb detection of gaseous analytes is required.

A common problem with many sulfur selective detectors is hydrocarbon interference, especially from co-elution [4]. The measurement challenge is acute when the interfering hydrocarbon comprises the majority of the sample, as in the analysis of impurities in ethylene and propylene. In most cases, an accurate determination of the sulfur compound is not possible. However, the use of the 5973 inert in selected ion monitoring (SIM) mode can largely overcome quenching caused by co-elution for many applications.

## Experimental

The 5973 inert equipped with a new deactivated source was used for all experiments. The 3-mm drawout lens was used to achieve low ppb sensitivity while maintaining linearity over the ppb to low ppm concentration range needed for most sulfur measurements.

The sulfur calibration mix consisted of the following components at 5 ppm each: hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, carbonyl sulfide, t-butyl mercaptan, and tetrahydrothiophene. The blend in helium was purchased from DCG Partnership, Pearland, TX.

A 6-port gas-sampling valve was connected directly to the volatiles interface on the 6890N with Siltek™ 1/16-inch tubing. See the sample introduction diagram in Figure 1. The sample loop, tubing, and inlet are Siltek treated for inertness.

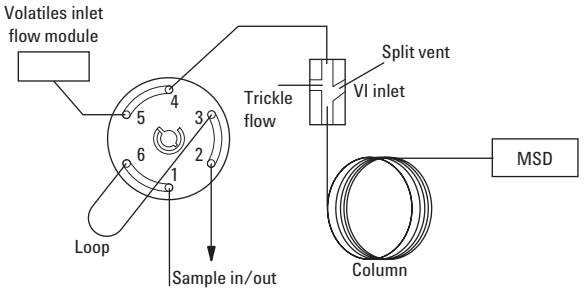


**Figure 1. Sample introduction scheme.**

Gaseous blends of the sulfur standard in helium or other matrices such as natural gas, propylene, and refinery gas were prepared using dynamic blending at the point and time of use. Diluent (matrix) gases are mixed with the calibration standard using an Aux EPC module on the 6890N GC. This system and the hardware employed have been described in detail [2].

Positioning of the column in the MSD must be carefully done to avoid loss of sulfur sensitivity. To position the column just inside the source, 2 mm to 3 mm of the column should be visible at the MSD end of the transfer line. See Reference 5 for installation details. See Table 1 for instrument conditions.

## Results and Discussion

### System Calibration

First, the system was calibrated and checked for linearity by analyzing the sulfur mix at various concentrations. The dynamic blending system was used to prepare seven and five level calibrations using helium and natural gas as diluents, respectively. Table 2 lists the concentrations used. Calibrations were focused in the ppb range since this is where most analytical problems for sulfur analysis are found. SIM acquisition mode was used.

**Table 1. Instrument Conditions**

| **6890N GC** | |
|---|---|
| **Injection port** | **Volatiles interface** |
| Temperature | 150 °C |
| Split ratios | 1:1 up to 50:1 |
| Carrier gas | Helium |
| Constant Flow Mode | 1.9 mL/min |
| **Injection source** | **6-port gas sampling valve** |
| Material | Hastelloy C |
| Temperature | 150 °C |
| Loop | Siltek, 0.5 cc |
| **Column** | **60 m × 0.320 mm × 5.0 µm DB-1** |
| Initial temperature | 40 °C |
| Initial time | 5 min |
| Temperature ramp | 25 °C/min |
| Final temperature | 270 °C |
| Final time | 2 min |

| **5973 *inert* MSD** | |
|---|---|
| Mass range | 33–100 and 12–100 amu |
| Scans | 13.1/s and 15.9/s |
| Samples | 2 |
| Threshold | 150 |
| EM Voltage | BFB.U tune voltage |
| Solvent delay | 3.00 min |
| Source | Surface deactivated |
| Drawout lens | 3 mm |
| Source temperature | 230 °C |
| Quad temperature | 150 °C |
| Transfer line | 280 °C |

Calibrations are linear in both matrices for all eight sulfur compounds. Refer to Table 3 where the regression coefficient $r^2$ values are shown. This is an indication that not only is the system response linear, but also that adsorption is not occurring in the GC or MSD from active sites. If adsorption were present, then one would expect a drop off at the lower end of the calibration curve. This is a direct benefit of the new inert MSD source.

Two calibration plots, as produced by the MSD ChemStation, are shown in Figures 2 and 3 for the calibration of $H_2S$ and COS in natural gas, respectively. These are two challenging compounds with respect to activity, and they help illustrate the effectiveness of the inert system.

### The 3-mm Drawout Lens

The 3-mm lens offers excellent sensitivity-optimized performance for this application. The 3-mm drawout was chosen for this work to meet the objective of reliable low ppb sulfur analysis. In addition, linearity over only a part of the MSD's dynamic range was required. Calibrations from 20 ppb to 5 ppm cover expected impurity ranges in real world samples and show excellent linearity with the 3-mm lens including samples run in a natural gas matrix where significant hydrocarbon fragmentation occurs.

**Table 2. Calibration Levels for Checking System Linearity. Sulfur Concentrations in ppb.**

| Cal Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Conc. in helium | 21 | 35 | 46 | 57 | 95 | 1600 | 3600 |
| Conc. in nat gas | 88 | 242 | 475 | 880 | 1170 | -- | -- |

**Table 3. Calibration Regression Coefficient $r^2$ Values**

| Compound | Helium | Natural gas |
|---|---|---|
| $H_2S$ | 0.998 | 0.998 |
| COS | 0.998 | 0.999 |
| $CH_3SH$ | 0.997 | 0.999 |
| EtSH | 0.996 | 0.998 |
| DMS | 0.998 | 0.998 |
| CS2 | 0.998 | 0.998 |
| t-ButylSH | 0.996 | 0.993 |
| THT | 0.996 | 0.992 |

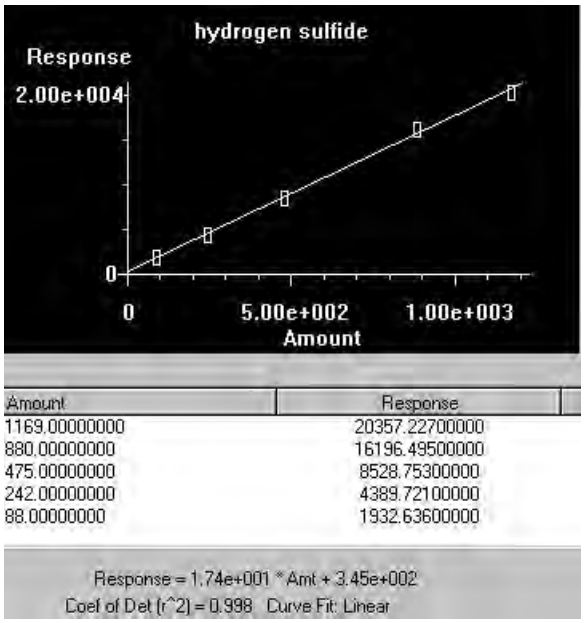


**Figure 2. Five level calibration plot of $H_2S$ in natural gas diluent. Calibration range is from 88 ppb to 1170 ppb.**

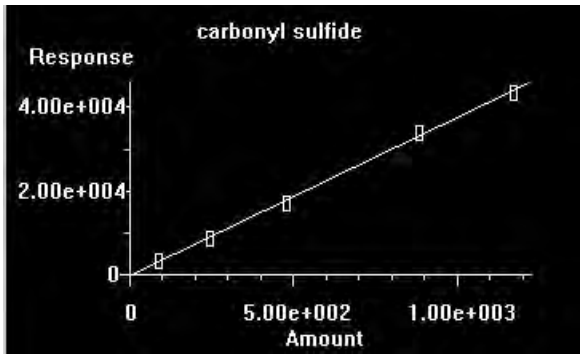


**Figure 3. Five level calibration plot of COS in natural gas diluent. Calibraton range is from 88 ppb to 1170 ppb.**

### Scan Results

The total ion chromatogram (TIC) of the eight-component sulfur mix at 1.3 ppm in helium using a split ratio of 0.5 to 1 is shown in Figure 4. As is evident in the figure, $H_2S$ is close to the minimum detection level (MDL) for this particular set of operating conditions. Symmetric peak shapes are seen for all components including adsorptive $H_2S$ and COS.

### Application of SIM

SIM provides the best sensitivity and selectivity for target analytes. Since sulfur determinations will normally be done in hydrocarbon matrices, care must be taken to select ions that ideally have no hydrocarbon contribution. If this can be done, excellent selectivity can be achieved even in cases where co-elution of sulfur species and hydrocarbon occur. This is an important distinction and advantage of the MSD compared to some of the common gas chromatographic sulfur selective detectors. Both the FPD and PFPD will suffer from quenching if co-elution occurs, making accurate quantitation of low-level sulfur problematic [2]. Even the SCD will have problems measuring low ppm sulfur in the presence of a dominant co-eluting hydrocarbon. In situations where a unique sulfur ion cannot be found, refinement of the method and chromatographic column/conditions to achieve separation from the interfering hydrocarbon should be attempted [2]. Also, when operating the MSD in SIM mode, it is usually best to select low resolution for maximum sensitivity at the expense of some resolution loss.

Refer to Reference 6 for guidelines for setting SIM parameters and instructions on using the AutoSIM feature available in the MSD ChemStation, G1701DA.

The SIM ions used for each sulfur compound are listed in Table 4. These ions were chosen to minimize interference from hydrocarbons. To arrive at the ions shown in the table, a scan of the sulfur mix in helium is acquired to identify target ions. Library spectra can also be consulted. Hydrocarbon mixes, such as natural gas and refinery gas, are then run separately using the SIM table to look for ions that may match those selected for sulfur. The table may be further refined if hydrocarbon interferences appear. These are not the only possible ions that can be used. For some of the compounds, other choices or additional ions could be included in the SIM table. While not necessary for this relatively simple sulfur example, the use of second and third qualifier ions may give the analyst a higher level of confidence of a compound's identity by comparing ion ratios to library spectra for a particular compound.

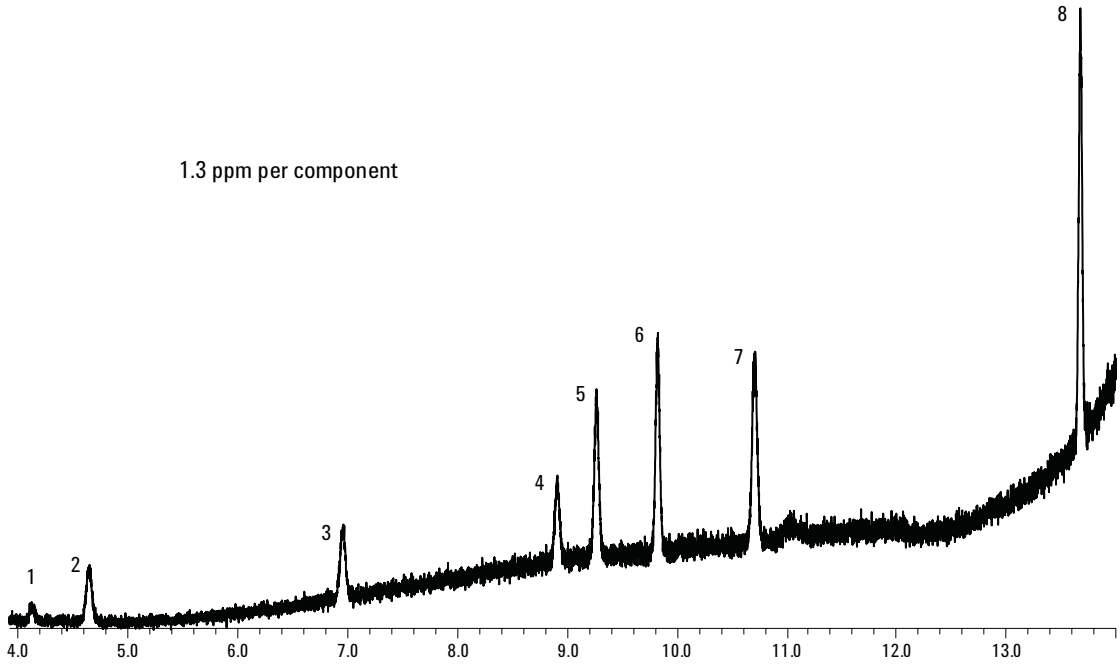


**Figure 4. TIC of the eight-component sulfur mix at 1.3 ppm per component. Scan 33–100 amu. Peak labels: 1. hydrogen sulfide, 2. carbonyl sulfide, 3. methyl mercaptan, 4. ethyl mercaptan, 5. dimethyl sulfide, 6. carbon disulfide, 7. t-butyl sulfide, 8. tetrahydrothiophene.**

**Table 4. Optimized SIM Table for Selective Sulfur Detection in Hydrocarbon Streams. Dwell Time for Each Ion is 100 ms.**

| Group | Start time (min) | Target and qualifier ions | Compound |
|---|---|---|---|
| 1 | 3.00 | 33,34 | $H_2S$ |
| 2 | 4.20 | 60 | COS |
| 3 | 6.00 | 45,47 | MeSH |
| 4 | 8.00 | 47 | EtSH |
| 5 | 9.10 | 45,47,62 | DMS |
| 6 | 9.70 | 44,76 | $CS_2$ |
| 7 | 10.20 | 57,90 | t-ButylSH |
| 8 | 11.80 | 45,60,88 | THT |

The sulfur mix chromatogram shown in Figure 5 was produced using the SIM parameters shown in Table 4. The offsets seen in the baseline are a result of the MSD switching from group to group and are not chromatographic. Excellent signal-to-noise and peak shape are seen for all components at the 46-ppb level. The sulfur mix was then further diluted to 16 ppb per component. The resulting chromatograms for $H_2S$, COS, and THT, the most challenging analytes, appear in Figure 6. At these levels, any problems with system or source activity would be evident. Sensitivity and peak shape are maintained, indicating excellent source inertness.

### Natural Gas and Refinery Gas: Composition and Impurities

The TIC of a natural gas scan and sulfur mix SIM runs are overlaid for illustration purposes in Figure 7. Note that with the 60 m × 0.32 mm × 5.0 µm DB-1 all hydrocarbons and $CO_2$ are separated. Natural gas compounds in order of elution are: $O_2/N_2$, $CH_4$, $CO_2$, ethane, propane, I-butane, N-butane, I-pentane, and N-pentane. From the overlay, it can be seen that seven of the eight sulfurs do not co-elute with natural gas components; only COS and propane have nearly identical retention times. Even with co-elution, SIM makes it possible to quantify the COS; this will be addressed in the following section on propylene impurities.

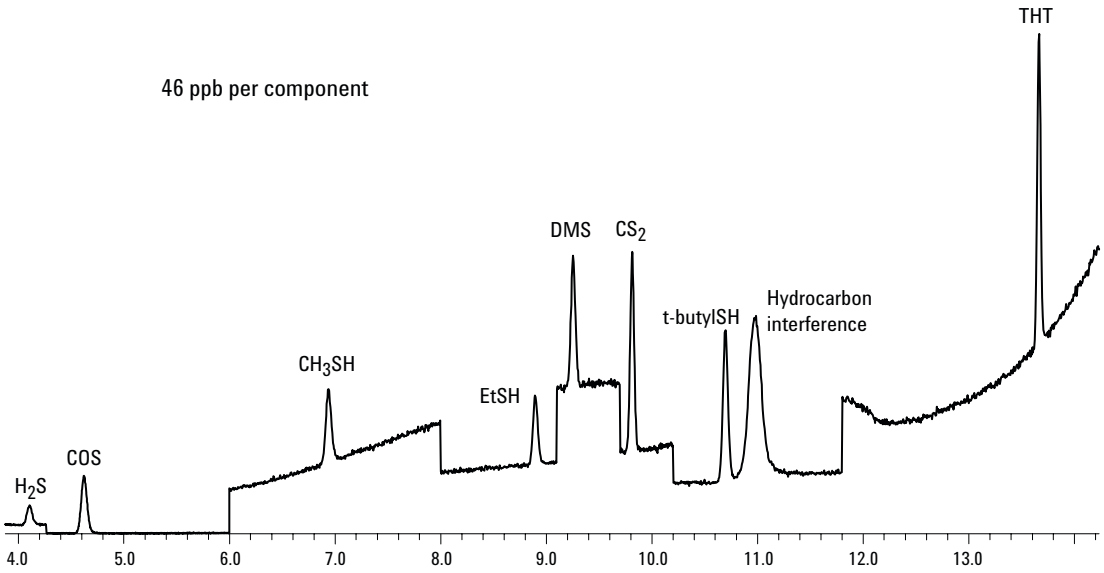


**Figure 5. Eight-component sulfur mix in helium at 46 ppb per component in SIM mode. Split ratio 0.5:1. Refer to Figure 4 for peak identification.**

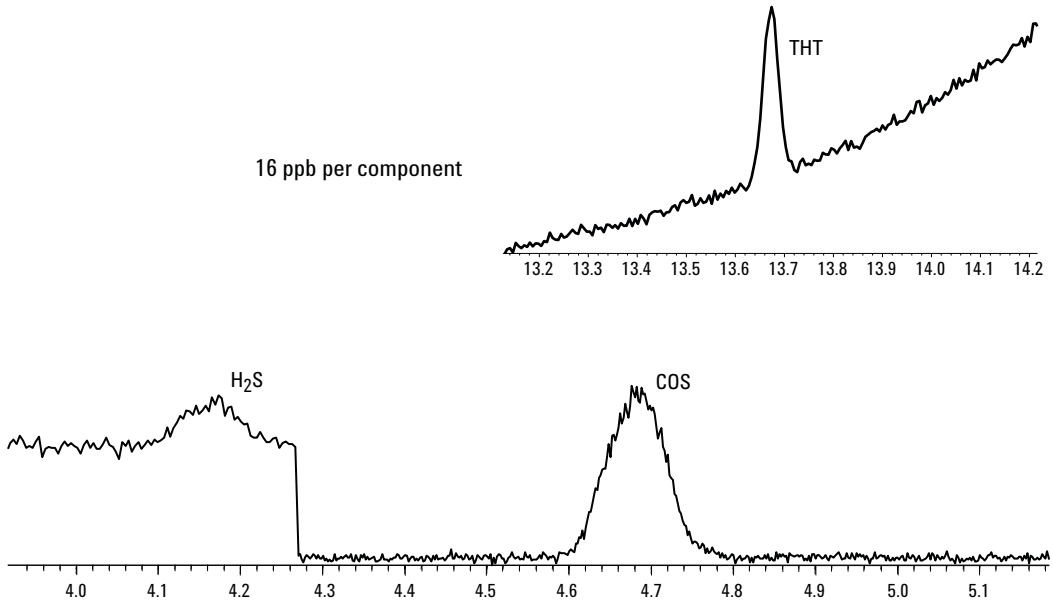


**Figure 6. $H_2S$, COS and tetrahydrothiophene (insert) at 16 ppb each.**

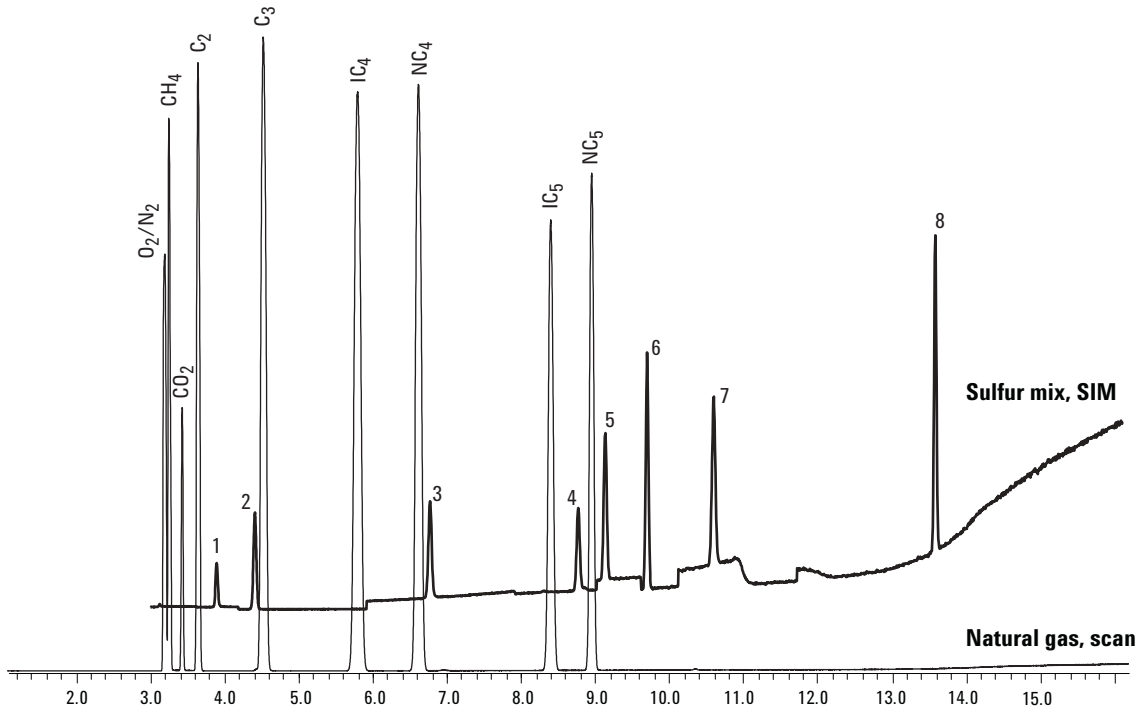


**Figure 7. Overlay of two runs: natural gas scan (12–100 amu), and sulfur mix at 4.5 ppm in SIM mode. Split ratio 20:1. Peak numbering same as Figure 4.**

Low level (350 ppb) sulfur gases in a representative refinery gas matrix are shown in Figure 8. Again, good peak shape and signal-to-noise are seen. Only methyl mercaptan is lost to hydrocarbon interference.

### Analysis of COS in Propylene

Measurement of ppb COS and $H_2S$ in propylene or propane can be challenging due to the co-elution of COS/propylene and the reactivity of $H_2S$. The COS co-elution is illustrated in Figure 9, where two independent separate runs are superimposed.

SIM (ion 60) was employed for the analysis of COS. To avoid overloading the source, the split ratio was increased to 50:1. To determine the effect of co-eluting propylene on COS response, two runs were performed at identical concentrations of 105 ppb COS. The diluents for the first and second runs were helium and propylene, respectively. Chromatograms for both runs are shown in Figure 10. The helium chromatogram shows the true COS area unaffected by co-elution. This area is then compared to that of COS in propylene diluent using the area ratio (COS propylene/COS helium) to indicate how co-elution has affected the 5973 inert response. This ratio of 0.77 indicates that COS in propylene response is suppressed by only 23% probably due to a reduction in ionization efficiency. Moreover, a subsequent experiment that constructed a five level calibration of COS in propylene showed linear behavior over the range of 20 ppb to 1200 ppb. Therefore, using a carefully constructed SIM method, the 5973 inert equipped with 3-mm drawout has the capability of quantifying ppb level COS in co-eluting propylene. Co-eluting active analytes do not preclude quantification even when concentration differences exceed 105 provided unique ions can be identified for the component of interest.

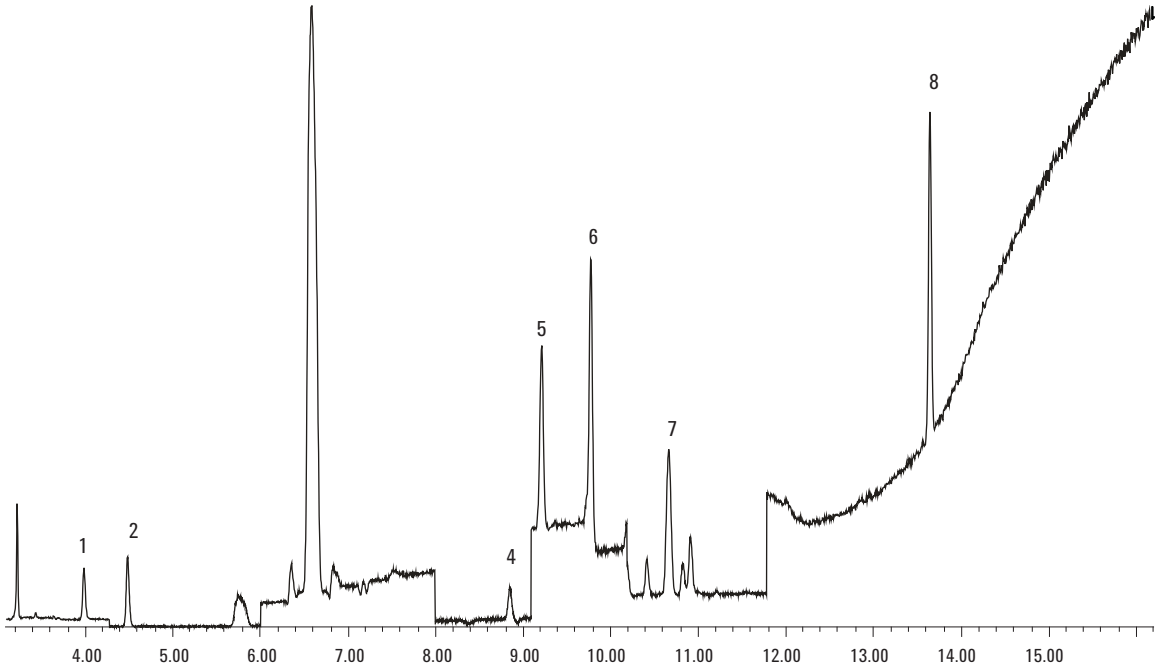


**Figure 8. Three hundred fifty ppb sulfur mix in refinery gas. Peak identifications same as Figure 4. Good peak symmetry and sensitivity seen.**

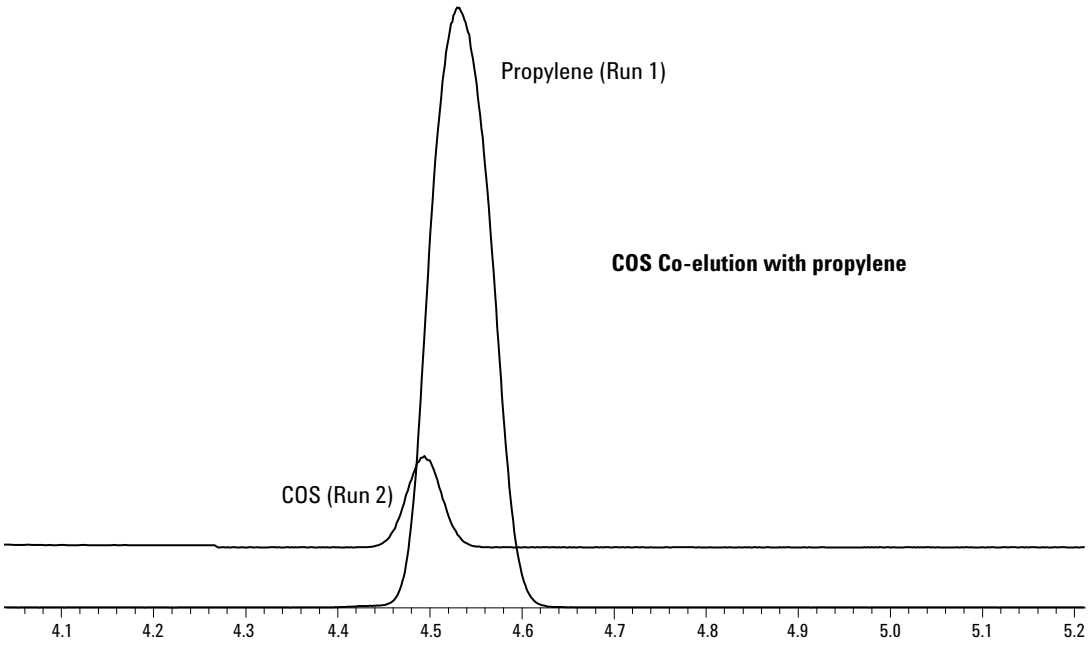


**Figure 9. Two separate chromatograms superimposed showing the co-elution of COS with propylene. Split ratio 50:1.**

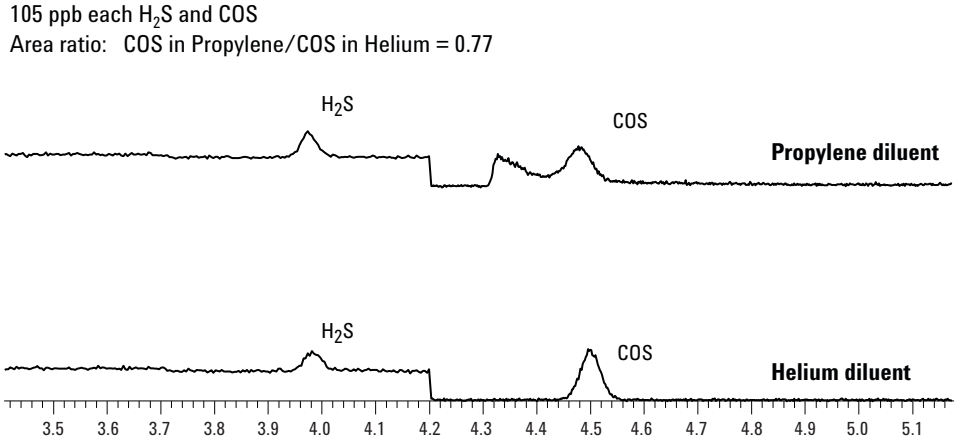


**Figure 10. Comparison of COS response (SIM mode) in helium and propylene. Split ratio 50:1.**

## Conclusions

The importance of inertness cannot be over emphasized when analyzing and quantifying ppb level volatile sulfur compounds. The 5973 inert has excellent capabilities as a sensitive, repeatable, and selective detector for active gaseous analytes at low levels. Sulfur detection at low ppb levels is easily achieved through use of a time programmed SIM table consisting of unique ions for the compounds of interest. This minimizes hydrocarbon interference making it possible to quantitate low-level analytes such as COS with co-eluting propylene.

Use of the new inert source leads to excellent detection limits of active, adsorptive compounds with minimal peak tailing. Good peak symmetry is maintained at the ppm and ppb level for $H_2S$, COS, and other light organo-sulfur compounds. Detection of low-level polar analytes in general will improve with the 5973 inert.

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Agilent Technologies

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

Application

**Hydrocarbon Processing**


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## Abstract

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


## Introduction

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

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

## Experimental

### Injection Device

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

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

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

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

**Guideline** for choosing Aux flow source

**7890AGC**

G3471A Pneumatic Control Module (PCM) or

G3470A Aux EPC module

**6890GC**

G1570A Aux EPC or

G2317A PCM module

The PCM is the preferred source for both GCs.

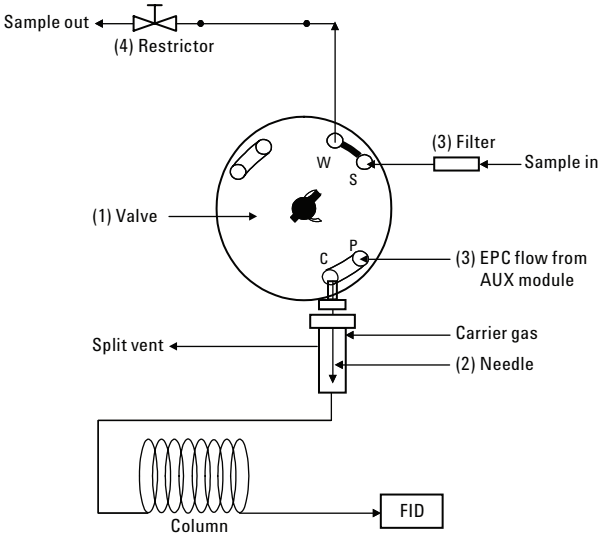



**Figure 1. Flow diagram of the HPLI device.**

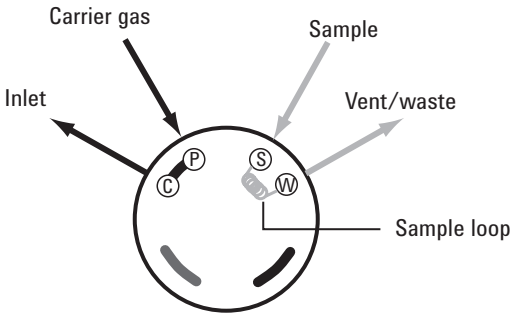
**Samples for System Evaluation**

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

**Operating Process**

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

**Load**




**Inject**

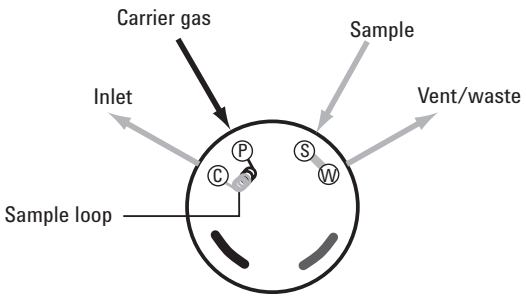



**Figure 2. Pneumatic and sample paths in load and inject positions.**

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

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

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

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

**Table 1. Instrumental Conditions**

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

**Table 2. Columns and Parameters**

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

## Results and Discussion

### Check for Carryover

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

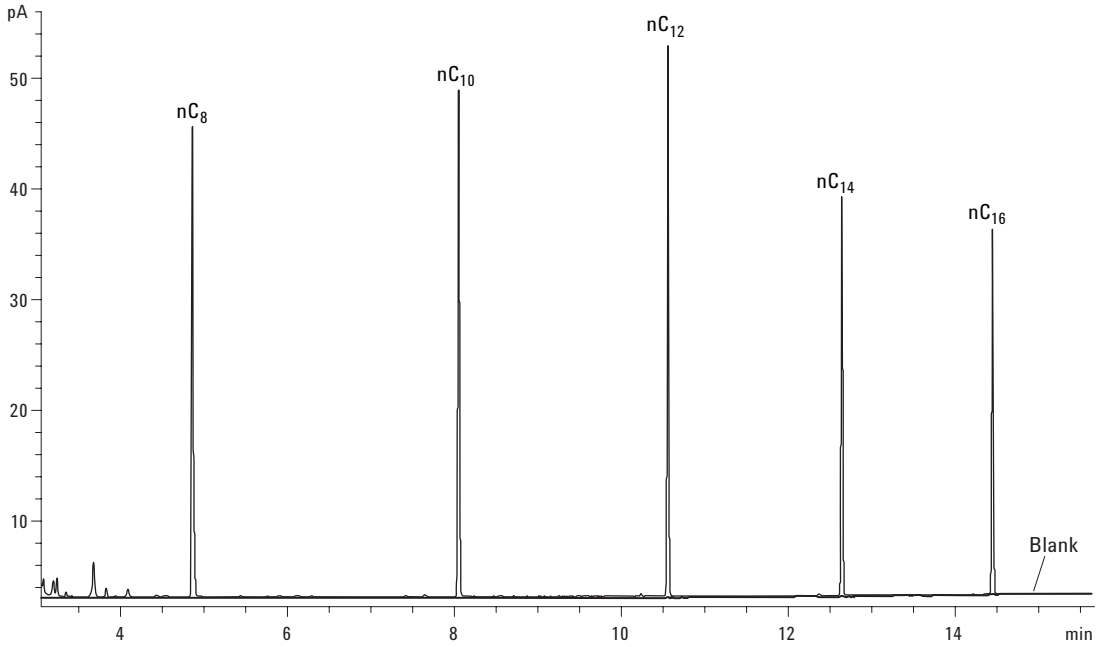



**Figure 4. Overlay of standard versus blank (100 ppm each in cyclohexane).**

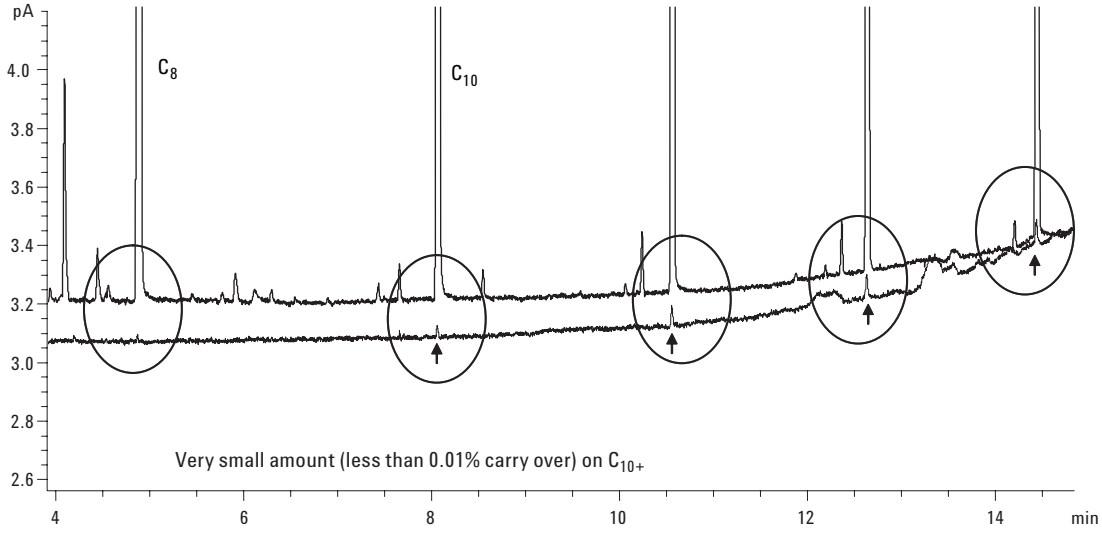



**Figure 5. Carryover less than 0.01% on $C_{10+}$.**

### Sample Analysis

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

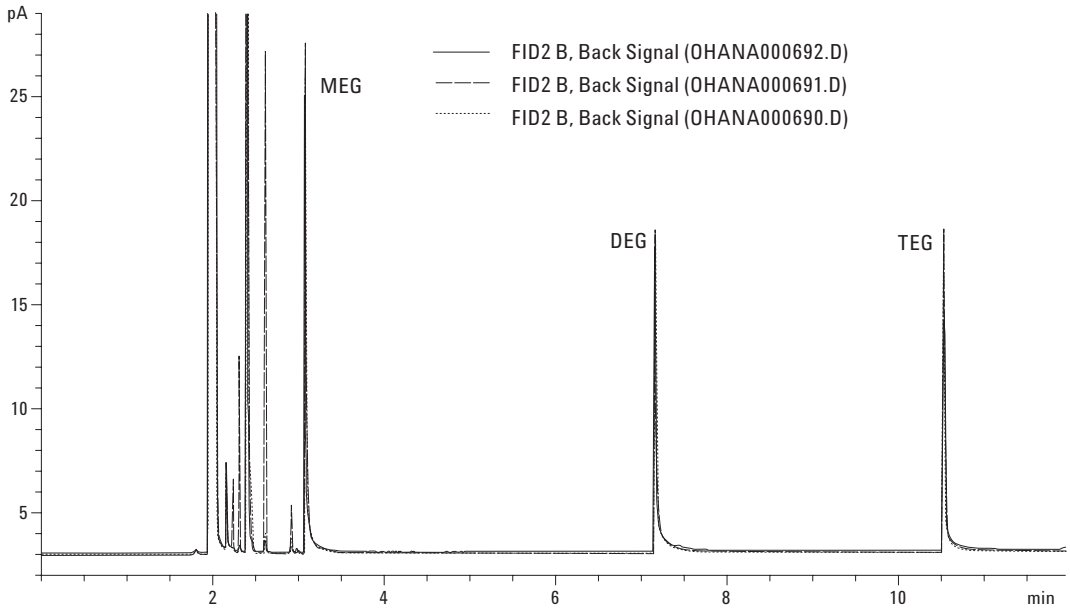



**Figure 6. Triplicate run of 100 ppm each of MEG, DEG, and TEG in IPA.**

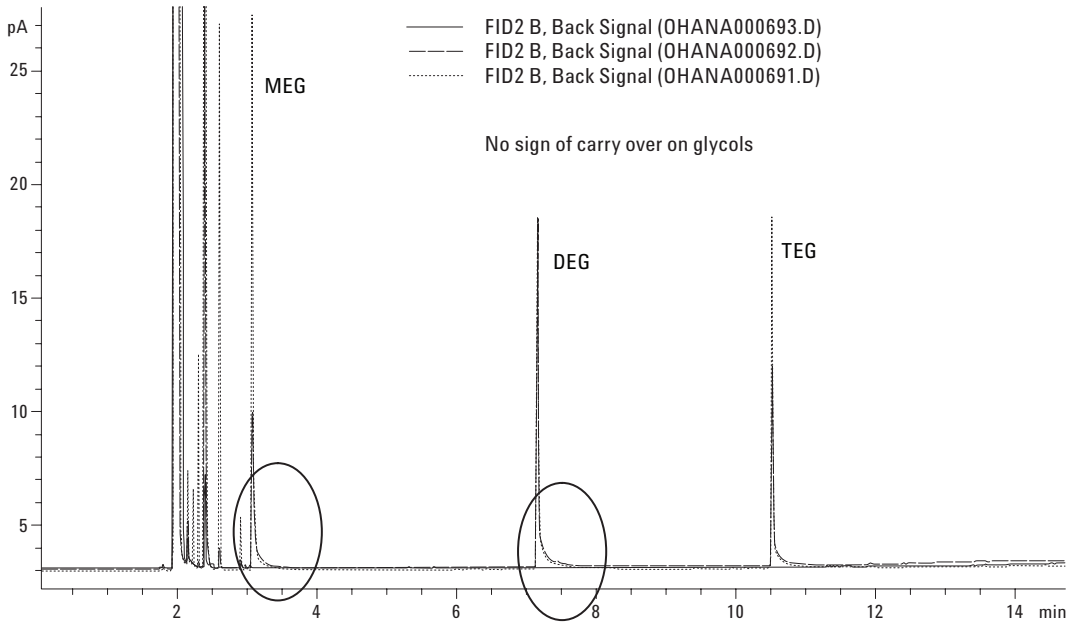



**Figure 7. Glycols versus blank. Two standard duplicates, blank run immediately after injection of standard.**

### A. Liquefied Natural Gas

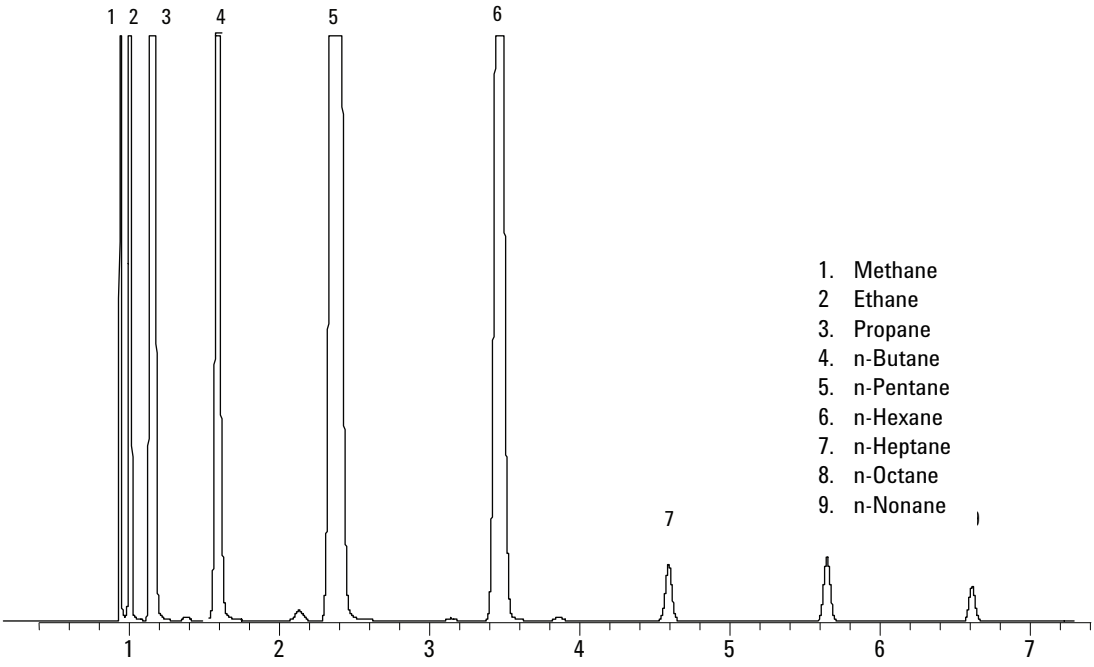



**Figure 8. Chromatogram of liquefied natual gas (calibration standard).**

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

**B. Liquefied Ethylene**

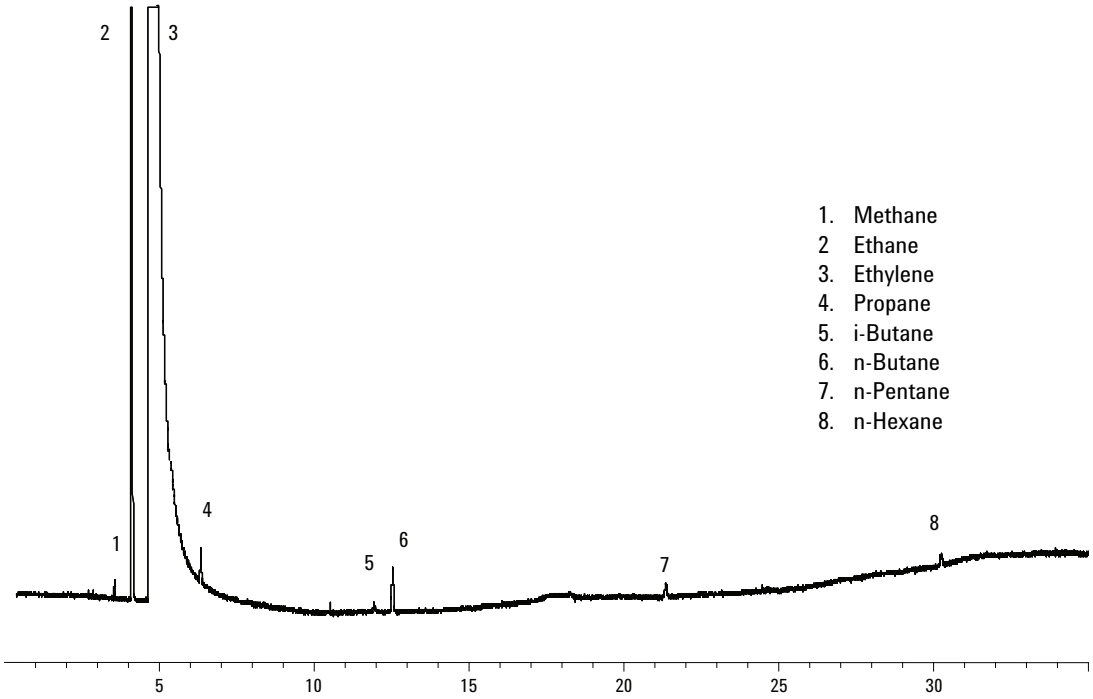



**Figure 9. Chromatogram of liquefied ethylene.**

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

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

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

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

### C. Pressurized Propylene

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

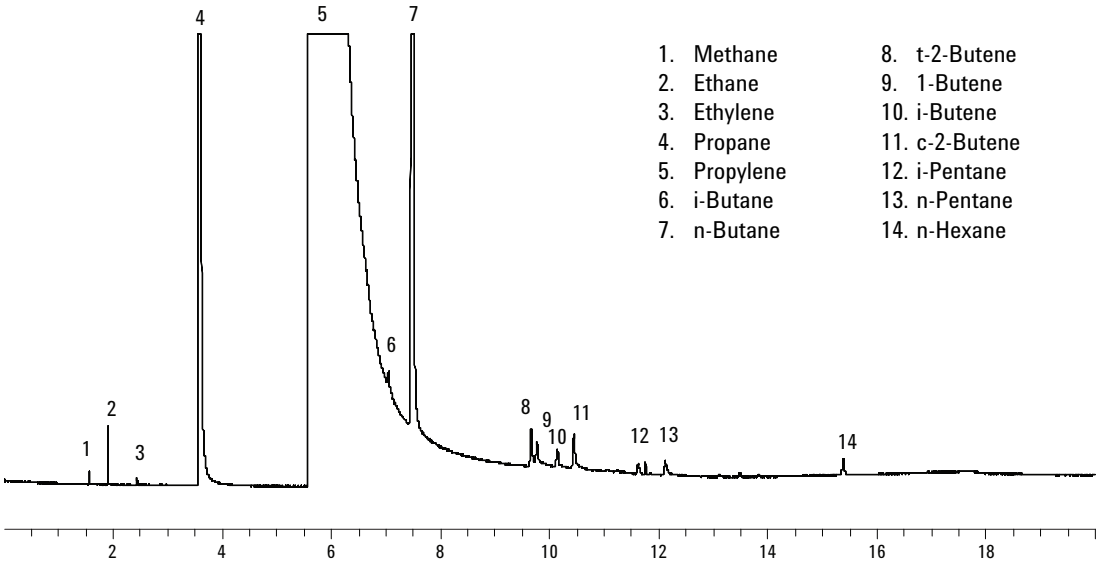



**Figure 10. Chromatogram of pressurized propylene.**

### D. Pressurized 1,3-Butadiene

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

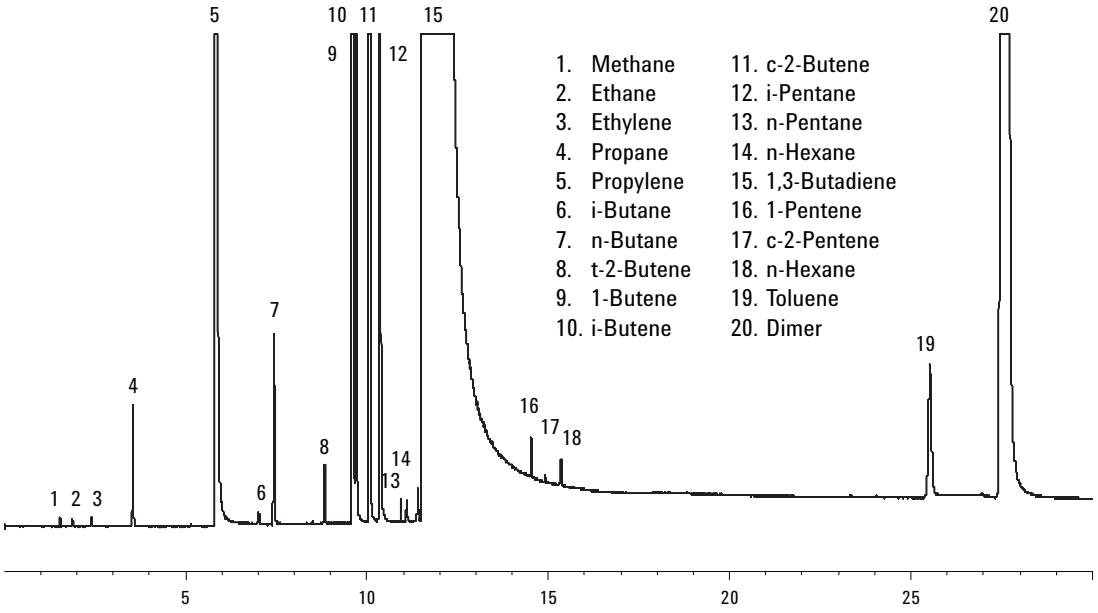



**Figure 11. Chromatogram of pressurized 1,3-butadiene.**

### E. Pressurized Propane + n-Butane

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

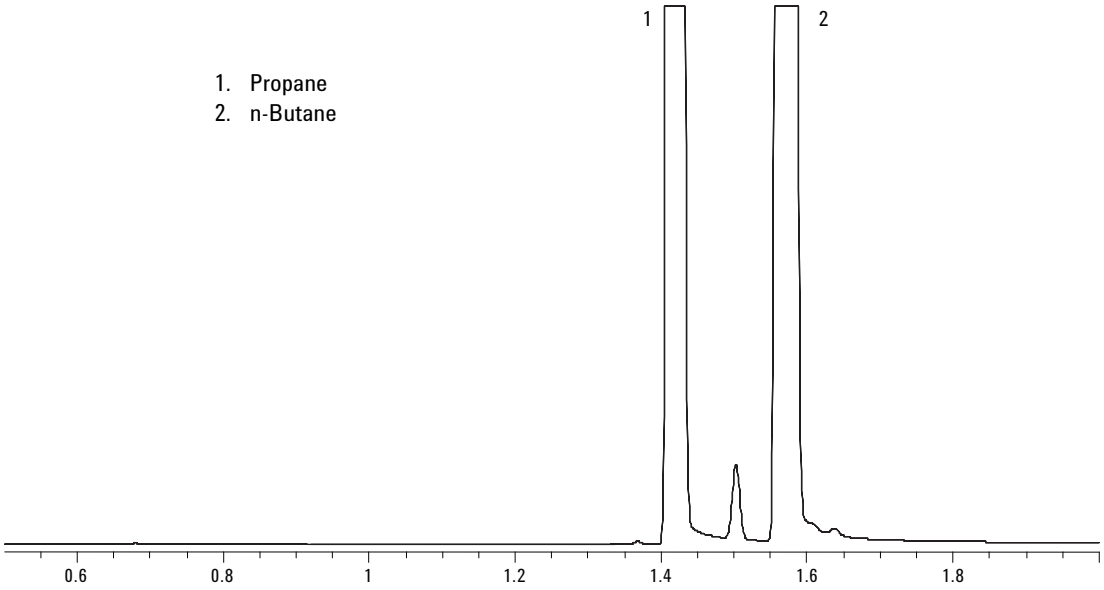



**Figure 12. Chromatogram of pressurized propane + n-butane.**

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

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

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

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

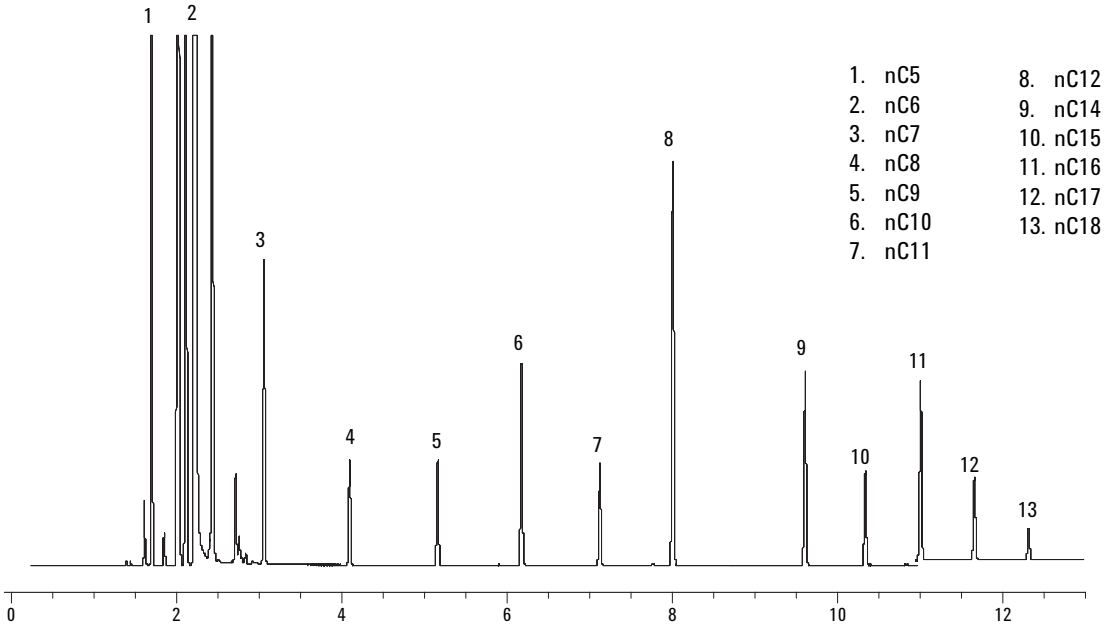



**Figure 13. Chromatogram of n-hexane + 1.0% BP standard.**

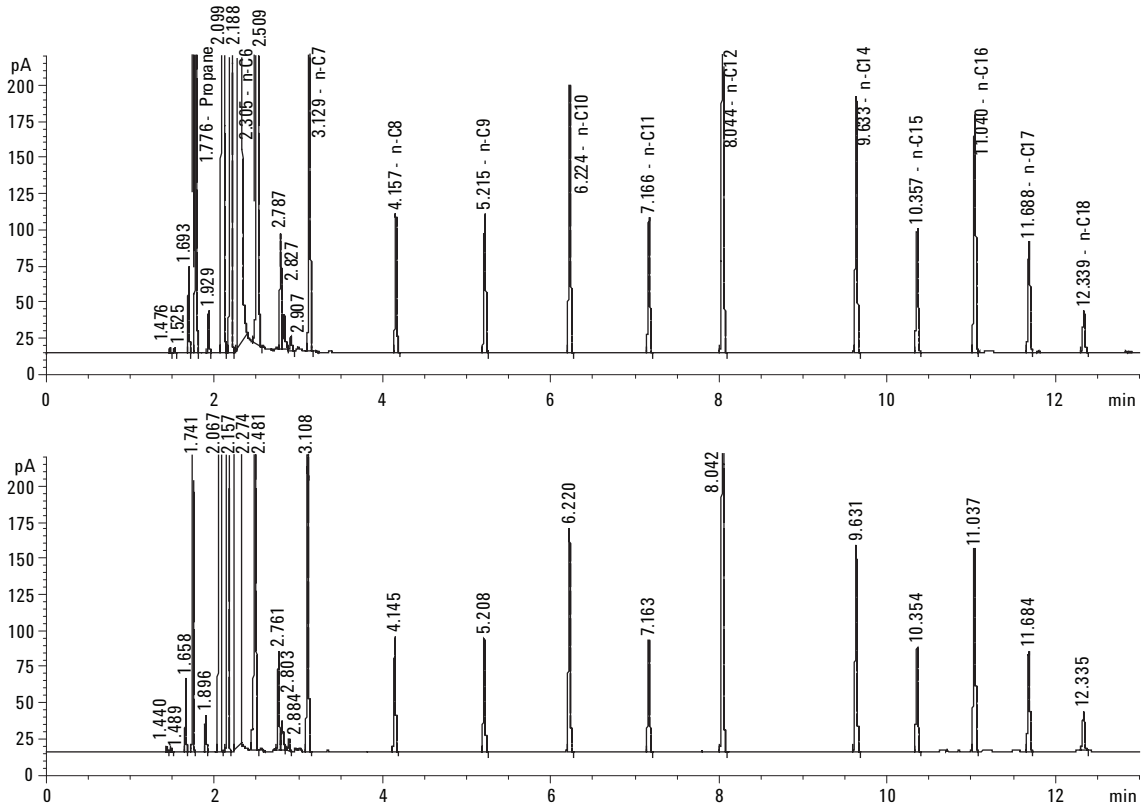



**Figure 14. Chromatograms of n-hexane + 1.0% BP standard. Top: HPLI. Bottom: ALS (syringe).**

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

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

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

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

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

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

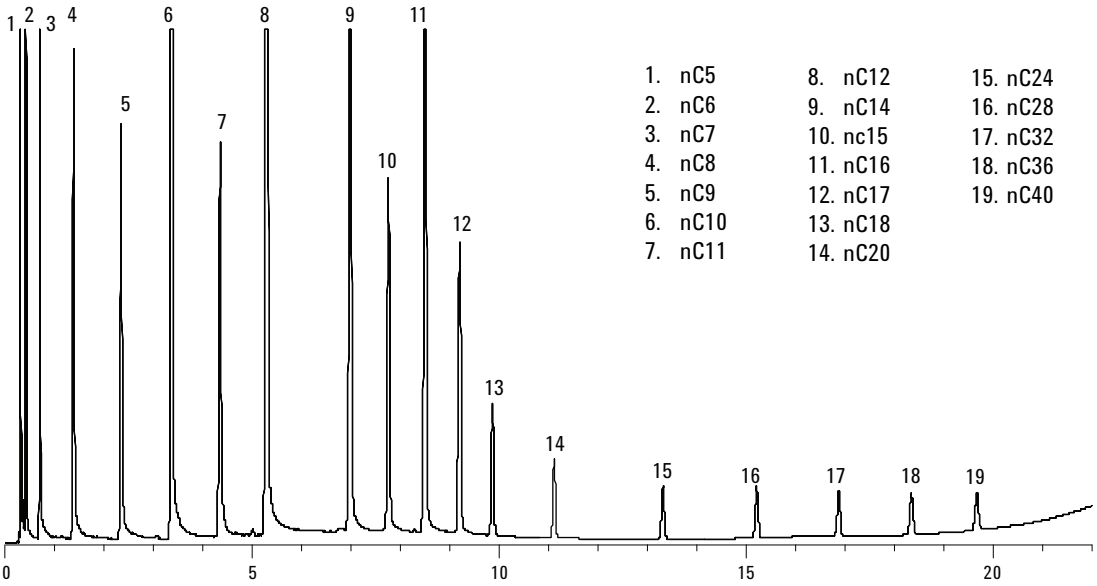



**Figure 15. Chromatogram of nC5-nC40 (D2887 BP standard diluted by $CS_2$).**

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

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

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

## Conclusions

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

## References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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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# Simultaneous Analysis of Trace Oxygenates and Hydrocarbons in Ethylene Feedstocks Using Agilent 7890A GC Capillary Flow Technology

## Application Brief

James McCurry

The presence of trace hydrocarbons in ethylene can have damaging effects on both the process catalysts and the final polymer products. Test methods such as ASTM D6159 are used to ensure the quality of these feedstocks [1]. However, the analysis of other key contaminants, such as oxygenates, requires GC methods that run on separate instruments. This can be time consuming and expensive for the process analysis lab.

The Agilent 7890A GC serves as the ideal platform when analyzing different classes of trace compounds in ethylene. Maximum productivity can be realized by:

- Using Capillary Flow Technology to perform analysis of trace oxygenates and hydrocarbons in a single run through 2-D Deans switch chromatography.
- Automating the preparation of multilevel calibration standards using the new auxiliary electronic pneumatics control (EPC) modules.
- Protecting the sensitive and expensive alumina PLOT column by preventing polar oxygenates from entering the column.

### Enhancing ASTM Method D6159 with Capillary Flow Technology 2-D GC

ASTM Method D6159 uses a methyl silicon column in series with an alumina PLOT column to resolve light hydrocarbons in ethylene. Polar oxygenated compounds cannot be analyzed on this column set because methyl silicon has insufficient selectivity and the alumina column will adsorb oxygenates, resulting in column damage. Wax-type liquid phases such as HP-INNOWax can easily separate polar compounds from light hydrocarbons using 2-D GC [2]. A wax column placed before an alumina column will retain polar compounds while the light hydrocarbons elute near the void volume. Therefore, if a Deans switch is placed between the columns, the hydrocarbons can be heart-cut from the wax to the alumina columns while oxygenates are held by the wax column. The optimized thermal and pneumatic performance of the Agilent 7890A Deans switch is a result of Capillary Flow Technology. This provides the high levels of retention time precision and narrow peak shape needed for optimal heart-cutting 2-D GC (Figure 1).

## Highlights

- The Agilent 7890A GC Capillary Flow Technology combined with enhanced electronic pneumatics control (EPC) provide greater productivity and flexibility in the analysis of trace contaminants in ethylene.
- Multiple auxiliary EPC channels provide the ability to automatically generate gas calibration standards for trace level impurities.
- Enhancement of ASTM D6159 method with 2-D GC Deans switching measures trace oxygenates and hydrocarbons in a single run.

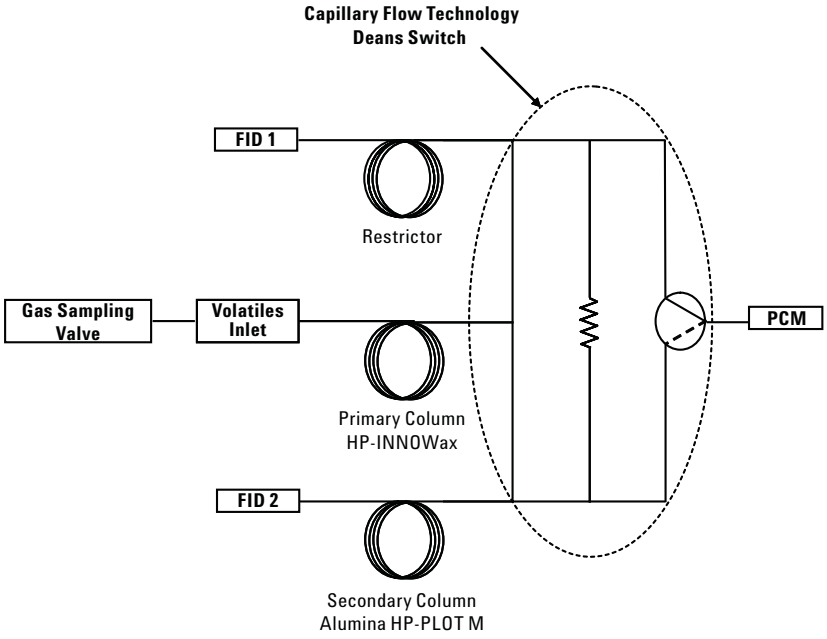


**Figure 1. Configuration of Agilent 7890A for the 2-D GC analysis of trace oxygenates and hydrocarbons in ethylene.**

### Method Parameters for Enhanced ASTM D6159 Method

| | |
|---|---|
| Primary column: | HP-INNOWax, 30 m × 0.32 mm id × 0.5 µm film (19091N-213) |
| Primary column flow: | Helium at 2.5 mL/min |
| Secondary column: | Alumina HP-PLOT M, 30 m × 0.53 mm id × 15 µm (19095P-M23) |
| Secondary column flow: | Helium at 6 mL/min |
| Oven temperature program: | 40 °C for 6 min, 4 °C/min to 125 °C |
| Volatiles inlet conditions: | 150 °C, 5:1 split |
| Sample loop: | 250 µL at 65 °C |
| Detector temperature: | 250 °C |
| Capillary Flow Technology: Deans switch cut time | 2.3 to 4.5 min |

### Automating the Preparation of Trace-Level Calibration Standards

Another advantage of the Agilent 7890A GC is the expanded capabilities in EPC. These extra channels of auxiliary EPC are used with the dynamic blending system hardware to allow automated preparation of ppmV gas standards for calibration. This approach has been described for the automated preparation of trace sulfur compounds in various gas matrices [3].

## Results

Figure 2 shows the 2-D GC analysis of methanol and C1 to C4 hydrocarbons in a sample of technical grade ethylene. The HP-INNOWax column first separates the polar methanol from the unresolved hydrocarbon peaks. The Deans switch transfers the hydrocarbons to the Agilent alumina HP-PLOT M column, where the C1 to C4 hydrocarbons are easily separated. This column is also shown to provide better separation of trace hydrocarbons from the large ethylene peaks, while maintaining excellent peak shape and intensity for the acetylene. The performance of this alumina column is maintained over many injections since the HP-INNOWax column prevents polar oxygenates (water, alcohols) from damaging the sensitive stationary phase. Table 1 shows very good precision using this method for a sample containing approximately 2 ppmV.

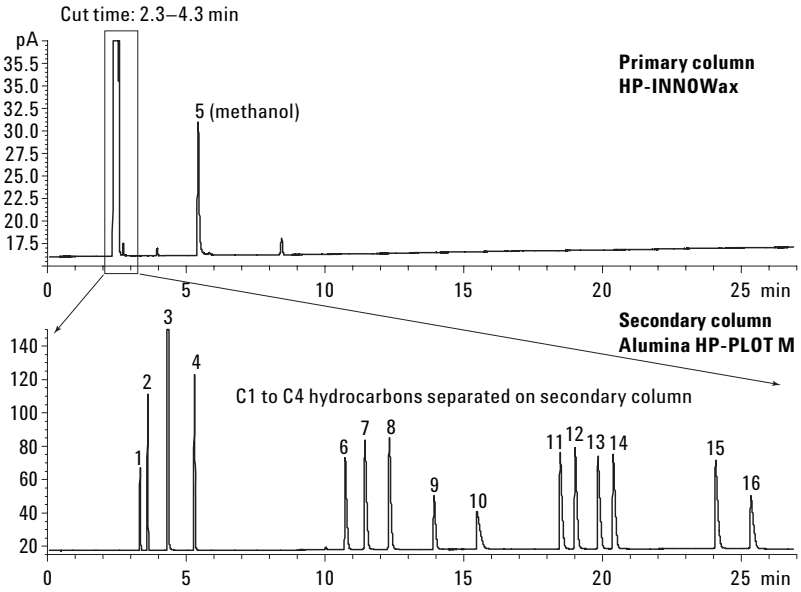


**Figure 2. Capillary Flow Technology Deans switch used to separate 100 ppmV oxygenate and hydrocarbon impurities in ethylene.**

**Table 1. Method Precision for 2-D GC Analysis of Ethylene Impurities**

| Peak No. | Name | Avg. (ppmV)* | Std Dev* | %RSD* |
|---|---|---|---|---|
| 1 | Methane | 2.1 | 0.011 | 0.5 |
| 2 | Ethane | 21.5 | 0.049 | 0.2 |
| 3 | Ethylene | Balance | Balance | Balance |
| 4 | Propane | 2.1 | 0.062 | 3.0 |
| 5 | Methanol | 2.1 | 0.081 | 3.8 |
| 6 | Propylene | 2.1 | 0.023 | 1.1 |
| 7 | Isobutane | 2.1 | 0.015 | 0.7 |
| 8 | n-Butane | 2.0 | 0.011 | 0.5 |
| 9 | Propadiene | 2.1 | 0.025 | 1.2 |
| 10 | Acetylene | 1.9 | 0.036 | 1.9 |
| 11 | Tran-2-butene | 2.1 | 0.011 | 0.5 |
| 12 | 1-Butene | 2.0 | 0.013 | 0.7 |
| 13 | Isobutylene | 2.1 | 0.016 | 0.8 |
| 14 | cis-2-butene | 2.1 | 0.017 | 0.8 |
| 15 | 1,3-Butadiene | 2.1 | 0.018 | 0.9 |
| 16 | Methylacetylene | 2.0 | 0.015 | 0.7 |

*Sample run 20 times

## References


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Agilent Technologies

# 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.

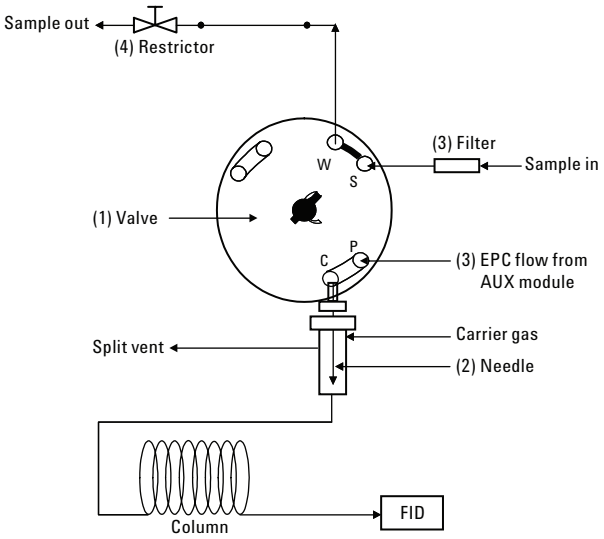



**Figure 1. Flow diagram of the high-pressure injection device (HPLI).**

**Typical Instrumental Conditions**

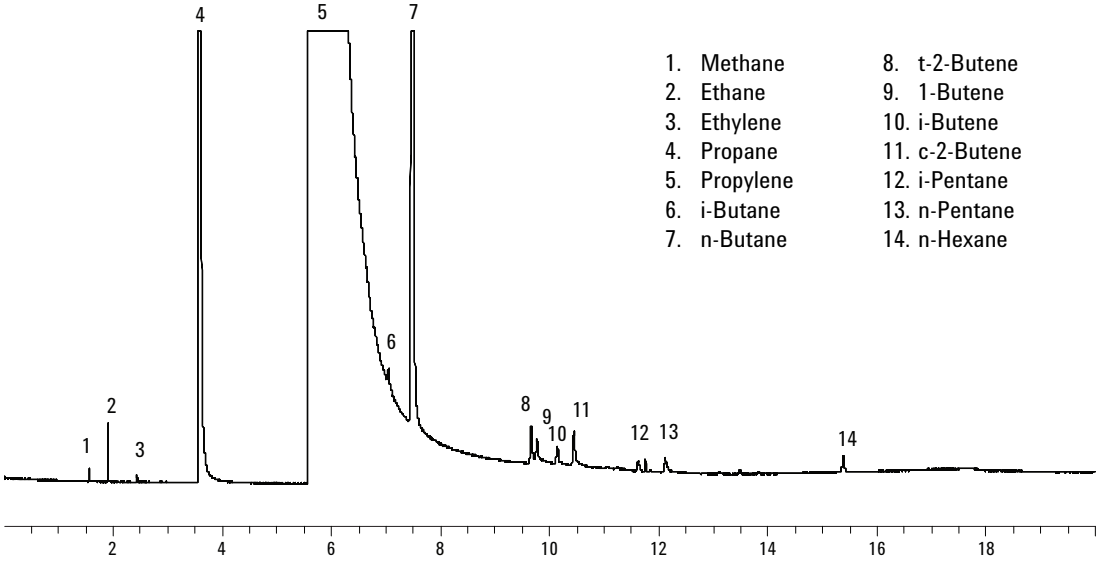
| | |
|---|---|
| Gas chromatograph | Agilent 7890A |
| Injection source | High-pressure injection device (HPLI) at near ambient temperature |
| Injection port | Split/splitless, 250 °C (350 °C for C5–C40) |
| Sample size | 0.06 µL |
| Carrier gas | Helium |
| Aux or PCM | 150 mL/min (Helium) |
| FID | 250 °C (350 °C for C5–C40)<br>$H_2$, 35 mL/min<br>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.




1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. i-Butane
7. n-Butane
8. t-2-Butene
9. 1-Butene
10. i-Butene
11. c-2-Butene
12. i-Pentane
13. n-Pentane
14. n-Hexane

**Figure 2. Chromatogram of pressurized propylene.**

### Pressurized 1,3-Butadiene

Figure 3 is an example of C4 hydrocarbons analysis showing 1.3 butadiene purity.

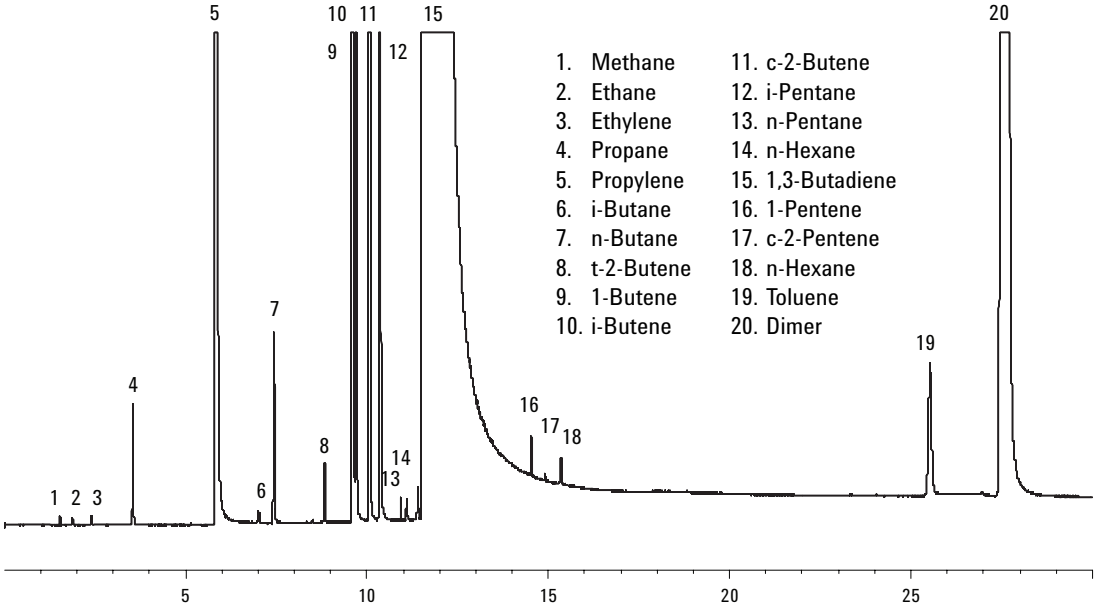



**Figure 3. Chromatogram of pressurized 1,3-butadiene.**

## 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 $C_{16}$)
- 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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**Agilent Technologies**

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

Application

**Gas Chromatography**


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## Abstract

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


## Introduction

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

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

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

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

## Experimental

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

hydrocarbon trap (Agilent p/n 5060-9096) were installed. Agilent ChemStation was used for all instrument control, data acquisition, and data analysis.

## Results and Discussion

### Analysis of Normal Hydrocarbons and Methanol

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

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

**Table 1. Conditions for Normal Hydrocarbons and Methanol Analysis**

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

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

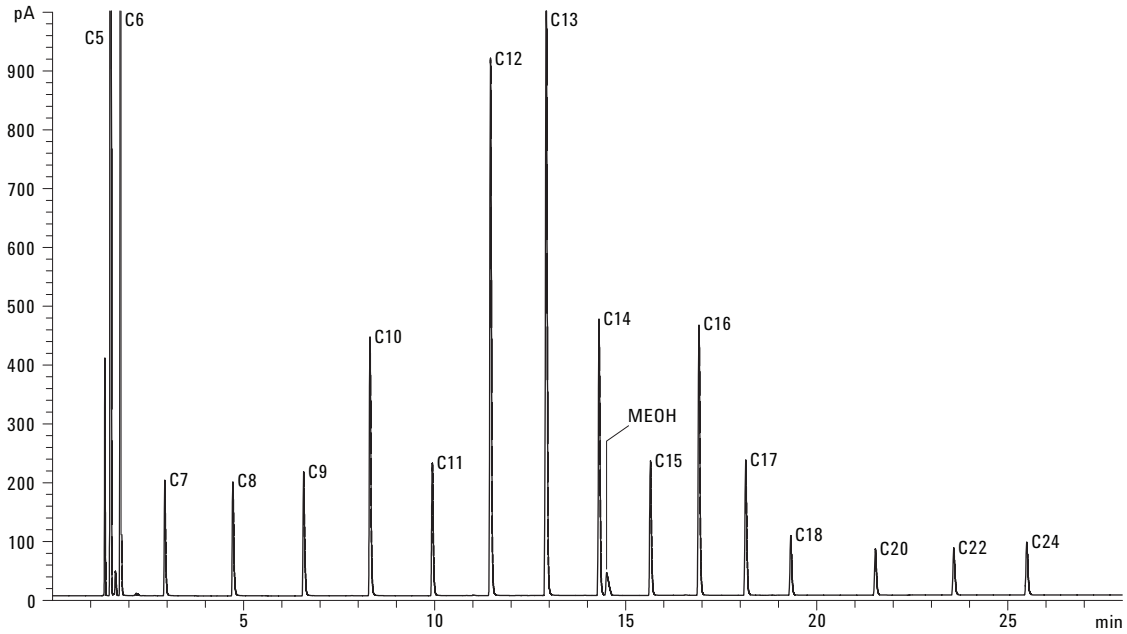


**Figure1. Analysis of methanol and normal hydrocarbons on a GS-OxyPLOT column, 10 m × 0.53 mm × 10 µm.**

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

### Analysis of Alcohols

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

### Sample

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

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

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

**Table 2. Conditions for Alcohols Analysis**

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

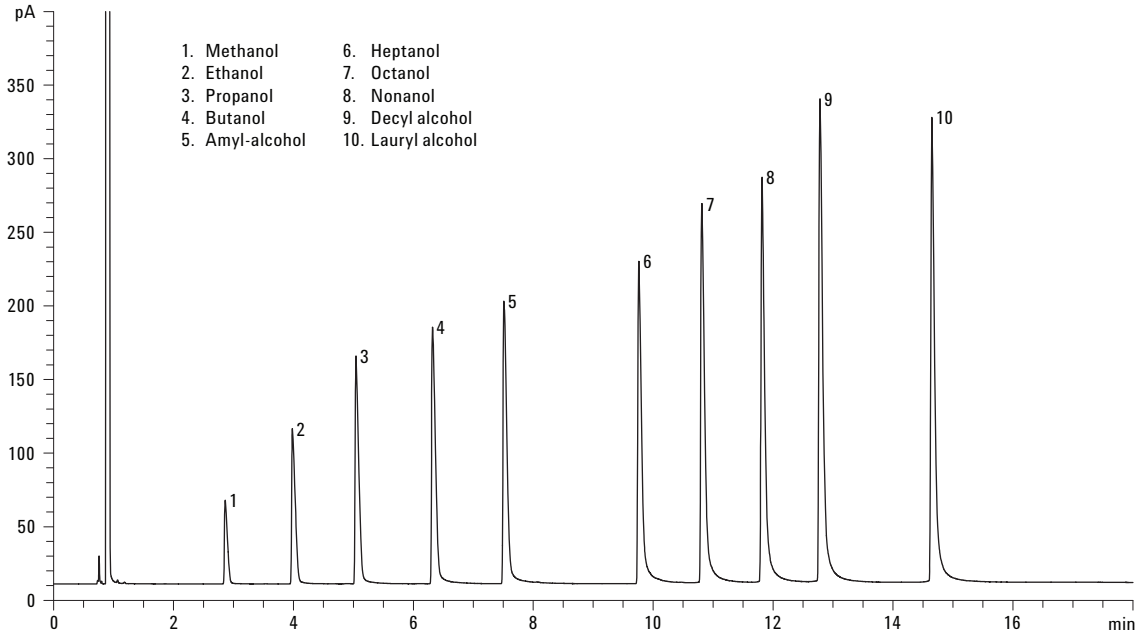


**Figure 2. Separation of alcohols using GS-OxyPLOT, 10 m × 0.53 mm × 10 µm.**

### Influence of Temperature on the Selectivity of GS-OxyPLOT

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

**Table 3. Conditions for Kovats Retention Indices Test**

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

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

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

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

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

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

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

### Influence of Moisture on GS-OxyPLOT

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

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

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

**Table 5. Conditions for Moisture Test**

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

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

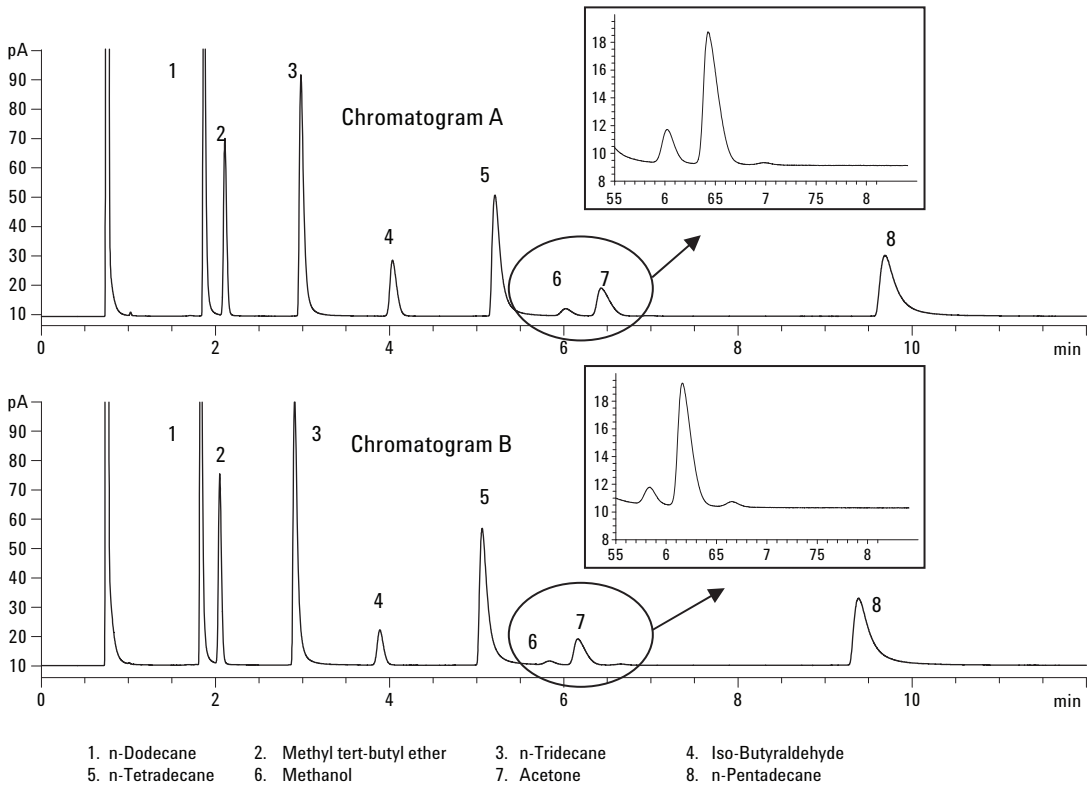


**Figure 3. Comparison of test mixture separation before (A) and after (B) 100 injections of water.**

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

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

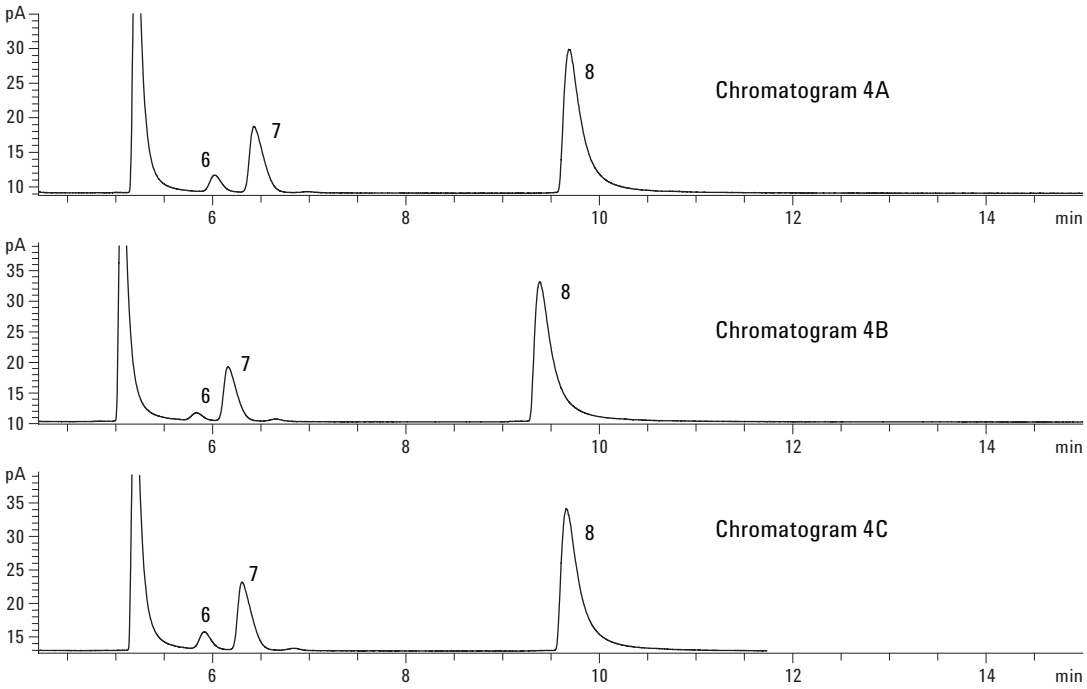


**Figure 4. Expanded view shows comparison of test mixture separation on GS-OxyPLOT.**
4A. Before injection of water. 4B. After 100 injections of water. 4C. After conditioning the column.

**Table 6. Comparison of Test Mixture Separation**

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

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

### Determination of Methanol

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

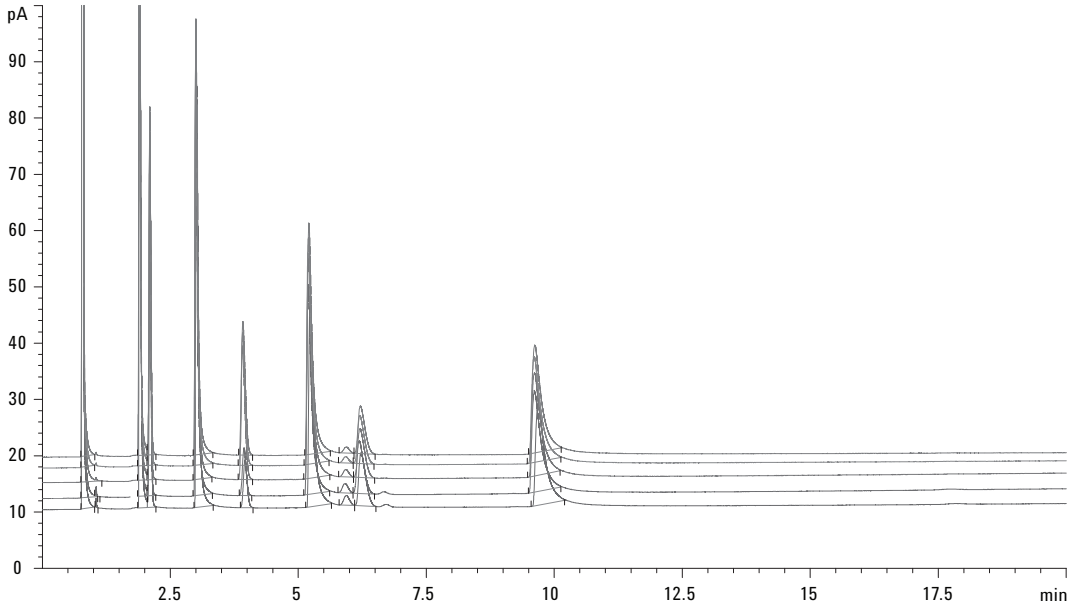


**Figure 5. Fifth run overlaid using GS-OxyPLOT (after conditioning column).**

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

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

### Reagents and Materials

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

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

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

### Linearity

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

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

**Table 8. System Settings for the Calibration Curve**

| | |
|---|---|
| Column | GS-OxyPLOT, 10 m × 0.53 mm × 10 µm |
| Carrier gas | Helium, constant flow mode,<br>50 cm/s at 150 °C |
| Inlet | Split/splitless at 250 °C<br>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 |

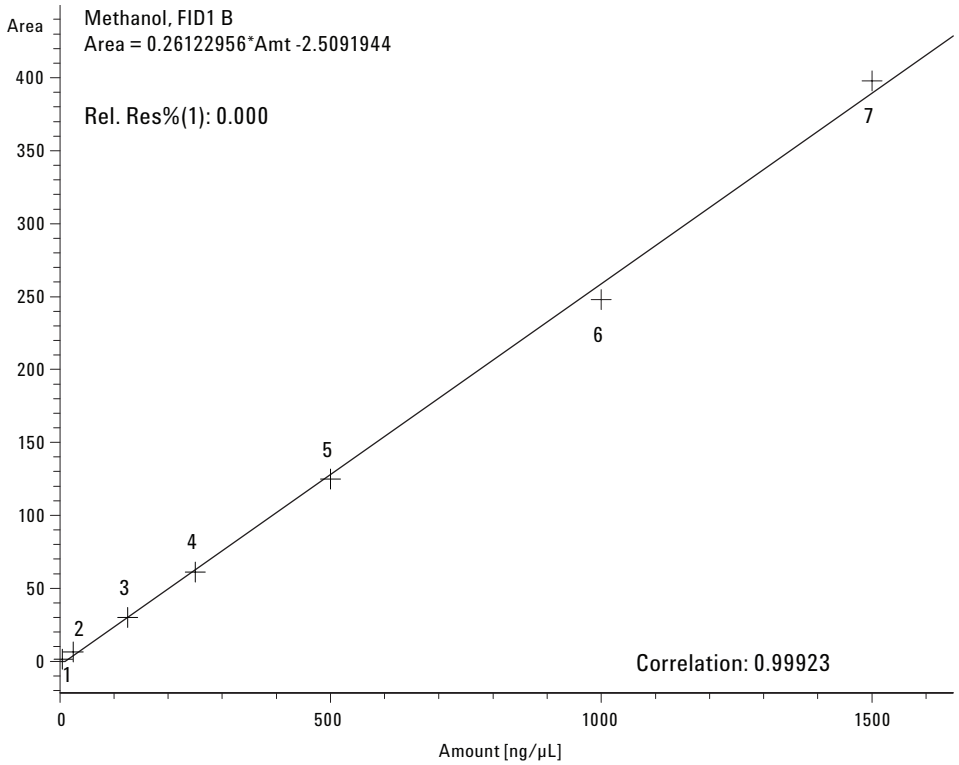


**Figure 6. The calibration curve of methanol in toluene.**

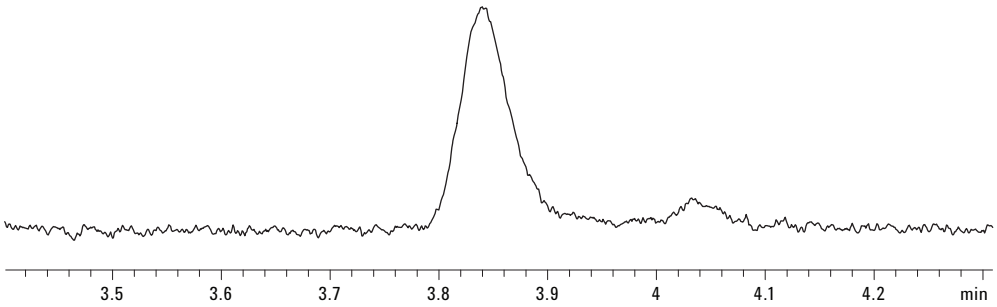


**Figure 7. Test mixture of 5 ppm methanol in toluene.**

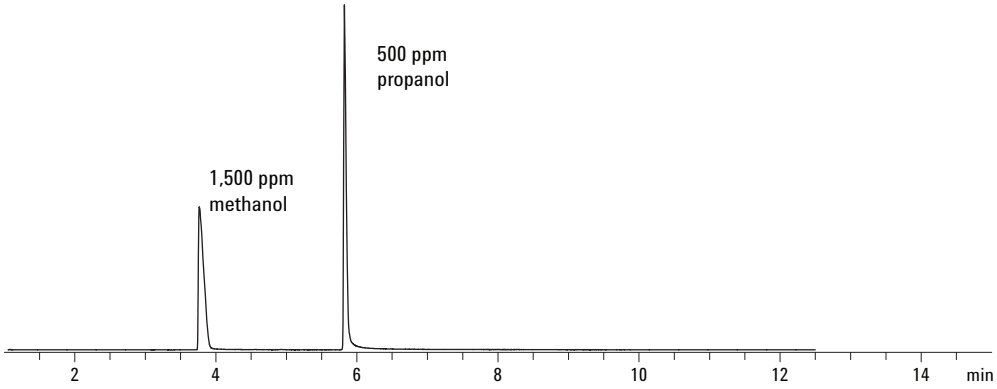


**Figure 8. Test mixture of 1,500 ppm methanol in toluene.**

### 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 | |

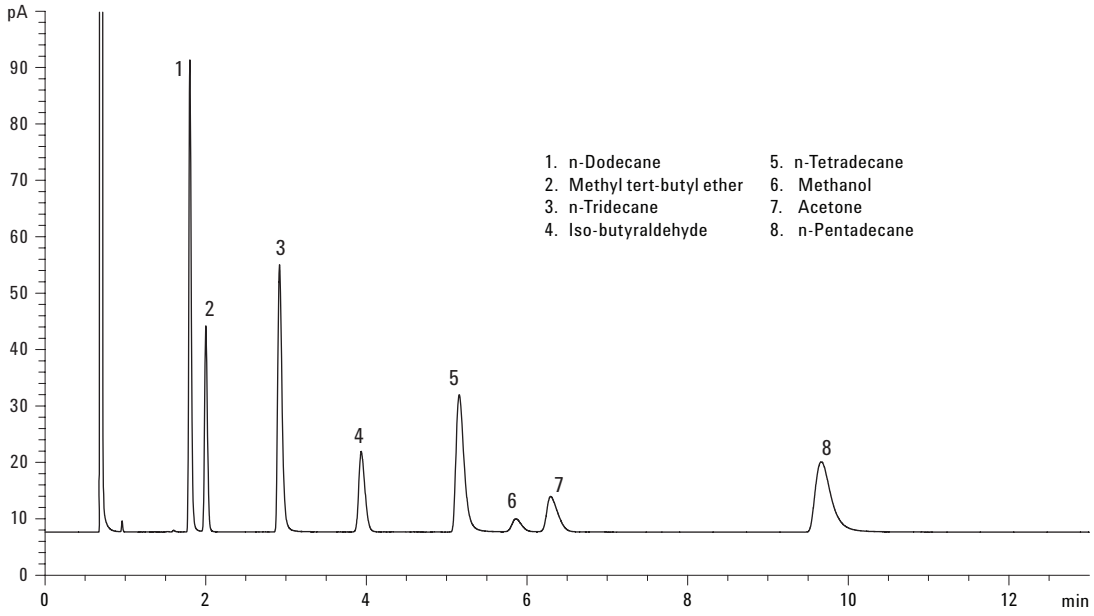


**Figure 9. Chromatogram of performance mixture after 1,500 injections.**

## 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.

## References


1. A. K. Vickers, “GS-OxyPLOT: A PLOT Column for the GC Analysis of Oxygenated Hydrocarbons,” Agilent Technologies publication 5989-6447EN, March 2007
2. “Agilent J&W GS-OxyPLOT Capillary GC Columns,” Agilent Technologies publication 5989-6489EN
3. A. K. Vickers, “A ‘Solid’ Alternative for Analyzing Oxygenated Hydrocarbons — Agilent’s New Capillary GC PLOT Column,” Agilent Technologies publication 5989-6323EN, February 2006
4. Standard test method for the determination of methanol in crude oils by multidimensional gas chromatography, ASTM D7059-04, July 2004


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# Chemical and Specialty Gas

## Additives/Polymer

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# Gradient LC analysis of herbicides and polyaromatic hydrocarbons by isocratic Capillary Electrochromatography

**Gordon Ross,**
**Thomas Adam**
**and Monika Dittmann**

**Environmental/chemical**

**Abstract**
Capillary Electrochromatography (CEC) combines the separation principle of HPLC (partitioning between mobile and stationary phases) with the high efficiency of capillary electroseparation methods. In CEC the electroosmotic flow (EOF) inherent in capillary electrophoretic separations is used to transport solute and mobile phase through a packed capillary column. The properties of the EOF provides higher efficiencies than can be realized with LC. This can be sufficient to allow the transfer of methods conventionally performed by gradient LC to be performed by isocratic CEC.

**Experimental**
All CEC experiments were performed using the Agilent CE system, equipped for CEC operation and with a built in diode array detector. The system includes an Agilent ChemStation for system control, data collection and data analysis. CEC columns were supplied by Agilent Technologies. Buffer salts were of the highest purity available and organic solvents were HPLC grade. All buffers were filtered and degassed prior to use. Buffers/mobile phase were adjusted to pH prior to the addition of organic modifiers.

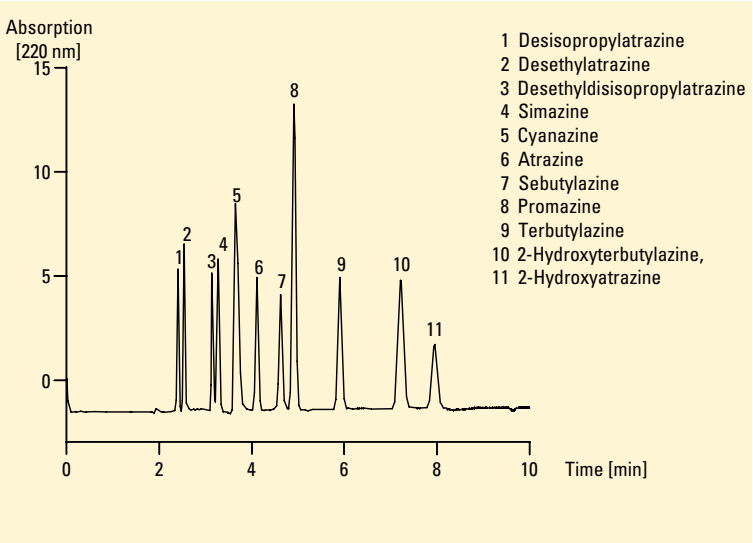


Figure 1
Isocratic CEC alternative to gradient HPLC separation of herbicides

Figure 1 shows the separation of a series of herbicides by CEC. The separation is normally achieved using gradient elution LC. The same is true for figure 2. Here the analysis is of polyaromatic hydrocarbons

## Conditions

**Column**
250 mm × 100 µm; Sperisorb ODS1
**Mobile Phase**
60 % acetonitrile/40 % 25 mM TRIS pH 8
**Voltage**
30 kV
**Temperature**
15 °C

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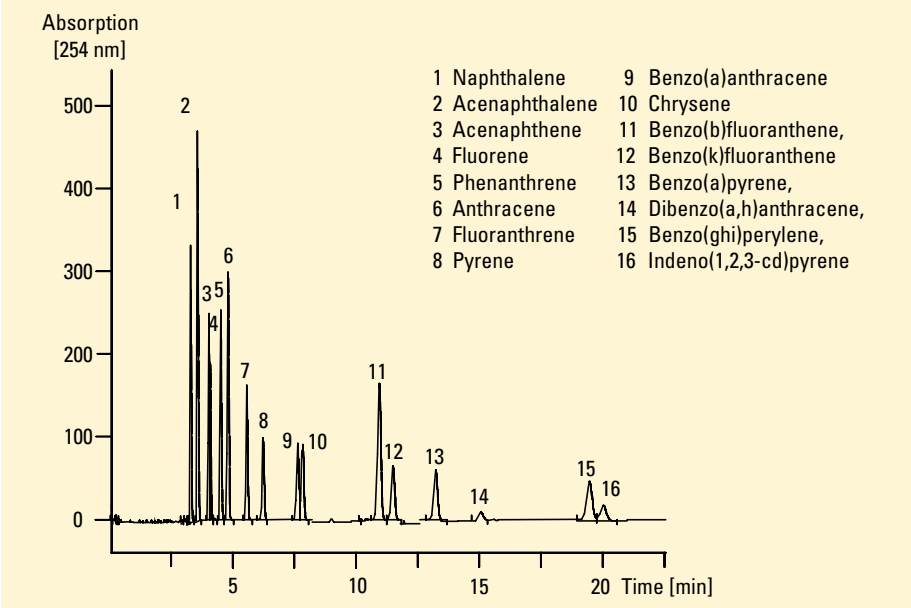



Figure 2
Fast CEC separation of EPA 16 PAH standard on CEC hypersil C18

which are of environmental significance and interest. Conventional analysis of these compounds can be achieved in a similar time however with isocratic CEC operation there is no inter-analysis time required for re-generation of the LC column.

## Conclusions

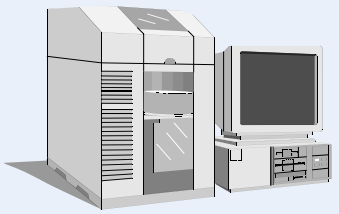
Some gradient LC separations can be succesfully performed using isocratic CEC. Very similar separations can be achieved in the same time frame. Time for re-equilibration of the LC column is not needed and therefore the overall analysis time is reduced.

## Conditions

**Column**
CEC Hypersil C18, 250 mm (350 mm) × 0.1 mm i.d., 2.5 µm
**Cell** Standard
**Eluent**
90 % TRIS-HCl 50 mM, pH 8
**Voltage** 30 kV
**Temperature** 20 °C
**Pressure** 10 bar both sides

## Equipment

- Agilent Capillary Electrophoresis System
- Agilent ChemStation + software



Monika Dittmann is an R&D chemist and Gordon Ross is an application chemists at Agilent Technologies, Waldbronn, Germany. Thomas Adam is at the University of Mainz, Germany.

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# Analysis of Antioxidants and UV Stabilizers in Polymers using HPLC

**Angelika Gratzfeld-Huesgen**

**Polymer /chemical industry**


## Abstract

Additives are frequently used to protect polymers against thermo-oxidative degradation and destruction caused by UV irradiation. The following antioxidants and UV stabilizers were analyzed using reversed phase liquid chromatography and diode-array detection in technical styrene.

• Uvinol 3000 • Tinuvin P • Irganox 1098 • Uvinol 3008 • Lavinix BHT • Tinuvin 320 • Irganox 1010 • Irganox 1076 • Irgafos 168


Irganox 1010 for example, is a highly effective, non-discoloring stabilizer for organic substrates such as plastics, synthetic fibers, elastomers, waxes, oils and fats. Tinuvin P can be used to protect plastics against UV irradiation as it absorbs the UV light and transfers it into thermal energy which cannot destroy the polymer. Both compound classes have a wide ranging molecular structure and molecular weight. Irganox 1010 has a molecular weight of 1178 and its chemical structure is [3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate]. Tinuvin P has a much lower molecular weight of 225 and its chemical structure is 2-(2'-hydroxy-5'-methyl-phenyl)-benzotriazol.

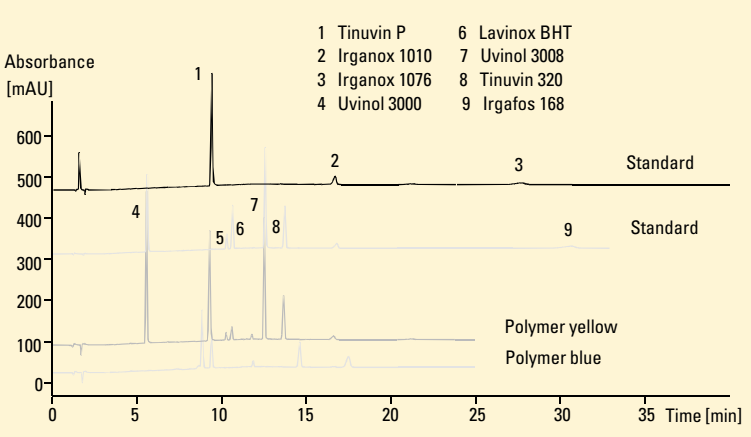


Figure 1
Analysis of antioxidants and stabilizers with the same conditions

## Conditions

**Column** 125 x 3 mm BDS, 3 µm
**Mobile Phase** A = Water + 0.001 m Tetrabutylammoniumhydrogensulfate, pH = 3.0 with $H_2SO_4$, B = Acetonitrile
**Gradient**
Start with 30 % B, to 98 % B in 10 min
**Flow Rate** 0.5 ml/min
**Injection Vol** 5 µl
**Oven Temp** 40 ºC
**UV-Detector** DAD, 280/20 nm
Reference 900/50 nm

**Sample preparation**
Polymer samples were dissolved in Tetrahydrofurane and filtered after extraction with ultra-sonic bath for 30 min

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Antioxidants and UV stabilizers are typically added to polymers as a mixture of several compounds, which also includes costabilizers and antistatic agents. The application range of these additives is broad and can be found in most polymers.

All mentioned compounds are soluble in organic solvents and can be analyzed using reversed phase HPLC with ion-pairing modifier. In addition to the identification by retention time, UV spectra were used.

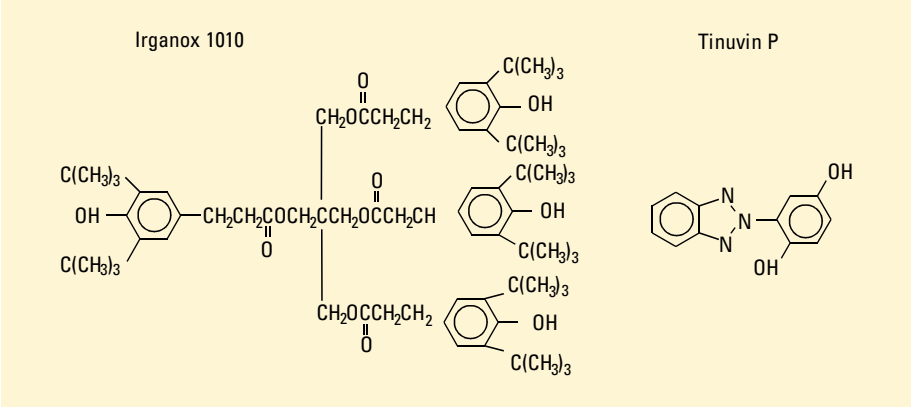



Figure 2
Formula of Antioxidants

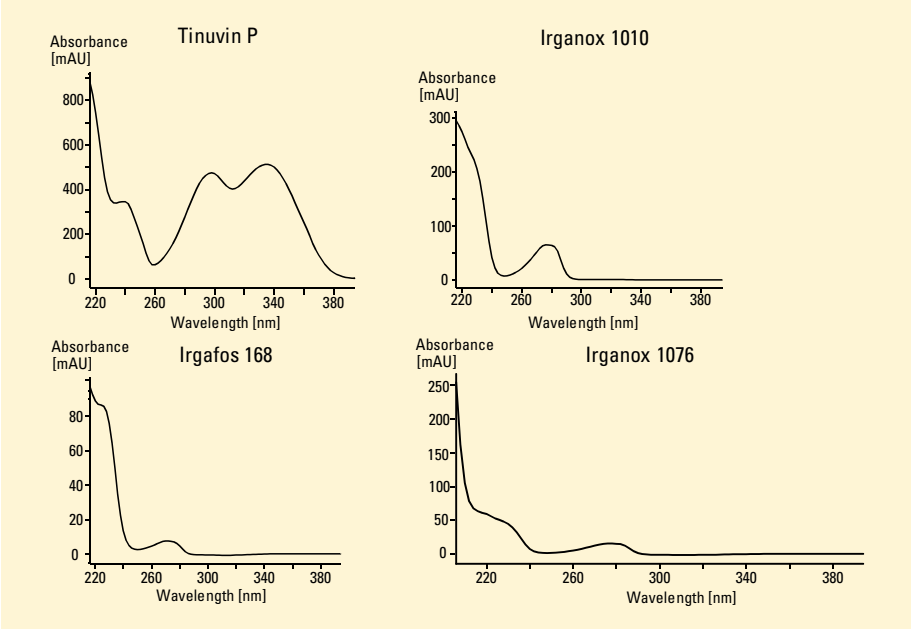



Figure 3
Spectra of antioxidants

## Method performance

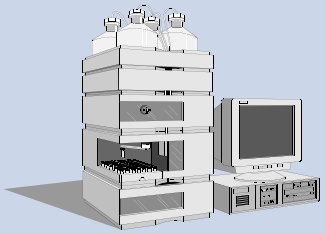
Limit of Detection (LOD) = < 1 ng
Precision of retention times (rsd) = 0.2 %
Precision of areas (rsd) = < 3 %

## Equipment

**Agilent 1100 Series**

- degasser
- binary pump
- autosampler
- thermostatted column compartment
- diode array detector

Agilent ChemStation + software



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# Analysis of Dyes in Plastics using HPLC

**Angelika Gratzfeld-Huesgen**

**Polymer /chemical industry**


## Abstract

Dyes which are used for coloring plastics have to fulfill special requirements. They have to be heat resistant, resistant against UV-irradiation and weatherproof. In addition, they should show strong coloring power and high brilliance. The analyzed colors in this application brief are soluble in organic solvents but are practically insoluble in water. This is important if the colored plastics are to be used in food packaging materials or in toys. Some of these colors are also used as coloring agents for polyamide fibers and other engineering plastics. The following colors were analyzed:


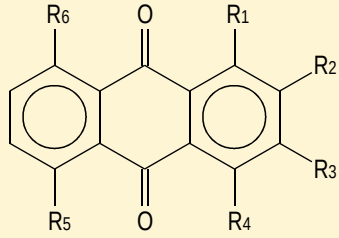


Figure 2
Chemical structure of dyes

| Name | Color Index | Structure |
|---|---|---|
| Solvent yellow 21 | | Monoazo 1:2 chromo complex |
| Filamid violet RB | | Monoazo 1:2 chromo complex |
| Disperse yellow 54 | 47020 | Chinophthalon |
| Solvent red 52 | 68210 | Anthraquinone |
| Macrolex blue 3R | | Anthraquinone |
| Solvent blue 97 | | Anthraquinone |

Table 1
Chemical structure of dyes

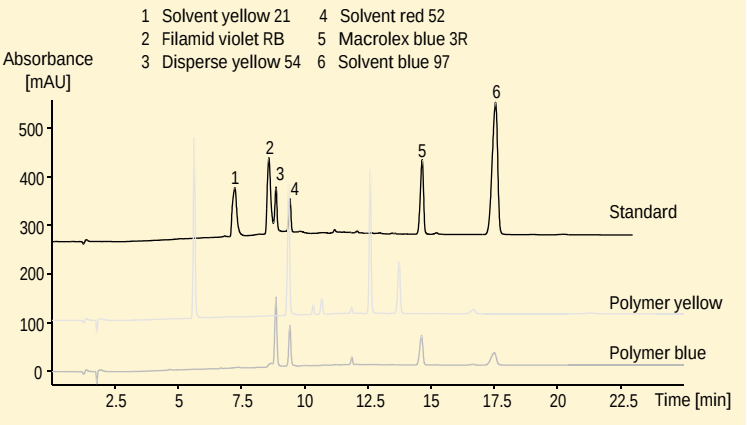


Figure 1
Standard chromatogram

## Conditions

**Column** 125 x 3 mm BDS, 3 µm
**Mobile Phase** A = Water + 0.001 m Tetrabutylammoniumhydrogensulfate, pH = 3.0 with $H_2SO_4$, B = Acetonitrile
**Gradient**
Start with 30 % B, to 98 % B in 10 min
**Flow Rate** 0.5 ml/min
**Injection Vol** 5 µl
**Oven Temp** 40 °C
**UV-Detector** DAD,
280/20 nm Reference 900/50 nm
350/40 nm Reference 900/50 nm
465/40 nm Reference 900/50 nm
540/40 nm Reference 900/50 nm
600/40 nm Reference 900/50 nm
**Sample preparation**
Polymer samples were dissolved in Tetrahydrofurane and filtered after extraction with ultra-sonic bath for 30 min

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• Solvent yellow 21 • Filamid violet RB • Disperse yellow 54
• Solvent red • Macrolex blue 3R • Solvent blue 97

These dyes have different chemical compound classes, for example Anthraquinone type, Chinophthalon type and Monoazo-1:2-chromo complex type.

### Method performance

The dyes in this analysis were analyzed using reversed phase HPLC with ion pairing compound in the mobile phase. A diode array detector was used as the detection system. Spectra which are very characteristic of this compound group were used as identification tools, in addition to the retention times.

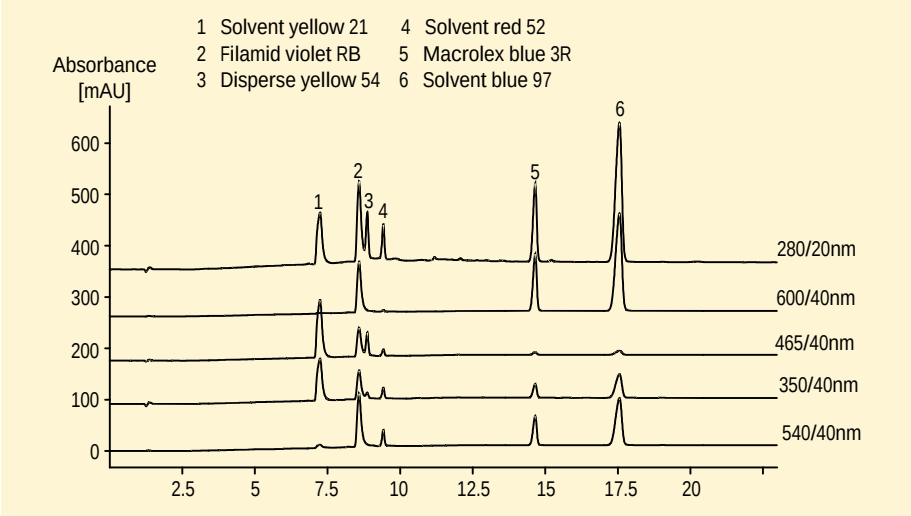



Figure 3
Analysis of dyes at different wavelengths

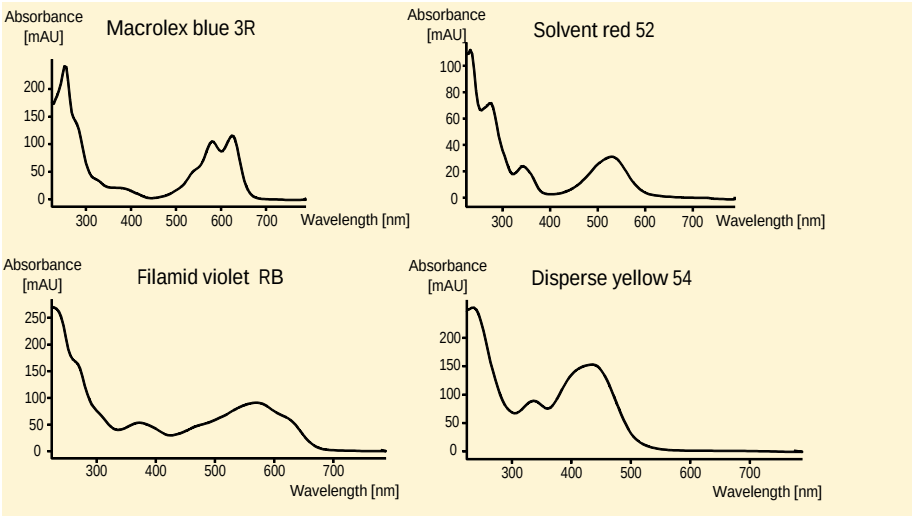



Figure 4
Spectra of polymer dyes

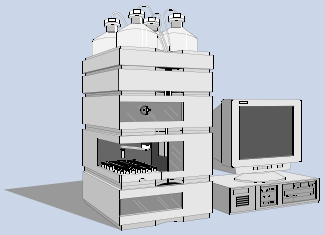
## Method performance

Limit of Detection (LOD) = < 1 ng
Precision of retention times (rsd) = 0.2 %
Precision of areas (rsd) = < 3 %

## Equipment

**Agilent 1100 Series**
- degasser
- binary pump
- autosampler
- thermostatted column compartment
- diode array detector

Agilent ChemStation + software



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# Analysis of Polymethylmethacrylate (PMMA) using Gel Permeation Chromatography

**Angelika Gratzfeld-Huesgen**

**Polymer /chemical industry**


## Abstract

Polymethylmethacrylates are used as homo and co-polymers for the production of safety glasses, Plexiglas and glasses for optics, cars and dishes. The mol masses vary from 120000 to 180000 g/mol. In 1988 1.5 Mio.t. were used worldwide.

The performance of PMMA depends on the molecular weight of the polymer. To ensure quality, molecular weight (MW) data has to be evaluated for each batch of polymer that is produced. Gel Permeation Chromatography is an analytical tool for the characterization of polymers which are soluble in organic solvents. The separation is based on the differences in size of the polymer molecules, and provides primary result molecular weight distribution curves. This means that molecular weight data and quantitative data are calculated after calibration with standards of known molecular weight.


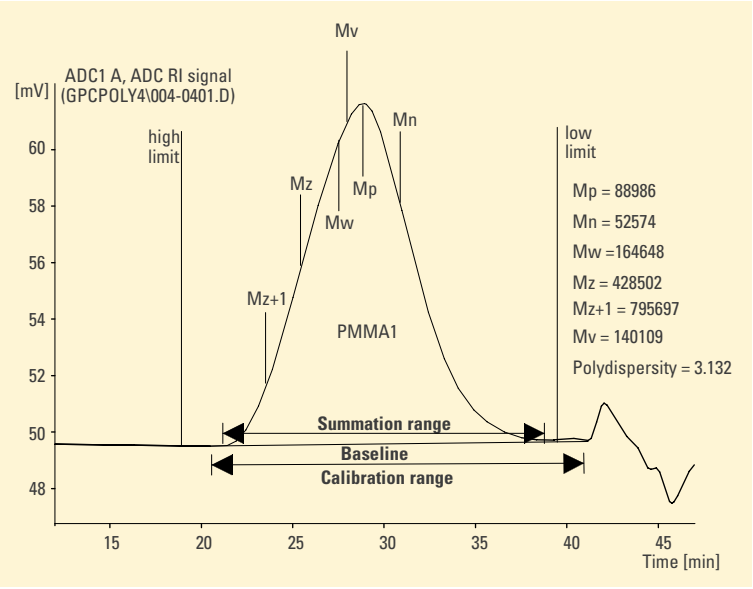


Figure 1
Standard Chromatogram

## Conditions

**Column**
3 ˘ PSS GPC 8 ˘ 300 mm, 5 µm, $10^6$, $10^5$, $10^3$ A
**Mobile phase**
Tetrahydrofurane (THF)
**Flow rate**
0.8 ml/min
**Oven Temp**
20 ºC
**Injection vol** 10 µl
**Refractive index detector**

**Sample preparation**
26 mg sample dissolved in 1 ml THF
Polystyrene standards from PSS were used for narrow standard calibration

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## Method Performance

Having set up the chromatographic and GPC calculation procedures including the calibration, the polymer can be analyzed and MW and MWD (molecular weight distribution) data can be calculated. After analysis of the polymer, the baseline and summation range have to be defined. The baseline points should be selected within a flat part of the graph before and after the polymer peak. The summation range should be within the calibrated range and marked either side with lines indicating the high and low limits. The start and end points of the peak need to be carefully selected.

## Method performance

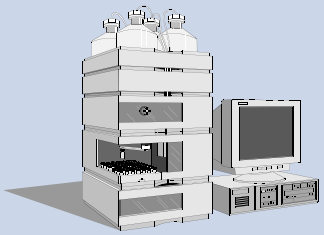
Precision of weight average molecular weight (rsd of Mw) = < 1 %
Precision of number weight average molecular weight (rsd of Mn) = < 2 %

## Equipment

**Agilent 1100 Series:**

- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector

Agilent ChemStation + software + polymer labs GPC software



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# Analysis of Polybutadiene using Gel Permeation Chromatography

**Angelika Gratzfeld-Huesgen**

**Polymer /chemical industry**

## Abstract

Polybutadiene is used as homo- and co-polymers for the production of tyres (70 %), moving belts and soles of shoes. In 1989 1.1 Mio.t. were used worldwide.

For example, the performance of tyres depends strongly on the molecular weight (MW) of the polybutadiene used and its additives. To ensure highest quality and consequently highest safety MW data need to be evaluated for each batch of produced polymer. Gel Permeation Chromatography (GPC) is an analytical tool used to characterize polymers which are soluble in organic solvents. In general an isocratic pump is sufficient for GPC analysis, however for ease of solvent change and rinsing, a pump with two or more channels would be advantageous. The pump should be able to pump the selected flow rate with a precision of typically < 0.15 %. Solvent degassing is recommended either offline or even better online with vacuum degassing. For high sample throughput the use of an autosampler would be beneficial. The temperature of the column oven needs to be very stable to avoid retention time shift and therefore MW errors—a peltier controlled thermostat is ideal for highest temperature stability especially at and below ambient temperatures

For detection a UV detector and/or a refractive index detector can be used. In this example we used both detectors to demonstrate, that results can be quite different, depending on the detection system used. The use of a diode array system enables the taking of spectra as an additional identification tool. This can help to identify for example remaining monomers (figure 1).

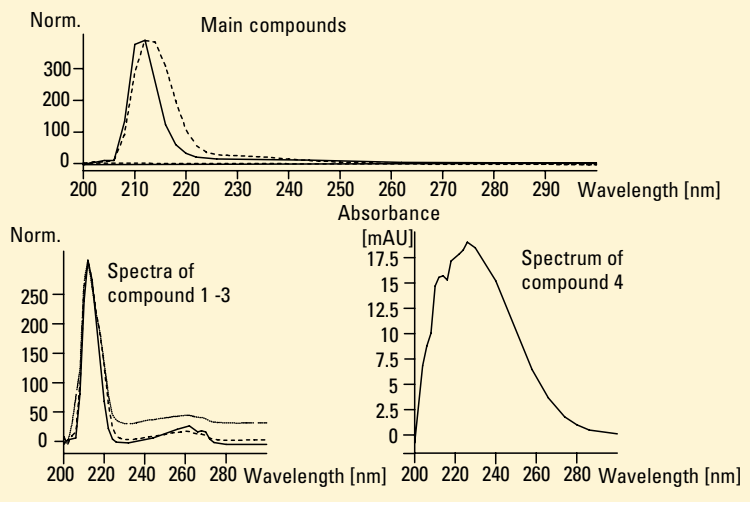


Figure 1
Spectra of oligomers and monomers

## Method Performance

In figure 2 the different signal traces of UV-DAD and refractive index detection are shown. It can be seen that the calculated MW data differ significantly. In addition to MW data like Mw and Mn, GPC evaluation software also calculates molecular weight distribution curves (MWD),

which offer information about the relation between for example height percentage and log molecular weight or cumulative height percentage versus log molecular weight. (figure 3).

### Method performance

Precision of weight: average molecular weight (rsd of Mw) = < 1 %
Precision of number weight average: molecular weight (rsd of Mn) = < 2 %

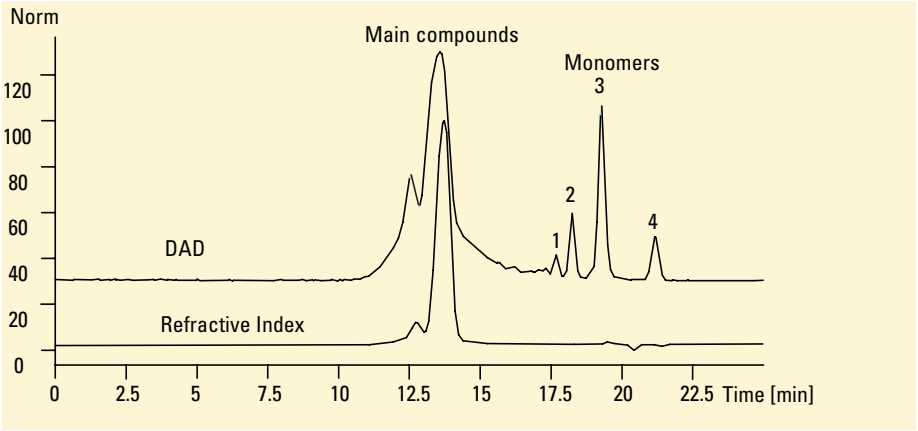


Figure 2
Analysis of polybutadiene using UV and refractive index

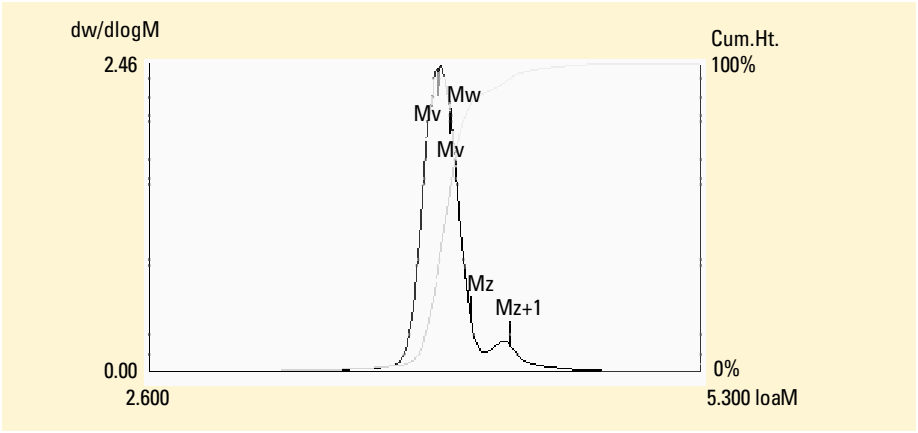


Figure 3
Molecular weight data based on refractive index detection

| MW data | Refractive index | UV Detection |
|---|---|---|
| Mp | 10283 | 10000 |
| Mn | 10543 | 6567 |
| Mw | 12054 | 13565 |
| Polydispersity | 1.143 | 2.066 |
| Mz | 14804 | 22037 |
| Mz + 1 | 21860 | 35784 |
| Mv | 11780 | 12579 |

Table 1
Molecular weight data refactive index versus UV detection

## Conditions

**Column** 2 × PLgel mixed-D, 7.5 × 300 mm, 5 µm
**Mobile phase**
Tetrahydrofurane (THF)
**Flow rate** 1 ml/min
**Oven Temp** 20 °C
**Injection vol** 20 µl
**UV detector** DAD 254/100 nm, reference 360/100 nm
**Refractive index detector**
**Sample preparation**
33 mg sample dissolved in 1 ml THF; Polystyrene standards from PSS were used for narrow standard calibration

## Equipment

**Agilent1100 Series:**
- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector

Agilent ChemStation + software + polymer labs GPC software

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# Analysis of Polystyrene using Gel Permeation Chromatography

**Angelika Gratzfeld-Huesgen**

**Polymer /chemical industry**

## Abstract

Polystyrene is used as homo-, co-polymers, thermoplastic elastomers and foamed polystyrene (EPS) for the production of cabinets, housings, furniture, packing boxes and food packaging material. In 1988 7.1 million tons were used worldwide. The mol masses vary from 170000 to 1000000 g/mol.

Polystyrene has been around since 1839, but the current macromolecular structure of the molecules was discovered a lot later in 1920 by Staudinger. The first industrial product based on polystyrene was introduced in 1930, then in 1950, the first foamed polystyrene product was made commercially available. This was called styropor.

Since then the usage of this plastic has increased drastically and nowadays when used as co-polymer its application range is almost universal. To ensure the highest quality, molecular weight (MW) data have to be evaluated for each batch of produced polymer. Gel Permeation Chromatography (GPC) is an analytical tool used to charact-erize polymers which are soluble in organic solvents.

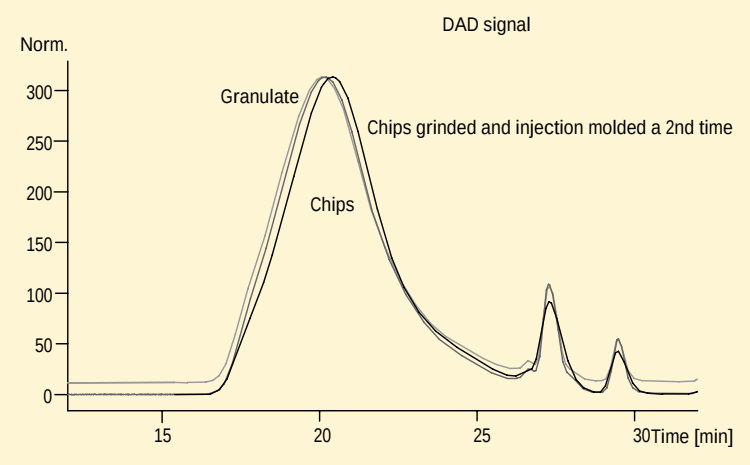


Figure 1
Different processed polystyrenes

## Conditions

**Column**
3 ˘ PLgel mixed-B, 7.5 ˘ 300 mm, 5 µm
**Mobile phase**
Tetrahydrofurane (THF)
**Flow rate** 1 ml/min
**Oven Temp** 20 °C
**Injection vol** 10 µl
**Refractive index detector**

**Sample preparation**
Sample dissolved in 1 ml THF
Polystyrene standards from PSS were used for narrow standard calibration

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## Method Performance

Figure 1 shows the signal traces of different treated polystyrenes. A granulate was used to produce colorless chips. These chips were grinded and injection molded a second time. The influence of these production procedures on the MW data are shown in table 1.

## Method performance

Precision of weight: average molecular weight (rsd of Mw) = < 1 %
Precision of number weight: average molecular weight (rsd of Mn) = < 2 %

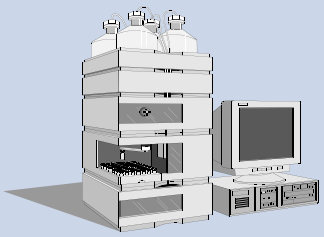
| MW data | Granulate | Chips | Chips, grinded and injection molded a second time |
|---|---|---|---|
| Mp | 109776 | 87563 | 103049 |
| Mn | 59152 | 49062 | 55036 |
| Mw | 159590 | 133565 | 149385 |
| Polydispersity | 2.698 | 2.722 | 2.714 |
| Mz | 327846 | 297500 | 311084 |
| Mz + 1 | 545718 | 539583 | 533941 |
| Mv | 141380 | 117205 | 132243 |

Table 1
Molecular weight data

## Equipment

**Agilent 1100 Series:**
- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector

Agilent ChemStation + software + polymer labs GPC software



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# Analysis of Polycarbonate using Gel Permeation Chromatography

**Angelika Gratzfeld-Huesgen**

**Polymer /chemical industry**

**Abstract**

Polycarbonate is chemically a polyester of carbonic acid and aliphatic or aromatic hydroxy compounds that it is used for the production of cabinets, housings, packing boxes, light transparent roofs, noise protection walls, inside paneling and microwave compatible dishes. In 1989, 470000 tons were used worldwide, with the mol masses varying from 10000 to 200000 g/mol.

To ensure the highest quality, molecular weight (MW) data has to be evaluated for each batch of produced polymer. Gel Permeation Chromatography is an analytical tool used to characterize polymers which are soluble in organic solvents.

## Method Performance

Figure 1 shows the signal traces of four different batches of polycarbonates. The differences in MW data for each of these four batches is shown in table 1. For one polycarbonate, MW data was determined by absolute methods. This data was used for a broad standard calibration.

The following explains the different calibration types.

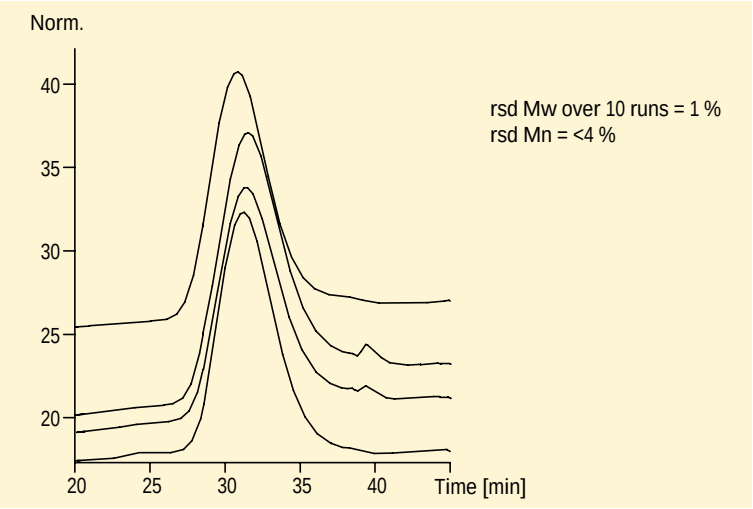


Figure 1
Molecular weight data analysis of four different polycarbonates

## Conditions

**Column** 3 ˘ PSS GPC, 8 ˘ 300 mm, 5 µm, $10^6$, $10^5$, $10^3$ A
**Mobile phase** Tetrahydrofurane (THF)
**Flow rate** 0.8 ml/min
**Oven Temp** 20 °C
**Injection vol** 10 µl
**UV DAD** 254/100 nm
**Refractive index detector**

**Sample preparation**
Sample dissolved in 1 ml THF
Polystyrene standards from PSS were used for narrow standard calibration

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The accuracy of MW data, is measured by conformity with data measured compared with absolute methods, and is mainly influenced by the calibration procedure used.

In an ideal situation narrow standards are available for the polymer of interest, however this is normally not true. In many cases where organic solvents are used narrow polystyrene standards are used for calibration. This means that the accuracy is often poor. This is seen when you look at the comparison with absolute MW from light scattering or viscometer measurements. A solution for this is to use the broad standard calibration, where a polymer of the same chemical structure and known Mw and Mn data is used as calibration compound (see figure 2). In this case broad standard calibration with a chemically identical polymer with known Mw and Mn would provide the best conformity.

On the software side, care should be taken in selecting the right calibration curve fit. Baseline setting and summation start and end points should be selected correctly.

| Narrow standard calibration | | Broad standard calibration | |
|---|---|---|---|
| **Mw** | **Mn** | **Mw** | **Mn** |
| 44096 | 17996 | 30000 | 12000 |
| 33306 | 10709 | 22604 | 6697 |
| 34494 | 10787 | 23616 | 7176 |
| 38556 | 16446 | 26602 | 10547 |

Table 1
Molecular weight analysis of four different polycarbonates

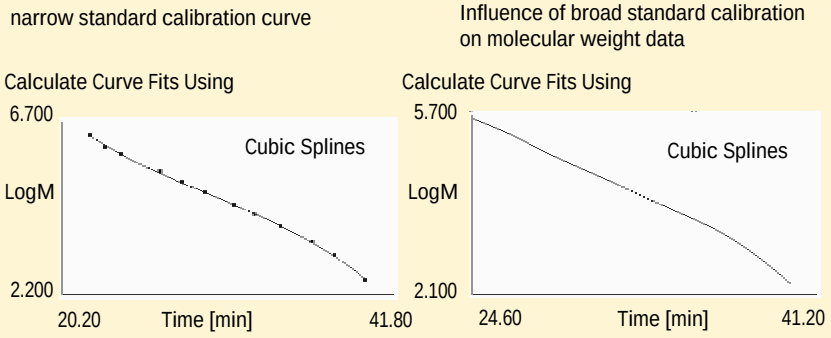



Figure 2
Influence of calibration on molecular weight data

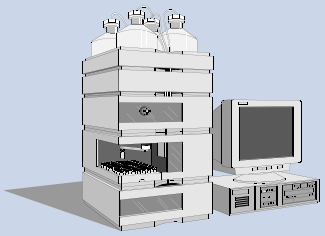
**Method performance**

Precision of weight: average molecular weight (rsd of Mw) = < 1 %
Precision of number weight: average molecular weight (rsd of Mn) = < 1 %

## Equipment

**Agilent 1100 Series:**
- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector

Agilent ChemStation + software + polymer labs GPC software



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# Analysis of Polyvinylchloride using Gel Permeation Chromatography

**Angelika Gratzfeld-Huesgen**

**Polymer /chemical industry**

**Abstract**

Polyvinylchloride (PVC) can be divided into two main groups—hard and soft PVC, which is used for the production of for example tubings, cables, cars, furniture, foils, artificial leather and the covering of wall papers. In 1990, 11.4 million tons were used worldwide. The mol masses vary from 30000 to 130000 g/mol. Chlorinated PVC with a maximum concentration of 73 % of chloride is used whenever the plastic material needs to have drastically increased solubility compared to normal PVC. Chlorination also improves thermal stability and mechanical stability. Examples of products made from this modified PVC are resins, foil and fibers. To ensure the highest quality, molecular weight (MW) data have to be evaluated for each batch of produced polymer. Gel Permeation Chromatography is an analytical tool used to characterize polymers which are soluble in organic solvents.

## Method Performance

Figure 1 shows the signal traces of 3 different batches of polyvinylchloride. The production process started with a normal PVC. In the second step this PVC was chlorinated and in the final process it was formed into tubes. MW data from these 3 production processes were evaluated. The differences in MW data are shown in table 1. It is interesting to note that the UV absorption increases during the manufacturing process, see figure 2.

| PVC type | Mw data | Mn data | Polydispersity |
|---|---|---|---|
| PVC | 111852 | 53648 | 2.085 |
| Chlorinated PVC | 107355 | 52145 | 2.059 |
| Chlorinated PVC as tube | 124378 | 61005 | 2.039 |

Table 1
Analysis of PVC with refractive index detector

## Influence of flow and temperature stability

The following in which PVC was analyzed, demonstrates the importance of stable flow rates and stable oven temperatures.

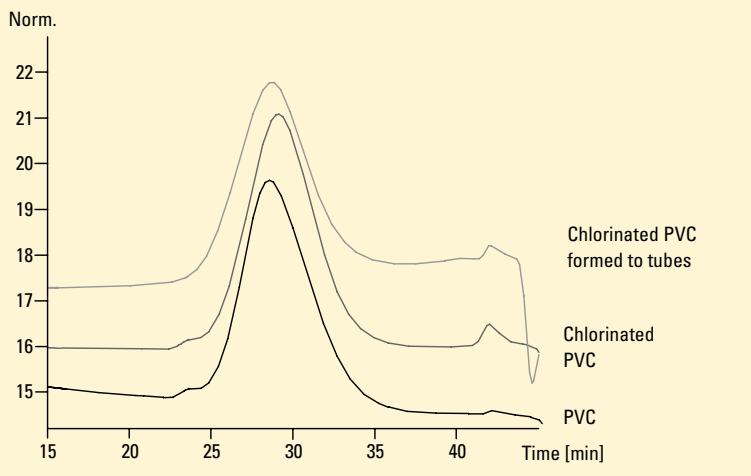


Figure 1
Analysis of PVC with refractive index detector

## Conditions

**Column** 3 ˜ PSS GPC, 8 ˜ 300 mm, 5 µm $10^6$,$10^5$,$10^3$ A
**Mobile phase** Tetrahydrofurane (THF)
**Flow rate** 0.8 ml/min
**Oven Temp** 20 °C
**Injection vol** 10 µl
**UV DAD** 254/100 nm
**Refractive index detector**
**Sample preparation**
Sample dissolved in 1 ml THF, filtered with 0.45 µm filter. Polystyrene standards from PSS were used for narrow standard calibration
**Method performance**
Precision of weight: average molecular weight (rsd of Mw) = < 1 %
Precision of number weight: average molecular weight (rsd of Mn) = < 1 %

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The precision of MW data, measured by relative standard deviation of for example Mw and Mn is mainly influenced by the stability of flow rate. To demonstrate the importance of stable flow rates and constant oven temperatures, experiments were done where for each parameter slight changes were made. It soon became obvious that flow changes even smaller than 0.5 % had an influence on the precision, whereas temperature changes below 1 °C did not have a major influence (see figure 3). Consequently the precision of the flow rate should be better than 0.1 %. 20 consecutive injections were made and the precision of the Mw data were < 0.4 %. (see figure 4.) Data was obtained using an HP 1090 Series HPLC system.

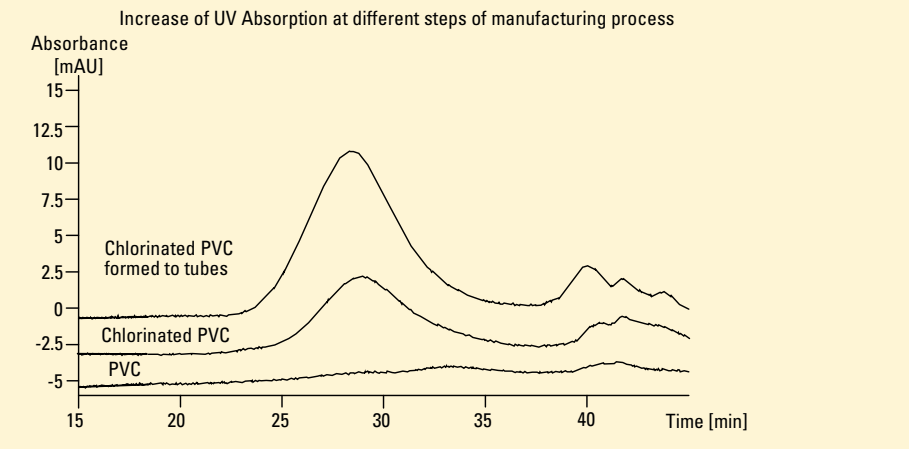


Figure 2
Different PVC types analyzed with UV DAD

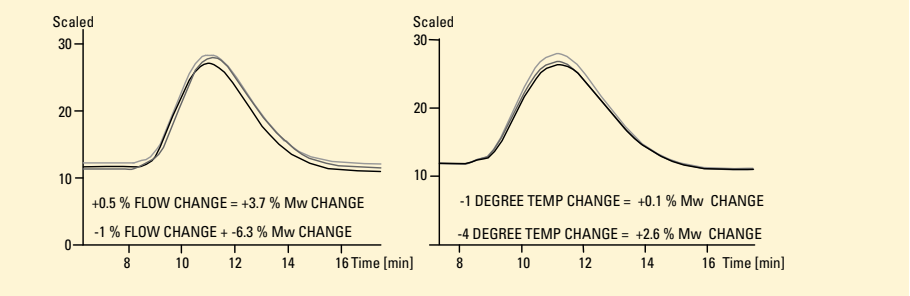


Figure 3
Influence of flow and temperature variations on precision of MW data

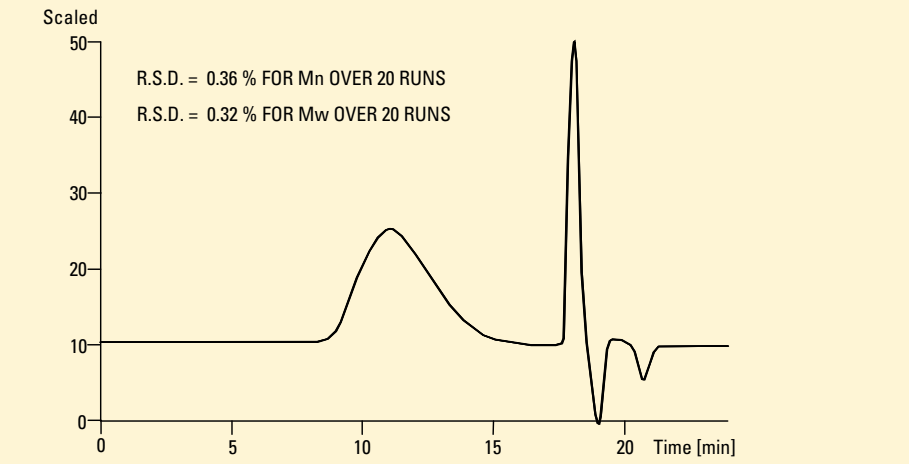


Figure 4
Precision for optimized conditions

## Conditions

**Column** 7.5 ˜ 300 mm, $10^4$ PLGel
**Mobile phase**
Tetrahydrofurane (THF)
**Flow rate** 0.2 ml/min
**Oven Temp** 40 °C
**Injection vol** 40 µl

## Equipment

**Agilent 1100 Series:**
- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector Agilent ChemStation + software + polymer labs GPC software

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# Analysis of Acrylonitril-Butadiene-Styrene Copolymer using Gel Permeation Chromatography

**Angelika Gratzfeld-Huesgen**

**Polymer**


## Abstract

Acrylonitril-Butadiene-Styrene (ABS) copolymers are thermoplastic and elastic polymer blends that are used in the production of cars, housings , tubings, foils, sport kits and toys, where high impact strength, stability of shape and resistance against heat is required.

To ensure the highest quality, molecular weight (MW) data have to be evaluated for each batch of produced polymer. Gel Permeation Chromatography is an analytical tool used to characterize polymers which are soluble in organic solvents.


| MW data | Colored product | Starting product |
|---|---|---|
| Mp | 61665 | 80398 |
| Mn | 33321 | 46523 |
| Mw | 101677 | 108226 |
| Polydispersity | 30.51 | 2.326 |
| Mz | 279324 | 222124 |

Table 1
Molecular weight data of two ABS polymers

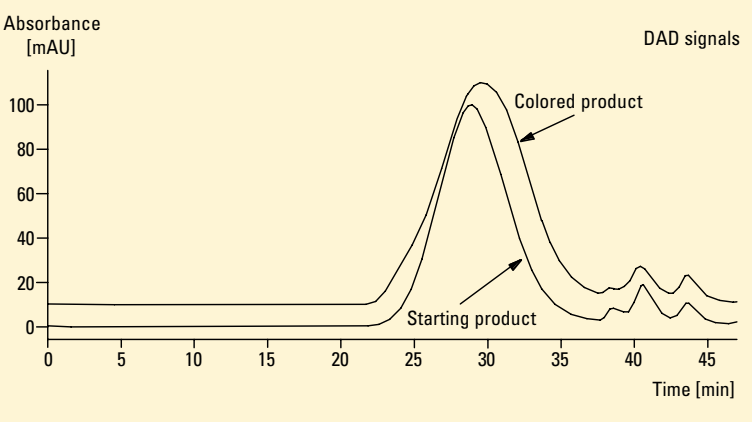


Figure 1
Molecular weight data of two ABS polymers

## Method Performance

Figure 1 shows the overlay of a starting product and the respective colored end product. The differences in MW data are shown in table 1.

## Conditions

**Column**
3 ˘ PSS GPC, 8 ˘ 300 mm, 5 µm
$10^6$, $10^5$, $10^3$ A
**Mobile phase** Tetrahydrofurane (THF)
**Flow rate** 0.8 ml/min
**Oven Temp** 20 ºC
**Injection vol** 10 µl
**UV DAD** 254/100 nm
**Refractive index detector**

**Sample preparation**
Sample dissolved in 1 ml THF, filtered with 0.45 µm filter
Polystyrene standards from PSS were used for narrow standard calibration

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## Method performance

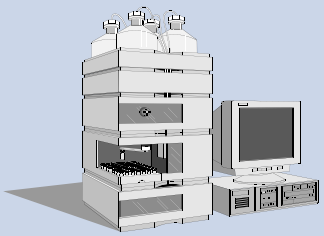
Precision of weight: average molecular weight (rsd of Mw) = < 1 %
Precision of number weight: average molecular weight (rsd of Mn) = < 2 %

## Equipment

**Agilent 1100 Series:**

- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector

Agilent ChemStation + software + polymer labs GPC software



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# Analysis of Styrene-Acrylonitrile-Copolymer using Gel Permeation Chromatography

**Angelika Gratzfeld-Huesgen**

**Polymer/ chemical industry**


## Abstract

Styrene-Acrylonitrile-Copolymer (SAN) contains 25 to 35 % acrylnitril, it is highly resistant against oil and fuel and used for the production of housings, show cases, food packaging, cosmetics and pharmaceutics. In 1989 65 000 tons were used in western Europe.

To ensure the highest quality, molecular weight (MW) data have to be evaluated for each batch of produced polymer. Gel Permeation Chromatography is an analytical tool used to characterize polymers which are soluble in organic solvents.


## Method Performance

Figure 1 shows the signal traces of different treated SAN plastics. A granulate was used to produce colorless chips. The chips were then grinded and injection molded a second time. The influence of these production procedures on the MW data are shown in table 1.

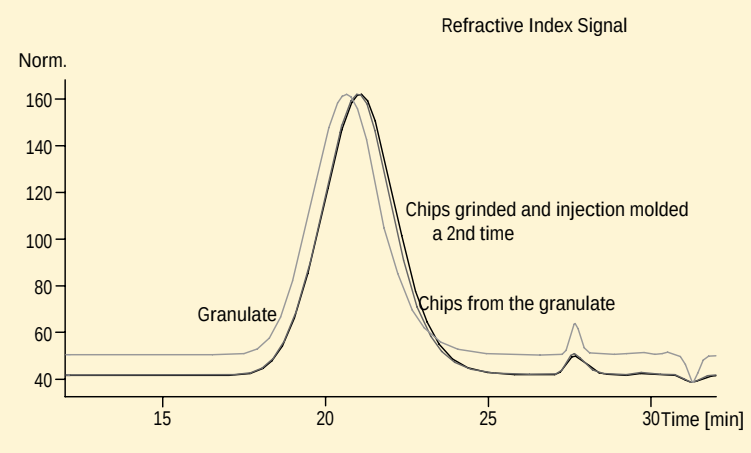


Figure 1
Styrene acrylonitrile from different production processes

## Conditions

**Column**
3 ˘ PLgel mixed-B, 7.5 ˘ 300 mm, 5 µm
**Mobile phase**
Tetrahydrofurane (THF)
**Flow rate**
1 ml/min
**Oven Temp**
20 °C
**Injection vol**
10 µl
**Refractive index detector**

**Sample preparation**
Sample dissolved in 1 ml THF
Polystyrene standards from PSS were used for narrow standard calibration

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## Method performance

Precision of weight: average molecular weight (rsd of Mw) = < 1 %
Precision of number weight: average molecular weight (rsd of Mn) = < 2 %

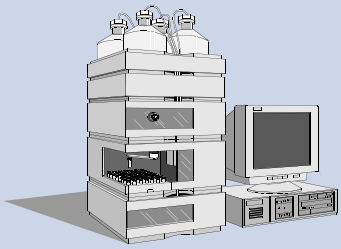
| MW data | Granulate | Chips | Chips, grinded and injection molded a second time |
|---|---|---|---|
| Mp | 86480 | 65812 | 62563 |
| Mn | 55525 | 42478 | 39616 |
| Mw | 117654 | 94559 | 91626 |
| Polydispersity | 2.119 | 2.226 | 2.313 |
| Mz | 224934 | 196436 | 195664 |
| Mz + 1 | 408416 | 376650 | 393504 |
| Mv | 106412 | 84598 | 81671 |

Table 1
The influence of the production procedures on the molecular weight data

## Equipment

**Agilent 1100 Series:**
- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector

Agilent ChemStation
+ software
+ polymer labs GPC software



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# Analysis of Epoxy Resins using Gel Permeation Chromatography

**Angelika Gratzfeld-Huesgen**

**Polymer /chemical industry**


## Abstract

Epoxy resins are produced through the reaction of bisphenol A and epichlorohydrin to macromolecules, (figure 1). These products are then used in the production of duroplasts, which are highly resistant against oil and fuel. Examples of products made from this material include, casting resins for the electrical industry, laminates for cars and airplanes, inner coatings for containers and tubings for the chemical industry. In 1987 85 000 tons were used in Germany.

To ensure the highest quality, molecular weight (MW) data have to be evaluated for each batch of produced polymer. Gel Permeation Chromatography is an analytical tool used to characterize polymers which are soluble in organic solvents.


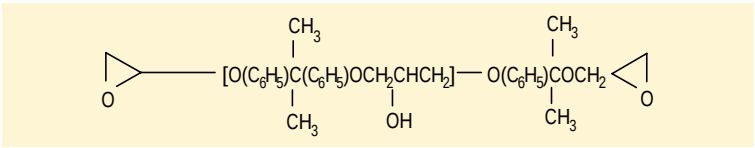


Figure 1
Epoxy resins

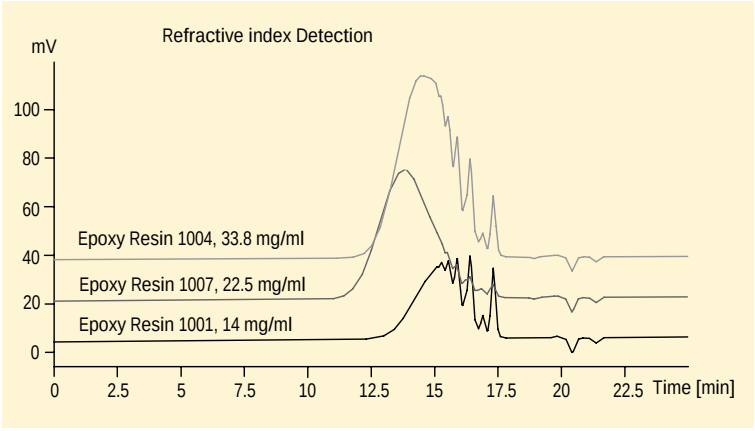


Figure 2
Analysis of three different epoxy resin qualities

## Conditions

**Column**
2 ˜ PLgel mixed-D, 7.5 ˜ 300 mm, 5 µm
**Mobile phase** Tetrahydrofurane (THF)
**Flow rate** 1 ml/min
**Oven Temp** 20 °C
**Injection vol** 20 µl
**UV detector**
DAD 254/100 nm, reference 360/100 nm
**Refractive index detector**

**Sample preparation**
Sample dissolved in 1 ml THF
Polystyrene standards from PSS were used for narrow standard calibration

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## Method Performance

Figure 2 shows an overlay of 3 different batches of epoxy resin. It can be seen that the epoxy resin 1001 has a relatively low molecular weight compared to the others. The epoxid 1007 has a high molecular weight whereas Epoxid 1004 falls in the middle. The molecular weight data of these three batches are combined in table 1. The precision of the molecular weight data was tested for batch 1001, and the MW data of 10 consecutive runs was evaluated. Figure 3 shows an overlay of the chromatograms. The rsd of Mw and Mn was calculated and found to be:

rsd of Mw over 10 runs = 0.66 %

rsd of Mn over 10 runs = 2.5 %

## Method performance

Precision of weight: average molecular weight (rsd of Mw) = < 1 %
Precision of number weight: average molecular weight (rsd of Mn) = < 3 %

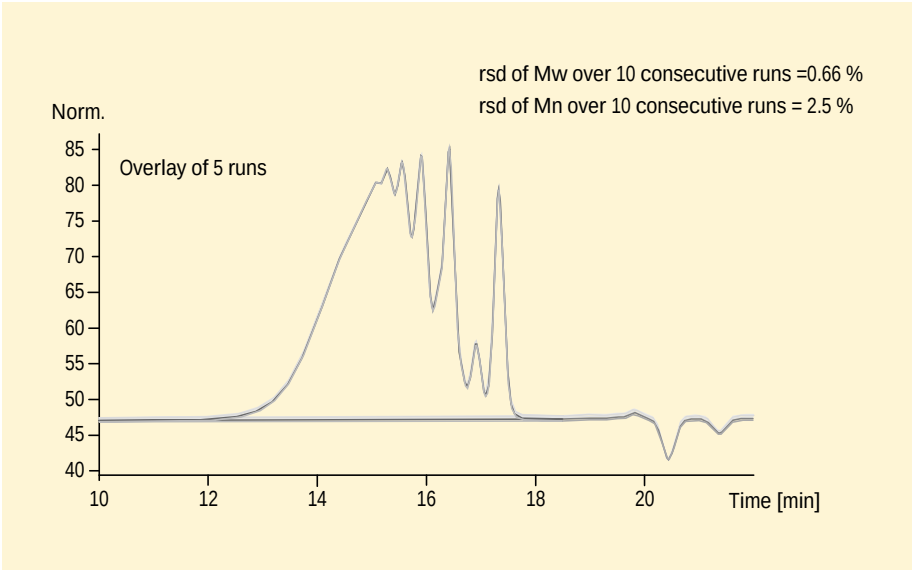
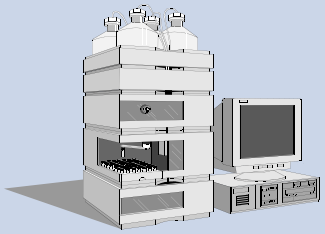



Figure 3
Precision of molecular weight data

## Equipment

**Agilent 1100 Series:**
- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector

Agilent ChemStation
+ software
+ polymer labs GPC software



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# Analysis of a Brenzcatechol Additive in Styrene using HPLC

**Angelika Gratzfeld-Huesgen**

**Polymer/ chemical industry**

## Abstract

Brenzcatechol (TBC) or Benzene-1,2-diol is used as an antioxidant for polymers. The concentration range of Brenzcatechol used varies between 10 and 100 ppm.

## Method Performance

Figure 1 shows the HPLC chromatogram of the analyzed styrene sample and the standard chromatogram of Brenzcatechol. For additional identification purposes, spectra can be taken and a comparison with the standard spectrum can be made. For this application, 2.1 mm columns were used in order to improve sensitivity so that the detection of 1 ng with signal to noise of 2, could be achieved.

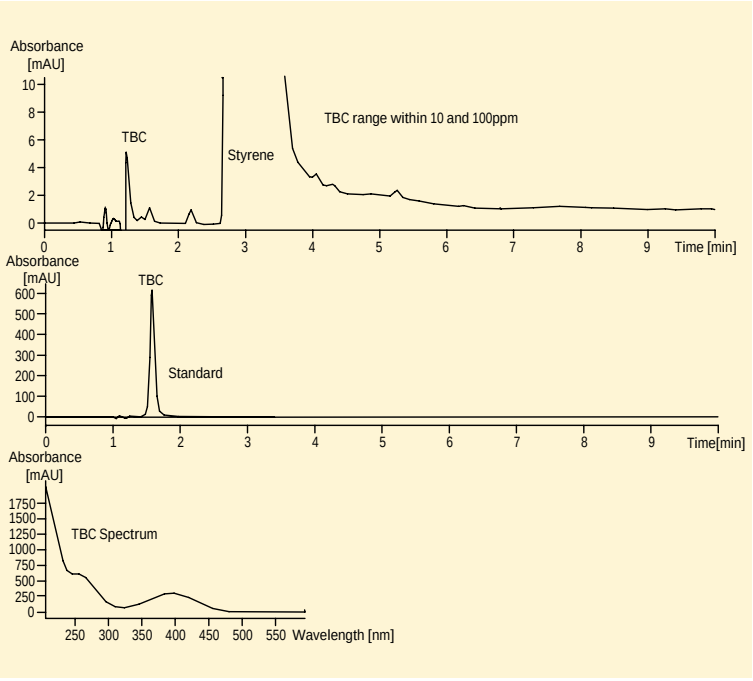


Figure 1
Analysis of brenzcatechine (TBC) additive in styrene

## Conditions

**Column**
200 x 2.1 mm Hypersil ODS, 5 µm
**Mobile Phase**
A = Water, B = Acetonitrile
**Gradient**
at start 50 % B, at 10 min 99.9 %B, at 20 min 50 %B
**Post Time** 6 min
**Flow Rate** 0.5 ml/min
**Oven Temp** 40 °C
**Injection Vol** 1 µl
**Diode array detector**
280/30 nm; Reference 500/50 nm

**Sample preparation**
1 ml styrene sample was diluted with 1 ml Tetrahydrofurane (THF)

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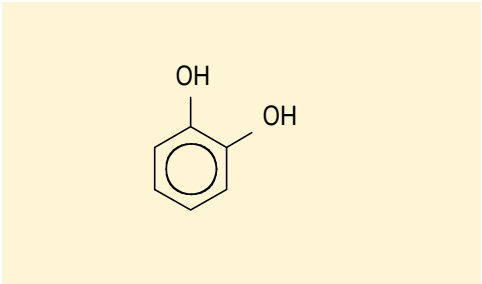



Figure 2
Brenzcatechin (Benzene-1,2-diol)

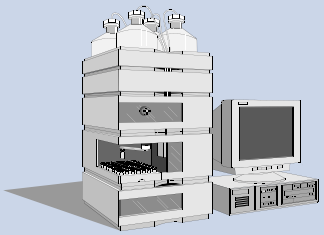
## Method performance

LOD: 1 ng or 1 ppm with signal/noise = 2
red RT <0.2 %
rsd area <2 %

## Equipment

**Agilent 1100 Series**
- degasser
- binary pump
- autosampler
- thermostatted column compartment
- diode array detector

Agilent ChemStation + software



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# Measuring intraday and interday precision of GPC-SEC analysis data

## Application

Heinz Goetz

**Abstract**

The daily (intraday) and day-to-day (interday) precision of $M_n$ and $M_w$ molecular weight data obtained by GPC-SEC has increased significantly over the past years. This Application Note describes what is possible nowadays in the area of intraday and interday precision of molecular weight data using state-of-the-art equipment. Typcial GPC conditions with organic eluents were chosen to obtain realistic-data.

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## Introduction

Precision of molecular weight data obtained by GPC-SEC is of great interest to polymer chemists since the advent of the technique in the late 1960s.[1,2,3,4] Due to a special calibration procedure using a linear elution volume (retention time) on the x-axis versus a logarithmic molecular weight on the y-axis, each deviation of the elution volume has an exponential effect on the precision of the molecular weight data. Therefore, demands on the hardware are more stringent than in other HPLC modes.

## Equipment

An Agilent 1100 Series GPC-SEC system consisting the following modules was used:

- Agilent 1100 Series vacuum degasser for efficient degassing of the mobile phase
- Agilent 1100 Series isocratic pump with large solvent cabinet
- Agilent 1100 Series autosampler with single valve design
- Agilent 1100 Series thermostatted column compartment for precise column temperatures
- Agilent 1100 Series refractive index detector with automatic recycle valve
- Agilent ChemStation Plus with GPC-SEC data analysis software

## Results and discussion

Table 1 shows the strong influence of flow deviations on the weight average molecular weight $M_w$ measured for a polystyrene sample. The system was calibrated at a flow rate of 1.0 mL/min. When analyzing the sample exactly at this flow rate the $M_w$ value is 35400. Table 1 shows that, for example, for a flow deviation of only +0.60 % or +1.30 % errors of 11 % and even 23.6 % occur. The column temperature stability between calibration and sample run is also important. A 4 °C change, as it can easily occur if the column compartment is not thermostatted, will create an error of 2.6 %. Hardware and software parameter effects on precision of molecular weight data are discussed in references 4 and 5.

As outlined before an excellent inter- and intraday precision of the retention times (elution volumes) is a fundamental prerequisite. To measure the retention time precision we injected a technical poly(styreneacrylonitrile) (SAN) automatically every day over 20 days. Figure 1 shows the plot of the retention times versus the run number. Table 2 shows the calculated relative standard deviations for retention time, $M_n$ and $M_w$. The very good interday (between days) precision from the 1st to the 20th day was 0.06 9%. The intraday (within day) precision was always below 0.05 % with

| Flow [mL/min] | Flow deviation [%] | $M_w$ | $M_w$ deviation [%] |
|---|---|---|---|
| 1.013 | +1.30 | 43400 | +23.6 |
| 1.006 | +0.60 | 39300 | +11.0 |
| 1.00 | 0 | 35400 | - |
| 0.992 | -0.80 | 31100 | -12.2 |
| 0.985 | -1.50 | 27700 | -21.80 |

**Table 1**
**Influence of flow variations on $M_w$**

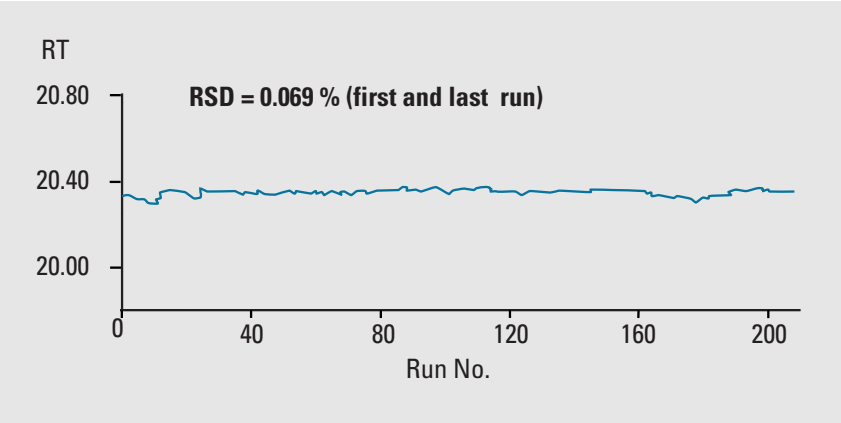


**Figure 1**
**Intra-and interday precision of retention times for a poly(styreneacrylonitrile) copolymer (SAN) over 20 days**

the exception of days 1, 2 and 15 but still below 0.08 %.

Figure 2 shows the precision of the styreneacrylonitrile analyses. It is an overlay of the injections made on days 1, 5, 10 and 20. The calculated relative standard deviations from day 1 to day 20 are shown for all injections. It should be pointed out that these very good data take almost all injections from day 1 to day 20 into account. Only about 10 injections had to be filtered out. They were stray points, for example, caused by a vial not filled correctly.

## Conclusion

The intra- and interday precision of $M_n$ and $M_w$ molecular weight data obtained by GPC-SEC has increased significantly in recent years. With the Agilent 1100 Series GPC-SEC system intra-(within one day) and interday precision data (over 20 days) for $M_n$ and $M_w$ below 1.5 % were calculated in completely automated analyses for broad distributed polymers with THF as eluent. These results are mainly based on

- HPLC pumps with an intra- and interday flow stability better than 0.1 % (based on polymer retention time),
- column thermostats with a temperature precision better than 0.5 °C,
- automated eluent recycling after the analysis which results in a better conditioned system,

| Day | % RSD retention time | % RSD for $M_n$ | % RSD for $M_w$ |
|---|---|---|---|
| 1 | 0.071 | 1.16 | 1.12 |
| 2 | 0.075 | 1.43 | 0.78 |
| 3 | 0.020 | 0.92 | 0.72 |
| 4 | 0.032 | 0.82 | 0.83 |
| 5 | 0.030 | 1.18 | 0.97 |
| 6 | 0.038 | 0.95 | 0.78 |
| 7 | 0.037 | 1.13 | 1.08 |
| 8 | 0.030 | 0.58 | 0.81 |
| 9 | 0.043 | 0.91 | 0.66 |
| 10 | 0.025 | 0.73 | 0.32 |
| 11 | 0.022 | 1.43 | 0.43 |
| 12 | 0.021 | 0.81 | 0.35 |
| 13 | 0.016 | 0.89 | 0.59 |
| 14 | 0.029 | 0.88 | 1.19 |
| 15 | 0.065 | 1.08 | 1.27 |
| 16 | 0.002 | 0.68 | 0.70 |
| 17 | 0.045 | 0.99 | 0.85 |
| 18 | 0.038 | 0.94 | 0.78 |
| 19 | 0.041 | 0.95 | 0.80 |
| 20 | 0.009 | 0.70 | 0.71 |
| **Average %RSD per day** | **0.035** | **0.96** | **0.78** |

**Table 2**
**Calculated relative standard deviations (intraday) for retention time, $M_n$ and $M_w$**

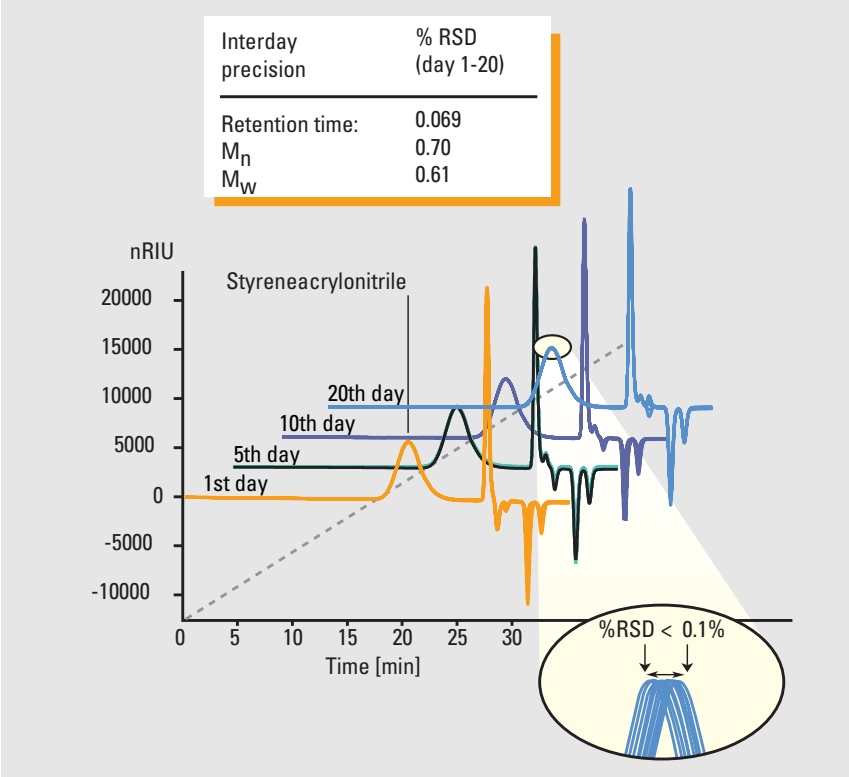


**Figure 2**
**Overlay of all analyses of the poly(styreneacrylonitrile) sample on days 1, 5, 10 and 20. A zoom into the analyses of day 20 is shown in the bottom right.**

- refractive index detectors with low noise (± $2.5 \times 10^{-9}$ RIU)* and low drift ($200 \times 10^{-9}$ RIU/h)* for correct and repeat able baseline and integration window setting,
- software with flexible and repeatable integration and cal culation algorithms to adapt to broad polymer peaks, and
- full automation capabilities reducing human errors.

Good precision data not only improves the reliability of the results but also the productivity because less time-consuming recalibrations are needed.[5]

* According to ASTM E-1303-95 "Practice for Refractive Index Detectors used in Liquid Chromatography". Reference Conditions: response time 4 s, 35 °C, 1 ml/min water, restriction capillary

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# Process control of polystyrenes

**Application**

**Heinz Goetz and Angelika Gratzfeld-Huesgen**

Polystyrenes are widely used for the production of packaging materials, household goods, cases of electronic equipment, toys, and insulation materials. Polymerization can be performed with pure styrene or by copolymerization with butadiene, acrylonitrile, rubber and methylstyrene. The properties of the product strongly depends on the monomers used, the molecular weights and the molecular weight distribution.

Figure 1 shows an overlay of 3 chromatograms of a technical polystyrene – the original granulate, one after 1st injection moulding and one after second injection moulding. After the first injection moulding there is almost no change in the chromatogram and therefore the molecular

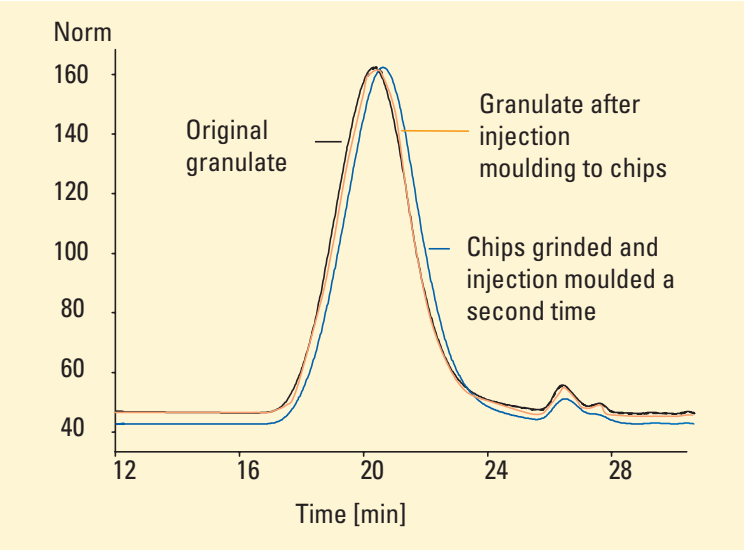


Figure 1
Overlay of three chromatograms of a technical polystyrene

## Conditions

**Sample preparation**
Sample was dissolved in THF. Polystyrene EasyCal Vial standards (Agilent p/n 79911-60500 and 79911-60501) were used for narrow standard calibration.

**Column**
3 x PLgel mixed B, 7.5 x 300 mm, 10 µm (Agilent p/n 79911GP-MXB) in series

**Mobile phase**
Tetrahydrofuran

**Flow rate**
1.0 mL/min

**Column compartment temperature**
20° C

**Injection volume**
10 µL

**Detector**
Refractive index detector, alternatively VWD, 254 nm

weight distribution. After grinding the chips, and injection moulding a second time there is a significant change which will have an effect on the properties. The visual information is supported by the number average molecular weight, $M_n$, as calculated by the ChemStation data analysis software:

$M_n$ (original granulate): 59000
$M_n$ (after second process): 55000

To characterize such small differences in polymers reliably a GPC-SEC instrument with excellent precision, such as the Agilent 1100 Series GPC-SEC system, is required. Further information on the precision of this system is given in application brief “Precision in GPC-SEC analysis”, Agilent publication number 5988-0109EN.

## HPLC performance

| | |
|---|---|
| RSD of $M_w$ | < 1% |
| RSD of $M_n$ | < 2% |

## Equipment

**Agilent 1100 Series GPC-SEC system**
consisting of

- vacuum degasser for efficient degassing of the mobile phase
- isocratic pump with large solvent cabinet
- autosampler with single valve design
- thermostatted column compartment for precise column temperatures
- refractive index detector with automatic recycle valve
- ChemStation Plus with GPC-SEC data analysis software

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# Process control of polyamide-6,6

**Application**

**Heinz Goetz**
**and R. Schewe**

Polyamide-6,6 is a synthetic polyamide typically produced by polymerizing hexamethylendiamine and adipinic acid. It is widely used for the production of fibres, foils and raw materials. Typical applications are in the clothing industry for stockings and sports apparel, in the building industry for synthetic carpets and in the electronic industry for housings. The properties of polyamide-6,6 strongly depend on molecular weight and molecular weight distribution.

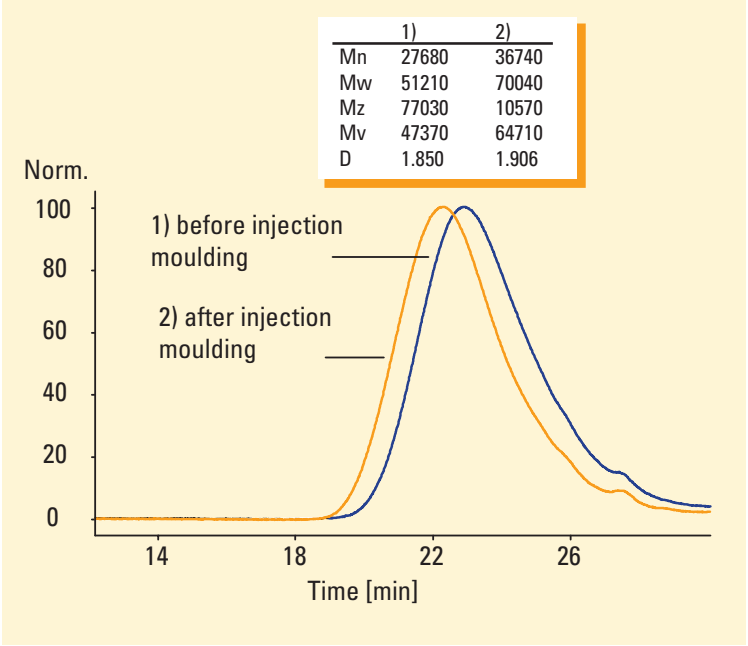


Figure 1
Overlay of two chromatograms of a technical polyamide-6,6 used for producing the housing of drilling machines

## Conditions

**Sample preparation**
Samples were dissolved in the mobile phase and filtered (0.45 µm).
Polystyrene EasyCal vial standards (Agilent p/n 5064-8281) were used for narrow standard calibration.

**Column**
PFGgel $10^3$ A, 8 x 300 mm, 5 µm in series with a PFGgel 300 Å, 8 x 300 mm, 5 µm and a PFGgel 100 A, 8 x 300 mm, 5 µm

**Mobile phase**
Trifluoroethanol and 1 g/l potassiumtrifluoroacetate

**Flow rate**
1.0 mL/min

**Column compartment temperature**
35 ° C

**Injection volume**
10 µL

**Detector**
Variable wavelength detector, 254 nm

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Figure 1 shows an overlay of two chromatograms of a technical polyamide-6,6 used for the production of the housing of drilling machines. One chromatogram was obtained with the original granulate and the other one after injection moulding. The picture and table clearly show that the moulding process changes the chromatograms and the molecular weight data. For a consistent product quality the moulding process needs to be optimized and controlled by GPC-SEC. Because of the insolubility of polyamide-6,6 in typical GPC-SEC eluents such as tetrahydofuran, toluene or dimethylformamide trifluoroethanol was used. To reduce the number of adsorptive sites on the stationary phase 1g/l of potassiumtrifluoroacetate was added to the mobile phase.

## HPLC performance

| | |
|---|---|
| RSD of $M_w$ | < 1% |
| RSD of $M_n$ | < 2% |

## Equipment

**Agilent 1100 Series GPC-SEC system**
consisting of
- vacuum degasser for efficient degassing of the mobile phase
- isocratic pump with large solvent cabinet
- autosampler with single valve design
- thermostatted column compartment for precise column temperatures
- refractive index detector with automatic recycle valve
- ChemStation Plus with GPC-SEC data analysis software

*Columns supplier:*
Polymer Standards Service, Mainz, Germany

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# Quality control of paint resins

**Application**

**Heinz Goetz**

Resins such as alkyd or acrylic resins are essential ingredients of paints. The rapid determination of the resin quality is of particular interest. The capability to respond quickly to quality control requirements increases productivity and therefore profit. This example shows the quality control analysis of two resins used for high quality paints in the car industry. One resin showed good adhesion properties while the other one failed. The poor quality resin failed because the high molecular weight fraction was not present (figure 1, hatched area).

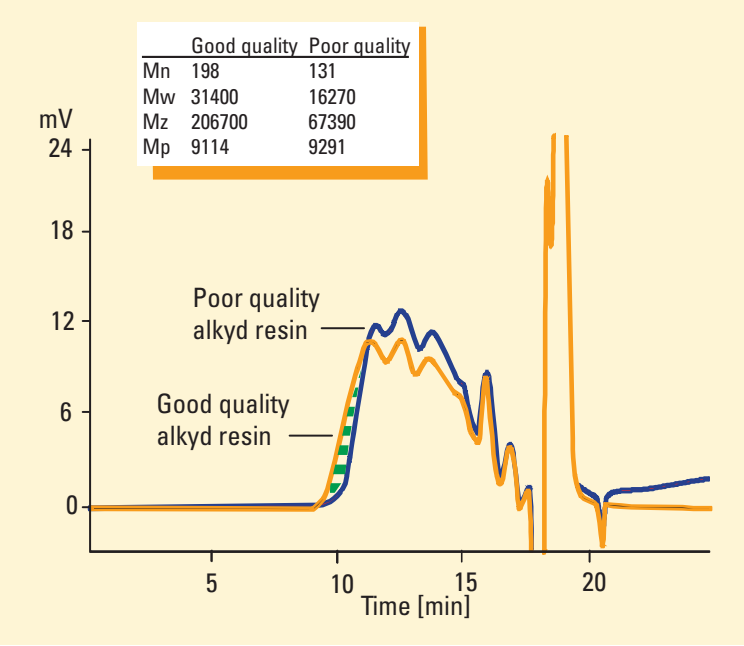


Figure 1
Quality control of two resins

## Conditions

**Sample preparation**
Resins were dissolved in THF. Polystyrene EasyCal vial standards (Agilent p/n 5064-8281) were used for narrow standard calibration.

**Column**
PLgel $10^2$ Å, 7.5 x 300 mm, 5 µm (Agilent p/n 79911GP-501) in series with a PLgel 5 x $10^3$, 7.5 x 300 mm, 5 µm (Agilent p/n 79911GP-502) and a PLgel $10^4$ Å, 7.5 x 300 mm, 5 µm (Agilent p/n 79911GP-504)

**Mobile phase**
Tetrahydrofuran

**Flow rate**
1.5 mL/min

**Column compartment temperature**
20 °C

**Injection volume**
100 µL

**Detector**
Refractive index detector

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The ChemStation GPC data analysis software provides the conventional graphical information of the chromatograms with the additional rapid numeric data in form of molecular weight averages and the report subsets. With the report subsets we could easily determine that the high molecular weight fraction (between the arrows) was 22 % for the high quality polymer but only 14 % for the low quality polymer.

## HPLC performance

RSD of $M_w$ < 1%
RSD of $M_n$ < 2%

## Equipment

**Agilent 1100 Series GPC-SEC system**
consisting of

- vacuum degasser for efficient degassing of the mobile phase
- isocratic pump with large solvent cabinet
- autosampler with single valve design
- thermostatted column compartment for precise column temperatures
- refractive index detector with automatic recycle valve
- ChemStation Plus with GPC-SEC data analysis software

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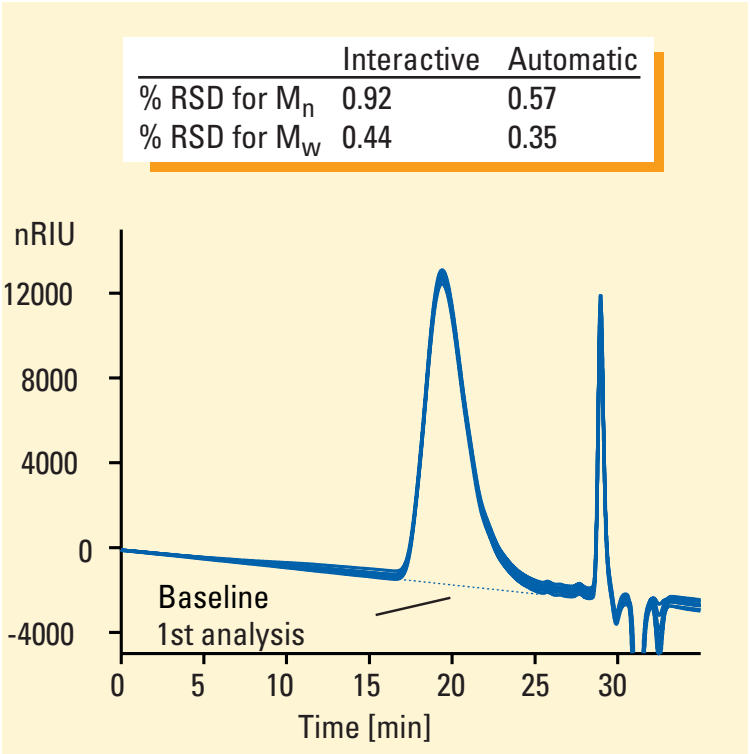
# Automatic versus manual (interactive) data evaluation in GPC-SEC analysis

**Application**

**Heinz Goetz**

**Abstract**
It is widely accepted among polymer analysts that the data acquisition part of the analysis can be automated with modern, state-of-the-art GPC hardware without any loss of accuracy and precision. Regarding data evaluation there is still some discussion on whether automatic or interactive baseline setting should be used. In this note we have analyzed a technical polystyrene sample 10 times with interactive and another 10 times with fully automatic data evaluation. The figure shows an overlay of the 10 chromatograms for the technical polystyrene




## Conditions

**Sample**
Technical polystyrene, 0.1 % in THF
**Eluent**
Tetrahydrofuran (HPLC grade)
**Column**
3 × PLGel mixed B in series, 7.8 × 300 mm, 10 µm (Agilent p/n 79911GP-MXC)
**Flow rate**
1 ml/min
**Column compartment temperature**
20° C
**Injection Volume**
100 µl
**Polymer standards**
Polystyrene EasyCal Vial standards (Agilent p/n 5064-8281)

Figure 1
Technical polystyrene sample analyzed with interactive and automatic baseline

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sample and the intraday precision data for automatic and interactive baseline setting. We see that the precision data for the automatic mode is slightly better than for the interactive mode for both $M_n$ and $M_w$. We also found a similar superiority for other polymers. This is however not the case for every sample, such as a polymer with a strong tailing peak or when the peak height is small due to low sample concentration or low refractive index.

In most cases the ChemStation's *Enhanced Integrator* is perfectly suited to detect the start and end of a polymer peak correctly and to ensure reliable automation. It provides the following improved capabilities:

- optimized baseline tracking using parameters from the individual method and data files,
- better peak allocation,
- additional initial parameters to remove noise-generated peaks
- ease of use–the *Enhanced Integrator* algorithm has a new user interface based on tool bars and automatically focuses on key information.

Typical advantages of completely automated analysis (from data acquisition to reporting) are:

- often at least similar precision,
- less room for human interpretation and errors,
- higher traceability and consistency, and
- improvement of efficiency by freeing trained staff from time-consuming work

## Equipment

**Agilent 1100 Series GPC-SEC system**
consisting of

- vacuum degasser for efficient degassing of the mobile phase
- Isocratic pump with large solvent cabinet
- Autosampler with single valve design
- Thermostatted column compartment for precise column temperatures
- Refractive index detector with automatic recycle valve
- Variable wavelength detector, 254 nm, standard cell
- ChemStation Plus with GPC-SEC data analysis software

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# Molecular weight characterization of polyacrylamides

**Application**

**Peter Kilz**
**and Heinz Goetz**

The analyzed polyacrylamides are used for drag reduction effects of ships and submarines. They are sprayed onto the ship's surface and reduce drag and therefore noise and fuel consumption. A further application of polyacrylamides is in water clarification purposes as setting aids. The polymer acts as flocculants to help remove contaminants from the water stream. All three polyacrylamides have a very high weight average molecular weight $M_w$.The GPC-SEC method

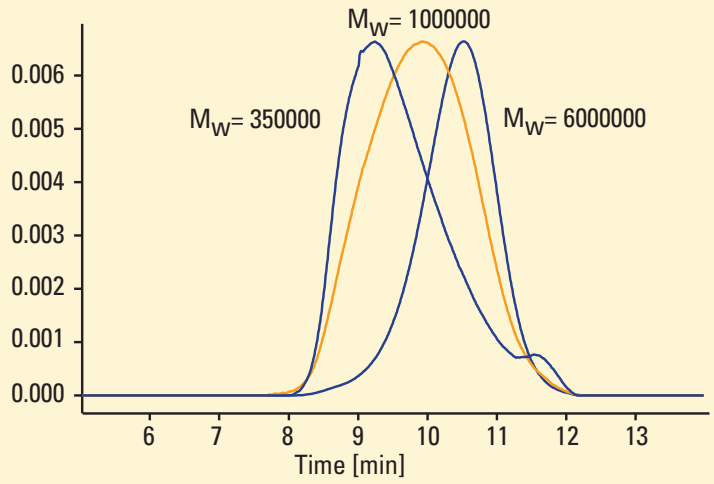


Figure 1
Overlay of high molecular weight polyacrylamides chromatograms

## Conditions

**Sample preparation**
Sample was dissolved in mobile phase (concentration 0.1 %).
**Column**
PSS Suprema $10^4$, 8 x 300 mm, 10 µm
**Mobile phase**
0.3 M $NaNO_3$
**Flow rate**
0.5 mL/min
**Column compartment temperature**
25 ° C
**Injection volume**
100 µL
**Detector**
Refractive index detector
**Polymer standards**
PSS broad polyacrylamide standards

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presented here shows an easy but reliable and precise analysis for the molecular weight characterization of polyacrylamides. Besides the weight average molecular weight $M_w$ the ChemStation GPC-SEC data analysis software calculates data as Mn, Mz, Mp, Mv, polydispersity D, differential and integral molecular weight distribution. The software allows internal standard and detector delay corrections, and includes narrow, broad, universal and integral calibration.

## HPLC performance

| | |
|---|---|
| RSD of $M_w$ | < 2% |
| RSD of $M_n$ | < 5% |

## Equipment

**Agilent 1100 Series GPC-SEC system**
consisting of

- vacuum degasser for efficient degassing of the mobile phase
- isocratic pump with large solvent cabinet
- autosampler with single valve design
- thermostatted column compartment for precise column temperatures
- refractive index detector with automatic recycle valve
- ChemStation Plus with GPC-SEC data analysis software

*Columns supplier:*
Polymer Standards Service, Mainz, Germany

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# Analysis of polyvinyl alcohol

**Application**

**Heinz Goetz**

Polyvinyl alcohols (PVA) are industrially synthesized by the catalytic reaction of polyvinyl acetates with alcohols, typically methanol. Due to properties such as excellent biological degradeability, water solubility , toxilogical harmlessness they are widely used as emulgators, binding agents in adhesives, salves and haircream. The properties can be varied with the molecular weight distribution and the molecular weight which ranges from 20000 to 100000 g/mol. Both parameters can be fast and reliably monitored by aqueous SEC. This is a convenient method for quality control analyis, and is more informative in production control and end-use performance evaluation than single-point viscosity measurements.

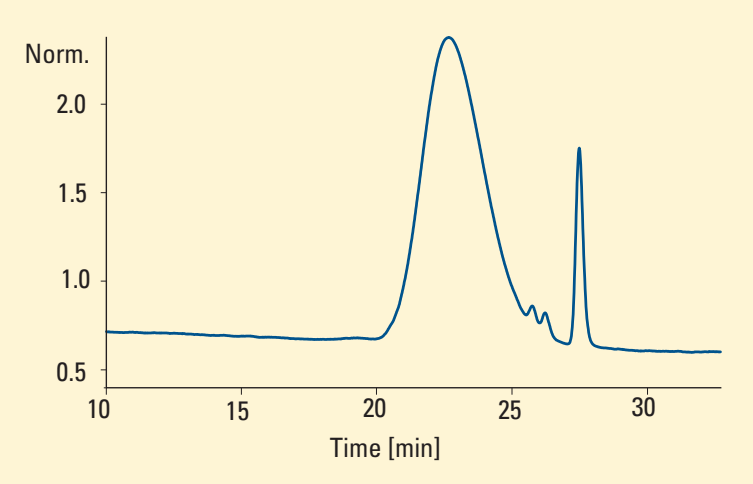


Figure 1
SEC chromatogram of polyvinyl alcohol

## Conditions

**Sample preparation**
PVA was dissolved in the mobile phase (concentration 0.1 %)

**Column**
3 × PL aquagel-OH 30 in series, 7.5 × 300 mm, 8 µm (Agilent p/n 79911GF-MXA) in series with PL aquagel-OH 30, 7.5 × 300 mm, 8 µm (Agilent p/n 79911GF-083)

**Mobile phase**
0.2 M $NaNOH_3$, $NaH_2PO_4$, pH 7

**Flow rate**
1 mL/min

**Column compartment temperature**
25 ° C

**Injection volume**
100 µl

**Detector**
Refractive index detector

**Polymer standards**
Polyethylene oxide EasyCal standards in vials for calibration (Agilent p/n 5064-8280)

## HPLC performance

| | |
|---|---|
| RSD of $M_w$ | < 1.5 % |
| RSD of $M_n$ | < 3 % |

## Equipment

**Agilent 1100 Series GPC-SEC system**
consisting of

- vacuum degasser for efficient degassing of the mobile phase
- isocratic pump with large solvent cabinet
- autosampler with single valve design
- thermostatted column compartment for precise column temperatures
- refractive index detector with automatic recycle valve
- ChemStation Plus with GPC-SEC data analysis software

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# Screening and Qualitative Identification of Antioxidant Polymer Additives by HPLC with UV/VIS and APCI-MS Detection

Application

**Consumer Products**


## Author

Michael Woodman
Agilent Chemical Analysis Solutions
Wilmington, DE
USA



## Abstract

**Liquid chromatography with ultraviolet/visible spectroscopy and mass selective detection is a powerful approach to antioxidant analysis and identification. Examples illustrate that mobile-phase conditions affect the quality and usability of the acquired data. Unknown compounds can be identified with sufficient MS data and additive degradation can be quickly evaluated.**


## Introduction

Plastic products are an essential part of our lives today. Whether they are used for automotive components, CDs, toys, or biocompatible replacement parts for humans, they are the subjects of intense research into new and improved polymers and blends. Equally important is the selection and quantity of chemical additives which are used to provide color, density, opacity, stiffness, flexibility, resistance to heat, light and air, flame retardance, and to improve processing properties during pellet creation and final product fabrication.

This application note examines several antioxidant (AO) types, their chemical composition, and suitable high-performance liquid chromatography (HPLC) conditions for assessing their concentration and identity, as well as their degradation products.

AOs arise from various compound classes including small hindered phenols, large hydrophobic hindered phenols, and phosphite or phosphonate linked aromatics. Examples appear in Tables 1 and 2.

**Table 1. AO Studied with Structures**

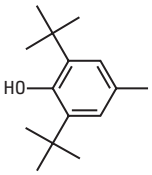
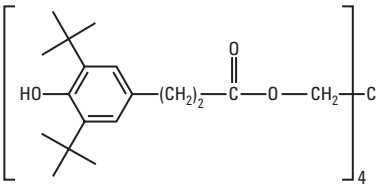
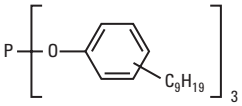
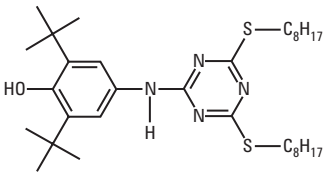
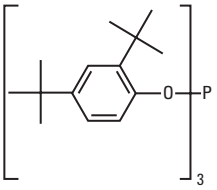
| | | |
|---|---|---|
| Name: | BHT | Butylated hydroxytoluene |
| Formula: | $C_{15}H_{24}O$ |  |
| Molecular Weight: (MW) | 220.2 | |
| Trade name: | Irganox 1010 (CibaGeigy) | Pentaerythritol tetrakis(3-(3,5-di-tert- butyl-4-hydroxyphenyl) propionate) |
| Formula: | $C_{73}H_{108}O_{12}$ |  |
| Molecular Weight: (MW) | 1176.8 | |
| Trade name: | Naugard P (Uniroyal) | Tris nonylphenyl phosphite |
| Formula: | $(C_{15}H_{23}O)_3P$ |  |
| Molecular Weight: (MW) | 688.5 | |
| Trade name: | Irganox 565 (CibaGeigy) |  |
| Formula: | $C_{33}H_{56}N_4OS_2$ | |
| Molecular Weight: (MW) | 588.4 | |
| Trade name: | Irgafos 168 |  |
| Formula: | $C_{42}H_{63}O_3P$ | |
| Molecular Weight: (MW) | 646.5 | |

**Table 2. Other Common AOs**

| Name | Formula | MW |
|---|---|---|
| BHA | $C_{11}H_{16}O_2$ | 180.1 |
| t-BHQ | $C_{10}H_{14}O_2$ | 166.1 |
| Cyanox 1790 | $C_{42}H_{57}N_3O_6$ | 699.4 |
| Ethanox 330 | $C_{54}H_{76}O_3$ | 772.6 |
| Irganox 1076 | $C_{35}H_{62}O_3$ | 530.5 |
| Sandostab P-EPQ | $C_{68}H_{92}O_4P_2$ | 1034.6 |

Gas chromatographs with conventional detectors or mass spectrometers (MS) can readily analyze many small molecules; however, the increased molecular weight (MW) and decreased volatility of many AOs makes gas chromatography (GC) generally unsuitable. Liquid chromatography (LC) is a common choice because it can analyze materials exhibiting a wide MW range and varied solubility. Since LC is generally a nondestructive technique, it offers the possibility of compound isolation and recovery.

Many AOs contain functionalized aromatic groups and offer distinctive ultraviolet/visible spectroscopy (UV/VIS) spectral opportunities. This detector type is an essential part of an additive analysis system. Since UV/VIS detectors are relatively insensitive to the chromatographic mobile phase, they are readily compatible with gradient-elution separation methods.

The presence of functionalized aromatic rings, oxygen, nitrogen, phosphorous, and sulfur in many of the AOs also makes them ideal candidates for investigation by atmospheric pressure ionization mass spectrometry (API-MS). Compound identity can be supported by matching retention data, UV/VIS spectra, and from the MS, a molecular ion (essentially giving the molecular weight of the compound). Depending on the type of ionization and MS chosen, further identification can be made where higher energy is employed, causing fragmentation of the molecules. These fragments help experienced users propose chemical structures.

### Instrumentation and General Method

Agilent 1100 LC system:

- Quaternary gradient pump with low volume degasser
- Binary gradient pump with degasser, for pre-MSD reagent addition
- ALS automatic sampler with 2-mL vial tray
- Thermostatted column compartment with automated 6-port, 2-position switching valve
- Diode array UV/VIS spectrophotometer

General chromatographic conditions:

- Gradient elution of increasing organic-solvent strength with combinations of:

  Water/Acetonitrile (ACN)
  Water/Methanol (MeOH)
  Water/Methanol/Tetrahydrofuran (THF), HPLC grade

- UV/VIS spectral-data collection from 200–400 nm, 1-nm slit, 4 nm resolution
- UV/VIS single-wavelength collection for 210 and 280 nm, at 4 nm resolution

### ChemStation PC Data and Control System

Mass selective detector (MSD) SL single quadrupole MS with APCI interface

Fragmentor: 100 V, positive and negative ionization

Vaporizer: 400 °C

Nebulizer: 50 psi nitrogen

Drying gas: 6 LPM Nitrogen

Column: Zorbax XDB-C8, 4.6 mm id × 50 mm L, 3.5 µm particles

### Gradients:

**Method 1. "MeOH/THF", Column 30 °C, 25 min cycle**

| Flow | Time | % Water | % MeOH | % ACN | % THF |
|---|---|---|---|---|---|
| 1 | 0 | 40 | 50 | 0 | 10 |
| 1 | 15 | 0 | 90 | 0 | 10 |
| 1 | 20 | 0 | 90 | 0 | 10 |
| 1 | 21 | 40 | 50 | 0 | 10 |

**Method 2. "MeOH", Column 40 °C, 20 min cycle**

| Flow | Time | % Water | % MeOH | % ACN | % THF |
|---|---|---|---|---|---|
| 1 | 0 | 40 | 60 | 0 | 0 |
| 1 | 10 | 0 | 100 | 0 | 0 |
| 1 | 15 | 0 | 100 | 0 | 0 |
| 1 | 16 | 40 | 60 | 0 | 0 |

**Method 3. "ACN", column 50 °C, 20 min cycle**

| Flow | Time | % Water | % MeOH | % ACN | % THF |
|---|---|---|---|---|---|
| 1 | 0 | 40 | 0 | 60 | 0 |
| 1 | 10 | 0 | 0 | 100 | 0 |
| 1 | 15 | 0 | 0 | 100 | 0 |
| 1 | 16 | 40 | 0 | 60 | 0 |

## Experimental Results

Figures 1 through 3 are overlaid UV chromatograms for nine AOs, using three different gradients.

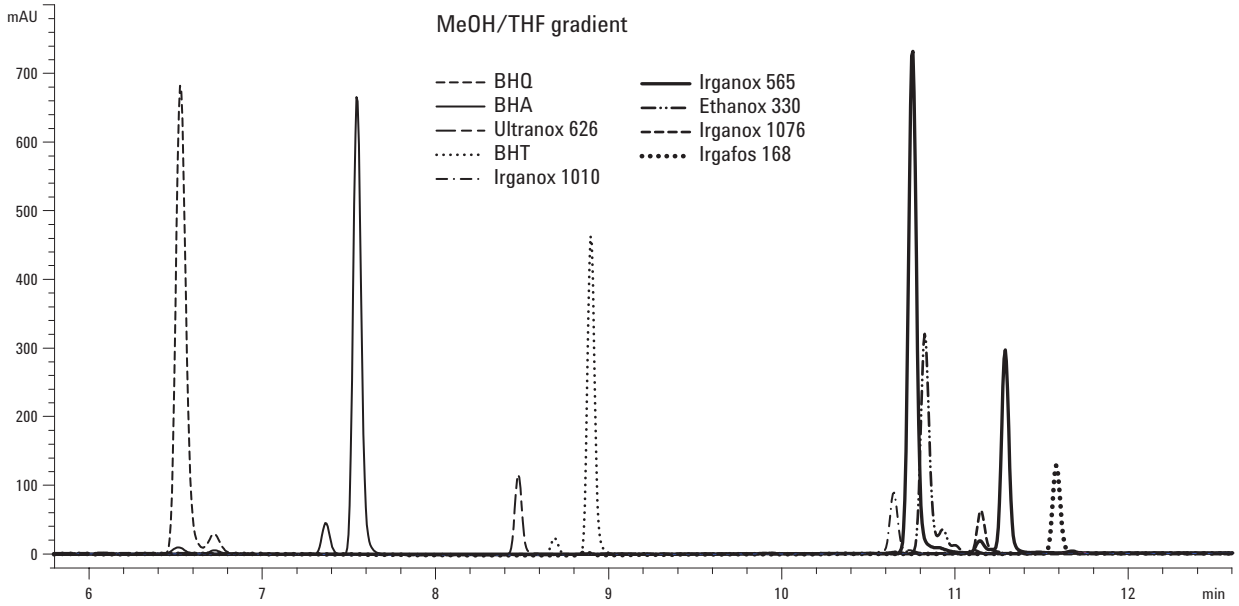



**Figure 1. Overlaid UV chromatograms for the selected AOs using the methanol/THF gradient.**

Many samples have minor peaks originating from impurities or degradation products having structures similar to the parent molecules. For the smaller molecules like BHA, BHQ, and BHT, there is no problem with resolution. For larger molecules, there is reduced resolution in the 10- to 12-minute region. These molecules have unique MWs, though, and can be analyzed using selective MS detection.

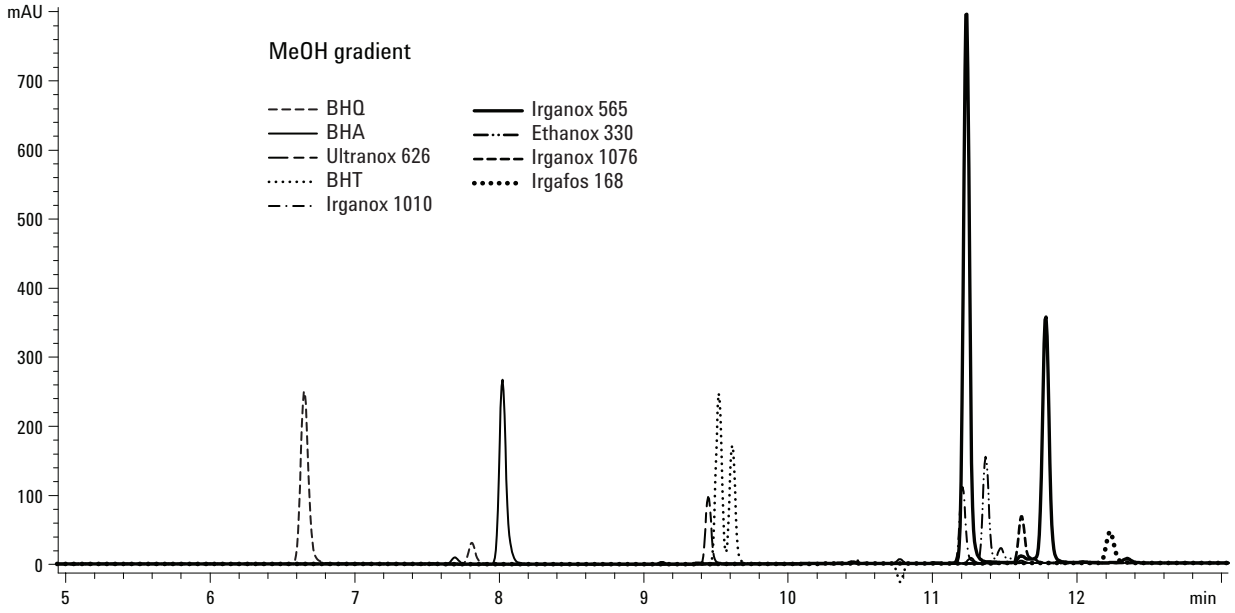



**Figure 2. Separation of AOs using the MeOH gradient.**

Using the MeOH gradient, relative separation is somewhat different, and as before, the smaller molecules are well resolved. The larger molecules in the 11- to12-minute region exhibit reduced resolution, but can be analyzed using selective MS detection.

Figure 3 shows the separation of the same AOs using the ACN gradient.

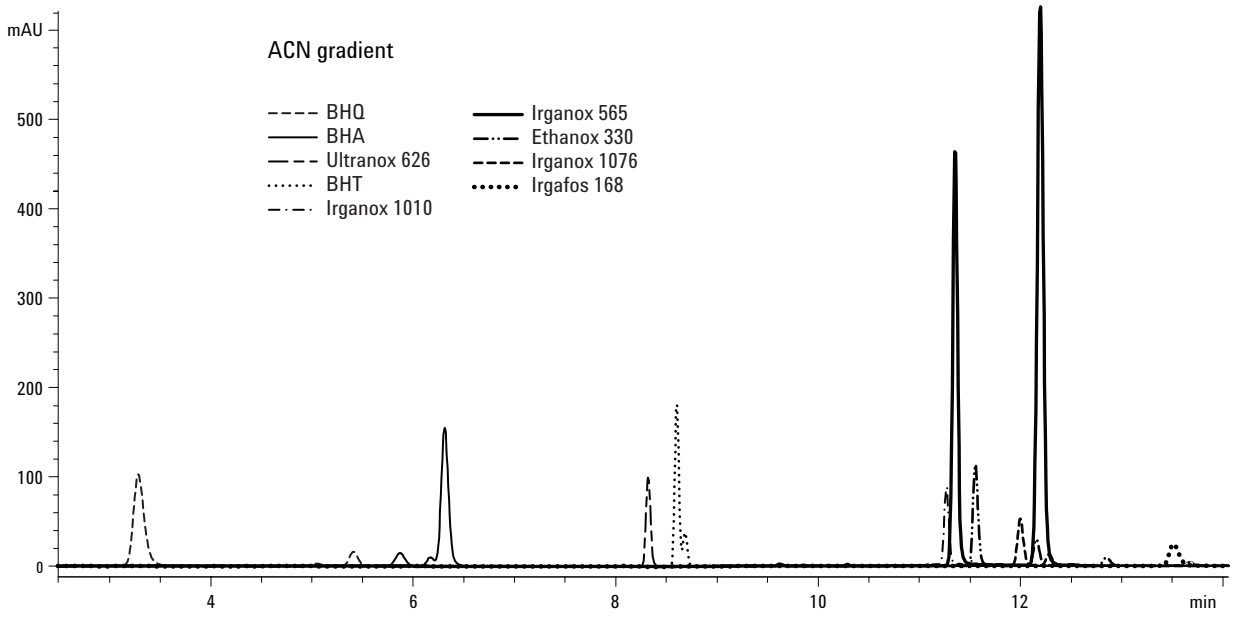



**Figure 3. Separation of AOs using the ACN gradient.**

Once again, no problem exists with resolution of the smaller molecules. For larger molecules in the 11- to 12-minute region there is somewhat better resolution. ACN has the best UV transparency at low wavelengths, maximizing baseline stability in the wavelength range where UV response would be observed for the AOs.

It is often attractive to use UV/VIS libraries to tentatively identify components in the sample mixture. This approach is especially useful when the various analytes have distinct spectra. Where many AOs have phenolic rings with characteristic UV/VIS spectra, distinguishing analytes by this approach is difficult and the user must rely on retention time data to support any identification attempt.

As we investigate various AO molecules, it is useful to note the general mass range for single- and multiple-ring structures. See Figure 4.

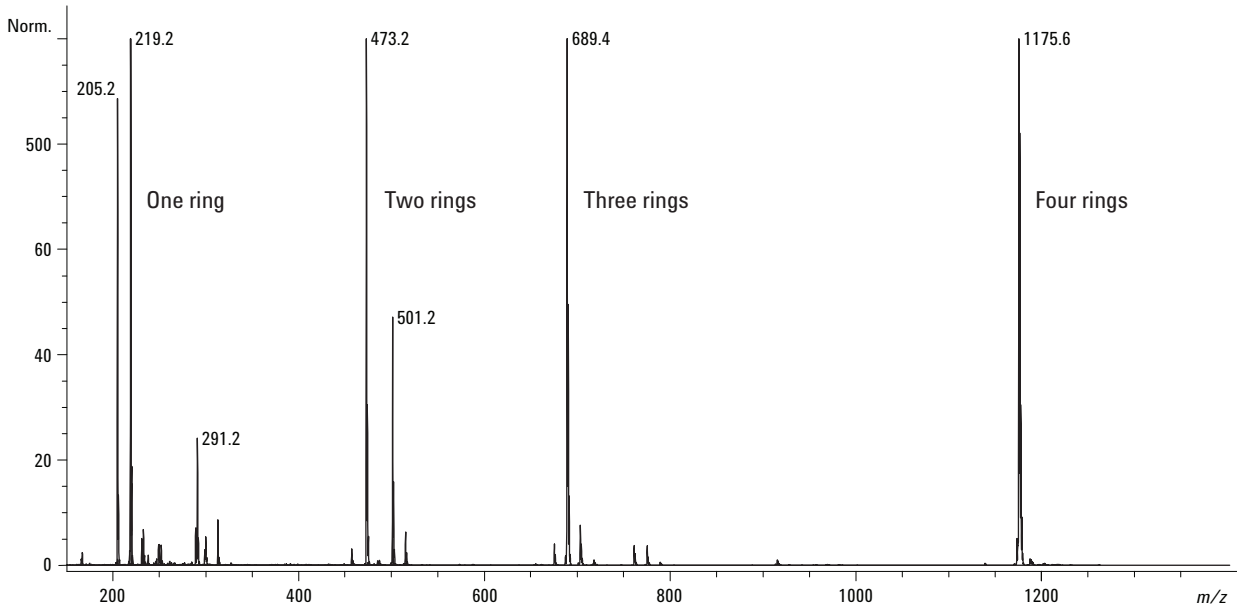



**Figure 4. Overlaid AO mass spectra, illustrating effect of ring number on observed mass range.**

In Figure 4 we see intact and fragmentation ions representing structures from one to four aromatic rings. The *m/z* 219 is $[M-H]^-$ for BHT while *m/z* 205, less one $CH_2$, is a fragmentation ion of a larger molecule having the hindered phenolic feature. The *m/z* 473 and *m/z* 501 are fragments discussed later in this text. The *m/z* 689 is Naugard P, $(C_{15}H_{23}O)_3P$. The *m/z* 1176, Irganox 1010, $(C_{73}H_{108}O_{12})$ has four rings and long alkyl chains that increase the mass and remind us that it is important to acquire mass data well over 1000 Da for general AO screening and analysis.

The mobile phase absorbance background invariably affects UV/VIS spectra. See Figure 5. In this example, the UV/VIS spectra for Irgafos 168 are shown for the three previously described solvent conditions.

Significant differences in response, especially in the important low UV range, are generally observed. This interference is also found with many ionic modifiers added to the mobile phase to control ionization of analytes, possibly improving the separation or enhancing ionization of the compounds in the MS.

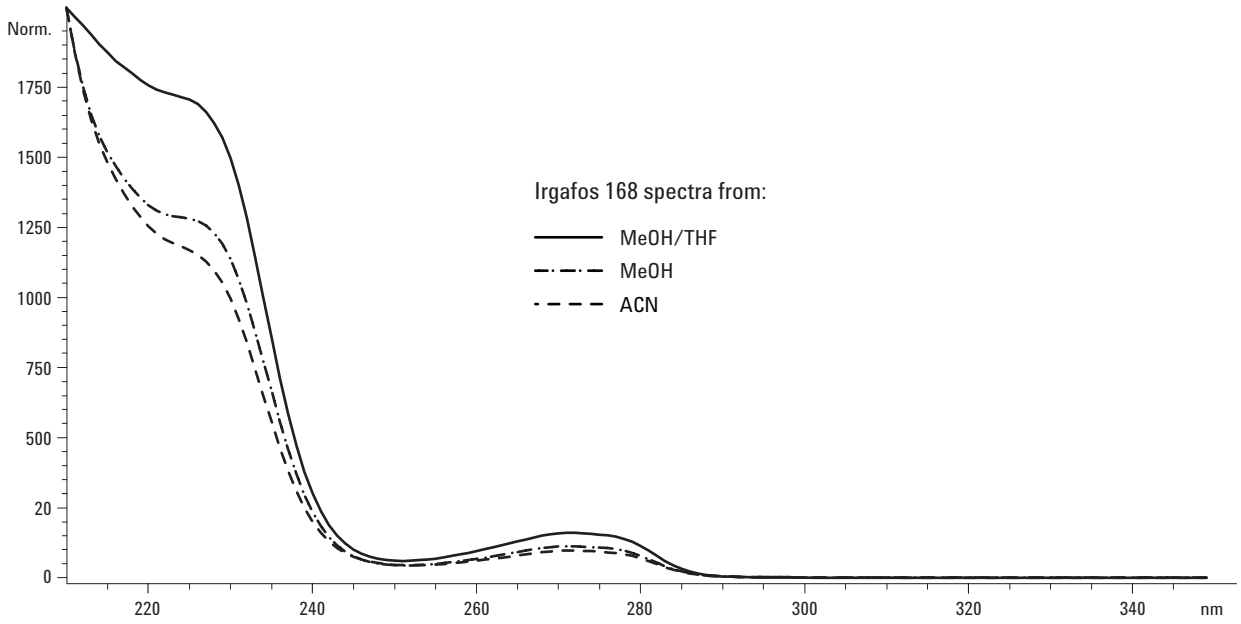



**Figure 5. Solvent effects on UV/VIS spectra for Irgafos 168.**

Ionization, and thus ion abundance in the MS, may also be affected by the mobile phase composition.

In Figure 6, the extracted positive-ion spectra for Irgafos 168 (molecular weight 646.5, detected as the $[M+H]^+$ ion) appear in the three previously described solvent conditions, where it elutes in high organic concentrations. Observe the significant differences in response, with the lowest response in ACN. Reduced response from the molecular ion may be from decreased ionization or increased fragmentation. It may be possible to add modifiers after the UV, and prior to the MSD inlet, to enhance MS response in circumstances where the solvent offers chromatographic or UV/VIS advantages but negatively impacts ionization in the MS.

The degree of fragmentation in the MS may also be affected by the mobile-phase composition. In Figure 7, the extracted negative-ion spectra for Irgafos 168 appear in the three previously described solvent conditions.

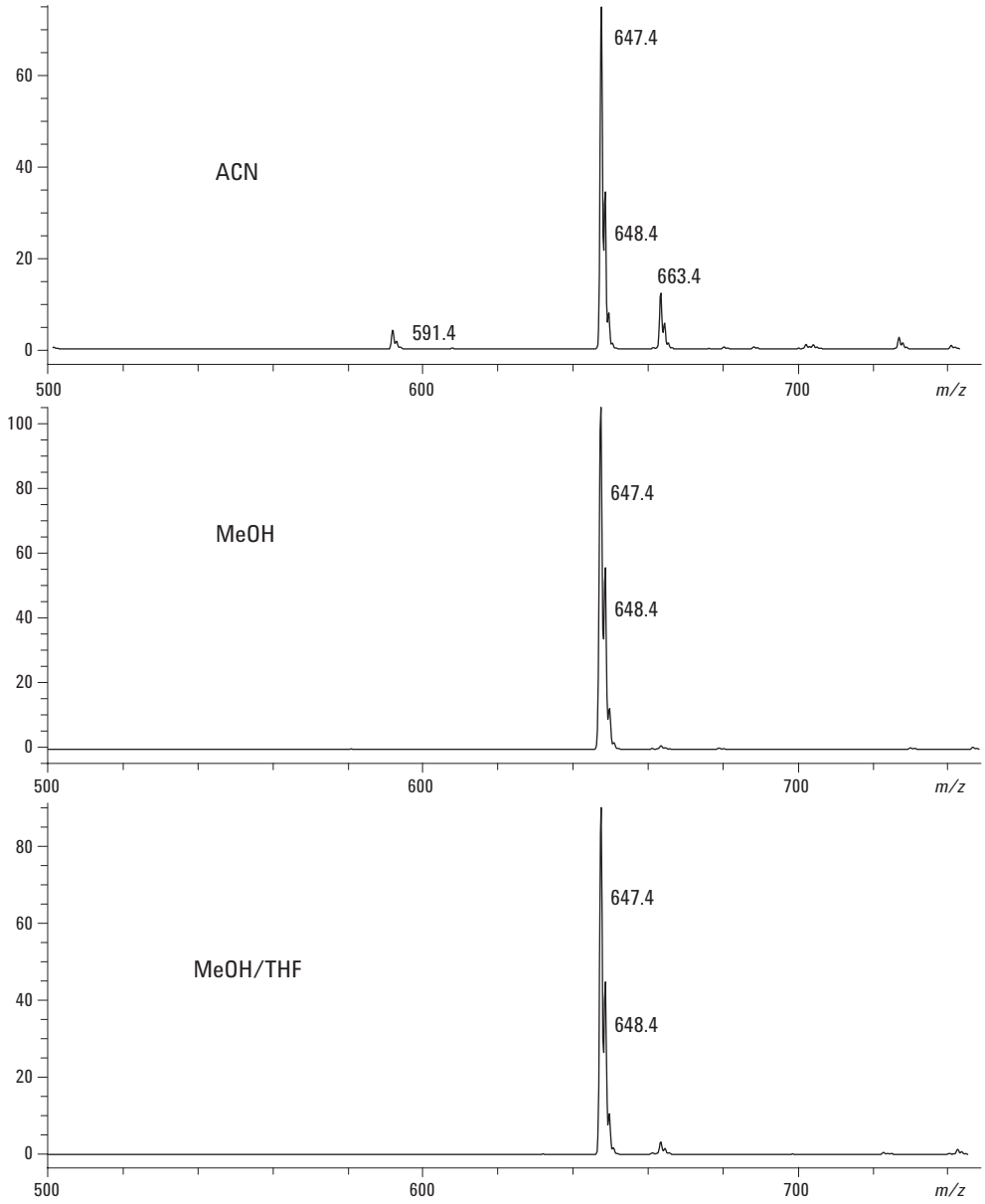



**Figure 6. Solvent effects on positive-ion MSD spectra for Irgafos 168.**

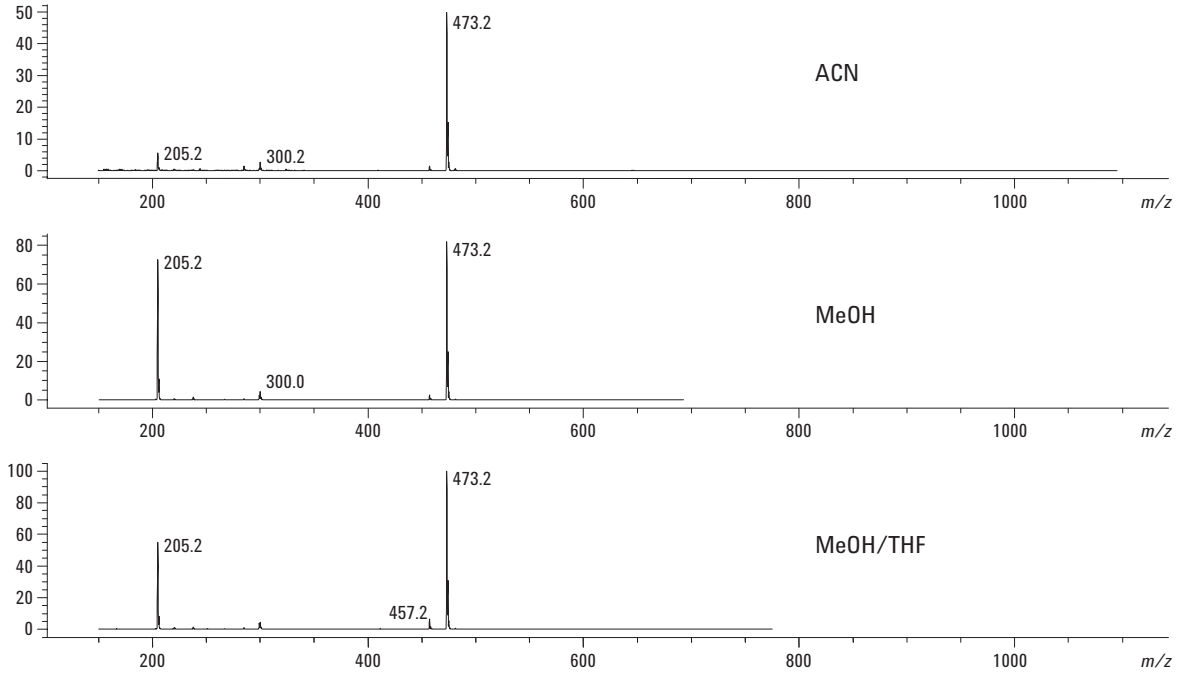



**Figure 7. Solvent effects on negative-ion MSD spectra for Irgafos 168.**

Note the significant differences in response with the lowest response in ACN. Reduced response for the molecular ion and fragment ions suggests that the ACN response is simply reduced ionization. Based on known degradation chemistry of Irgafos 168 and similar compounds, the *m/z* 473 fragment is likely $[C_{28}H_{42}O_4P]^-$ where an "arm" is lost (*m/z* 205) and an oxygen remains on phosphorous as P=O.

### Identification of Unknowns

Retention data may allow experienced chromatographers to suggest how an unknown peak might differ structurally from a group of knowns run under the same conditions, but identification invariably takes far more resources than simple elution patterns provide. From UV/VIS data, we can often suggest molecule class, especially so in our discussion of compounds commonly having the phenoxy group in the chemical structure. UV/VIS spectra may be suggestive but, when used without significant prior knowledge, lack sufficient resolution to confirm identity. MS data, on the other hand, have the spectral resolution necessary to infer structural details leading to actual chemical identification. The following examples describe several situations in which either detector would be helpful.

In the simple case of an unknown containing either BHA or BHT, the UV spectra (Figure 8) are sufficiently unique to allow a reasonable identification along with characteristic retention data. Nearly 1.5 minutes separate these two peaks in the conditions above and little doubt would remain.

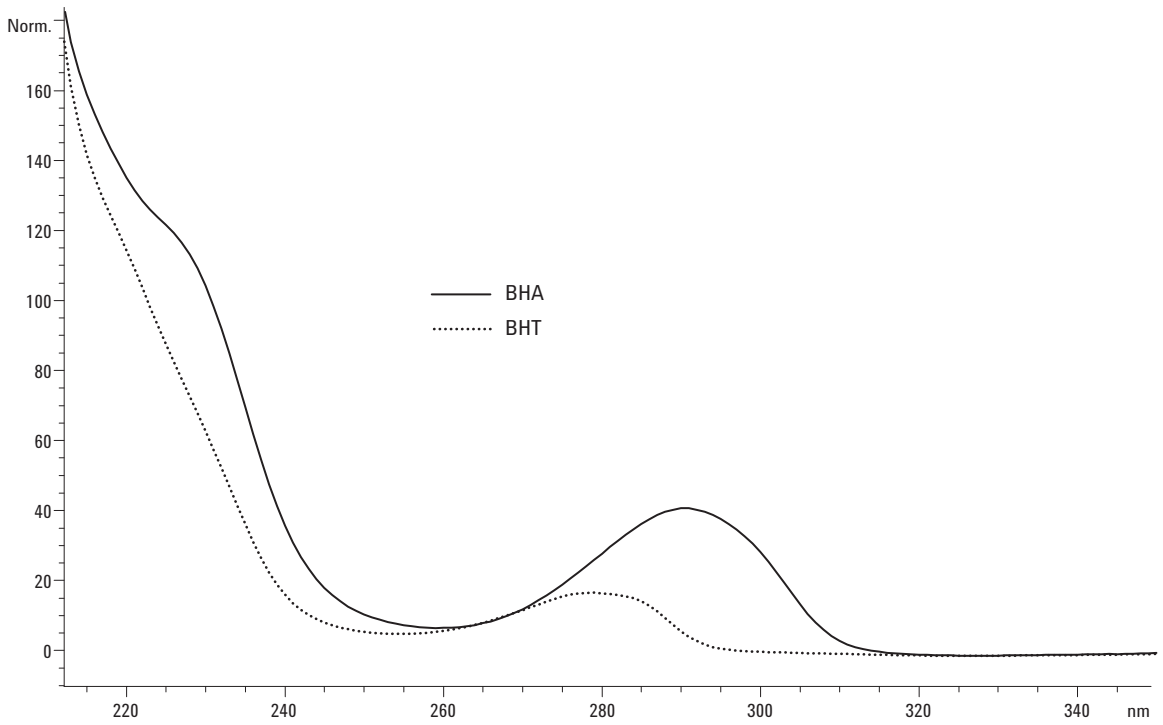



**Figure 8. Extracted UV spectra from mixture containing only BHA and BHT.**

Using MS data for the same sample, we would reach similar conclusions. See Figure 9.

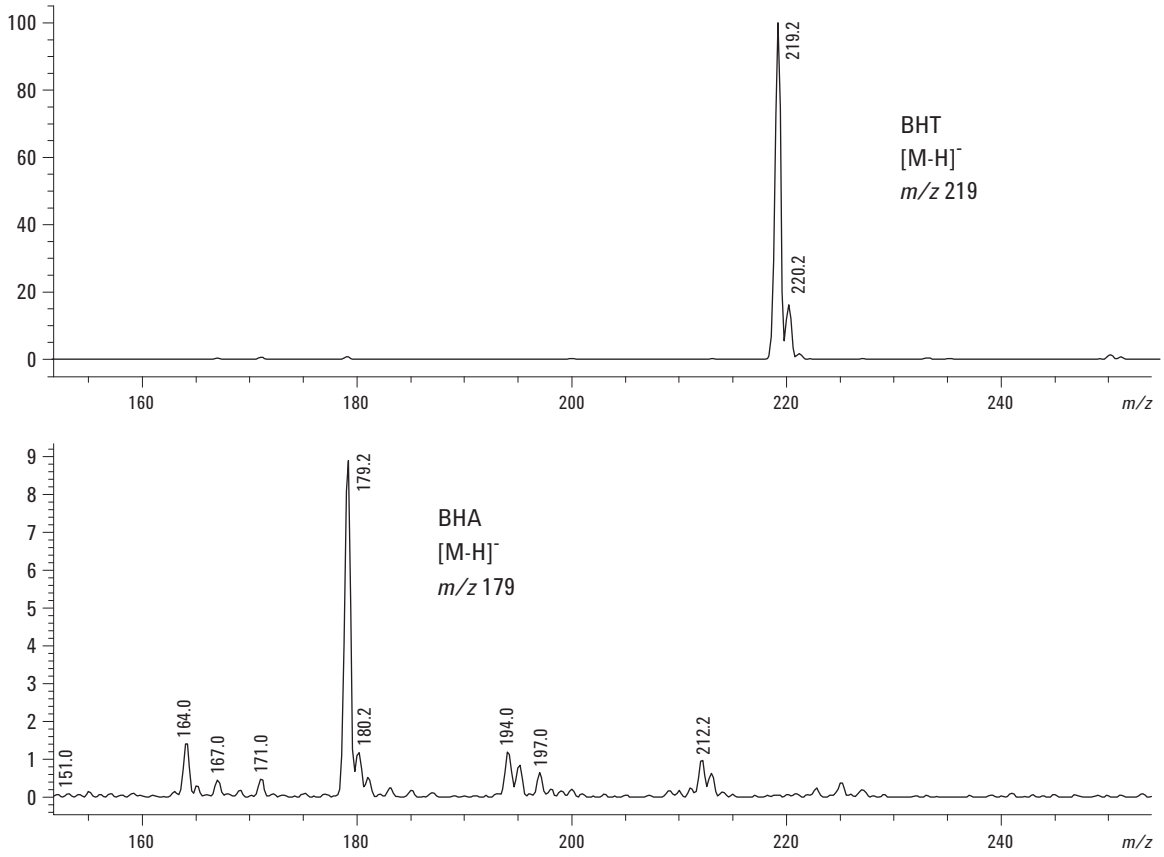



**Figure 9. Extracted negative-ion MS spectra from mixture containing only BHA and BHT.**

Retention data suggests two distinct molecules leading to an unambiguous identification without any need for MS fragmentation data.

When examining MS data, we generally expect to see classic molecular ions, either molecular mass+1 in positive-ion mode or mass-1 in negative-ion mode. These conditions, in the absence of significant adduct or fragment ion formation, often yield the best sensitivity and quantitative result. Such is the case in the Irganox 565 example shown in Figure 10.

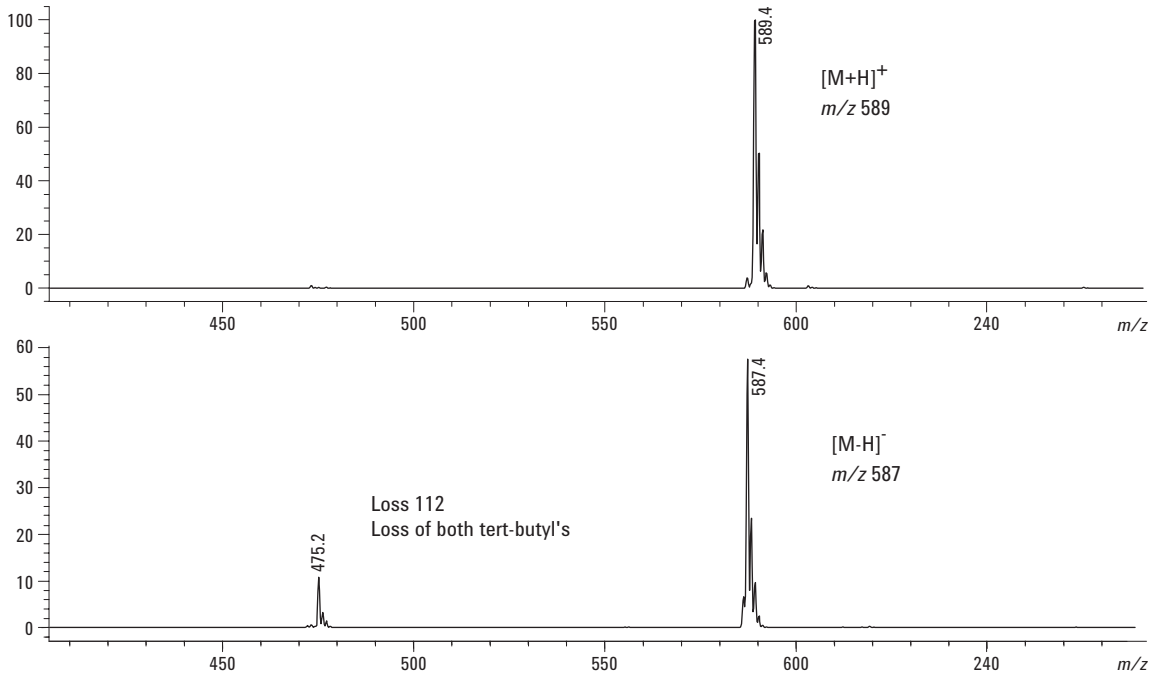



**Figure 10. Positive- (upper) and negative- (lower) ion spectra for Irganox 565, using MeOH/THF gradient.**

Only minor amounts of fragmentation are seen in the negative-ion spectrum, corresponding to the loss of both tert-butyl groups. In some cases, a radical ion is formed and the MS ion observed will correspond to the mass of the parent molecule. It is difficult to predict when this may occur, but the user must be prepared to interpret the spectral data with this situation in mind.

Irganox 1010 was run under the same conditions and produced minimal fragmentation in the negative-ion spectrum. An $[M\text{-}H]^-$ ion at *m/z* 1175.6 is detected for the expected MW 1176.8. See Figure 11.

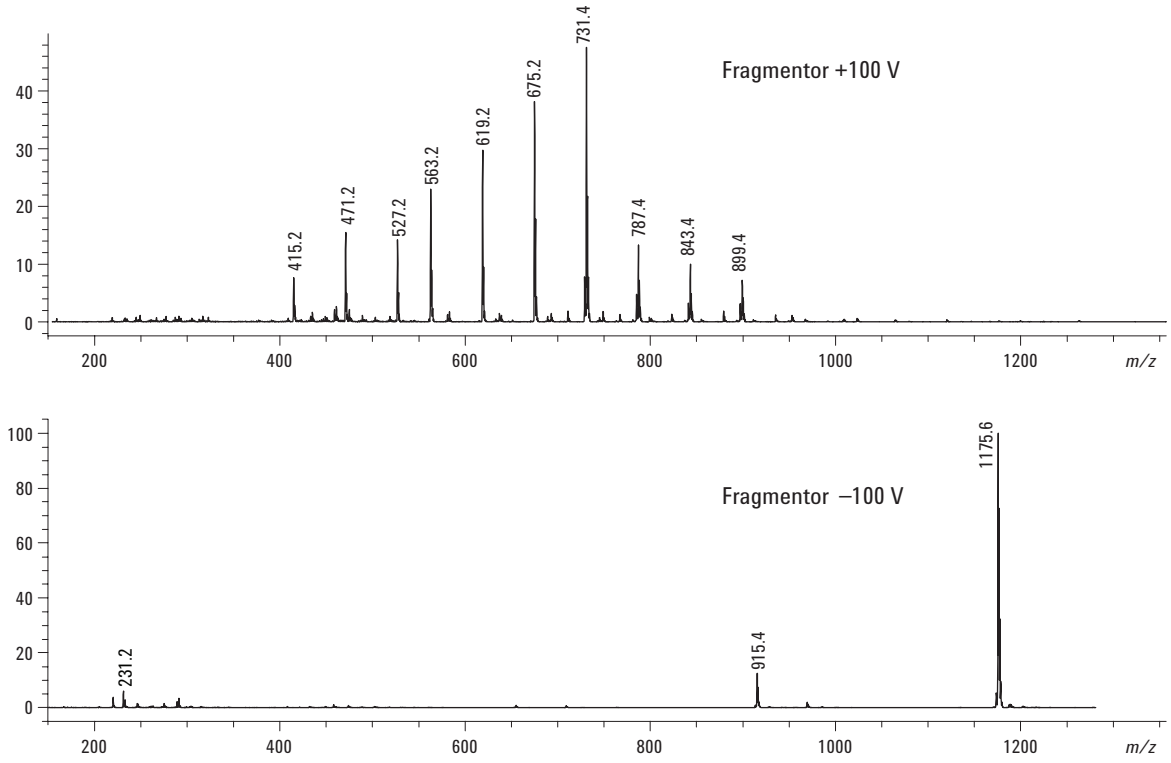



**Figure 11. Positive- (upper) and negative- (lower) ion spectra for Irganox 1010, using MeOH/THF gradient.**

The positive-ion spectrum, however, is devoid of any useful amount of the molecular ion. The resulting fragmentation pattern suggests a molecule with a significant number of tert-butyl structures which, with the molecular ion from negative ionization, is consistent for a tentative identification for the named compound.

Little change is observed in the fragmentation pattern by reducing the fragmentor voltage to 25 V, though overall ion production is reduced from the 100 V experiments. See Figure 12.

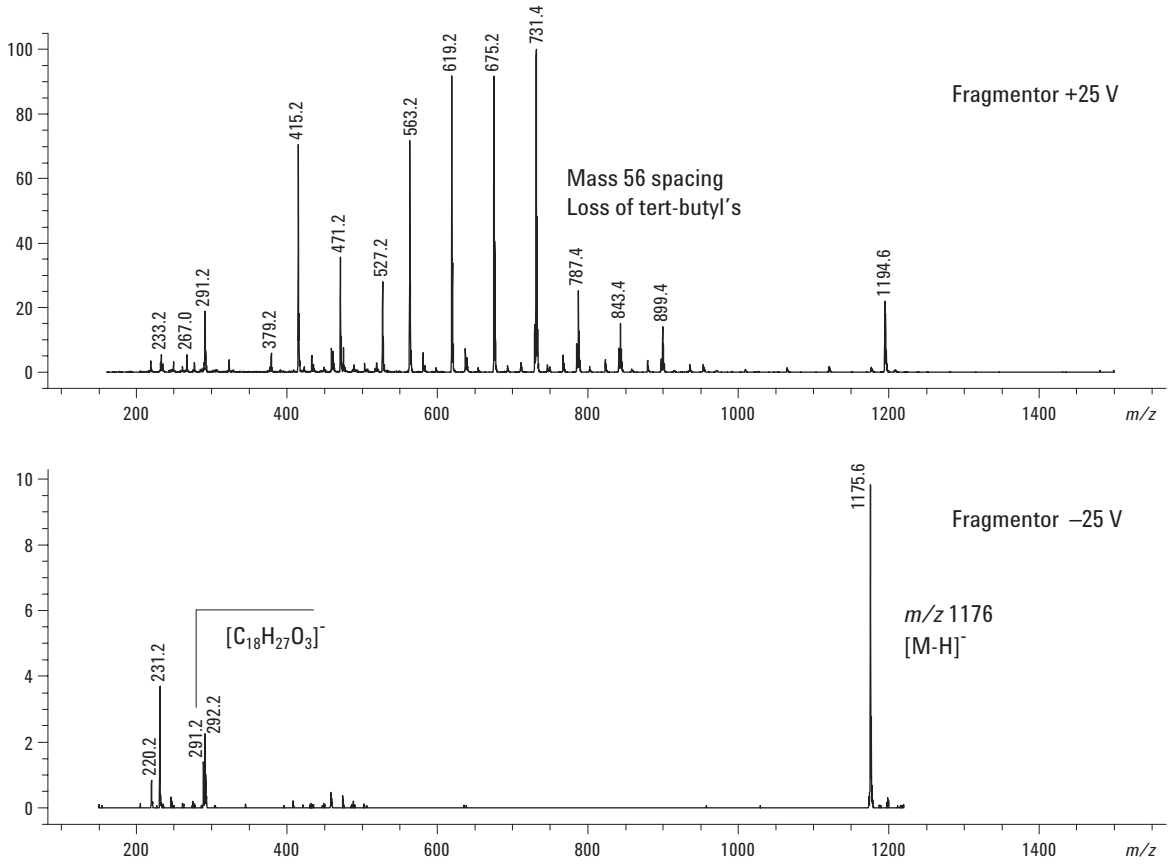



**Figure 12. Positive- (upper) and negative- (lower) ion spectra for Irganox 1010, using MeOH gradient.**

An *m/z* 291 fragment ion can be observed, which corresponds to one of the symmetrical "arms" of the molecule.

The positive- and negative-ion spectra extracted from the main peak in a degraded standard of Naugard P appear in Figure 13. Naugard P responds comparably to the Irganox 1010 in positive-ion mode, yielding an easily observed molecular ion.

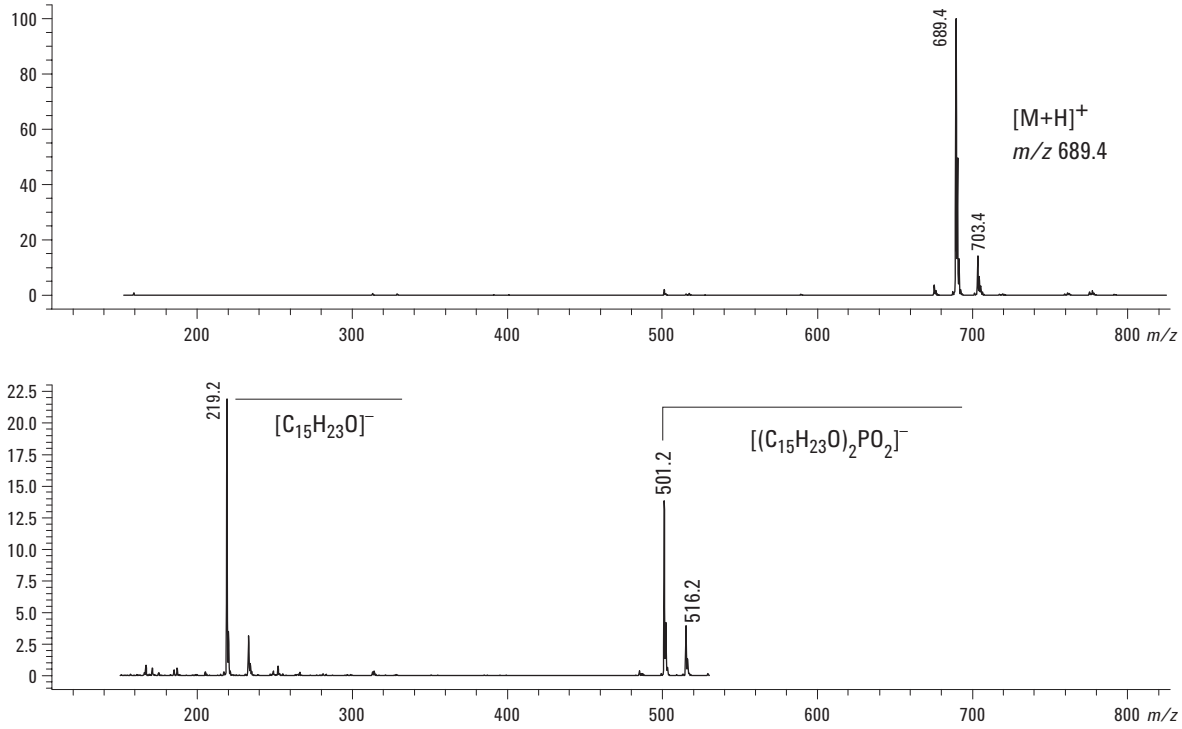



**Figure 13. Extracted positive- (upper) and negative- (lower) ion spectra from the main peak in a degraded Naugard P standard.**

Poor response in negative-ion mode is presumably due to excessive fragmentation, and no molecular ion is observed. Fragments and minor rearrangements found under these conditions are excellent markers for this sample type and would be good indicators if unknown samples were analyzed.

Peaks in the degraded Naugard P analysis have characteristic positive- and negative-ion spectra which could be studied to confirm typical or propose unknown degradation products. All the peaks seem to have the alkyl side chain present. The other variations presumably lie with the number of oxygen atoms attached to the phosphorous, as proposed in the spectra of the peak at 11.6 min in Figure 14.

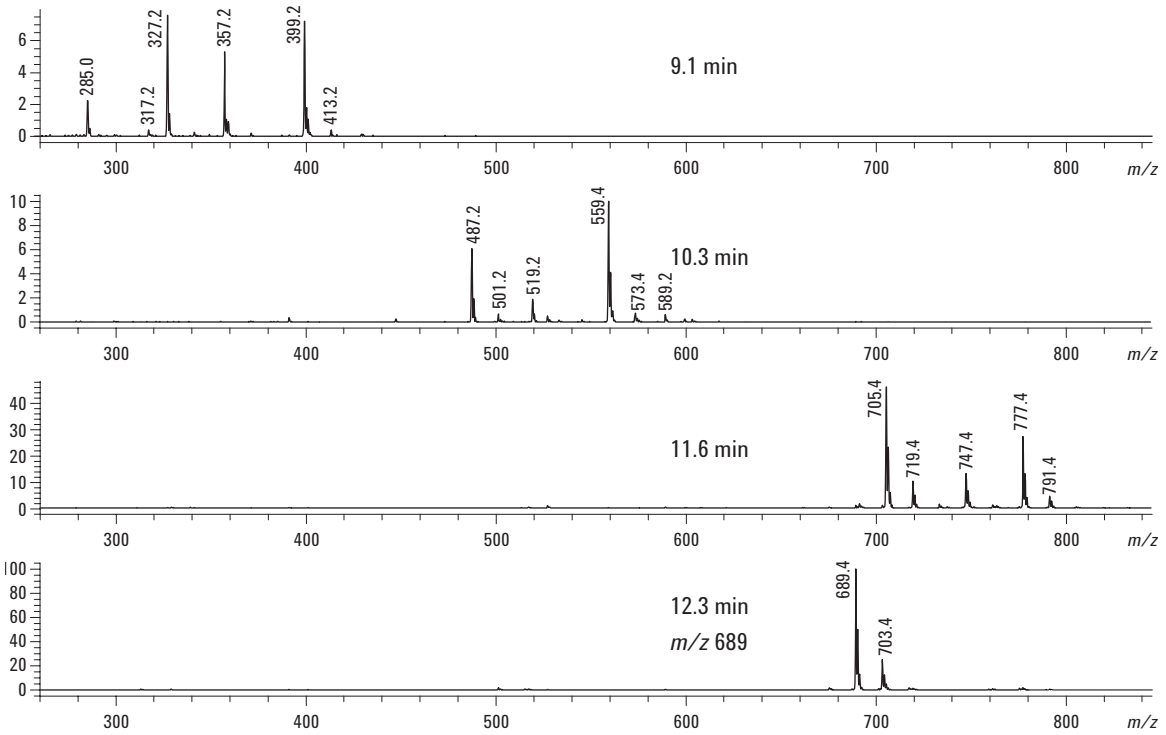



**Figure 14. Extracted positive-ion spectra for Naugard P.**

Likewise, the negative-ion fragmentation patterns shown in Figure 15 help simplify the investigation by showing differences in the alkyl chain or P-O bonds.

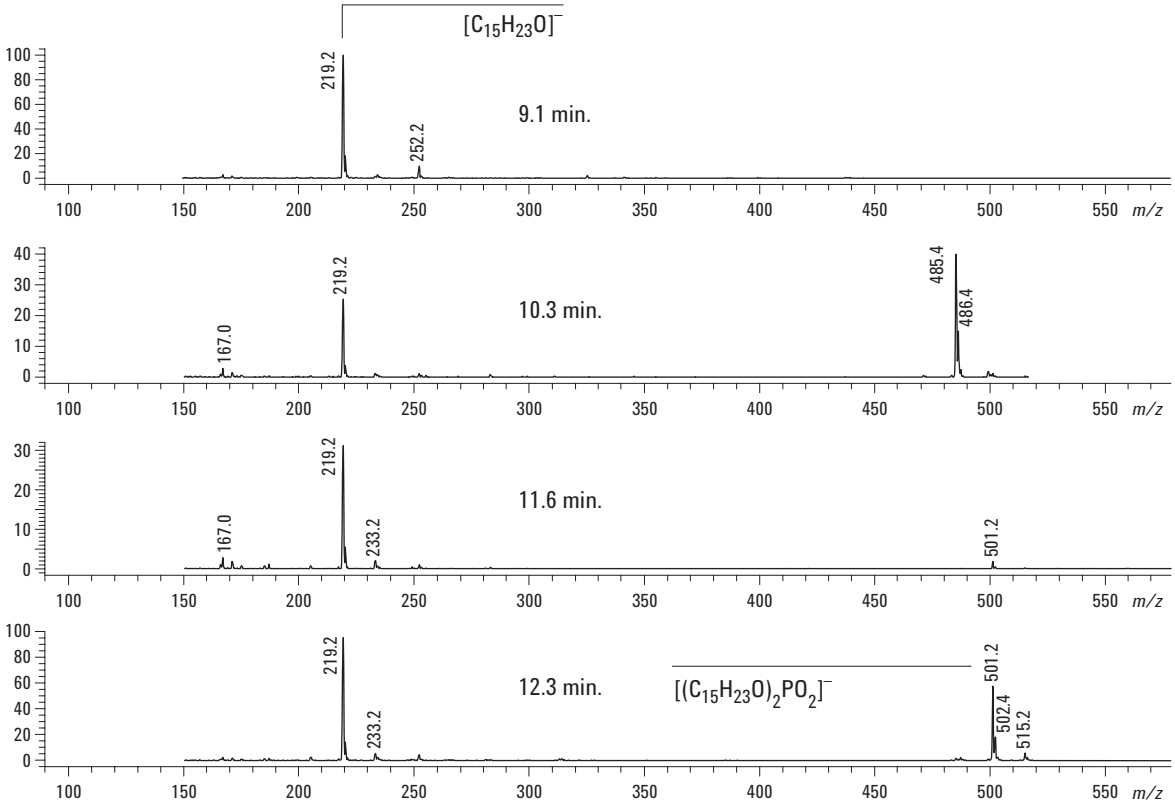



**Figure 15. Extracted negative-ion spectra for Naugard P.**

We received several unknown samples containing polymer additives. The prepared solutions were analyzed with a wide variety of known standards of AOs and other additive classes. Of all the analyzed standards, Naugard P chromatographic patterns, as shown in Figure 16, most closely matched the unknown samples. Additional spectral investigations followed.

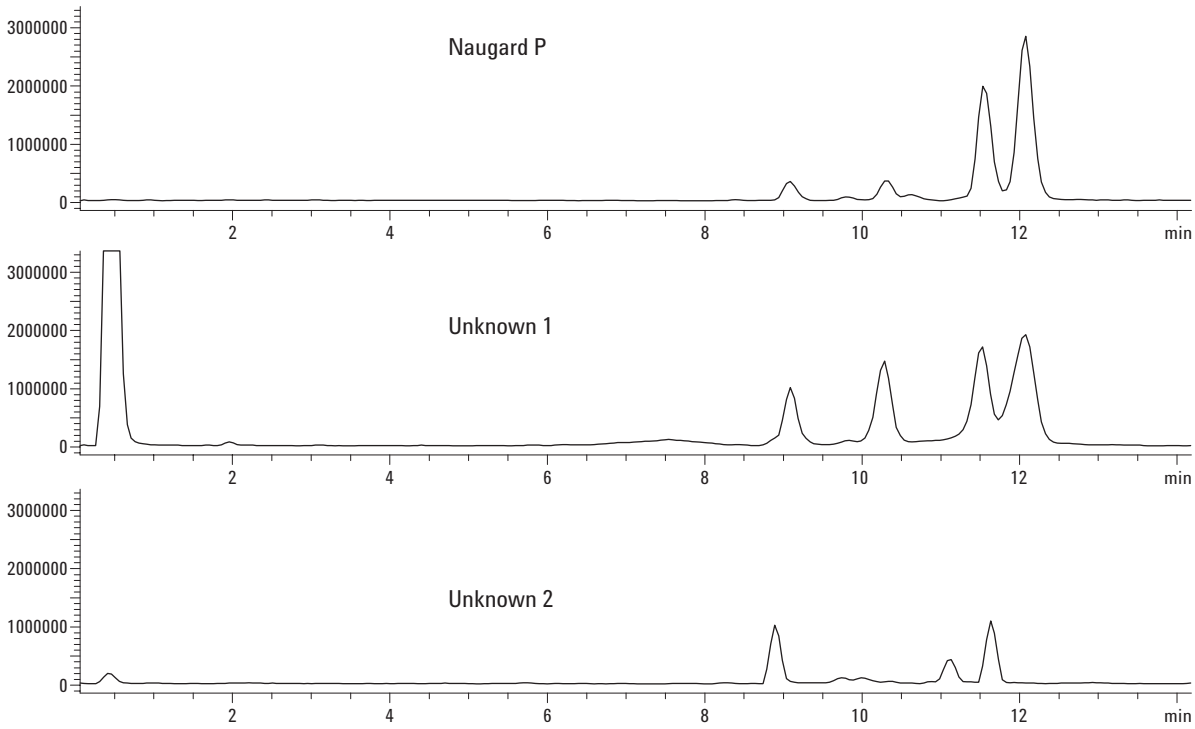



**Figure 16. Total positive-ion chromatograms of Naugard P and two unknowns are compared.**

The UV spectra for these same samples shown in Figure 17 are similar, though still generally characteristic of many aromatic compounds having minimal ring substitution. These data are interesting, but not conclusive.

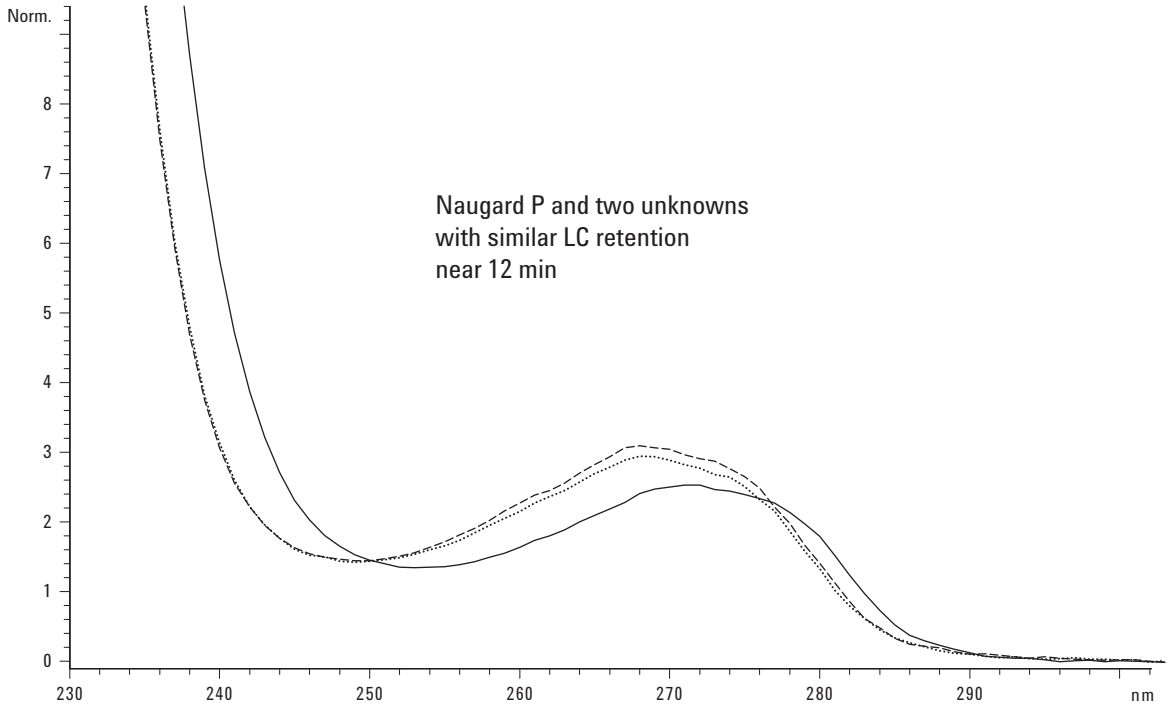



**Figure 17. UV spectra of Naugard P and the two unknowns.**

The positive-ion mass spectrum of Unknown 1, shown in Figure 18, is an excellent match to that of Naugard P, showing slightly more alkyl variation than the standard. This could be a different lot of Naugard P or a product from a different supplier. Unknown 2 has the primary positive-ion at *m/z* 647, reasonably due to a shorter alkyl chain, $C_8H_{17}$, compared to the $C_9H_{19}$ alkyl chain on Naugard P.

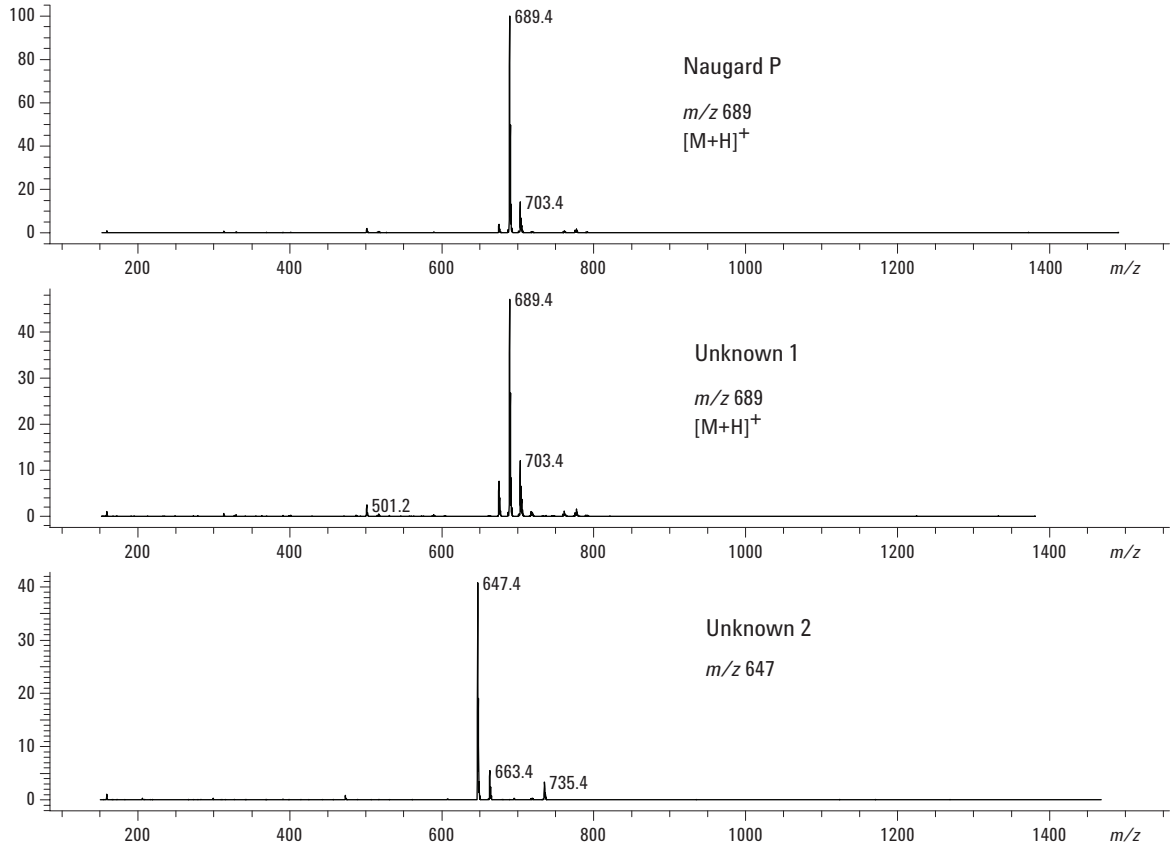



**Figure 18. The positive-ion mass spectra of Naugard P and the two unknowns.**

In negative-ion mass chromatograms, we see similarities to Naugard P in Unknown 1 and quite dissimilar data in Unknown 2. Recalling from earlier discussions that Naugard P is highly fragmented in negative-ion mode, the negative-ion mass spectra should be extremely helpful in supporting our initial thoughts taken from the positive-ion spectra. See Figure 19.

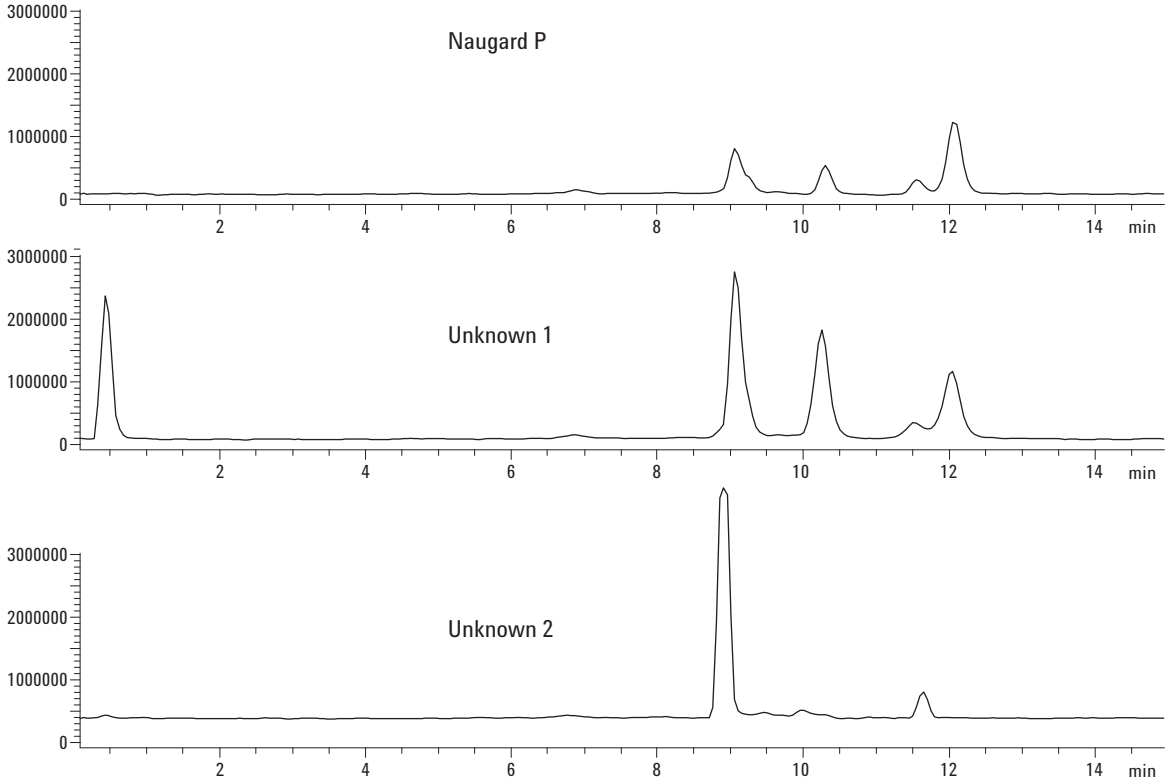



**Figure 19. Total negative-ion chromatograms of Naugard P and two unknowns are compared.**

The negative-ion spectra for Naugard P and Unknown 1 are an excellent match and probably offer the best support of that chemical identity and structural details. Unknown 2, however, speculatively presents two $CH_2$'s less in the *m/z* 501 fragment and one $CH_2$ less the *m/z* 219 fragment. See Figure 20. This is highly supportive of the proposed structure from the positive-ion data and allows us to conclude that, while similar to Naugard P, it is a unique product whose structure is most likely $(C_6H_4\text{-}C_8H_{17}\text{-}O)_3P$.

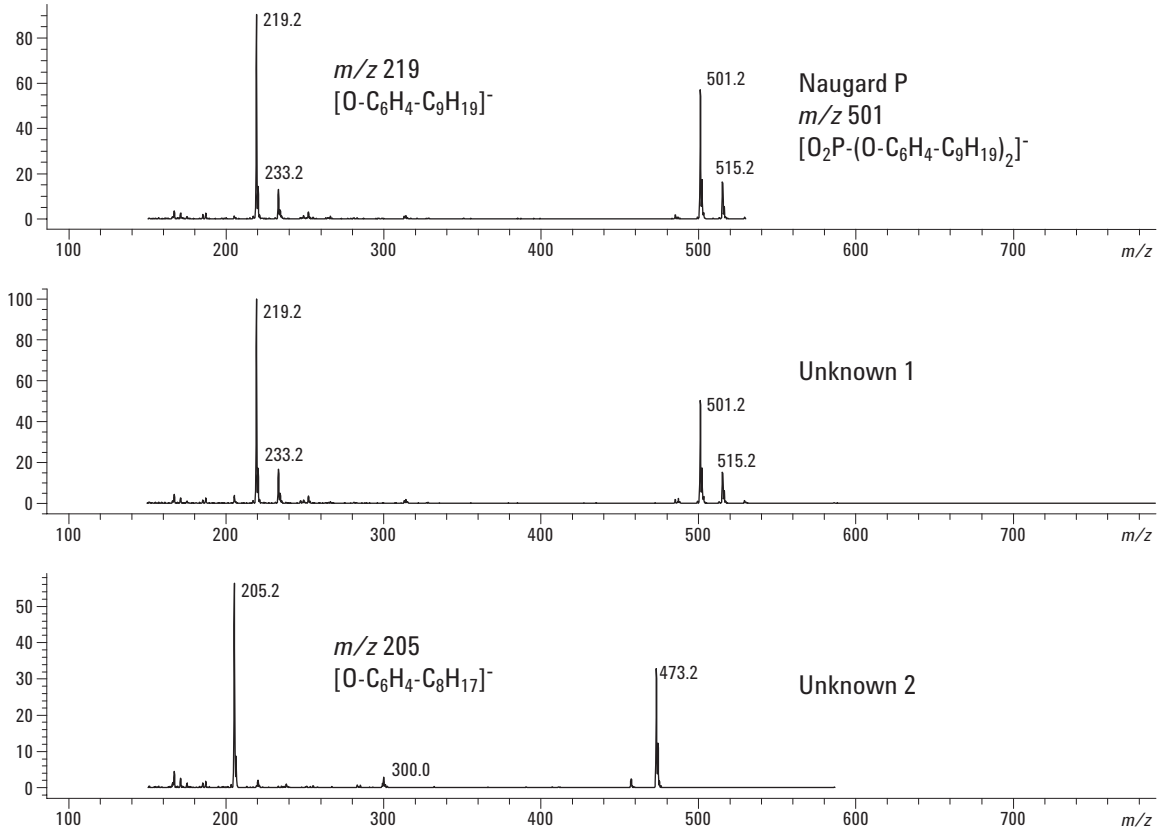



**Figure 20. Negative-ion fragmentation mass spectra of Naugard P and the two unknowns.**

## Conclusions

- LC with UV/VIS and MSD detection is a powerful approach to compound analysis and identification.
- Mobile phase conditions affect the quality and usability of the acquired data.
- Unknown compounds can be tentatively identified with MS data.
- Additive degradation can be quickly evaluated to optimize formulations for better performance.

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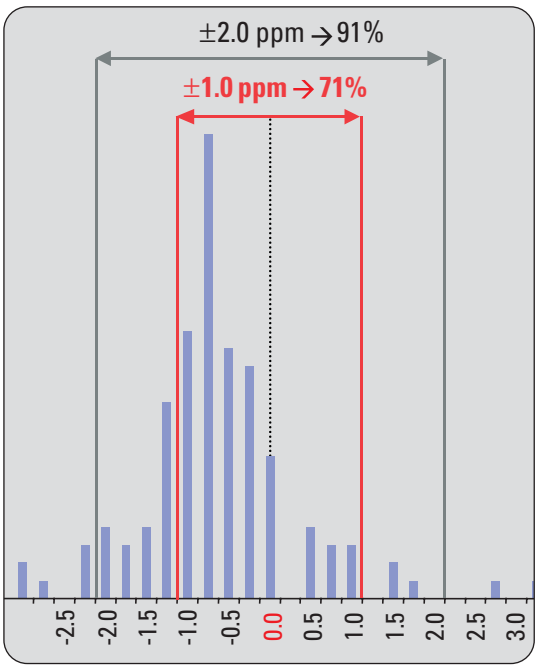
Agilent Technologies

# Agilent 1200 Series Rapid Resolution LC system and the Agilent 6210 TOF MS – Highest data content with highest throughput

## Application Note




Michael Frank

**Abstract**

Fast and unambiguous determination of purity and identity of compounds derived from screening libraries is a common task for many analytical labs in the pharmaceutical industriy. The method of choice to determine the identity of compounds is mass spectrometry, preferably with accurate mass. As yet, data quality was usually compromised by gaining higher throughput. This Application Note demonstrates how a daily throughput of far more than 1000 samples can be achieved together with full spectral data acquisition and accurate mass information with close to FT-MS mass accuracy.

Agilent Technologies

## Introduction

In the quest to achieve highest throughput in LC/MS analyses, the quality of the data is often compromised. There are certain approaches to increase the throughput of LC/MS systems. One approach is to do flow injection analysis. This probably delivers the highest possible throughput, however since no chromatographic separation occurs, the probability to loose compounds by the ion suppression effect during the ionization process is high. Orthogonal detection methods like UV detection do not succeed at all in flow injection analysis as all compound signals are overlaid. Approaches to achieve at least minimal chromatographic separation by using very short columns with 5 µm particles and ballistic gradients are an improvement in view of data quality, however, not state-of-the-art. Some manufactures have established parallel working instrumentation with a shared mass spectrometer and shared UV detector. Obviously, this also compromises data quality as the full acquisition rate of each instrument has to be shared on each LC channel[1].

With the introduction of an LC/MS system which facilitates the use of columns with sub two micron particles it is now possible to achieve short analyses times as well as high chromatographic resolution. Furthermore the system is able to acquire full UV spectral data and mass spectral data with accurate masses.

## Experimental

The Agilent 1200 Series Rapid Resolution LC system is set up for alternating column regeneration (ACR)[2] using 2.1-mm id columns. The pumps are in the low delay volume configuration with an internal volume of only ca. 120 µL. All other modules are optimized for lowest delay volumes by using the low delay volume capillary kit (G1316-68744) and the alternating column regeneration kit (G1316-68721). Consequently, from the injection valve on only capillaries of 0.12 mm id are used. In the thermostatted column compartment the newly introduced low dispersion heat exchangers consisting of 1.6 µL internal volume have been used as well as the high pressure rated 2-position/10-port valve.

The instrument set-up is shown in figure 1:

- Two Agilent 1200 Series binary pumps SL with the new Agilent 1200 Series micro vacuum degasser placed between the two pumps eliminates the need for long tubing to the pumps.
- Agilent 1200 Series high performance autosampler SL.
- An Agilent 1200 Series thermostatted column compartment SL, equipped with a high pressure, 2-position/10-port valve, facilitating alternating column regeneration.
- An Agilent 1200 Series diode-array detector SL allowing a data acquisition rate of 80 Hz and equipped with a 500 nano liter flow cell with 0.12-mm id connecting capillaries.
- Agilent 6210 Time-of-Flight mass spectrometer allowing a maximum data acquisition rate of 40 Hz and equipped with a dual ESI source for parallel ionization of the analyte and a reference mixture.
- Two ZORBAX SB C18, 2.1 mm id x 50 mm, 1.8 µm columns
- As mobile phase gradient grade water with 0.1 % trifluoro acetic acid and acetonitrile with 0.08 % trifluoro acetic acid was used. No additional filtering of the solvents was made.

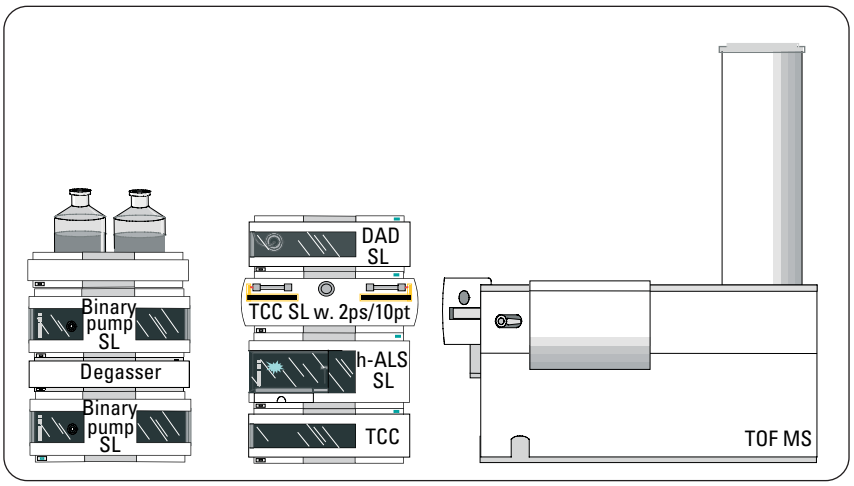



**Figure 1**
**Agilent 1200 Series Rapid Resolution LC system with Agilent 6210 TOF-MS with low delay volume for high speed applications using 2.1-mm id columns with lengths ranging from 20 to 50 mm.**

Instrument control and data acquisition was done by the Agilent TOF-software A02.01 running on a Hewlett-Packard xw 4300 workstation with an Intel dual core Pentium™ D840 CPU at 3.2 GHz.

## Results and discussion

By applying elevated temperatures the viscosity of the solvent can be reduced which allows higher flow rates and therefore shorter gradient times. A maximum temperature of 80 °C was applied, which allowed a flow rate of 1.8 mL/min without hitting the pressure limit of the pump. This results in a linear velocity of approximately 11 mm/s for the 2.1 mm x 50 mm column (1.8 µm). With the help of the regeneration pump and the 2-position/10-port valve in the column compartment cycle times could be reduced significantly because one column is flushed with high organic content solvent and then re-equilibrated again with the starting composition of the gradient while on the second column the separation of a sample occurs. After this sequence the 10-port valve is switched and both columns are exchanged in the flow path. Details of alternating column regeneration and the correct setting of time points are described in another Application Note[2]. Despite the high flow rate (1.8 mL/min), the column effluent was not split prior to reaching the mass spectrometer. The standard ESI source specifies a maximum flow rate of up to 1 mL/min, however even these higher flows are tolerated if the drying gas temperature and flow rate are set to maximum and little condensation occurs. Condensation of water is practically eliminated when using ACR because equilibration is done on the column which

| Data File | Sample Type | Inj Vol (µl) | Capillary | Fragmentor | Skimmer |
|---|---|---|---|---|---|
| opt_4000_215_60.wiff | Unknown | 1 | 4000 | 210 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 3000 | 210 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 2000 | 210 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 4000 | 180 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 3000 | 180 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 2000 | 180 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 4000 | 150 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 3000 | 150 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 2000 | 150 | 60 |
| opt_4000_215_60.wiff | Unknown | 1 | 4000 | 210 | 40 |
| opt_4000_215_60.wiff | Unknown | 1 | 3000 | 210 | 40 |

**Figure 2**
**Feature of the TOF software to modify the MS parameter from run to run.**

| | | | | |
|---|---|---|---|---|
| **Method:** | | | | |
| **Solvent:** | A = water (0.1% TFA), B = ACN (0.08% TFA) | | | |
| **Temperature:** | 80 °C | | | |
| **Flow:** | 1.8 mL/min | | | |
| **Gradient:** | 0.00 min 5%B<br>0.50 min 90%B<br>0.51 min 5%B<br>0.65 min 5%B | | **Regeneration:** | 0.00 min 5%B<br>0.01 min 95%B<br>0.20 min 95%B<br>0.21 min 5%B<br>0.65 min 5%B |
| **Stoptime:** | 0.65 min | | | no limit |
| **Posttime:** | off | | | off |
| **DAD:** | Wavelength: | 210 nm (8), ref. off | | |
| | Peak width: | >0.0025 min (0.05s responsetime), 80 Hz | | |
| | Spectra: | no | | |
| | Slit: | 8 nm | | |
| | Balance: | pre-run | | |
| **MS:** | Scan range: | 100-1000 m/z | | |
| | Acquisition rate: | 5, 20, 30 and 40 cycles/s | | |
| | Data type: | profile data | | |
| | Capillary voltage: | 3000 V | | |
| | Fragmentor: | 180 V | | |
| | Skimmer: | 40V | | |
| | Gas temperature: | 350 °C | | |
| | Gas flow: | 13 L/min | | |
| **Injection volume:** | 1µL | | | |
| **Injector:** | Overlapped injection, Automatic delay volume reduction, Sample flush out factor = 10 | | | |
| **Valve position:** | Next position | | | |

**Table 1**
**LC/MS method used for the data shown in figures 3-5. The method was also used to achieve the values in table 2.**

is not connected to the detector. Generally the use of an Agilent multi mode source with a specified flow rate up to 2 mL/min even with pure water is recommended. The chromatographic conditions in table 1 were used to achieve gradient times of 0.5 min. Under these conditions, the peak capacity for the MS detection is in the range of >40 in 39 s. With the use of a 5-µm particle size column of the same dimension the peak capacity would only be half!

The detector of the Agilent 6210 TOF MS would be saturated if the compound concentrations used here to give also significant UV signals would be injected into the MS without special settings. Saturation of the MS detector would produce incorrect results in mass determination. The solution is to intentionally desensitize the TOF MS. This can be done quite easily by applying the functionality of the TOF software to alter the MS parameters from one run to the other,

simply by adding one or more "MS-parameter" columns to the worklist (figure 2). Select "add columns" from the worklist and then chose "MS-parameter" and the desired parameter. As the reference mixture is also affected by these settings, the concentration of the reference mixture was increased. Only the capillary voltage, the fragmentor voltage and the skimmer voltage were varied. The optimal conditions determined by this approach can be found in the method parameters in table 1.

In figure 3 the total ion chromatogram and the UV chromatogram achieved with conditions above (80 Hz DAD, 30 Hz TOF data acquisition rate) is shown for a five-component sample (58 ng/µL atenolol, 85 ng/µL primidon, 62 ng/µL metoprolol, 125 ng/µL verapamil and 75 ng/µL beclomethasone-dipropionat). The peaks of the total ion chromatogram are inherently broader than the peaks of the UV chromatogram because of additional extra column volume from the flow cell and also from connecting the capillary between the UV detector and ESI interface. But as can be seen in figure 3, the additional peak broadening of the MS peaks is only minor. The peak widths at half height of the MS peaks obtained under the highest data acquisition rate (40 Hz) are shown in figure 4 with values from as little as 0.34 to 0.42 s. The chromatograms shown in figure 5 were produced under the same chromatographic conditions, but with different data acquisition rates of the time-of-flight MS. The peak form and resolution are improved by having high data acquisition

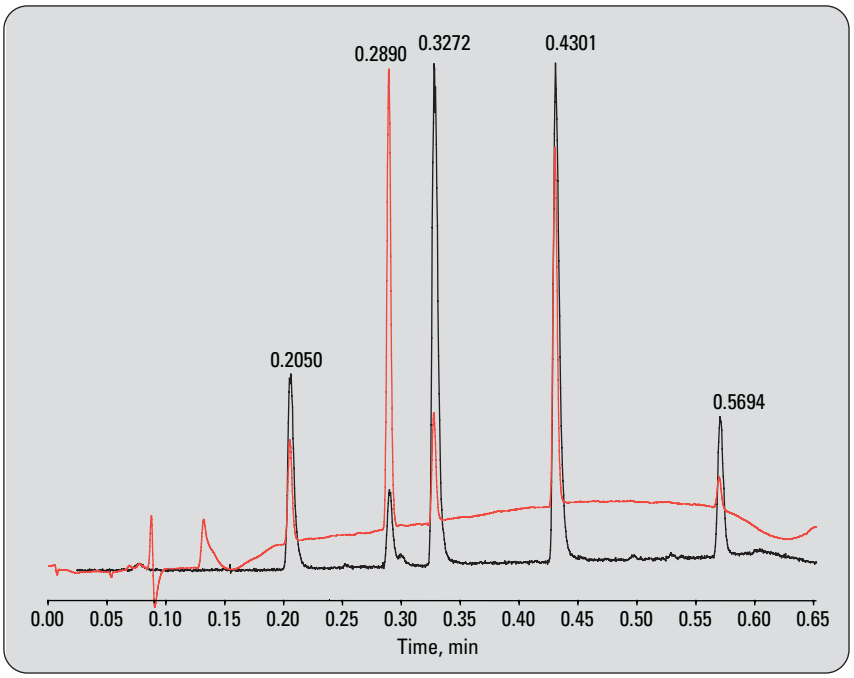



**Figure 3**
**Comparison of corresponding peaks in the UV (red trace) and the MS detection (black trace).**

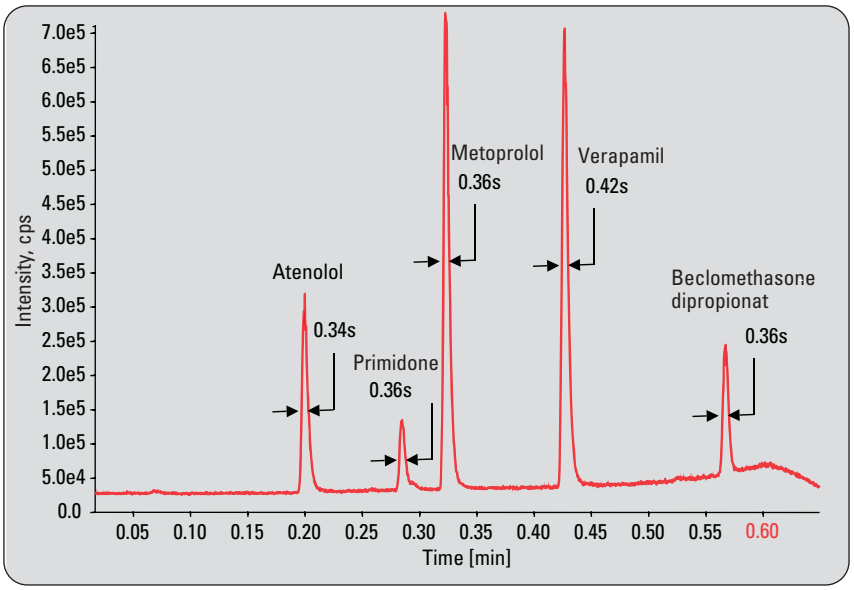



**Figure 4**
**MS total ion chromatogram of highest speed LC-TOF-MS analysis (40 Hz TOF data acquisition rate).**

rates in the MS which shows clearly in figure 5. The effect is nicely demonstrated on the little side peak next to the primidon peak – with 40-Hz data acquisition rate it is obvious that an additional compound shows up but with 5 Hz data acquisition rate this could not be differentiated from tailing of the primidon! The advantage, especially if MS quantization is necessary, is clear.

By applying the chromatographic conditions of table 1 and 80 Hz signal data acquisition of one wavelength and 30 Hz TOF centroid data, a cycle time of 49 s was achieved. The achievable cycle time is not only dependent on the used run time (that is the gradient time plus additional flush and re-equilibration times, or in Agilent terminology the stop time plus post time) but also very much dependent on the instrument overhead time. This is usually caused by communication between the data system and the individual LC/MS modules as well as the data system writing data to the hard disc and initiating certain processes. The overhead time caused by the data system can be significant if the computer's performance is not sufficient to handle the data amount or if other software programs or processes are consuming the power available. To decrease the cycle time it might be worth decreasing the amount of data acquired.

Table 2 shows the cycle times and the possible daily throughput depending on the DAD and MS settings. Since the MS data are constantly written to the hard disc during data acquisition, whereas the UV data are buffered and added to the data file after the stop time of

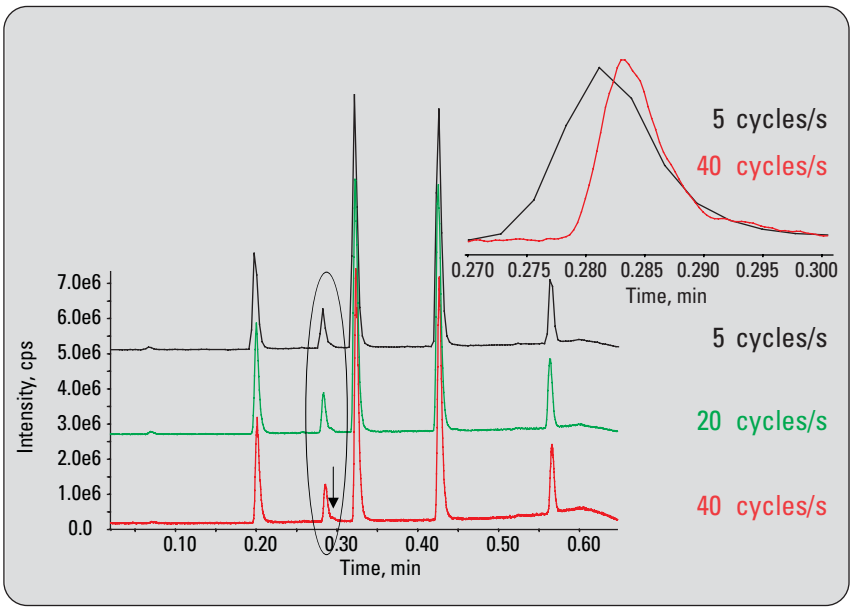



**Figure 5**
**Total ion chromatograms recorded with varying data acquisition rates – dependence of the MS peak shape and resolution on the data acquisition rate.**

| DAD (80 Hz) | | TOF (100 – 1000 Da) | | | Cycletime | Throughput |
|---|---|---|---|---|---|---|
| Type | Wavelength | Centroide | Profile | Data rate [Hz] | [s] | [Samples/day] |
| spectral | 190-900 (1) | | x | 20 | 62 | 1394 |
| spectral | 190-900 (1) | x | | 20 | 62 | 1394 |
| spectral | 190-400 (2) | | x | 20 | 59 | 1464 |
| spectral | 190-400 (2) | | x | 40 | 59 | 1464 |
| spectral | 190-400 (2) | | x | 30 | 58 | 1490 |
| signal | 210/254 | | x | 20 | 50 | 1728 |
| signal | 210 | x | | 30 | 49 | 1763 |

**Table 2**
**Dependence of the cycle time on the DAD and MS data acquisition settings, method stop-time was 0.65 min (39 s), pre-run balance was applied (ca. 2 s). The number in brackets for the DAD wavelength range stands for the scan width in nm.**

the method, the cycle time depends more on the UV data amount than on the MS data amount. The cycle time was calculated from the time stamp each file gets assigned from the WindowsXP™ operating system after closing the file following data acquisition.

If using a TOF MS the attention is certainly focused on the accurate mass. The question may arise if the possibility to obtain low mass accuracy errors might suffer from these high speed conditions. Figure 6 shows the achieved mass accuracy errors of the analysis of 140 members of a chemical library used in a screening campaign by a pharmaceutical company. The shown error-values have been extracted from an automated empirical formula confirmation report and involved no manual interference. Sixteen of the compounds could not be ionized under positive ESI conditions and two compounds showed large mass errors of 11 and 15 ppm, probably caused by co-eluting isobaric impu-

rities. The cycle time was 90 s and was determined by a required injector program which allowed an on-line dilution of the samples directly prior to the analysis. Chromatographic conditions applied a 5-100 % water-acetonitrile (0.1 % TFA) gradient in 0.7 min at a flow rate of 1.5 mL/min and 60 °C column temperature. UV data acquisition to determine purity was done in the wavelength range of 210 to 500 nm with an acquisition rate of 80 Hz. The MS data acquisition rate was at 8 Hz to reduce the file size. The scan range was 120 – 1200 Da, capillary voltage 4000 V and the fragmentor voltage at 215 V. No ACR was applied and the flow to the MS was splitted in a 1:7.5 ratio.

More compelling is the histogram of the mass errors of these samples as shown in figure 7. More than 91 % of the ionizable compounds (outliers included) have a mass accuracy error in the range of ±2.0 ppm. Excluding the outliers even 93 % of the analyzed samples lie in-between the ±2.0 ppm range. In the ±1.0 ppm range which is FT-MS-like mass accuracy 71 % of the samples can be found (72 % excluding the outliers).

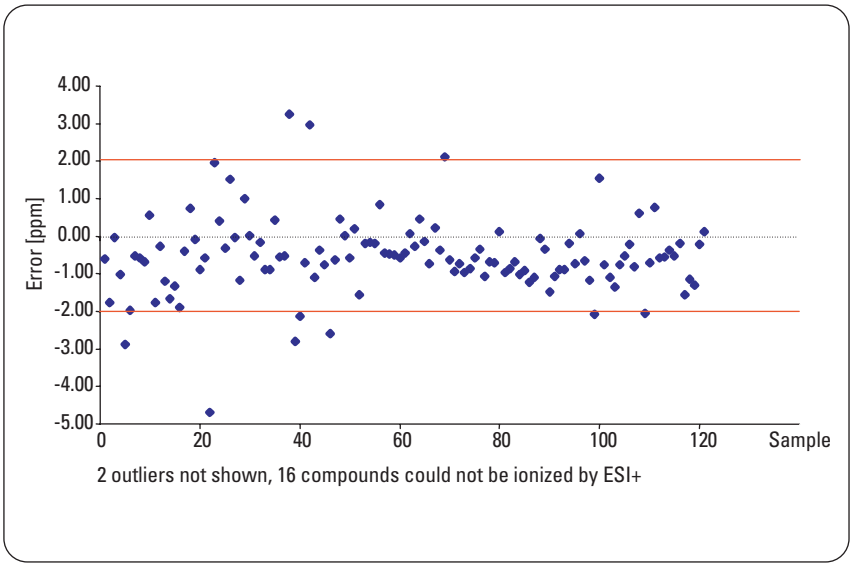



**Figure 6**
**Mass accuracy errors of the analyses of a set of chemical library members under fast-LC conditions.**

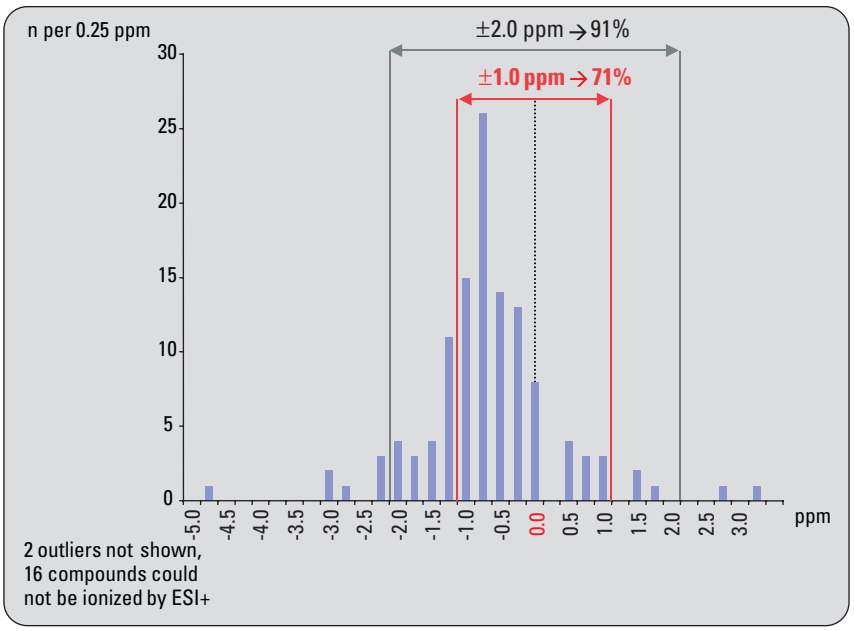



**Figure 7**
**Histogram of the mass accuracy errors of the analyses of a set of chemical library members under fast LC conditions. The given populations of the ±1.0 ppm and ±2.0 ppm range include the outliers.**

## Conclusion

The Agilent 1200 Series Rapid Resolution LC system together with the Agilent 6210 Time-of-Flight mass spectrometer allows acquisition of a wealth of data to unambiguously determine the purity and identity of compounds in samples as they are typical for the high throughput analytical departments of pharmaceutical companies. In the time range of one minute high chromatographic resolution, full spectral diode-array data from 190-900 nm wavelength in a band width of 1 nm at an 80 Hz acquisition rate plus full MS spectral data from 100-1000 m/z with high acquisition rate and with an accurate mass with a mass error below ±2.0 ppm for more than 91 % of the samples could be acquired.

Using features like alternating column regeneration, overlapped injection, high temperatures, high flow rates together with highest data acquisition rates and most importantly stable and easy-to-use accurate mass, this system outperforms other high throughput LC/MS techniques used as yet in throughput and/or data quality. The linear velocities achieved were in the range of 11 mm/s and cycle times were as fast as 49 s for a run time of 41 s. Due to the columns with particle sizes of 1.8 µm, the UV peak capacities were still in the range of fifty and even the MS peak capacities were in the range of forty for a gradient time of 39 s.

## References


1.

Jeremy R. Kenseth, Shelly J. Coldiron, "High-throughput characterization and quality control of small-molecule combinatorial libraries", *Curr. Opin. Chem. Biol. 8; 418-423*; **2004.**

Jill Hochlowski, Xueheng Cheng, "Current Application of Mass Spectrometry to Combinatorial Chemistry", *Anal. Chem. 74, 2679-2690;* **2002.**

2.

Udo Huber, „High throughput HPLC – Alternating column regeneration with the Agilent 1100 Series valve solutions" *Agilent Application Note, Publication number 5988-7831EN;* **2002.**



*Most of the data herein was presented as a poster, titled "Non-multiplexed DAD-ToF Analysis of 1400 Samples/day" by Michael G. Frank, Edgar Naegele (Agilent Technologies, Waldbronn, Germany), Doug McIntyre (Agilent Technologies, Santa Clara, USA), Thilo A. Fligge, Stefan Buehler, Markus Christ (Boehringer-Ingelheim, Biberach, Germany), CO-1152, at the Pittcon conference 2006 in Orlando, Florida, USA.*



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**Agilent Technologies**

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

Application


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## Abstract

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


## Introduction

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

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

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

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

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,

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

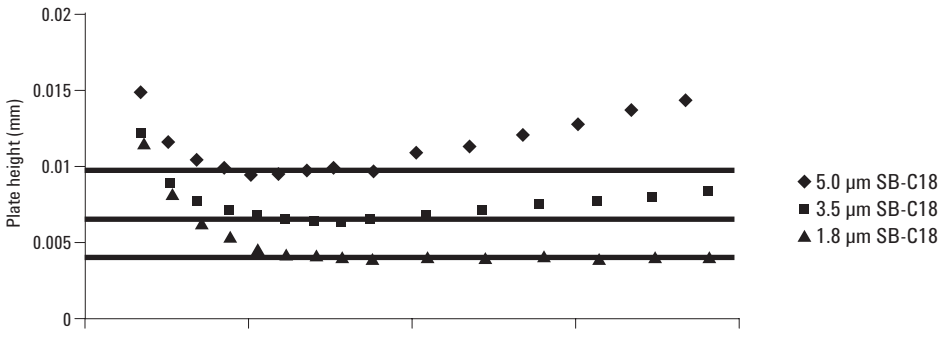
$$\text{Inj. vol.}_{\text{col. 1}} \times \left[\frac{\text{Volume}_{\text{column2}}}{\text{Volume}_{\text{column1}}}\right] = \text{Inj. vol.}_{\text{col. 2}} \quad \text{(eq. 2)}$$

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

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

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

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




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

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

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

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

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

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

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

### Experimental Conditions

#### System

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

#### Columns

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

#### Mobile phase conditions

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

#### Gradient Conditions

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

#### Sample

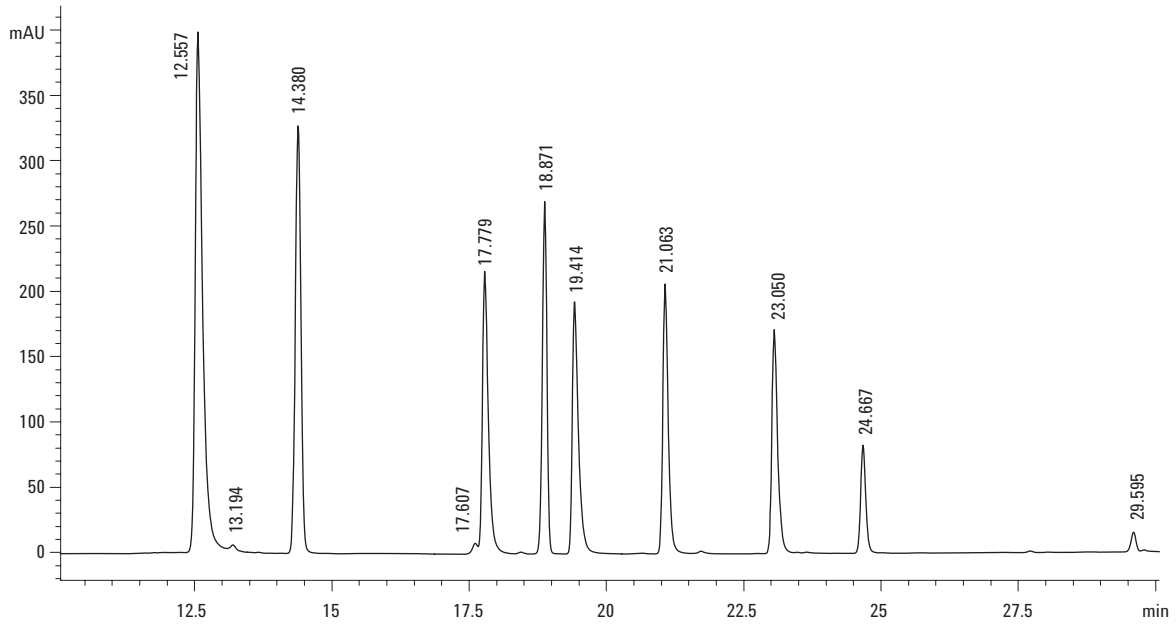
Standard mixture of chlorinated phenoxy acid herbicides, 100 µg/mL in methanol

## Results

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

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

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

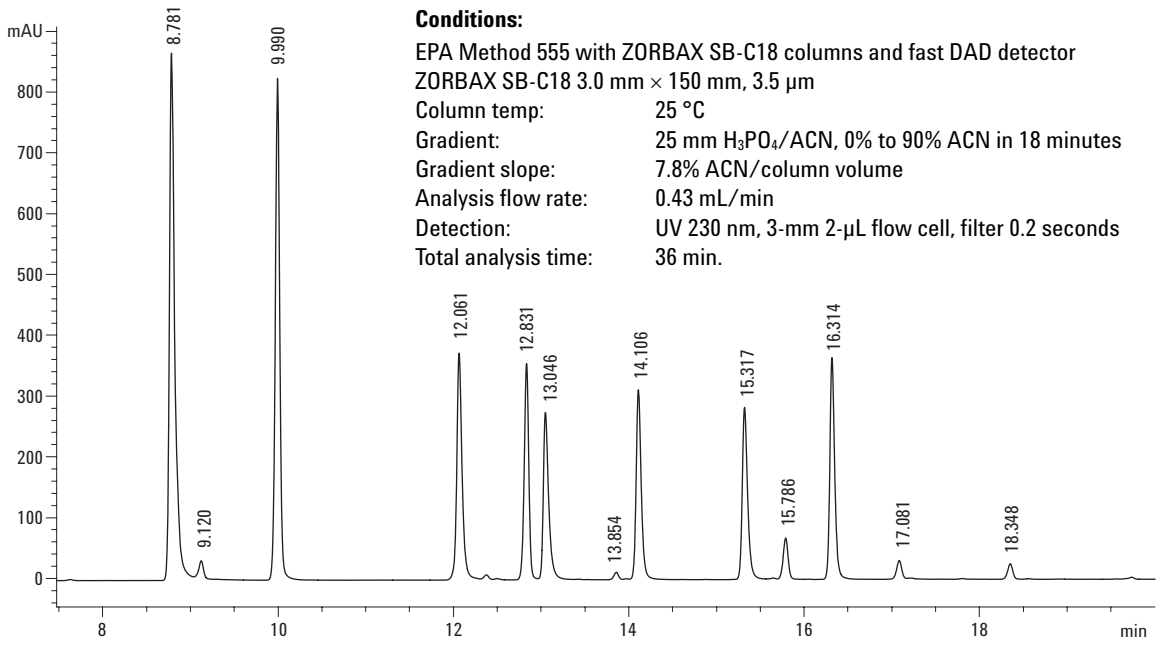



**Conditions**

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

| | |
|---|---|
| ZORBAX SB-C18 4.6 mm × 250 mm, 5 µm | |
| Column temp: | 25 °C |
| Gradient: | 10% to 90% ACN vs. 25 mM $H_3PO_4$ |
| Gradient slope: | 7.8% ACN/column volume |
| Analysis flow rate: | 1 mL/min |
| Group A Compounds | |
| Total analysis time: | 60 min |
| Detection: | UV 230 nm, 10-mm 13-µL flow cell, filter 2 seconds (default) |

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




**Conditions:**

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

| | |
|---|---|
| ZORBAX SB-C18 3.0 mm × 150 mm, 3.5 µm | |
| Column temp: | 25 °C |
| Gradient: | 25 mm $H_3PO_4$/ACN, 0% to 90% ACN in 18 minutes |
| Gradient slope: | 7.8% ACN/column volume |
| Analysis flow rate: | 0.43 mL/min |
| Detection: | UV 230 nm, 3-mm 2-µL flow cell, filter 0.2 seconds |
| Total analysis time: | 36 min. |

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

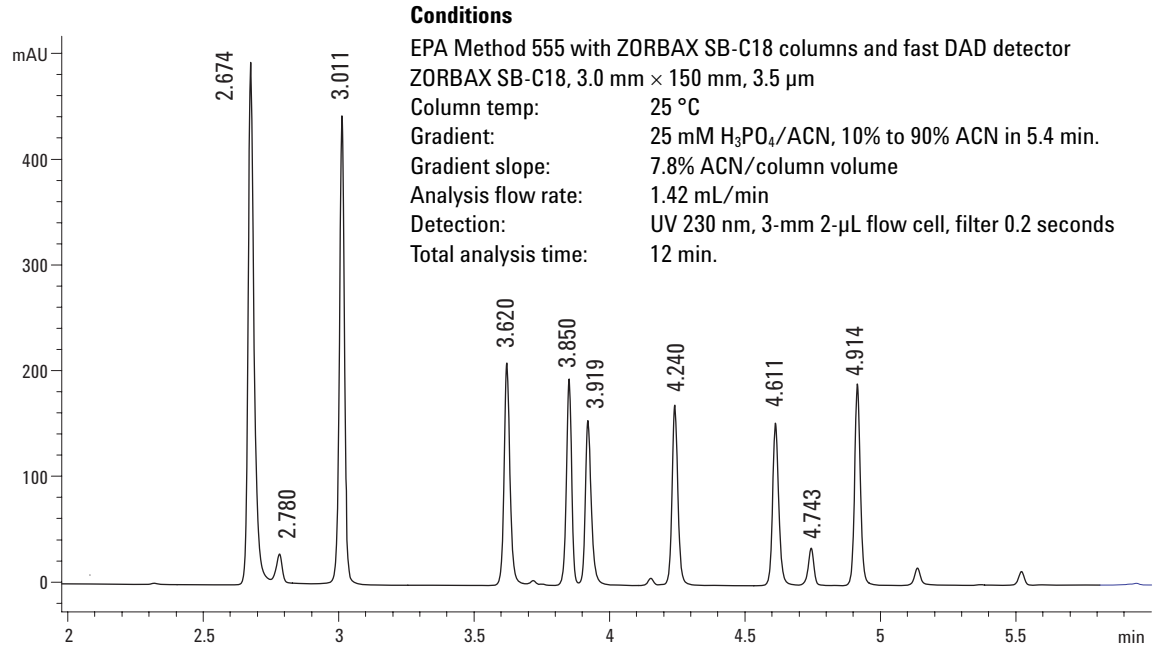



**Figure 4. High speed gradient separation of herbicides on 3.0 × 150 mm, 3.5-µm ZORBAX SB-C18.**

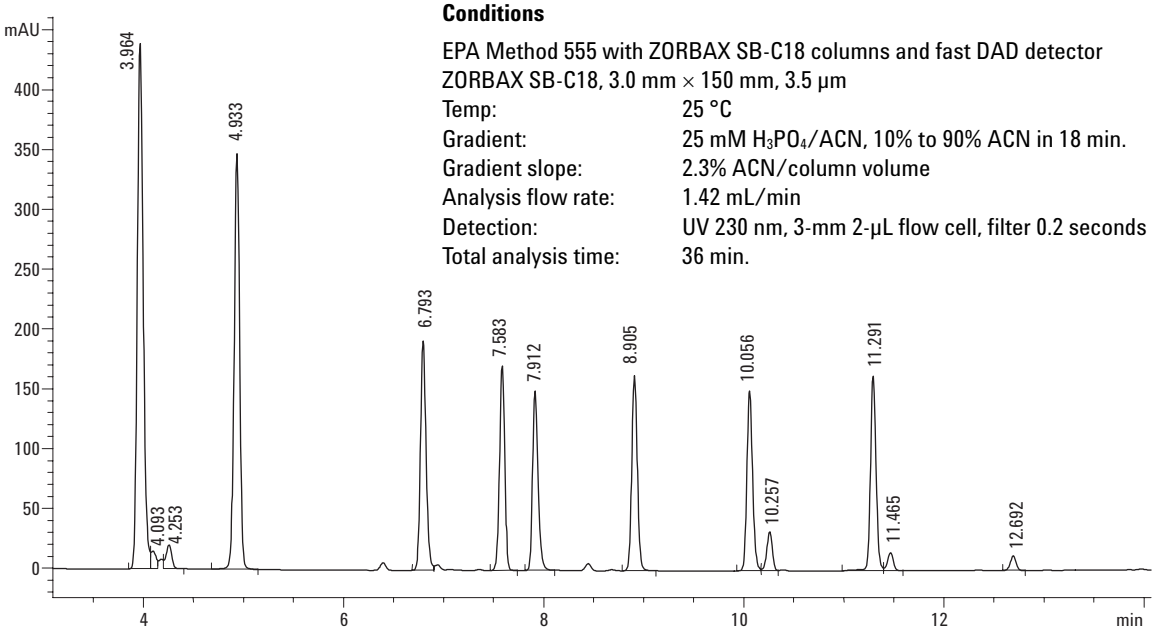



**Figure 5. Reduced slope gradient separation of herbicides on 3.0 × 150 mm, 3.5-µm ZORBAX SB-C18.**

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-µL injection of dilute actone is made to determine the bandspreading contribution of the system, with various flow cells. Multiple flow cells were tested, and the average result reported, where possible. The elution volume summarizes the total volume of all tubing in the system. While the absolute volume from the 2-µL to the 13-µL flow cells is 11 µL, we observe an increase of 15 to 16 µL because of the larger diameter inlet tubing integral to the larger volume flow cells.

**Table 1. Volumetric Measurements of Various Flow Cells**

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

## Conclusion

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

## References

1. J. J. van Deemter, F. J. Zuiderweg, A. Klinkenberg, Chemical Engineering Science 1956, 5, 271–289
2. The Influence of Sub-Two Micron Particles on HPLC Performance, Agilent Technologies, application note 5989-9251EN, May 2003

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# Process Monitoring of Bisphenol-A in Industrial Feedstock using High Throughput HPLC

Application

**Process Control**


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## Abstract

**The chromatographic method used to monitor the Bisphenol-A manufacturing process was improved using Agilent RRHT Eclipse XDB-C18 columns. These columns use 1.8-µm particles versus conventional 3.5-µm or 5-µm particles. The improved method allowed seven times faster analyses, improved resolution, and higher sensitivity.**


## Introduction

Bisphenol-A (Figure 1) is a highly versatile material used to manufacture many modern products. It is also known as 4,4"-Isopropylidenediphenol, 4,4"-(1-Methylethylidene) bisphenol, or simply BPA.

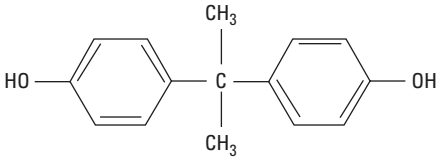


**Figure 1. Bisphenol A**

Every year, 2.8 million tons of BPA are produced. BPA is a building block for polycarbonate plastic and epoxy resins. Polycarbonate plastic is prized for its scratch resistance, optical clarity, and heat and electrical resistance. Because of these attributes, it is used for eyewear, CD/DVD disks, electronics, and food and drink containers. Epoxy resins are used for protective coatings because of their combination of inertness, chemical resistance, adhesion, and formability. For example, metal food cans are lined to protect taste. Epoxy resins are also used as a component in dental sealants and as a component in dental composites providing an alternative to mercury amalgam in veneers and fillings. Other uses include fungicides, polymer antioxidants, and components in automobiles and appliances.

BPA is produced through an acid-catalyzed condensation reaction of phenol with acetone. During condensation, a number of phenol-based byproducts are also formed. HPLC is used to determine the composition of many of the process streams in a commercial BPA plant.

Here we describe the use of new HPLC column technology for the possible improvement to one of the HPLC methods used in a commercial BPA facility.

## Method Optimization and Scalability

The existing HPLC method was proven and robust; however, it was complicated. We sought a similar chromatogram, based on the original method, but using simpler method parameters. Because of the challenge of changing many chromatographic parameters, essentially redeveloping the method, we chose a 4.6 × 50 mm, 1.8-µm Eclipse XDB-C18 column for experiments to reduce the time required. Smaller particles packed in shorter columns increase the speed of analysis and still provide enough efficiency to maintain resolution equivalent to longer columns packed with larger particles. After several trials, we developed a method that produced a chromatogram similar to the original. The short analysis time is a major advantage of Rapid Resolution High Throughput (RRHT) technology. Whereas a handful of experimental runs would take an entire work day using a typical analytical-sized column (50 min/run), the series of runs took about an hour (7.5 min/run), using an RRHT column.

We incrementally scaled up to a 4.6 × 250 mm column. Figure 2 shows an overlay of the sample analyzed by three 4.6-mm id columns of different lengths and particle sizes. Injection volume was also changed proportionally to length. The smaller ZORBAX particles speed up the analysis while maintaining resolution. In fact, resolution increased when using the RRHT columns despite their shorter length.

One reason this method can be easily scaled (up or down) is the uniform spherical Eclipse XDB-C18 packing. It has a proprietary engineered particle size distribution, based on ZORBAX silica with a controlled surface area and pore size. The robust proprietary packing material and proven column manufacturing techniques consistently yield reproducible columns with similar chromatographic performance, independent of the column dimensions.

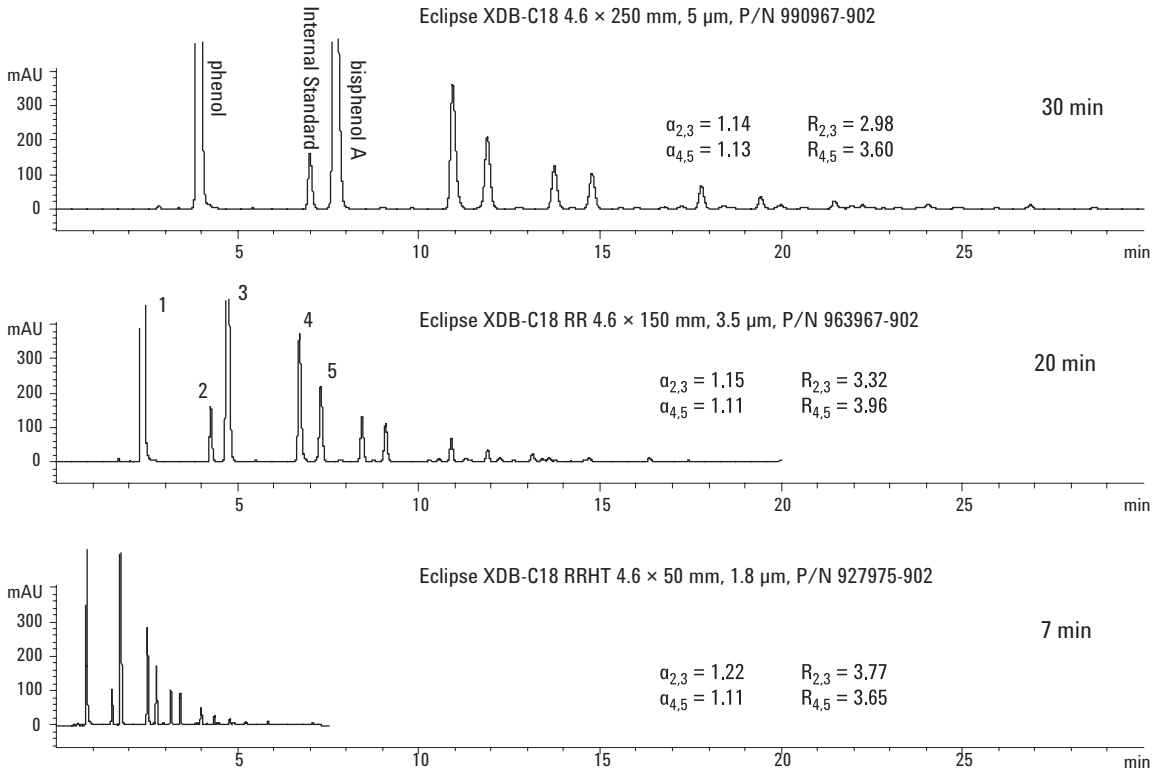


**Figure 2. RRHT column configuration increased both speed and resolution.**

Particle size does influence resolution. The influence can be noticed when comparing columns of identical dimensions, packed with three different particle sizes. Figure 3 shows the shortened Bisphenol-A analysis using different particle-sized Eclipse XDB-C18 columns. Resolution (Rs) is related to selectivity (α), efficiency (N) and retention (k´):

$$Rs = (1/4)(\alpha-1)\sqrt{N}\,[k'/(1+k')]$$

Factors affecting the selectivity term (stationary phase, mobile phase) and retention term (mobile phase, temperature) are constant for the three chromatograms. The efficiency term is influenced by column length, linear velocity of the mobile phase (both constant), and particle size (varied in Figure 3). N increases as particle size decreases. In Figure 3 the selectivity factors (α) and retention remain about the same, but resolution actually increases. The increase in resolution due to the decrease in particle size highlights the advantage of using smaller particles. The similar selectivity and retention highlight the suitability of ZORBAX Eclipse XDB-C18 columns for scaling methods, especially to more rapid, high-throughput methods.

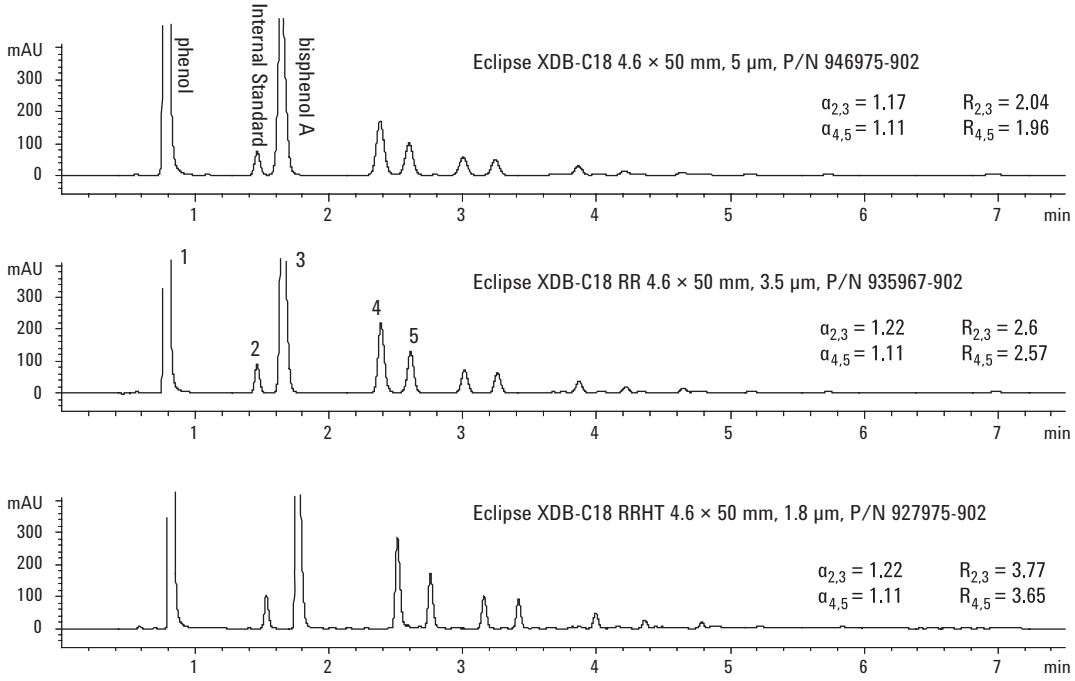


**Figure 3. Effect of particle size on resolution and selectivity.**

## Comparing the Existing Method to the RRHT Method

Figure 4 compares the original BPA separation to the RRHT separation. The top chromatogram is an example of the analysis using the original commercial method, and the bottom is an example of the process sample analyzed with the RRHT method. The method developed with the new column technology clearly increases productivity.

Analysis time is reduced at least six-fold; solvent consumption is reduced about 12.5 times, from 100 mL/analysis to only 7.5 mL/analysis. Interestingly, the peak shape of Bisphenol-A is more symmetrical using Eclipse XDB-C18 as compared to the current C18 column used in the original analysis. The more Gaussian peak shape eluted by the Eclipse XDB-C18 column is important for accurate quantification. Other method improvements such as a simplified gradient and a binary mobile phase are listed in Table 1.

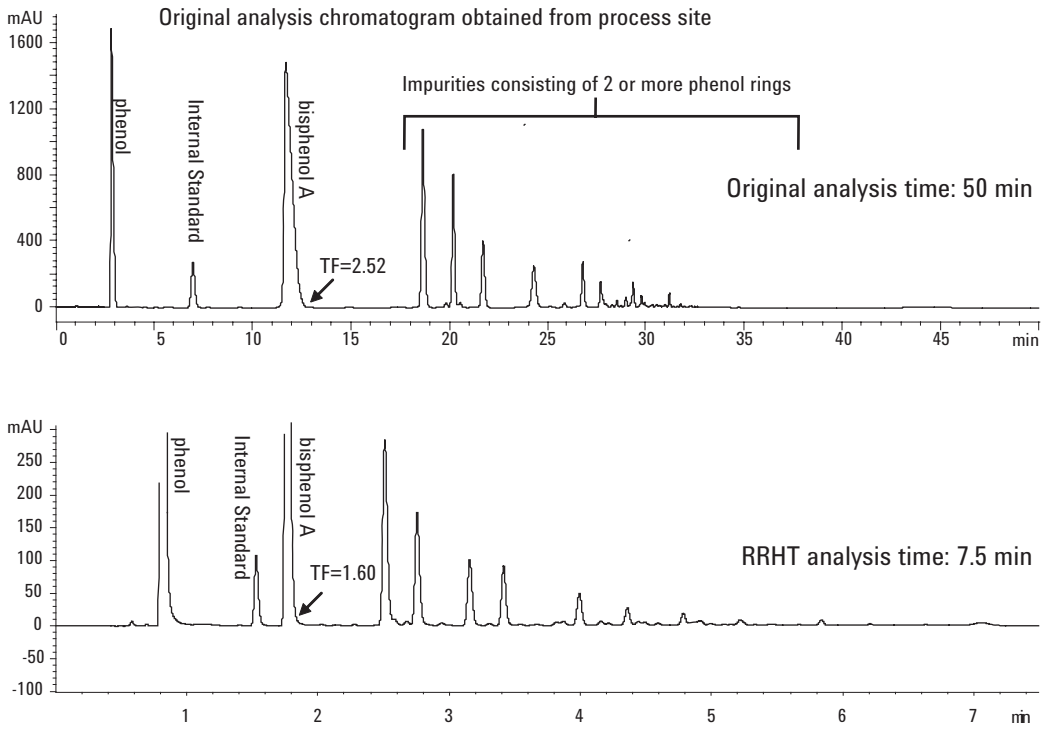


**Figure 4. Comparison of methods; original to RRHT.**

**Table 1. Current and Improved Method Parameters**

**Original**

- Column: Supelco LC-18, 4.6 × 250 mm, 5 µm
- Mobile phase: A: 0.025% $H_3PO_4$, B: ACN, C: MeOH
- Flow: 2 mL/min
- Temperature: 35 °C
- Sample size: 20 µL
- Gradient: segmented, has isocratic holds

| Time | % A:B:C |
|---|---|
| 0 | 65:25:10 |
| 13 | 65:25:10 |
| 18 | 50:40:10 |
| 23 | 50:40:10 |
| 27 | 30:50:20 |
| 32 | 0:70:30 |
| 35 | 0:70:30 |
| 36 | 0:60:40 |
| 40 | 0:50:50 |
| 43 | 0:20:80 |
| 48 | 65:25:10 |

**RRHT**

- Column: ZORBAX XDB-C18, 4.6 × 50 mm, 1.8 µm
- Mobile phase: A: 0.1% formic acid, B: ACN: MeOH (200:800)
- Flow: 1 mL/min
- Temperature: 25 °C
- Sample size: 2 µL
- Gradient: linear, no isocratic holds

| Time | % B |
|---|---|
| 0 | 60 |
| 6 | 95 |
| 6.01 | 60 |
| 8 | 60 |

## Conclusion

Converting an existing method to a high-throughput method is one way to improve lab productivity. Using RRHT columns initially for method development also improves productivity. Eclipse XDB-C18 RRHT columns are a good choice for converting existing C18 methods into high-throughput methods. Smaller particles packed into shorter columns provide comparable resolution to larger particles packed into longer columns in a fraction of the time. RRHT columns are advantageous for gradient method development because gradient re-equilibration is time-consuming and often overlooked in the total analysis time. Methods developed on Agilent RRHT columns can be scaled easily because of the highly uniform particles, bonded phase chemistry, and column manufacturing techniques. An existing method developed on a "traditional analytical-sized" column was easily converted to a high throughput method using an Eclipse XDB-C18 RRHT column. The method was incrementally scaled up to an analytical-sized column, and it performed with predictable results on various column dimensions and particle sizes. The predictability of the results supports Eclipse XDB-C18 RRHT columns' ability to easily improve applications and transfer them into high-throughput and high-resolution applications.

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**Agilent Technologies**

# Fast Analysis of Phenolic Antioxidants and Erucamide Slip Additives in Polypropylene Homopolymer Formulations Using 1200 Rapid Resolution Liquid Chromatography (RRLC) with Rapid Resolution High Throughput (RRHT) Columns and Method Translator

Application

**Hydrocarbon Processing**


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## Abstract

**Vitamin E (tocopherol), phenolic antioxidants and erucamide slip additives in polypropylene homopolymer formulations were resolved and detected using liquid chromatography with ultraviolet/visible detection, under guidelines suggested by ASTM Method D6042. Using the Agilent 1200 Rapid Resolution LC system with Agilent ZORBAX RRHT columns, the antioxidants could be rapidly separated with the same or improved resolution. The Agilent method translator was used to transfer the ASTM method into new methods based on the instrument parameters, column dimensions, and particle size in three modes: simple conversion and speed optimized and resolution optimized methods.**

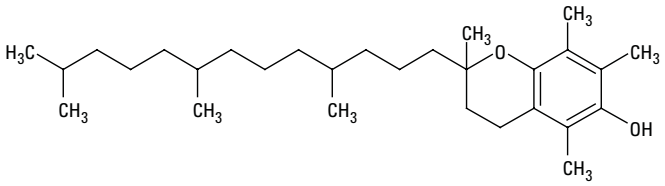

## Introduction

Polymers are very popular all over the world owing to their unprecedented physical properties. Various additives are blended into polymeric materials to modify certain properties of the polymer formulation. Erucamide, Irganox 3114, Irganox 1010, Vitamin E (tocopherol), Irganox 1076, and Irgafos168 are often used as antioxidants to prevent the degradation of polypropylene homopolymer formulations by light, heat, and oxygen. In this work, with the goal to shorten the analysis time and reduce solvent consumption without losing separation quality, the existing ASTM method was recalculated for new operating conditions based on columns packed with smaller particle sizes. The chemical information of the antioxidants and Tinuvin P as internal standard is displayed in detail in Table 1.

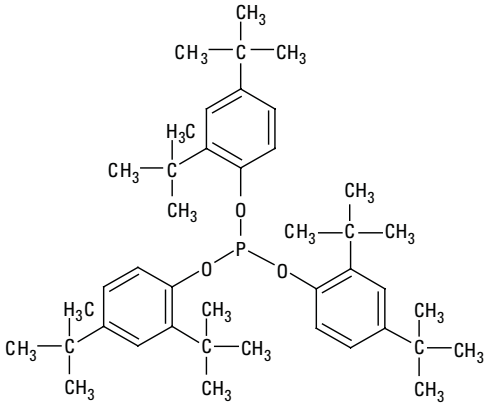
Specific additives and their concentrations in polymer formulations are critical to the properties of polymer, and careful analysis is required to ensure that the additives and levels are appropriate for the intended use. This application will compare two different stationary phases according to analyte retention characteristics and peak shape, show the influence of different injection volume of real sample on the peak shape, and then will focus on showing how to use the method translator. The latter is used to transfer the conventional method to new methods using smaller size columns to perform simple conversion and to extend the method to greater speed and higher resolution.

**Table 1. Chemical Information of Antioxidants and Tinuvin P**

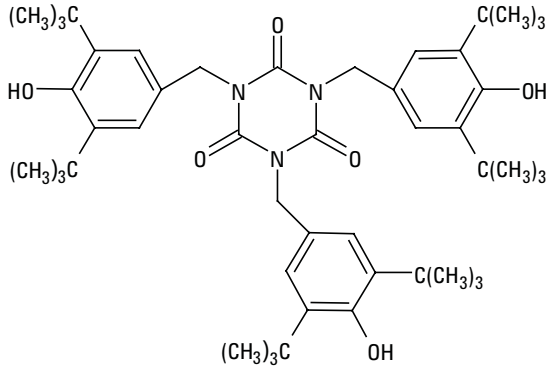
| | | |
|---|---|---|
| Name: | Vitamin E | DL-all-rac-α-Tocopherol |
| Formula: | $C_{29}H_{50}O_2$ | |
| Molecular Weight: | 430.71 | |
| CAS No.: | 10191-41-0 | |



| | | |
|---|---|---|
| Name: | Irgafos 168 | Tris(2,4 di-tert-butylphenyl) phosphite |
| Formula: | $[[(CH_3)_3C]_2C_6H_3O]_3P$ | |
| Molecular Weight: | 646.92 | |
| CAS No.: | 31570-04-4 | |



| | | |
|---|---|---|
| Name: | Irganox 3114 | Tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate |
| Formula: | $C_{48}H_{69}N_3O_6$ | |
| Molecular Weight: | 784.08 | |
| CAS No.: | 27676-62-6 | |



| | | |
|---|---|---|
| Name: | Erucamide | cis-13-docosenamide |
| Formula: | $CH_3(CH_2)_7CH=CH(CH_2)_{11}CONH_2$ | |
| Molecular Weight: | 337.58 | |
| CAS No.: | 112-84-5 | |

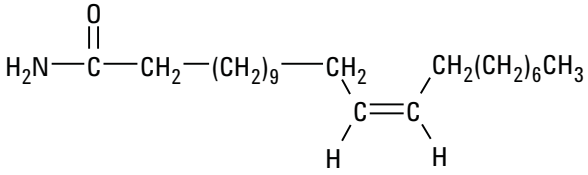
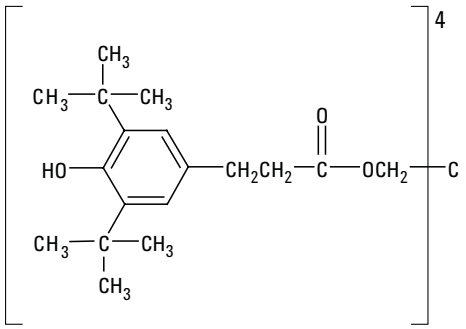
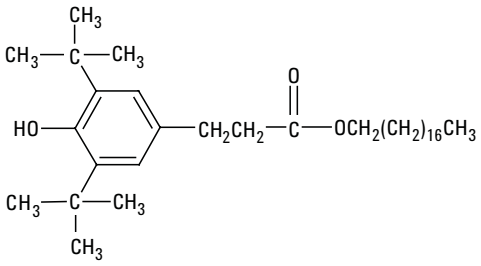
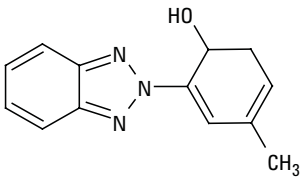


**Table 1. Chemical Information of Antioxidants and Tinuvin P** (Continued)

| | | |
|---|---|---|
| Name: | Irganox 1010 | Pentaerythritol tetrakis (3,5-di-tert-butyl-4-hydroxyhydrocinnamate) |
| Formula: | $[HOC_6H_2[C(CH_3)_3]_2CH_2CH_2CO_2CH_2]_4C$ | |
| Molecular Weight: | 1177.63 | |
| CAS No.: | 6683-19-8 |  |
| Name: | Irganox 1076 | Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate |
| Formula: | $[(CH_3)_3C]_2C_6H_2(OH)CH_2CH_2CO_2(CH_2)_{17}CH_3$ | |
| Molecular Weight: | 530.86 | |
| CAS No.: | 2082-79-3 |  |
| Name: | Tinuvin P | 2-(2-hydroxy-5-methylphenyl)benzotriazole |
| Formula: | $C_{13}H_{11}N_3O$ | |
| Molecular Weight: | 225.25 | |
| CAS No.: | 2440-22-4 |  |

# Experimental

### System

Agilent 1200 Series Rapid Resolution LC (RRLC), consisting of:
G1379B micro vacuum degasser
G1312B binary pump SL
G1367C high-performance autosampler SL
G1316B thermostatted column compartment SL
G1315C UV/VIS diode array detector SL with 3 mm, 2 µL flow cell
ChemStation 32-bit version B.02.01-SR1

### Columns

Agilent ZORBAX Eclipse XDB-C18, 4.6 mm × 150 mm, 5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 150 mm, 5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 100 mm, 3.5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 50 mm, 1.8 µm
Agilent ZORBAX Eclipse XDB-C8, 3.0 mm × 100 mm, 3.5 µm
Agilent ZORBAX Eclipse XDB-C8, 3.0 mm × 50 mm, 1.8 µm

### Mobile Phase

| | |
|---|---|
| Gradients: | A: water<br>B: acetonitrile (ACN) |
| Gradient conditions: | See individual chromatograms |
| Column temperature | See individual chromatograms |

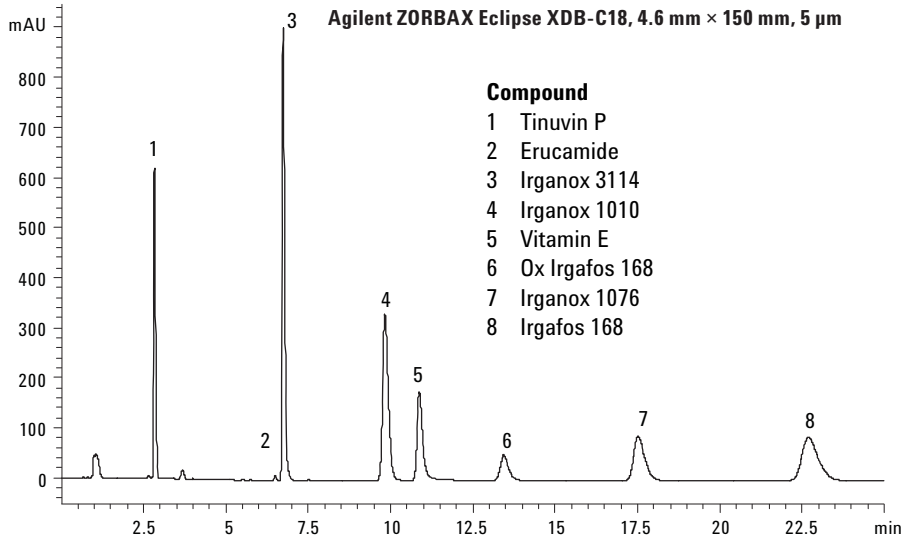
### Samples

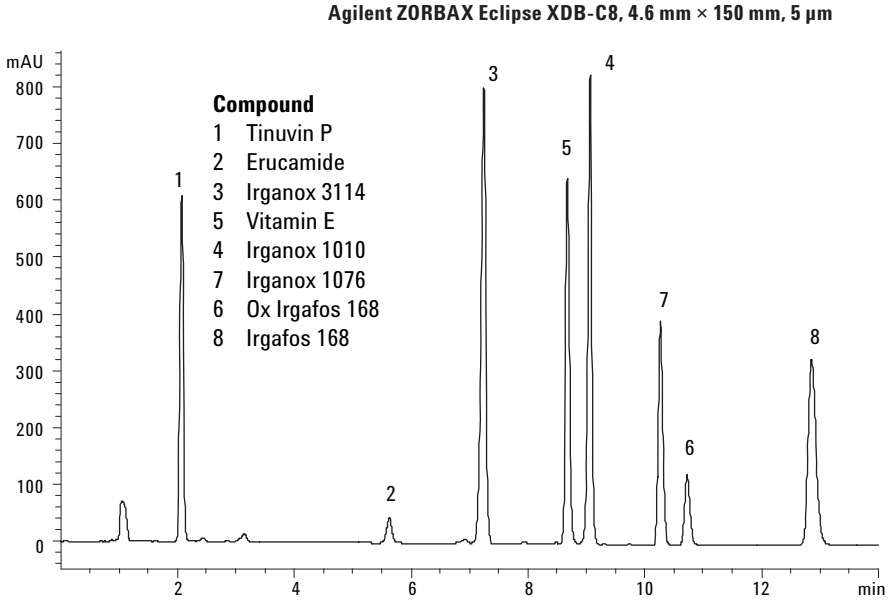
1. Standard mixture of Tinuvin P, Erucamide, Irganox 3114, Irganox 1010, Vitamin E, Irganox 1076, and Irgafos168, all 200 µg/mL in isopropanol
2. Polypropylene Homopolymer Formulation, from customer, extracted by ultrasonic according to the method ASTM D6042-04
3. Polypropylene extract spiked with 20 µg/mL standard mixture

## Results and Discussion

### Selection of Stationary Phase for the Separation of Antioxidants

It is desirable during method development to select a column that will provide the optimal analyte separation and shortest analysis time. Reversed phase C18 columns are recommended by ASTM D6042-04; however, in our application we determined that the retention characteristics of ZORBAX XDB-C18 columns were too strong for the specified solvents, resulting in broad peak shape and quantitation difficulties for late-eluting peaks. Compared with ZORBAX XDB-C18 columns, ZORBAX XDB-C8 columns showed better retention capability and peak shape. Therefore, we chose the ZORBAX XDB-C8 column for further method development. The different separations with ZORBAX XDB-C18 and ZORBAX XDB-C8 columns are shown in the Figure 1.




**Conditions**

| | | ZORBAX chemistry: Eclipse XDB-C18 | | Eclipse XDB-C8 | |
|---|---|---|---|---|---|
| Mobile phase: | A: water; B: ACN | Gradient: | Min | %B | Min | %B |
| Flow rate: | 1.5 mL/min | | 0.00 | 75 | 0.00 | 75 |
| Wavelength: | 200 nm | | 5.00 | 100 | 8.00 | 100 |
| Injection volume: | 10 µL | | 25.00 | 100 | 15.00 | 100 |
| Column temperature: | 50 °C | | 25.10 | 75 | 15.10 | 75 |
| Column size: | 4.6 mm × 150 mm, 5 µm | | 30.00 | 75 | 20.00 | 75 |
| Sample: | Standard mixture, 200 µg/mL in isopropanol | | | | | |

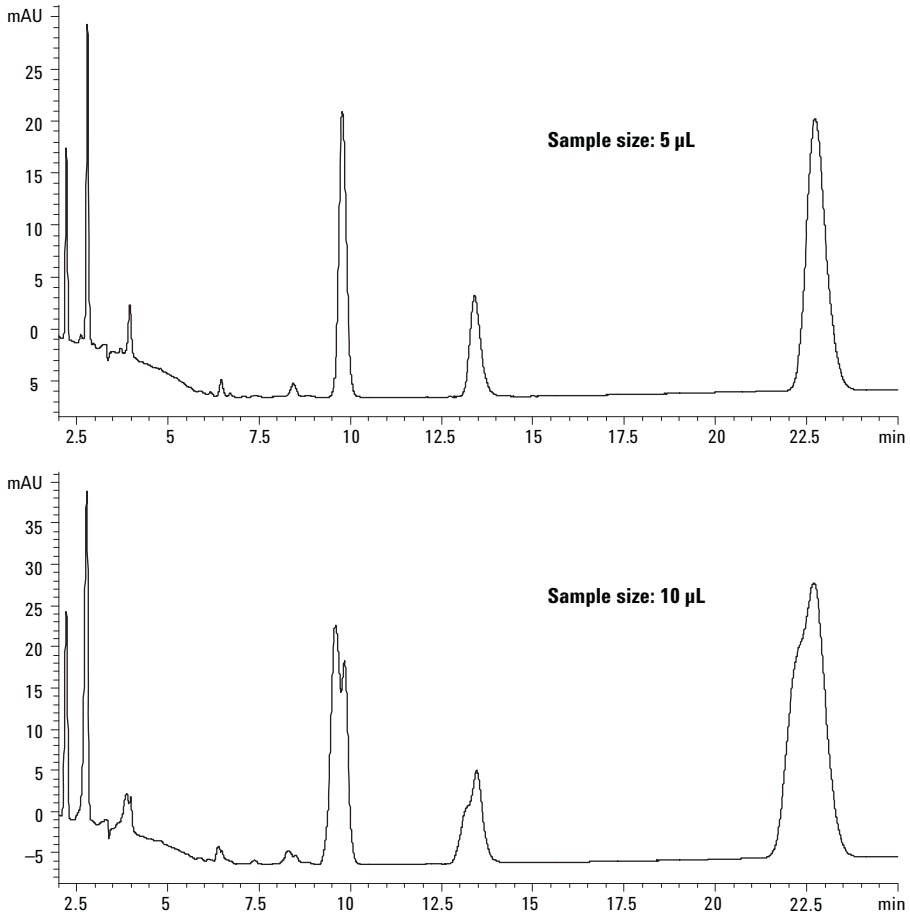
**Figure 1. ZORBAX stationary phase comparison for antioxidants.**

### Injection Volume Influence of Real Sample Extraction Solution on the Peak Shape

According to ASTM D6042-04 [1], a solvent mixture of methylene chloride and cyclohexane (1/1 v/v) is used as the extraction solvent and, after filtration, the extracted solution is directly injected into the LC. Neither methylene chloride nor cyclohexane is miscible in the acetonitrile and water mobile phase. Peak splitting was observed when the injection volume was 10 µL. We decreased the sample size of real sample and found that the volume of 5 µL was suitable and free of solvent influence. The split and nonsplit peaks are shown in Figure 2. At the same time, the influence of injection volume was not found in the standard solution, which was dissolved in isopropanol per ASTM method guidance.

### Fast Method Developed Based on New 1200 RRLC with Method Translator

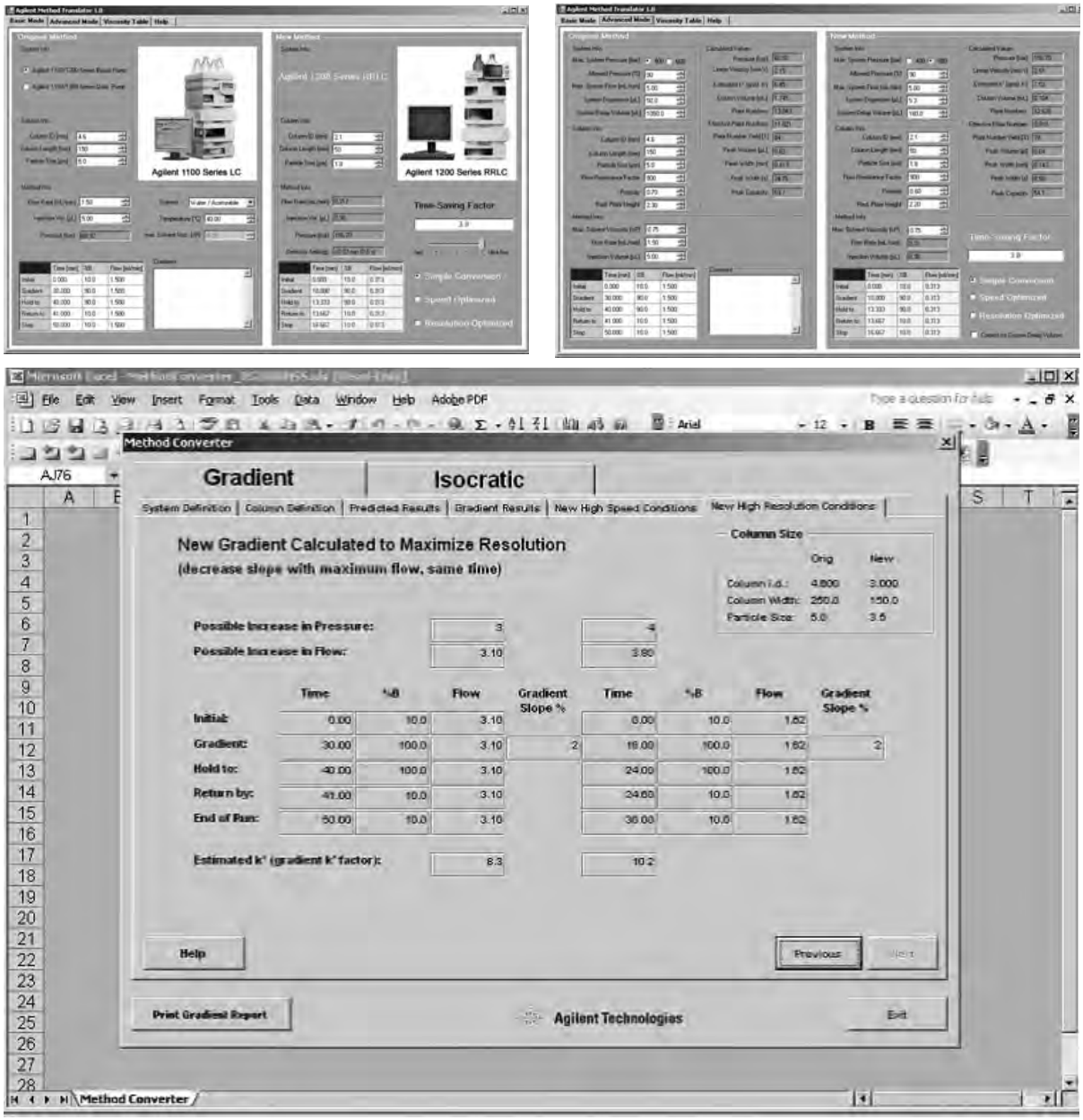
Due to the appearance of sub-two-micron columns and LC systems with higher pressure capabilities, the research of ultra-fast separation is more and more popular. Therefore, it is important to quickly and easily transfer conventional methods to fast or high-resolution methods. Agilent provides the users of RRLC systems with two versions of method translators; one is a Microsoft.net version, which requires that Net-Framework 2.0 be resident on the computer, the other is a Microsoft Excel version, which requires that Excel be resident on the PC. The interface of the two translators is displayed in Figure 3.




**Conditions**

| | | | |
|---|---|---|---|
| Mobile phase: | A: water; B: ACN | **Gradient**: | |
| Flow rate: | 1.5 mL/min | Min | %B |
| Wavelength: | 200 nm | 0.00 | 75 |
| Injection volume: | 5 or 10 µL | 5.00 | 100 |
| Column temperature: | 50 °C | 25.00 | 100 |
| Column: | ZORBAX Eclipse XDB-C18 4.6 mm × 150 mm, 5 µm | 25.10 | 75 |
| Sample: | Polypropylene extraction solution | 30.00 | 75 |

**Figure 2. Injection volume influence of real sample extraction solution on the peak shape.**




The upper one is the Microsoft.net version, the lower one is the Microsoft Excel version.

**Figure 3. Two different method translators.**

### Sample Preparation

The two versions of method translators provide three modes of method conversion; the first is the simple conversion, which has the same gradient slope as the conventional method, and changes the flow rate according to equation 1:

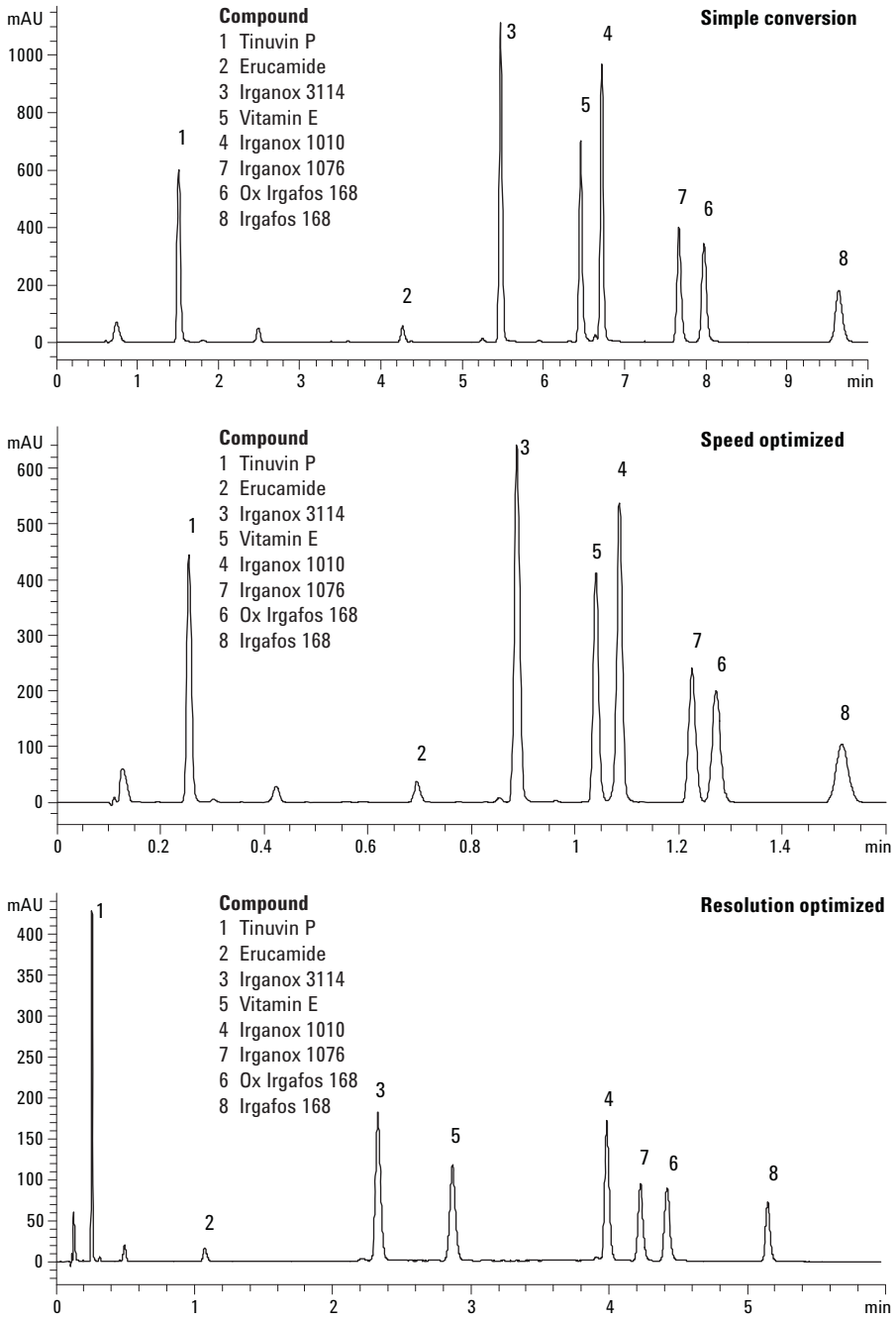
$$Flow_{Col.\,2} = \left[\frac{Diam_{Col.\,2}}{Diam_{Col.\,1}}\right]^2 \times Flow_{Col.\,1} \quad \text{(eq. 1)}$$

The second is the speed optimized conversion, which has the same gradient slope as the conventional method and maximizes the flow rate according the LC system pressure capability. The last is the resolution optimized conversion, which maximizes the flow rate according the LC system pressure capability and has the same gradient time as the simple converted mode, resulting in a reduced gradient slope that normally yields higher peak resolution. For the different columns, the injection volumes should be changed according to the relationship displayed in equation 2.

$$Inj.\ vol._{Col.\,2} = \left[\frac{Volume_{Col.\,2}}{Volume_{Col.\,1}}\right] \times Inj.\ vol._{Col.\,1} \quad \text{(eq. 2)}$$

As mentioned above, the method based on the ZORBAX Eclipse XDB-C8 4.6 mm x 150 mm, 5 µm, was selected as the initial method. Afterwards, the initial method was transferred with the method

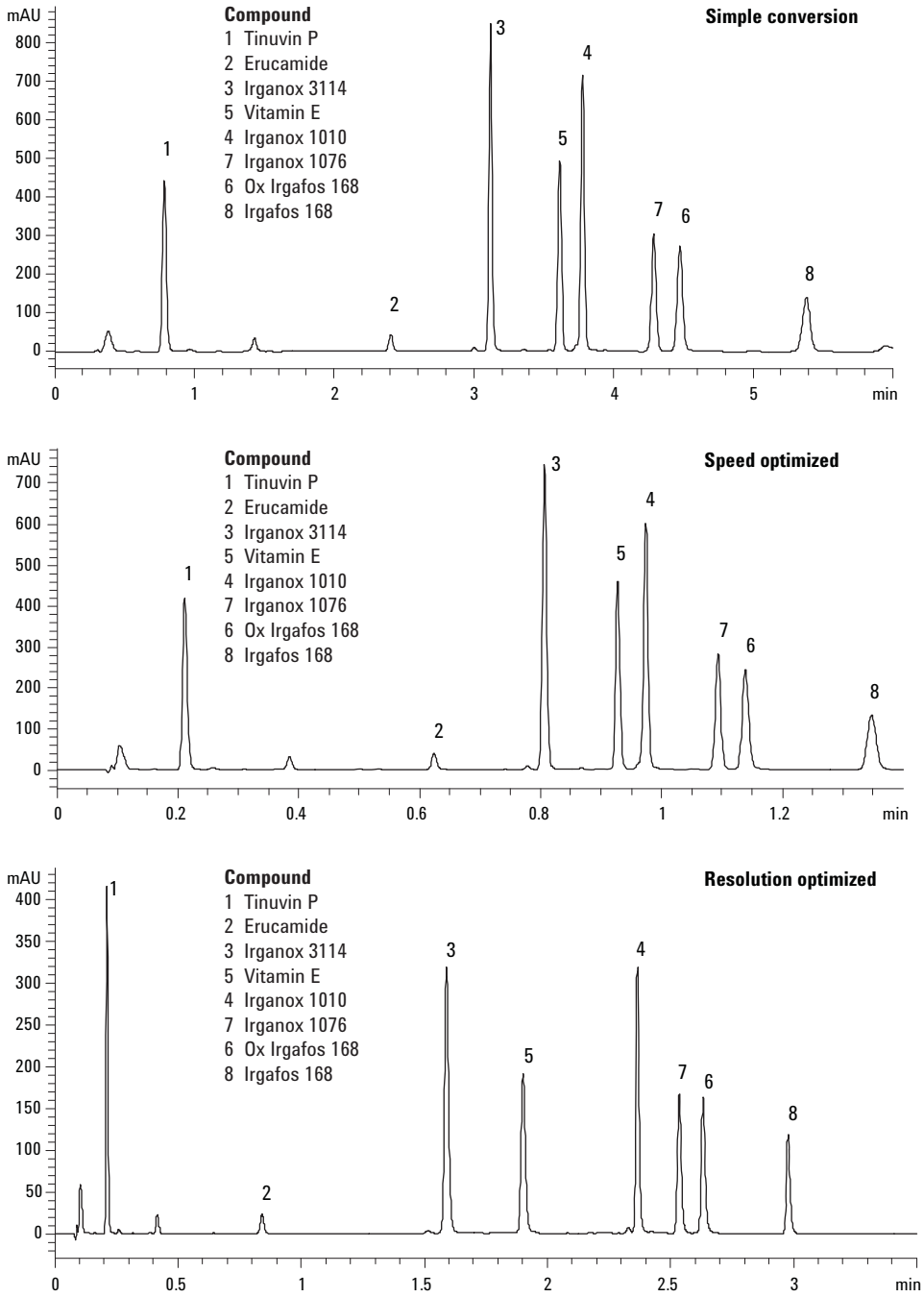
translator into three modes on different column lengths (100, 50 mm) and particle sizes (3.5, 1.8 µm), respectively. Figures 4 and 5 show the separation of antioxidants in smaller particle size columns with the recalculated methods.




**Conditions**

| | | | | |
|---|---|---|---|---|
| Sample: | Standard mixture, 200 µg/mL in isopropanol | | | |
| Mobile phase: | A: water; B: ACN | | | |
| Temperature: | 50 °C | | | |
| Wavelength: | 200 nm | | | |
| Injection volume: | 6.7 µL | | | |
| Column: | ZORBAX Eclipse XDB-C8 3.0 mm × 100 mm, 3.5 µm | | | |
| Mode: | Simple converted | Speed optimized | Resolution optimized | |
| Flow rate: | 0.64 mL/min | 4.00 mL/min | 4.00 mL/min | |
| | Pressure: | 110 bar | 460 bar | 460 bar |
| | Gradient slope: | 3.1% | 3.1% | 0.5% |
| | Analysis time: | 10 min | 1.6 min | 5.5 min |

**Figure 4. Separation of antioxidants on ZORBAX Eclipse XDB-C8 3.0 mm × 100 mm, 3.5 µm.**

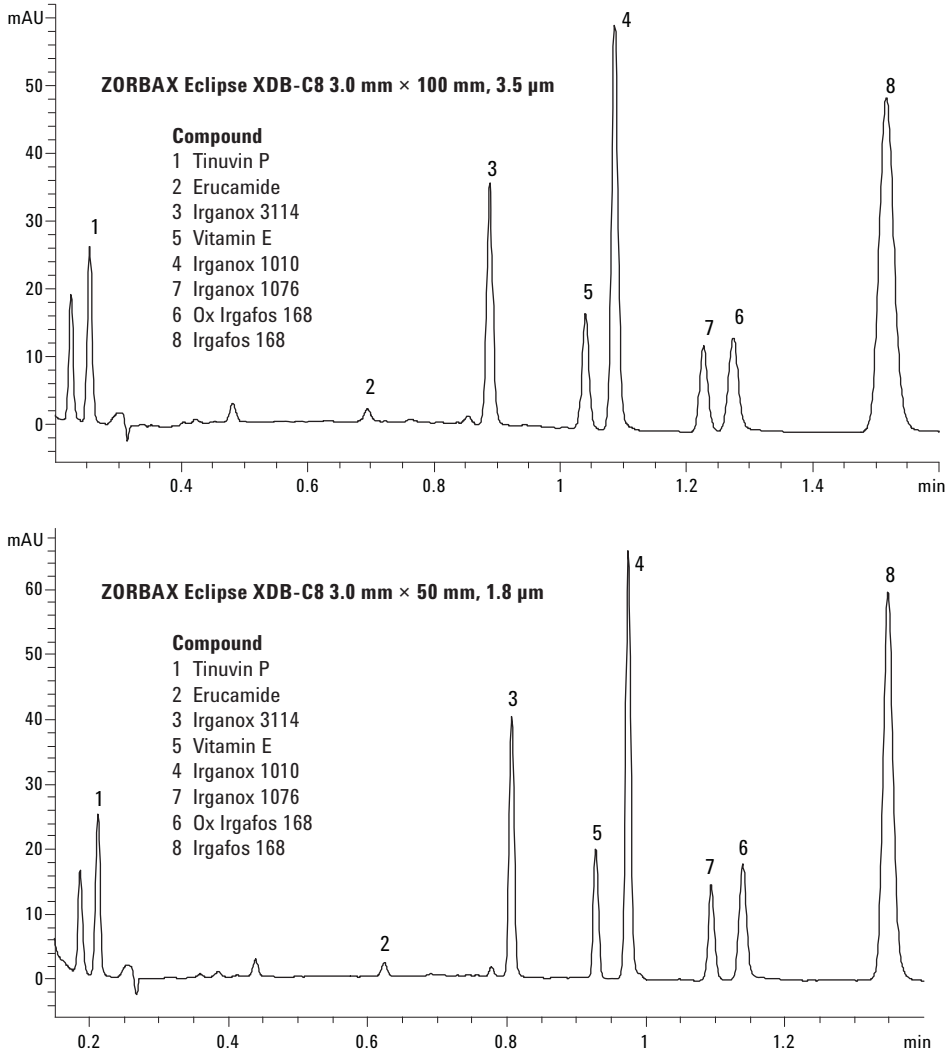



**Conditions**

| | | | |
|---|---|---|---|
| Sample: | Standard mixture, 200 µg/mL in isopropanol | | |
| Mobile phase: | A: water; B: ACN | | |
| Temperature: | 50 °C | | |
| Wavelength: | 200 nm | | |
| Injection volume: | 3.3 µL | | |
| Column: | ZORBAX Eclipse XDB-C8 3.0 mm × 50 mm, 1.8 µm | | |
| Mode: | Simple converted | Speed optimized | Resolution optimized |
| Flow rate: | 0.64 mL/min | 2.50 mL/min | 2.50 mL/min |
| Pressure: | 160 bar | 460 bar | 460 bar |
| Gradient slope: | 3.1% | 3.1% | 0.8% |
| Analysis time: | 6 min | 1.4 min | 3 min |

**Figure 5. Separation of antioxidants on ZORBAX Eclipse XDB-C8 3.0 mm × 50 mm, 1.8 µm.**

To identify the matrix influence on the separation, the polypropylene extract was spiked with 20 µg/mL standard mixture and injected into the LC system. Figure 6 depicts the separation of spiked sample with the speed optimized method, which shows a sufficient separation of antioxidant in polymer matrix with about 10 times faster speed than the conventional method mentioned above.




**Conditions**

| | | |
|---|---|---|
| Sample: | Polypropylene extract spiked with 20 µg/mL standard mixture | |
| Mobile phase: | A: water; B: ACN | |
| Temperature: | 50 °C | |
| Wavelength: | 200 nm | |
| Stationary phase: | ZORBAX Eclipse XDB-C8 | |
| Column size: | 3.0 mm × 100 mm, 3.5 µm | 3.0 mm × 50 mm, 1.8 µm |
| Injection volume: | 3 µL | 1 µL |
| Mode: | Speed optimized | Speed optimized |
| Flow rate: | 4.00 mL/min | 2.50 mL/min |
| Pressure: | 460 bar | 460 bar |
| Gradient slope: | 3.1% | 3.1% |
| Analysis time: | 1.6 min | 1.4 min |

**Figure 6. Separation of spiked polypropylene extract by the speed optimized method.**

## Conclusions

As an important innovation in the advancement of liquid chromatography, the Agilent 1200 Rapid Resolution LC system provides the customer not only a rapid separation with the same or similar resolution, but also includes a method translator to convert any initial conventional method to a fast or high-resolution method according to the requirements of the user. This note applies the method translation tool in the separation of polymer additives and demonstrates the ease-of-use and power of the method translator using separations of a standard mixture and spiked real sample.

## References

1. ASTM D6042-04, “Standard Test Method for Determination of Phenolic Antioxidants and Erucamide Slip Additives in Polypropylene Homopolymer Formulations Using Liquid Chromatography (LC)”
2. Michael Woodman, “Improving the Effectiveness of Method Translation for Fast and High Resolution Separations”
3. Michael Woodman, “Screening and Qualitative Identification of Antioxidant Polymer Additives by HPLC with UV/VIS and APCI-MS Detection”

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# Analysis of Phenolic Antioxidant and Erucamide Slip Additives in Polymer by Rapid-Resolution LC

Application

**Hydrocarbon Processing**


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## Abstract

**Liquid chromatography with ultraviolet/visible (UV/VIS) detection is a powerful approach for analyzing additives in polymer formulations. This application illustrates the use of the Agilent 1200 Series Rapid Resolution LC (RRLC) system for the separation of antioxidants and erucamide. The system can operate significantly faster than conventional HPLC without sacrificing resolution, precision, or sensitivity. The column chemistry and temperature influence on the separation and the sample preparation method are also discussed.**


## Introduction

Additives are incorporated into various polymeric materials to retard the degradation caused by ultraviolet light, heat, and oxygen or to modify processing characteristics. A rapid and accurate analytical method is required to ensure that the specified amount of an additive or combination of additives is incorporated into a polymer after the extrusion process. Conventional HPLC methods for additives [1,2] often require more then 30 minutes per analysis, while the application described here can achieve comparable results in as few as 3 minutes.

Agilent has developed an easy-to-use method conversion tool for transferring existing methods for higher speed and/or higher resolution. The tool was used for the method optimization in this application. [3]

This application examines additives mentioned in ASTM Methods D5815 and D1996. The chemical structures are shown in Table 1.

**Table 1. Polymer Additives in ASTM Methods D5815 and D1996**

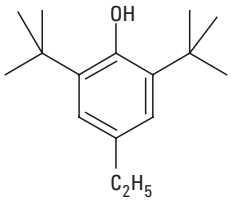
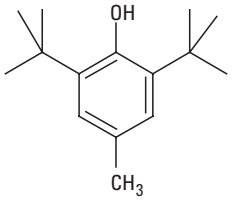
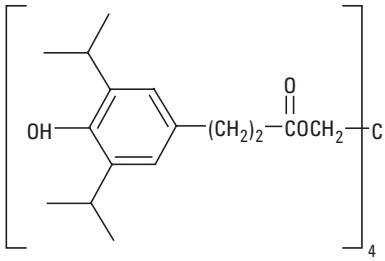
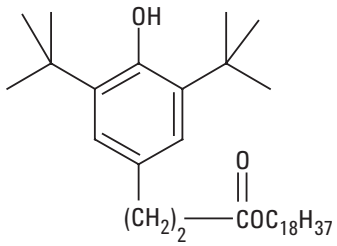
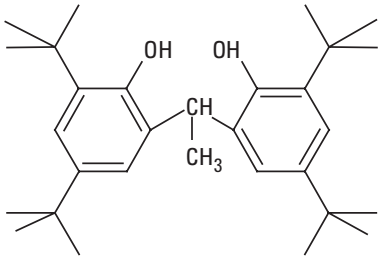
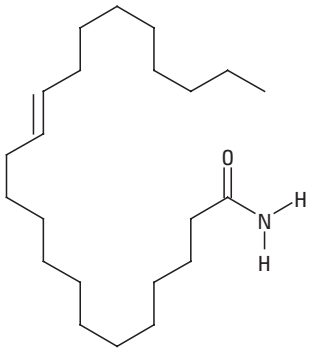
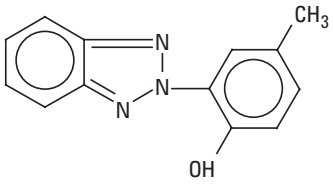
| Registered trade name | CAS no. | Chemical name | Chemical structure |
|---|---|---|---|
| BHEB | 4310-42-1 | 2,6-di-tert-butyl-4-ethyl-phenol or butylated hydroxyethyl benzene |  |
| BHT | 128-37-0 | 2,6-di-t-butyl-cresol or butylated hydroxy toluene |  |
| Irganox 1010 | 6683-19-8 | Tetrakis[methylene(3,5-di-t-butyl-4-hydroxy hydrocinnamate)] methane |  |
| Irganox 1076 | 2082-79-3 | Octadecyl-3,5-di-t-butyl-4-hydroxy hydrocinnamate |  |
| Isonox 129 | 35958-30-6 | 2,2-ethylidene bis (4,6-di-t-butyl phenol) |  |

**Table 1. Polymer Additives in ASTM Methods D5815 and D1996** (Continued)

| Registered trade name | CAS no. | Chemical name | Chemical structure |
|---|---|---|---|
| Kemamide-E | 112-84-5 | Cis-13-docosenamide or Erucamide or Fatty acid amide ($C_{22}H_{43}NO$) |  |
| Tinuvin P | 2440-22-4 | 2(2'-hydroxy-5'-methyl phenyl) benzotriazole |  |

## Experimental

### System

Agilent 1200 Series rapid-resolution LC configured with
G1379B microvacuum degasser
G1312B binary pump SL
G1367B high-performance autosampler SL
G1316B thermostatted column compartment SL
G1315C UV/VIS diode array detector SL
ChemStation 32-bit version B.02.01

### Column

ZORBAX Eclipse XDB-C18, 4.6 mm × 150 mm, 5 µm
ZORBAX Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm
ZORBAX SB-C18, 4.6 mm × 150 mm, 5 µm
ZORBAX SB-C18, 4.6 mm × 50 mm, 1.8 µm

### Mobile phase

| | |
|---|---|
| Gradients: | A: water<br>B: acetonitrile (ACN) |
| Gradient slope: | See individual chromatograms for flow rate and gradient time |
| Column temperature: | See individual chromatograms |

### Samples

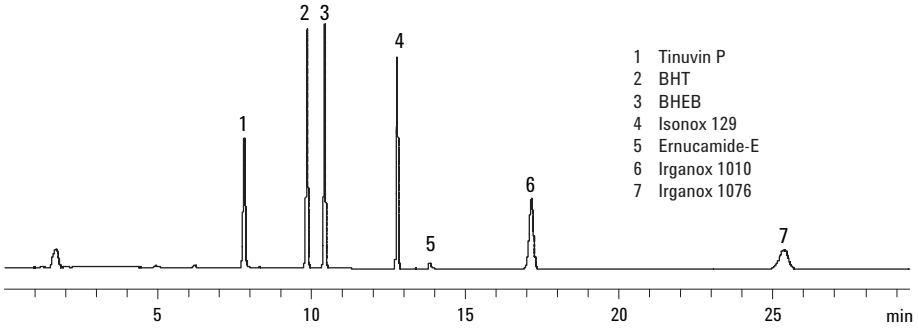
1. Standard mixture described in ASTM D5815 and D1996, 50 µg/mL, 200 µg/mL in isopropanol
2. Linear low-density polyethylene from customer, ground to 20 mesh, extracted by ultrasonic or reflux method

## Results and Discussion

### Fast Method Conversion

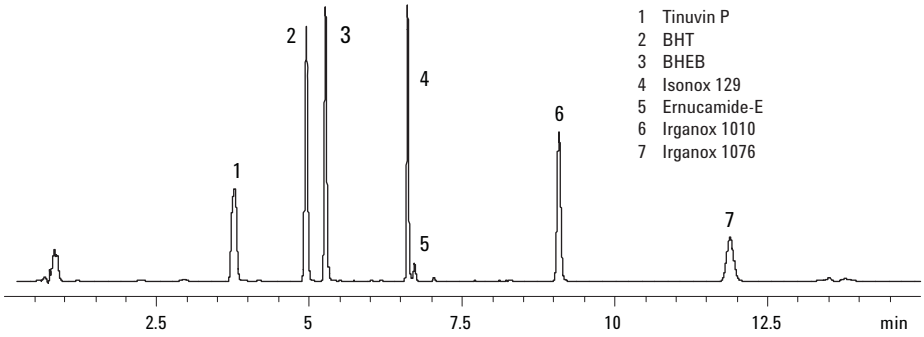
The separation was initially performed on a standard 4.6 mm × 150 mm, 5-µm ZORBAX Eclipse XDB-C18 column thermostatted to 60 °C (Figure 1) following the conditions in ASTM D5815 (or D1996). The method was then scaled in flow and time for exact translation to a 2.1 mm × 50 mm, 1.8-µm column (Figure 2). The analysis time was reduced from 25.5 to 12.5 minutes, and the solvent consumption was reduced from 25 to 2.5 mL.

The separation was then re-optimized for faster separation with the same gradient slope by increasing the flow rate from 0.21 to 0.9 mL/min and proportionately reducing the gradient time (Figure 3), achieving up to 10 times faster than conventional HPLC without sacrificing resolution, precision (showed in Table 2), or sensitivity. Figure 4 demonstrates that 1 ppm of additives can be determined with very good signal-to-noise response using the same condition in Figure 3, which exceeds the specification of 2 ppm of ASTM D5815 (or D1996). Peak 6, Irganox 1010, for example has a signal-to-noise response of 88 at 1 ppm.



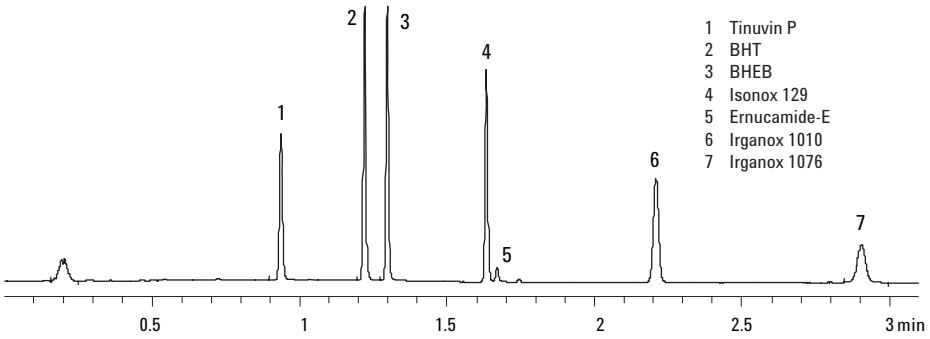

| | | Gradient | |
|---|---|---|---|
| Conventional method: | Follow ASTM D5815 (or D1996) method with | | |
| | ZORBAX Eclipse XDB-C18, | | %B |
| | 4.6 mm × 150 mm, 5 µm | 0 | 50 |
| Sample: | Standard 50 µg/mL | 11 | 100 |
| Sample size: | 10 µL | 28 | 100 |
| Detector: | UV 200 nm | 28.1 | 50 |
| Column temperature: | 60 °C | | |
| Mobile phase: | A: water | | |
| | B: acetonitrile | | |
| Flow rate: | 1 mL/min | | |

**Figure 1. Separation of additives standards on Eclipse XDB-C18, 4.6 mm × 150 mm, 5 µm.**




| | | Gradient | |
|---|---|---|---|
| Simple-converted: | Translate the conventional method to a | | |
| | ZORBAX Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm | | %B |
| Sample: | Standard 50 µg/mL | 0 | 50 |
| Sample size: | 2 µL | 5.2 | 100 |
| Detector: | UV 200 nm | 12 | 100 |
| Column temperature: | 60 °C | 12.1 | 50 |
| Mobile phase: | A: water | 15 | 50 |
| | B: acetonitrile | | |
| Flow rate: | 0.21 mL/min (73 bar) | | |

**Figure 2. Separation of additives standards on Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm.**

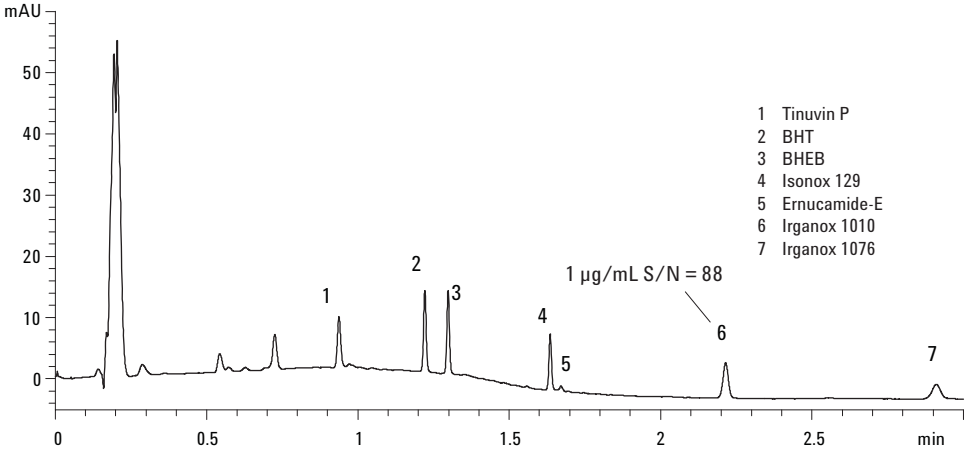



| | | Gradient | |
|---|---|---|---|
| Speed-optimized: | Optimize the conventional method for speed with ZORBAX Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm | | %B |
| | | 0 | 50 |
| Sample: | Standard 50 µg/mL | 1.3 | 100 |
| Sample size: | 2 µL | 3 | 100 |
| Detector: | UV 200 nm | 3.1 | 50 |
| Column temperature: | 60 °C | 3.5 | 50 |
| Mobile phase: | A: water<br>B: acetonitrile | | |
| Flow rate: | 0.9 mL/min (357 bar) | | |

**Figure 3. Fast separation of additives standards on Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm.**

**Table 2. Repeatability for the Methods of Conventional, Simple-Converted, and Speed-Optimized Methods (n = 5)**

| | Area, RSD% | | |
|---|---|---|---|
| **Compounds (50 ppm)** | **Conventional** | **Simple-converted** | **Speed-optimized** |
| Tinuvin P | 0.37 | 0.39 | 0.09 |
| Erucamide | 0.40 | 0.57 | 0.13 |
| Irganox 3114 | 0.44 | 0.49 | 0.22 |
| Irganox 1010 | 0.38 | 0.39 | 0.26 |
| Vitamin E | 0.58 | 0.80 | 0.68 |
| Irganox 1076 | 0.58 | 1.49 | 0.17 |
| Irgafos 168 | 0.53 | 0.77 | 0.32 |




Speed-optimized method for analysis of additives standards with concentration of 1 µg/mL LC conditions is identical to that in Figure 3

**Figure 4. Fast separation of 1 µg/mL additives standards on Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm.**

### Optimized Column Temperature

Increasing column temperature can lower both solvent viscosity and nonspecific column/analyte interactions. The new ZORBAX StableBond RRHT columns can operate at temperatures up to 90 °C. We tested operating temperatures at 60, 75, 85, and 90 °C with a ZORBAX SB-C8 4.6 mm × 150 mm, 5-µm column. The results (Figure 5) show that the analysis time obtained from 60 °C to 85 °C is reduced from 23.5 minutes to 17 minutes; at 90 °C, only an additional 0.5 minute is saved. Based on the combined speed reduction and optimized resolution of peaks 4 and 5, 85 °C is chosen as a suitable column temperature.

The method was then scaled in flow and time for exact translation to a 4.6 mm × 50 mm, 1.8-µm column (Figure 6). Finally, the separation was optimized for faster separation by increasing the flow rate from 1 mL/min to 3.5 mL/min, with only a 1.7-minute analysis time (Figure 7). This is really an excellent procedure for high-throughput screening and quantitation of a large number of samples. Figure 8, the separation of an extract of linear low-density polyethylene (LLDPE) spiked with 20 µg/mL of standard solution, shows excellent separation with real sample matrix.

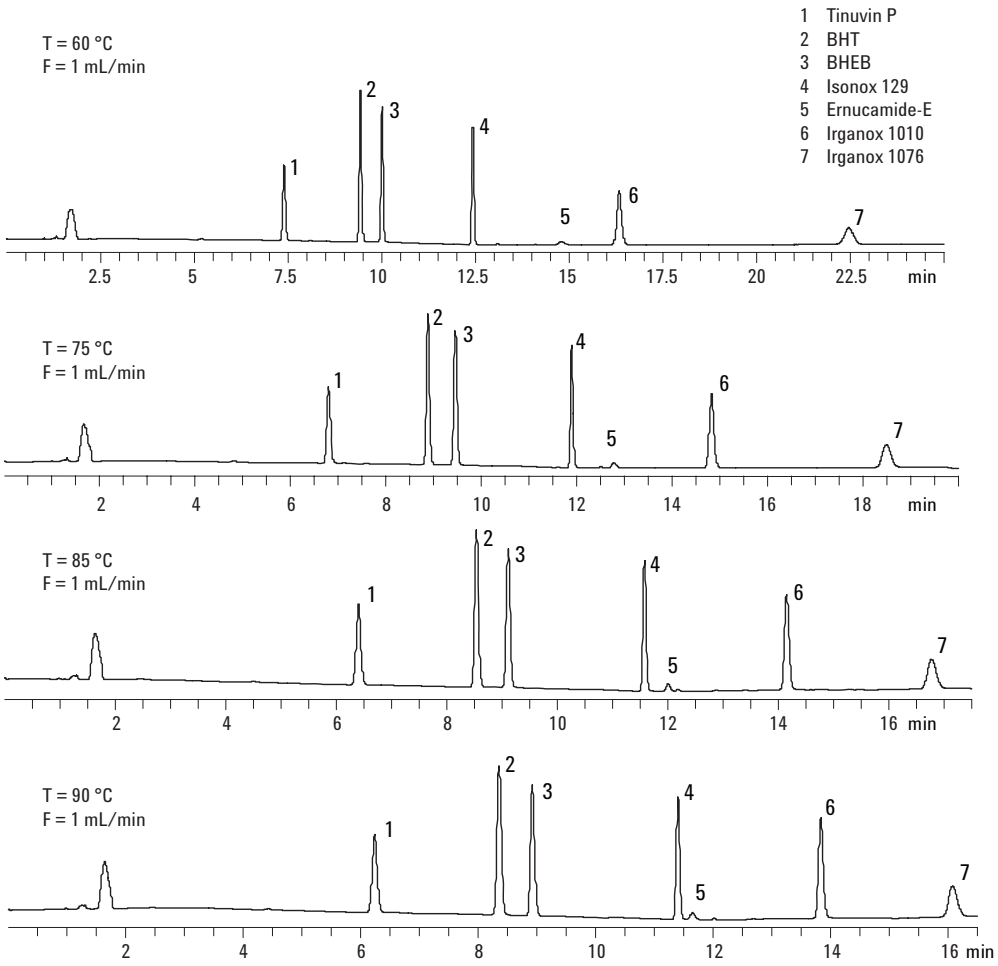
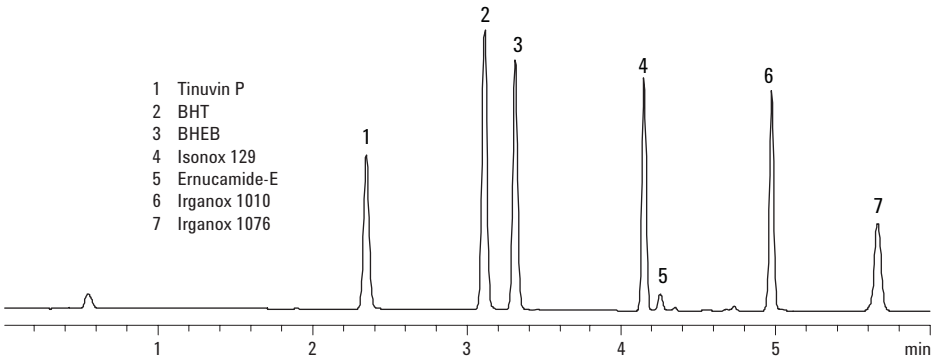
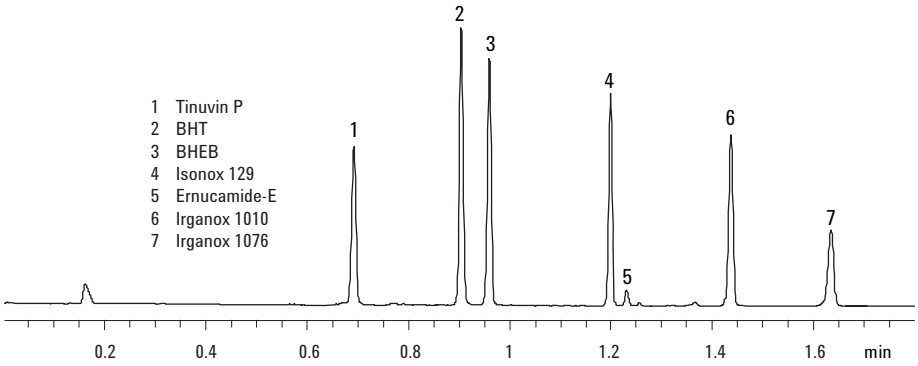



**Figure 5. Separation of additives standards on ZORBAX StableBond RRHT SB-C18, 4.6 mm × 150 mm, 1.8 µm.**



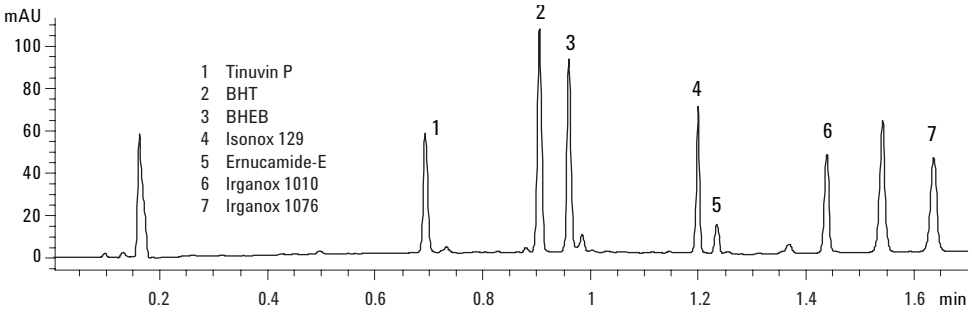

| | |
|---|---|
| Sample: | Standard 200 mg/mL |
| Sample size: | 2 µL |
| Detector: | UV 200 nm |
| Mobile phase: | A: water |
| | B: acetonitrile |
| Gradient slope: | 6.8% |
| Flow rate: | 1mL/min |

**Figure 6. Separation of additives standards on ZORBAX SB-C18, 4.6 mm × 50 mm, 1.8 µm, at 85 °C.**




| | |
|---|---|
| Sample: | Standard_200 mg/mL |
| Sample size: | 2 µL |
| Detector: | UV 200 nm |
| Mobile phase: | A: water |
| | B: acetonitrile |
| Gradient slope: | 6.8% |
| Flow rate: | 3.5 mL/min |

**Figure 7. Fast separation of additives standards on ZORBAX SB-C18, 4.6 mm × 50 mm, 1.8 µm, at 85 °C.**




LC conditions are identical with those in Figure 7.

**Figure 8. Fast separation of spiked real sample-LLDPE (20 µg/mL) on ZORBAX SB-C18, 4.6 mm × 50 mm, 1.8 µm, at 85 °C.**

### Sample Preparation

ASTM D5815 (or D1996) method recommends using a reflux apparatus for extracting additives in polymer. This requires periodic operator intervention over the 1.5-hour-long extraction period. To find a time-saving sample-preparation method, ultrasonic extraction was also tested, producing comparable results in 30 minutes. In terms of extraction efficiency, there is not much difference between these two methods. Figure 9 shows very good overlays of extractions by reflux and ultrasonic extraction methods for a LLDPE. Conditions are identical to those in Figure 1.

## Conclusions

Liquid chromatography with ultraviolet/visible detection is an effective tool for analyzing additives in polymer formulations. The Agilent 1200 Series RRLC system equipped with RRHT 1.8-µm columns was used to achieve up to 10 times faster than the conventional HPLC method. The ultrasonic extraction method allowed fast extraction without user intervention for a significant reduction in overall analysis time. Total time saved was more than 80 minutes per sample when compared to the conventional analysis and extraction methods.

## References


1. ASTM D5815-95, “Standard Test Method for Determination of Phenolic Antioxidants and Erucamide Slip Additives in Linear Low-Density Polyethylene Using Liquid Chromatography (LC).”
2. ASTM D1996-97, “Standard Test Method for Determination of Phenolic Antioxidants and Erucamide Slip Additives in Low-Density Polyethylene Using Liquid Chromatography (LC).”
3. Agilent Application Compendium CD, 5989-5130EN, June 2006.
4. Michael Woodman, “Improving the Effectiveness of Method Translation for Fast and High Resolution Separations,” Agilent Technologies, publication 5989-5177EN.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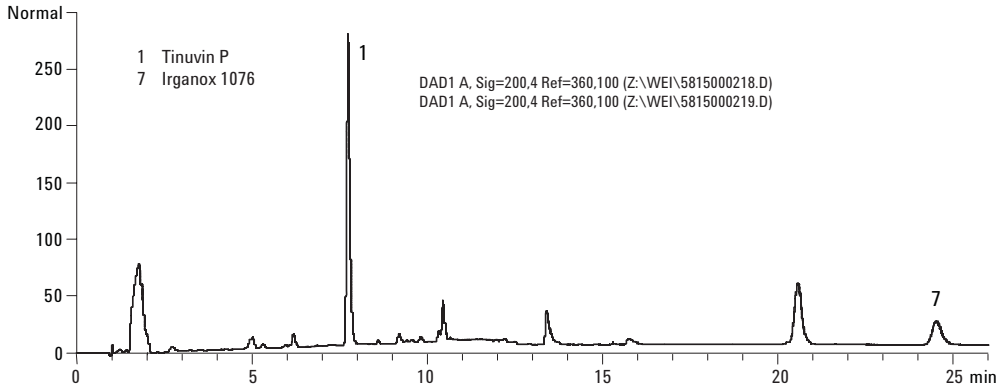


**Figure 9. Chromatogram Overlays of extractions by reflux and ultrasonic extraction methods for LLDPE.**



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# Fast Analysis Method for Rubber Chemical Antidegradants Using 1200 Rapid Resolution Liquid Chromatography (RRLC) Systems with Rapid Resolution High Throughput (RRHT) Columns

Application

**Hydrocarbon Processing**


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## Abstract

***p*-Phenylenediamine (PPD), a chemical antidegradant for rubber, and its analogs were found to be optimally determined using liquid chromatography with ultraviolet/visible detection according to the guidelines of ASTM Method D5666. Using the Agilent 1200 RRLC system with ZORBAX 1.8-µm columns, the PPDs could be separated in one run with a total analysis time up to 6.4 times faster than the conventional method based on a 5-µm column.**

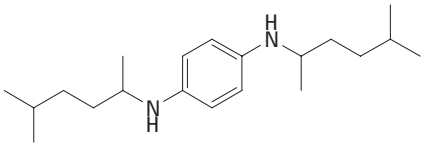
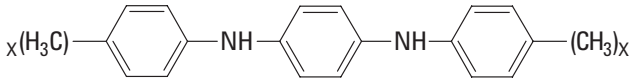
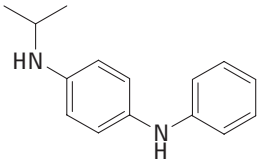
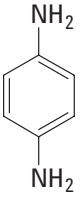
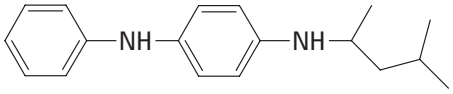

## Introduction

Various additives are artificially incorporated into polymeric materials to modify certain properties of the polymer. Therefore, the additives and their concentration in the formulation are crucial to the properties of the end product. 77PD, DTPD, IPPD, PPD, and 6PPD (see Table 1) are often used as chemical antidegradants for rubber materials. The chemical information for five PPDs is displayed in detail in Table 1.

Liquid chromatography with ultraviolet\visible detection is a powerful approach to the qualitative and quantitative analysis of chemical antidegradants in rubber. The isocratic LC method for five PPDs is introduced by ASTM D5666. In this method, the five PPDs are divided into three groups and determined by three different methods (Table 1, ASTM Method D5666-95, 2004).

Agilent 1200 RRLC systems use conventional or sub-two-micron columns, in various lengths up to 300 mm, and can typically provide ultra-fast separations with the same or better resolution as the original method. This application will compare the retention capability and peak shape of the two different stationary phases and will focus on showing the separation of five PPDs in one run, within five minutes, using the 1200 RRLC system with Agilent RRHT reversed phase columns.

**Table 1. Chemical Information of Five PPDs**

| Trade Name | CAS Number | Chemical Structure and Chemical Name |
|---|---|---|
| 77PD | 3081-14-9 | N,N'-bis-(1,4-dimethylpentyl)-*p*-phenylenediamine  |
| DTPD | 27417-40-9 | N,N'-ditolyl-*p*-phenylenediamine  |
| IPPD | 101-72-4 | N-isopropyl-N'-phenyl-*p*-phenylenediamine  |
| PPD | 106-50-3 | *p*-phenylenediamine  |
| 6PPD | 793-24-8 | N-(1,3 dimethylbutyl)-N'-phenyl-*p*-phenylenediamine  |

## Experimental

### System

Agilent 1200 Series Rapid Resolution LC, consisting of:
G1379B micro vacuum degasser
G1312B binary pump SL
G1367C high-performance autosampler SL
G1316B thermostatted column compartment SL
G1315C UV/Vis diode array detector SL with 3-mm, 2-µL flow cell
ChemStation 32-bit version B.02.01-SR1

### Columns

Agilent ZORBAX Eclipse XDB-C18, 4.6 mm × 150 mm, 5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 150 mm, 5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 100 mm, 3.5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 50 mm, 1.8 µm

### Mobile Phase Conditions

A: Water with 0.1 g/L ethanolamine
B: Acetonitrile (ACN) with 0.1 g/L ethanolamine

### Samples

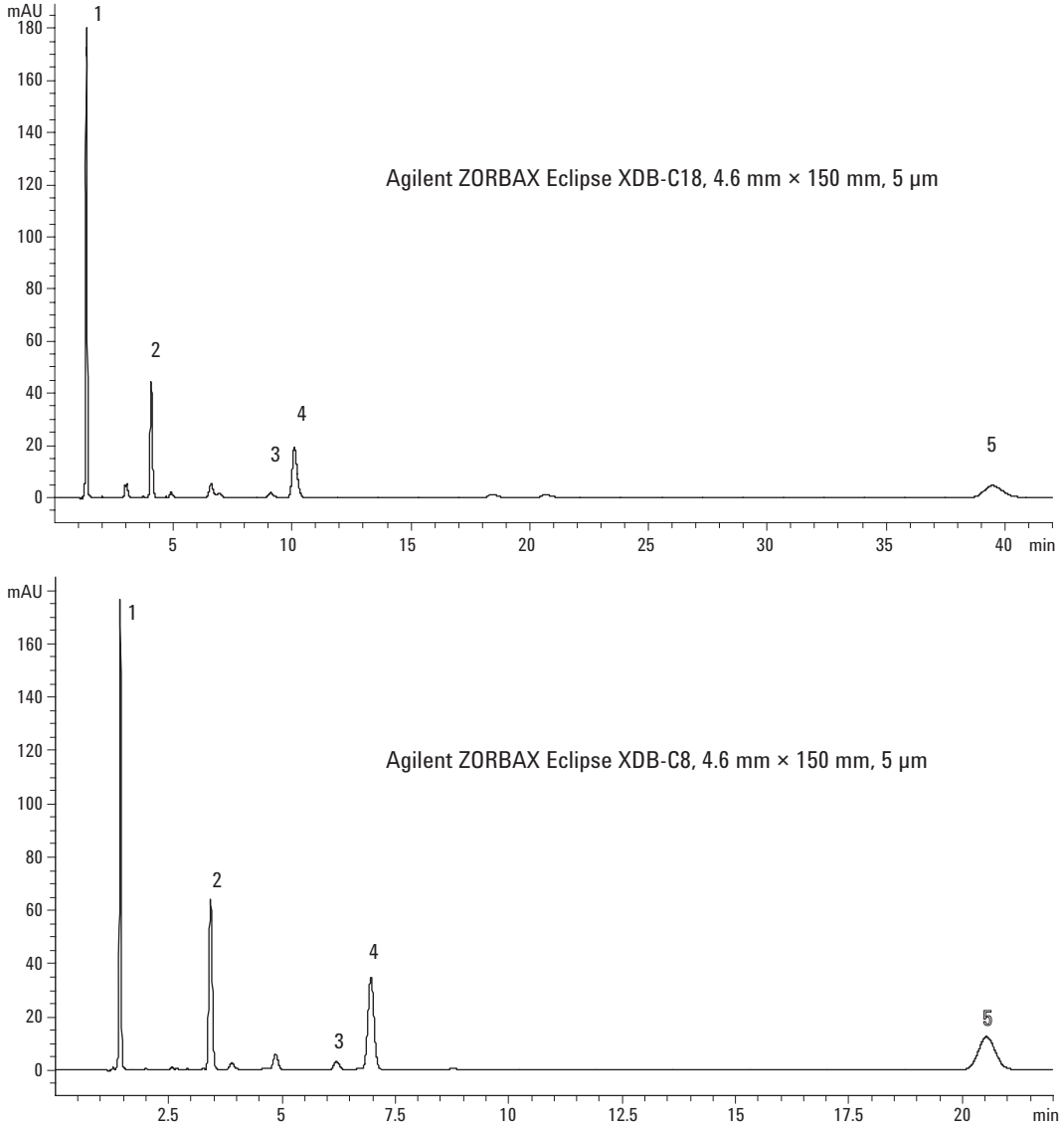
Mixture of 77PD, IPPD, PPD, DTPD, and 6PPD, all 50 µg/mL in acetonitrile. 77PD, IPPD, and PPD were standards from Sigma-Aldrich (St. Louis, Missouri, USA). DTPD and 6PPD were provided by a customer.

## Results and Discussion

### Selection of Stationary Phase for the Separation of Five PPDs

ASTM D5666-95 recommends a 10- to 15-cm long column packed with C18 grafted silica and 3- to 5-µm particle sizes. In our investigation, however, we observed that the retention characteristics of

ZORBAX Eclipse XDB-C18 were so strong that the total analysis time would be about 40 minutes or more. ZORBAX Eclipse XDB-C8 columns were found to have adequate resolution, and the retention time was only about half of the C18 column. Therefore, we chose the C8 column for further method development. The separations are shown in Figure 1.



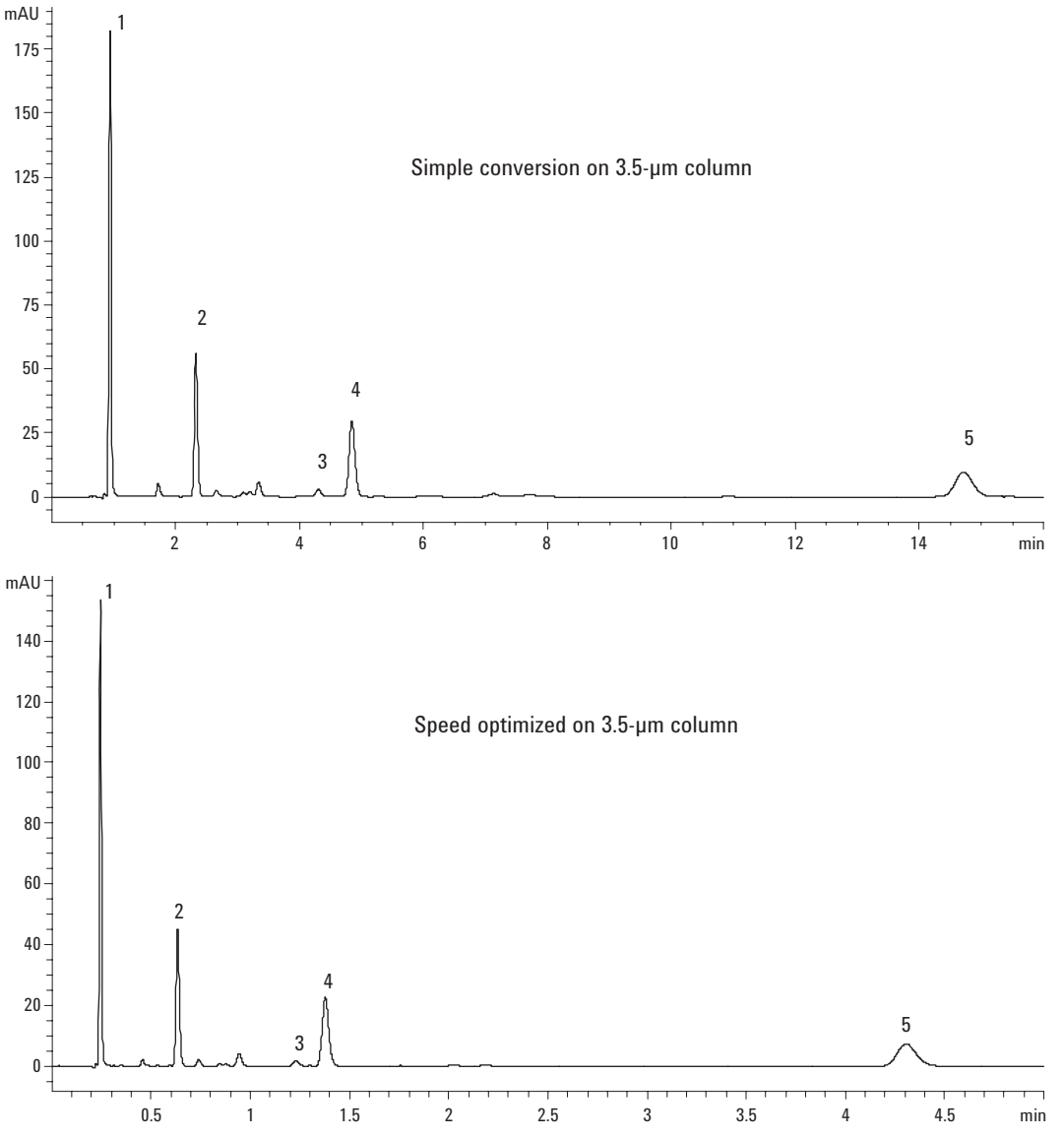

| Compound | Conditions | | |
|---|---|---|---|
| 1 PPD | Mobile phase: | A: water with 0.1 g/L ethanolamine<br>B: ACN with 0.1 g/L ethanolamine | |
| 2 IPPD | Flow rate: | 1.0 mL/min | |
| 3 DTPD | Wavelength: | 260 nm | |
| 4 6PPD | Injection volume: | 10 µL | |
| 5 77PD | Column temperature: | 35 °C | |
| | Sample: | Mixture, 50 µg/mL in ACN | |
| | Isocratic composition: | 30% A, 70% B (v/v) | |
| | Column size: | 4.6 mm × 150 mm, 5 µm | |
| | Stationary phase: | Agilent ZORBAX Eclipse XDB-C18 | Agilent ZORBAX Eclipse XDB-C8 |
| | Analysis time: | 42 min | 22.5 min |

**Figure 1. Column stationary phase comparison for five PPDs.**

### Fast Method Developed Based on New 1200 RRLC

The popular desire of chromatographers is to decrease the analysis time and increase the daily throughput with the same or similar resolution. Nowadays, the Agilent 1200 RRLC system with higher pressure capability and a higher temperature range can provide excellent chromatographic resolution with much shorter run times. Furthermore, a constant concern is how to quickly and easily transfer conventional methods to fast methods. Agilent provides two versions of method translators: one is a Microsoft.net version requiring that Net-Framework 2.0 be resident on the computer, and the other is a Microsoft Excel version requiring that Excel be resident on the PC. When the initial method is an isocratic method, the method translator can provide two modes of faster methods. One is simple conversion, with the scaled flow rate according to the column diameter; the other is speed optimized conversion, with the maximum flow rate and pressure. In gradient mode, an additional option is a resolution optimized conversion.

This application uses a set of Agilent ZORBAX Eclipse XDB-C8 columns, including 4.6 mm × 150 mm (5 µm), 4.6 mm × 100 mm (3.5 µm), and 4.6 mm × 50 mm (1.8 µm). The method translator is used to transfer the initial method on a 5-µm column to two fast methods on 3.5-µm and 1.8-µm columns, respectively. The resulting separation of five PPDs is depicted in Figure 2.

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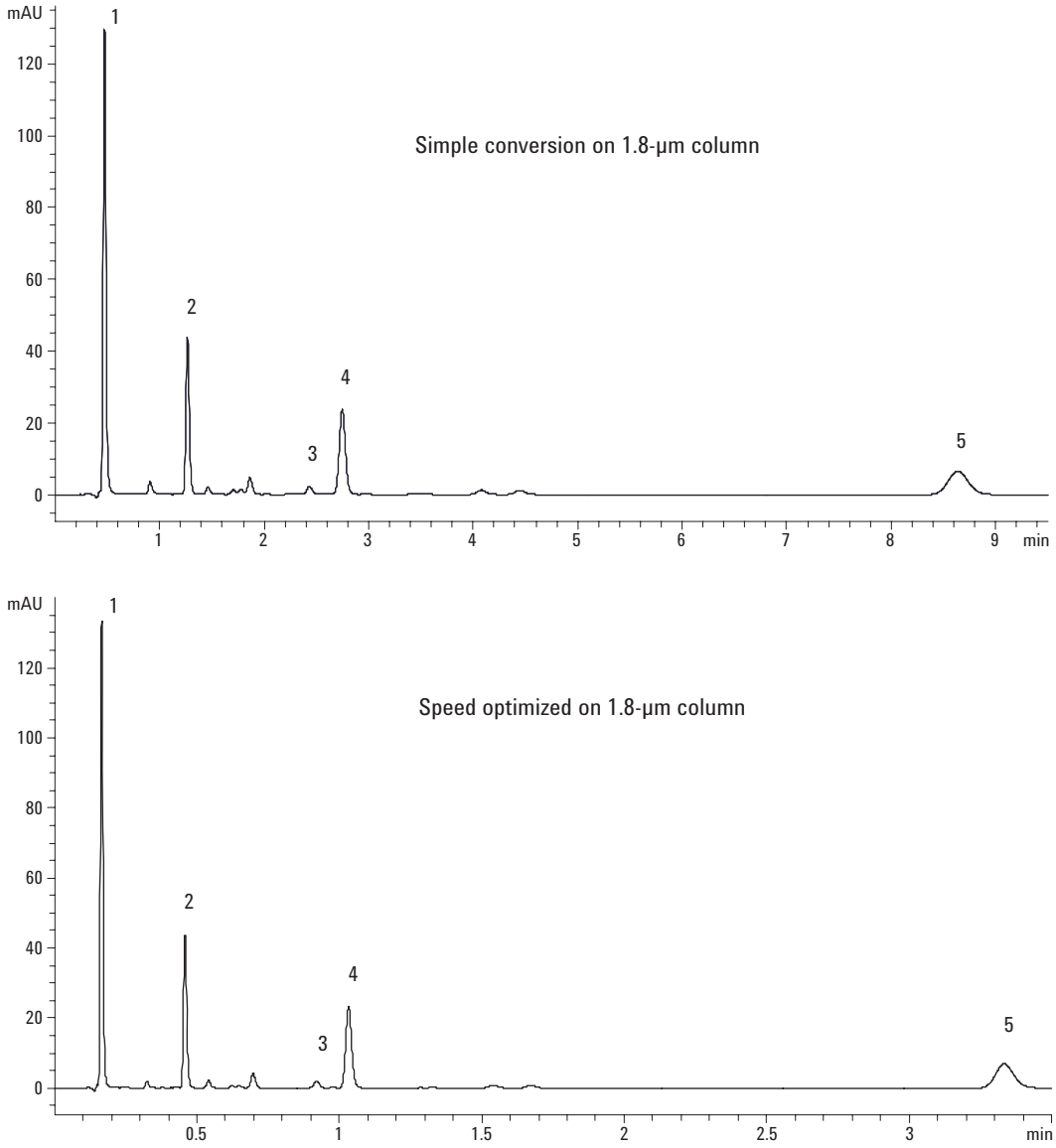


| Compound | Conditions | | | | |
|---|---|---|---|---|---|
| 1 PPD | Stationary phase: | Agilent ZORBAX Eclipse XDB-C8 | | | |
| 2 IPPD | Mobile phase: | A: water with 0.1 g/L ethanolamine | | | |
| 3 DTPD | | B: ACN with 0.1 g/L ethanolamine | | | |
| 4 6PPD | Isocratic composition: | 30% A, 70% B (v/v) | | | |
| 5 77PD | Column temperature: | 35 °C | | | |
| | Wavelength: | 260 nm | | | |
| | Column size | 4.6 mm × 100 mm, 3.5 µm | | 4.6 mm × 50 mm, 1.8 µm | |
| | Conversion mode: | Simple | Speed optimized | Simple | Speed optimized |
| | Flow rate: | 1.0 mL/min | 4.0 mL/min | 1.0 mL/min | 3.0 mL/min |
| | Injection volume: | 6.7 µL | 6.7 µL | 3.3 µL | 3.3 µL |
| | Analysis time: | 15 min | 5 min | 10 min | 3.5 min |

**Figure 2. Separation of five PPDs on a smaller particle size column using the transferred methods.**

## Conclusions

As a powerful approach, liquid chromatography with ultraviolet\visible detection is often used to determine the chemical antidegradants in rubber. Agilent 1200 RRLC systems typically provide the customer with a rapid separation having the same or similar resolution. The method translator can convert any isocratic or gradient method to fast method according to customer requirements. This application details the selection of stationary phases for the separation of five PPDs, separates five PPDs with the RRLC system in one run, and applies the method translator to develop fast methods based on smaller particle size columns. With 1.8-µm column, the total analysis time of five PPDs in one run is about 6.4 times faster than the original 5-µm column method.

## References

1. ASTM D5666-95 (Reapproved 2004) "Standard Test Method for Rubber Chemical Antidegradants - Purity of *p*-Phenylenediamine (PPD) Antidegradants by High Performance Liquid Chromatography"
2. Michael Woodman, "Improving the Effectiveness of Method Translation for Fast and High Resolution Separations," Agilent Technologies publication 5989-5177EN, 2006.

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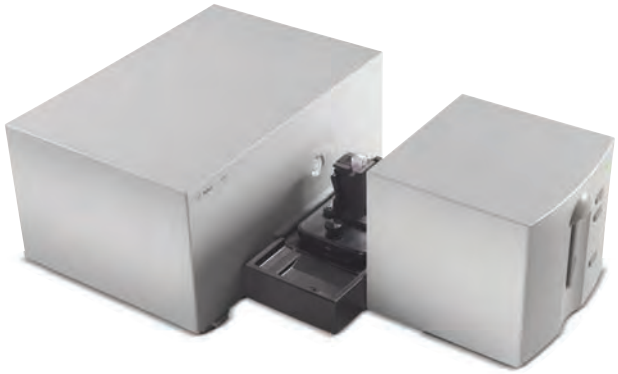
5989-6011EN

Agilent Technologies

# Accurate Measurement of Particle Sizes of Polymers with the Agilent 7010 Particle Size Analyzer

Application Note




## Abstract

Many properties of polymeric particles depend on particle size distribution (PSD), so it is important to be able to measure particle sizes in the nanometer to low micrometer range without error. When the PSD contains particles of more than one size population, traditional light scattering techniques are often unable to resolve them, and these instruments typically fail to detect a population of small particles in the presence of a population of large particles. The Agilent 7010 Particle Size Analyzer overcomes these limitations to quickly and accurately measure both particle sizes and concentrations in complex mixtures of fine polymeric particles.


Agilent Technologies

## Introduction

Applications of fine polymeric particles are diverse. Coatings, paints, adhesives, drug delivery systems, and medical diagnostics are just a few examples. Unerring characterization of particle sizes is critical because many properties of these materials depend on their particle size distributions (PSDs). For example, the final attributes of a latex product include stability, film-forming ability, covering capacity, viscosity, opacity, texture, mechanical resistance, and processability. All of these properties are affected by its PSD. And in polymerization processes, controlling the PSD allows the synthesis of high-solids-content latexes with improved rheological properties and viscosity.

By correctly manipulating the PSD of the final product, concentrated polymer dispersions (over 65% on a volume basis) can be produced without overly increasing the viscosity of the dispersion. Small latex particle size (< 200 nm) gives best gloss, binding, and adhesion. Large particle size (> 500 nm) gives useful rheological properties (thixotropy, film build, etc), but less efficient binding and low gloss.

Agilent has developed an accurate particle size analyzer that is built on its robust UV-Visible (UV-Vis) spectrometric instrument platform. The Agilent 7010 Particle Size Analyzer is simple to use and maintain, and excels at characterizing the particle size distribution in polymer dispersions.

## Measurement of reference monodisperse materials

Reference particles from several suppliers (Duke Scientific Corporation, Polymer Laboratories, Bangs Laboratories, Corpuscular Inc., Spherotech, Seragen Diagnostics) and ranging in size from 74 nm through 15 µm were extensively tested and measured with the Agilent 7010 Particle Size Analyzer. The particle sizes determined by the Agilent 7010 consistently agreed within 5% of the manufacturer-specified values and typically within 2%. The relative standard deviation for all these samples after five consecutive measurements was better than 1.5%. Figure 1 displays size analyses by the Agilent 7010 for a few of the many polystyrene reference sizes that were measured to check accuracy and precision in the range of 240 nm to 800 nm.

The Agilent 7010 accurately measures the particle size distribution of a variety of polymers, as shown in Figures 2 through 5. Fluorescent and dyed polystyrene particles commonly used for tagging applications in biotechnology are also measured easily; the absorptions of the dyes and fluorophores have a negligible effect on the scattering spectrum and do not alter the calculated particle size distribution, as shown in Figure 2. Figure 3 depicts the PSD for polymethylmethacrylate (PMMA) particles from Seragen Diagnostics. Various sizes of polybutadiene particles have also been tested. Figure 4 shows the particle size distribution for 160 nm, 400 nm and 590 nm polybutadiene particles dispersed in water. Melamine formaldehyde particles have been successfully measured, as shown in Figure 5 for 1.7 µm and 2.54 µm standards. Accurate measurement of polymer dispersions are not limited to dispersions in water, as is shown by measurement of polystyrene in 2-propanol in Figure 6.

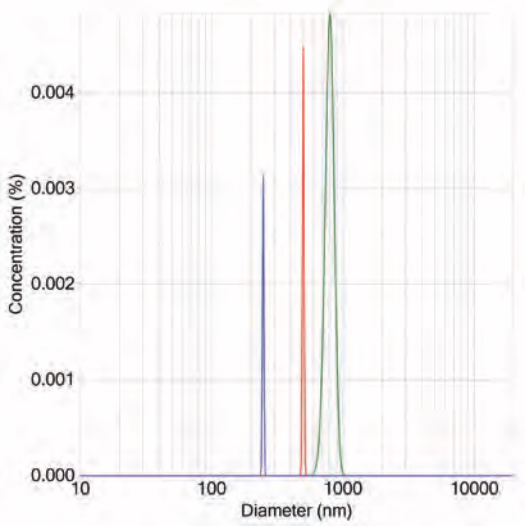



**Figure 1.** *Duke polystyrene 240 nm (blue), 500 nm (red), and 800 nm (green)*

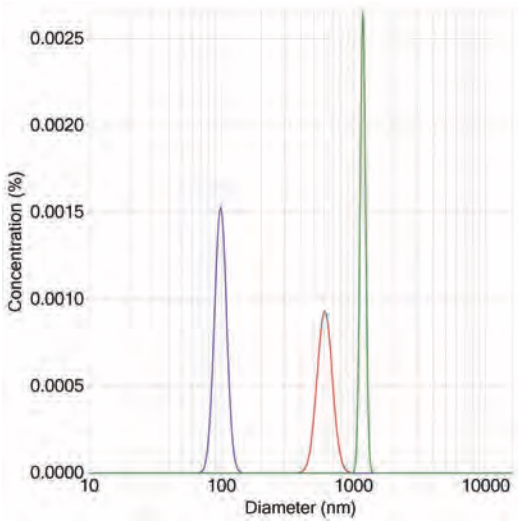



**Figure 2.** *Particle size distribution of blue-, red-, and green-dyed polystyrene.*

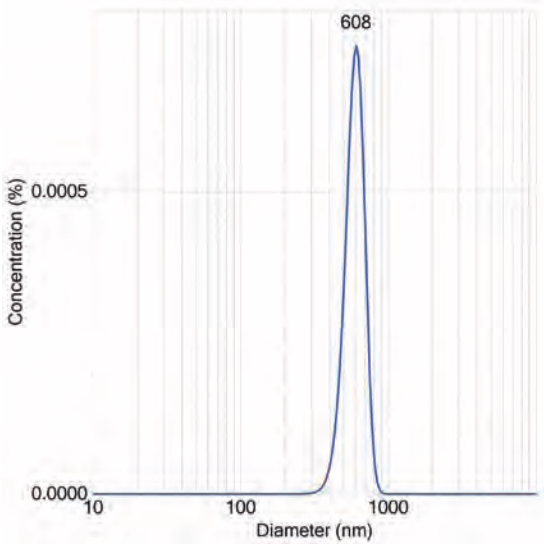



**Figure 3.** *Seragen polymethylmethacrylate (PMMA) at 586 nm*

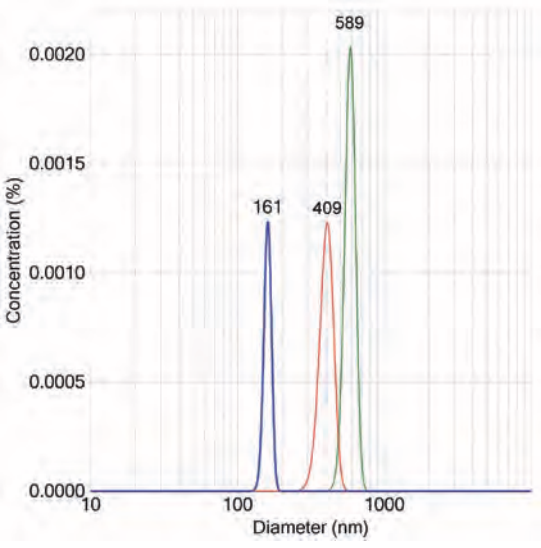



**Figure 4.** *Dow polybutadiene at 160 nm (blue), 400 nm (red), and 590 nm (green).*

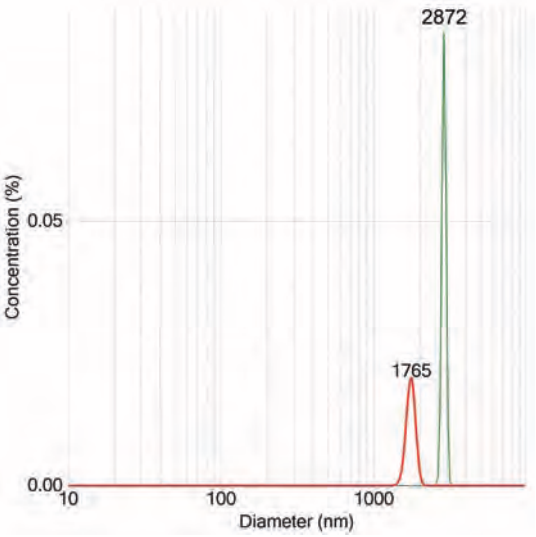



**Figure 5.** *Melamine formaldehyde at 1.7 µm (red) and 2.54 µm (green).*

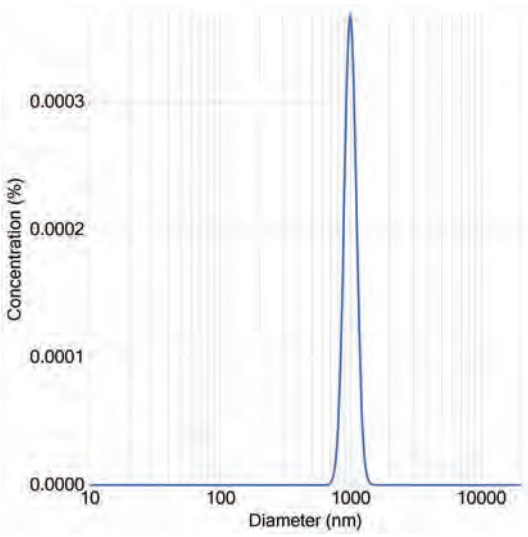



**Figure 6.** *1.2 µm polystyrene dispersed in 2-propanol.*

## Coarse and fine populations mixed in different proportions

Figure 7 depicts a mixture of two polystyrene reference particles (Duke Scientific Corporation) of sizes 92 nm and 3000 nm. These images were obtained with the Hitachi S-4500 Field Emission Scanning Electron Microscope (FE-SEM). Samples were prepared with varying proportions of the fine 92 nm and coarse 3000 nm particles from a ratio of 2%/98% to 98%/2%, respectively.

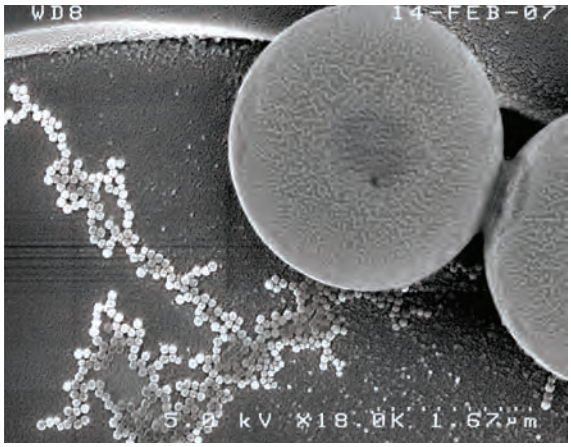



**Figure 7.** *Mixture of 92 nm and 3000 nm polystyrene particles (Hitachi S-4500 FE-SEM).*

Resolution of multimodal distributions is generally difficult for traditional light scattering techniques. Furthermore, the detection of fine particles in the presence of a large population of coarse particles is even more challenging since a few large particles can scatter too much light, masking the presence of the small particles. Figure 8 shows that the 7010 Particle Size Analyzer is able to detect even 9% of fine 92 nm particles in the presence of 91% of 3 µm particles.

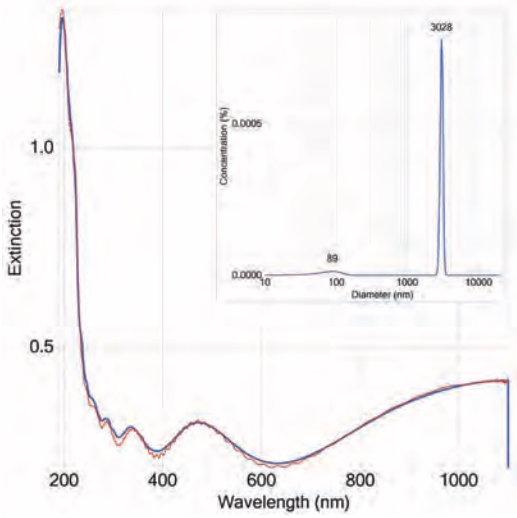



**Figure 8.** *Detection of 9% by volume of the fine 92 nm particles in a background of 91% of 3 µm particles.*

To understand how this UV-Vis spectroscopic technique is able to detect and resolve these complex dispersions, Figures 9 and 10 dissect the measurement. If the entire measured UV-near infrared (NIR) spectrum is to agree with theory within experimental accuracy, the instrument's size analysis must include the two populations. Static light scattering and dynamic light scattering instruments have difficulty detecting fine particles in the presence of a population of coarse particles because in visible wavelengths, the coarse particles scatter much more strongly than the fine particles. The Agilent 7010 does not have this difficulty because the respective signatures of the fine and coarse populations do not overlap throughout the wavelength range of the instrument.

Figures 9 and 10 assist in understanding why this instrument can discriminate two particle populations that are different in both size and concentration. In Figure 9, the 7010 Particle Size Analyzer was set to analyze the spectrum without considering the information in the wavelength range of 190 nm to 400 nm. The analysis delivered a peak at 3.028 µm. By analyzing the spectrum again and using only the wavelength range of 190 nm to 230 nm, Figure 10 shows a peak at 97 nm. Because those two peaks are very close to the actual sizes of the two populations, these measurements show that in the original spectrum, the signature associated with the fine population is predominantly in the UV region, while the signature associated with the coarse population is primarily in the visible region.

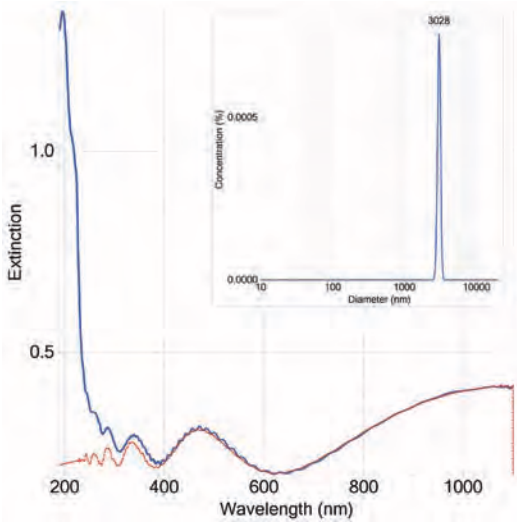



**Figure 9.** *Same measurement as in Figure 8, with elimination of information in the 190 nm to 400 nm range.*

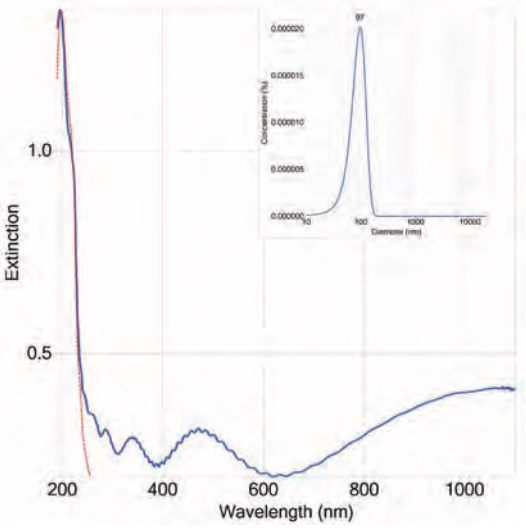



**Figure 10.** *Same measurement as in Figure 8, with elimination of information in the 230 nm to 1100 nm range.*

Figure 11 compares the size analysis for samples in which the volume percentage for the fine population was 4.8%, 9%, and 17%. From inspection of the spectra, it is apparent that as the proportion of fine particles increases, the spectral signature of the coarse particles becomes more and more insignificant in amplitude as the attenuation in the short wavelengths increases. The sharp decrease in extinction as a function of increasing wavelength in the UV range due to Rayleigh scattering of the fine particles is clearly observed. As the feature due to Rayleigh scattering of fine particles grows, the relative size of the signature for the coarse population decreases.

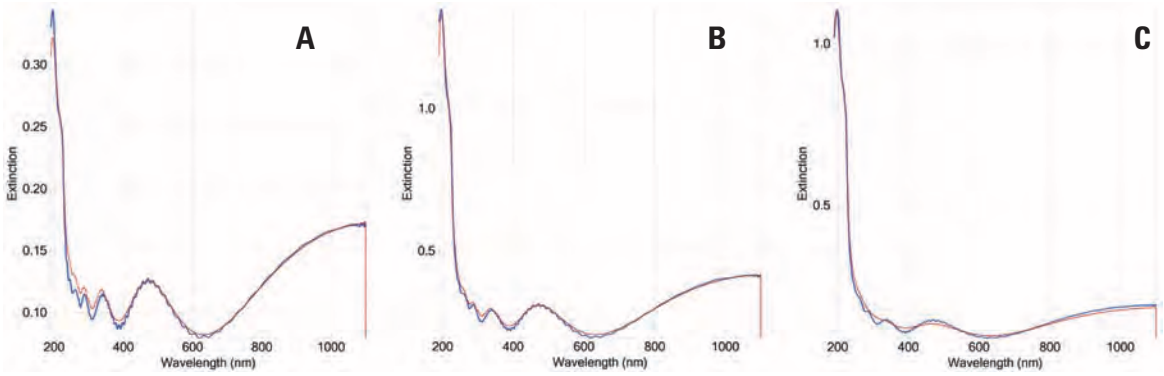



**Figure 11.** *A) 4.8% 92 nm and 95.2% 3 µm polystyrene. B) 9% 92 nm mixed with 91% 3 µm polystyrene. C) 17% 92 nm mixed with 83% 3 µm polystyrene.*

## Resolution test

The results shown up to this point demonstrate that the 7010 Particle Size Analyzer can resolve populations that differ greatly in particle size, as well as in their volume proportions. The following examples demonstrate how close in size two populations can be while still being resolved by the Agilent 7010. Polystyrene at 200 nm was mixed first with 1 µm polystyrene, and then with incrementally smaller polystyrene particles to determine the population size limits that the Agilent 7010 can resolve. Figure 12 illustrates the size resolution of 50%/50% polystyrene mixtures: 200 nm/1000 nm (blue); 200 nm/800 nm (red); 200 nm/600 nm (green); and 200 nm/500 nm (black). In fact, the Agilent 7010 has resolved two different size populations that are as close as a ratio of 1:1.5. This is demonstrated in Figure 13 for 1 µm and 2 µm (blue), 2 µm and 3 µm (red) and 3 µm and 5 µm (green) polystyrene particles. Comparing these distributions, it appears that the broadening of the 1 µm peak in the mixture is an artifact of the fitting algorithm. There appears to be a trend in close bimodal samples of the smaller peak becoming artificially broadened.

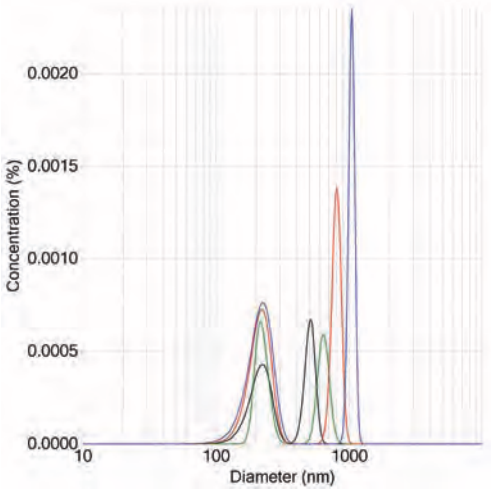



**Figure 12.** *Size resolution of 50% 200 nm polystyrene mixed with 50% 1 µm polystyrene (blue), 50% 800 nm polystyrene (red), 50% 600 nm polystyrene (green), and 50% 500 nm polystyrene (black).*

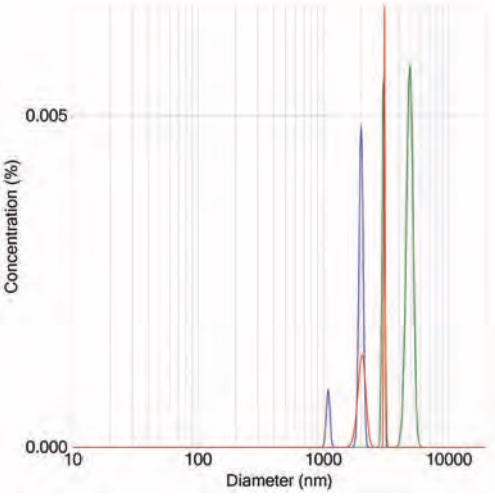



**Figure 13.** *Demonstration of 1:1.5 size resolution capability with polystyrene mixtures: 15% 1 µm mixed with 85% 2 µm (blue), 50% 2 µm mixed with 50% 3 µm (red), and 50% 3 µm mixed with 50% 5 µm (green).*

## Polymer dispersions with UV-absorbing additives

Very often, dispersions of polymer particles in water contain additives that absorb in the UV range. For example, biocides may be added to reduce bacterial growth, surfactants may be added to promote colloidal stability, or ligands with specific chemical functionality may be attached. These UV-absorbing features must be either subtracted or ignored in order to produce the best particle size results. If the software tries to fit the UV-absorbing features to particle scattering, phantom small-particle peaks may be created in the PSD.

One method to produce results that are more accurate is to measure a blank using the exact suspending medium of the dispersion. This may be accomplished by separately preparing a solution with the correct concentration of additive, or if the particles are sufficiently large and not buoyant, by centrifuging the particles and using the supernatant as a blank. Note that if the centrifugation is not complete and some particles are present in the blank, it is still possible to get a very good measurement of particle size, but the particle concentration will be underestimated and the dynamic range for the sample will be drastically reduced.

A simpler procedure to reduce artifacts caused by UV-absorbing additives is to use pure water as a blank and to remove the UV wavelengths from the calculation of particle size. This is especially advisable if the particles are in the micron size range and the spectral scattering features are not in the UV range. To disregard the UV wavelengths in the calculation, the Agilent 7010 software has a feature called "UV Autocorrect."

Figures 14A and 14B give an example of a commercial latex emulsion with a broad distribution that maximizes around 7 µm. The correct particle size distribution, verified by comparison with SEM image analysis, is found with UV Autocorrect selected (Figure 14A). With UV Autocorrect off, a poor spectral fit (red and blue lines not corresponding) is found and the wrong particle size distribution is produced (Figure 14B).

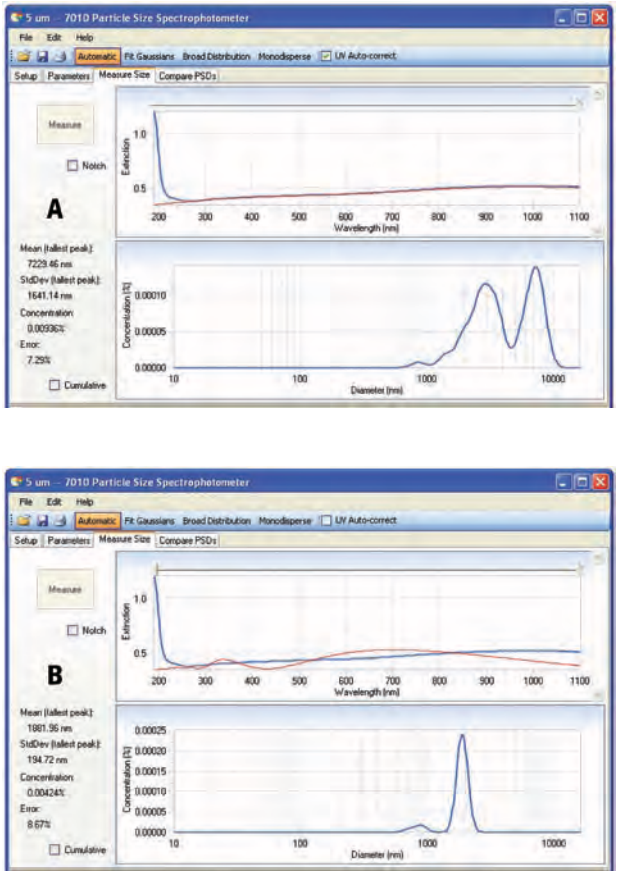



**Figure 14.** *Automatic mode measurement of commercial latex emulsion. A) Correct PSD found with UV Autocorrect on. B) Incorrect PSD found with UV Autocorrect off.*

The particle size distributions for several polystyrene reference standards in the range of 1 µm to 15 µm were also measured. Two of these are shown in Figures 15 and 16. Despite this, even if UV Autocorrect is off and pure water is used as the blank fluid, the size analysis in many cases will be accurate due to the high information content for monodisperse particles in this size range. However, the error will be higher than the advised range of 0 to 3% due to the discrepancy between measurement and theory in the UV wavelengths.

## When *not* to use UV Autocorrect

Although the default setting of UV Autocorrect is on, it may be advisable to deselect this feature when measuring small particles (< 200 nm) of nonmetals. These particles scatter strongly in the UV range and may be entirely ignored by UV Autocorrect.

The screen shots in Figure 17 show a mixture of 100 nm and 400 nm polystyrene latex in a 1:3 mixture. With UV Autocorrect on (Figure 17A), the particle size distribution algorithms completely ignore the 100 nm particles. With UV Autocorrect deselected, as shown in Figures 17B and 17C, the software correctly finds both the 100 and 400 nm polystyrene peaks, and correctly determines their relative concentrations as well.

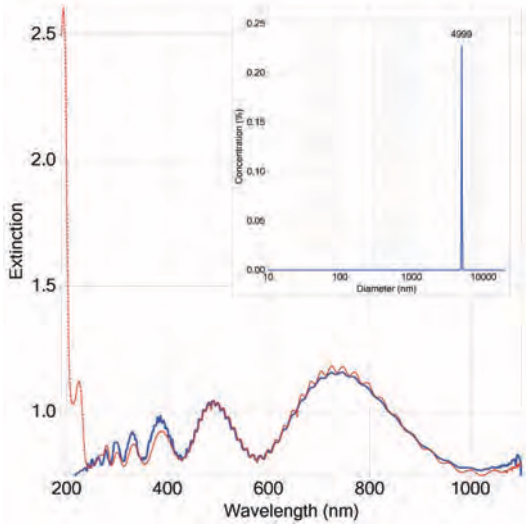



**Figure 15.** *5 µm polystyrene (Duke Scientific Corporation).*

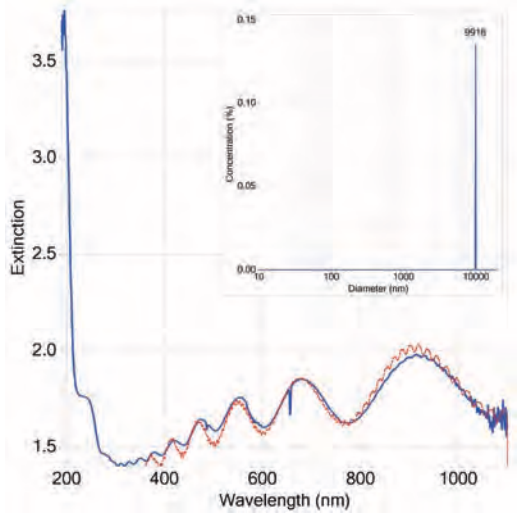



**Figure 16.** *10 µm polystyrene (Duke Scientific Corporation).*

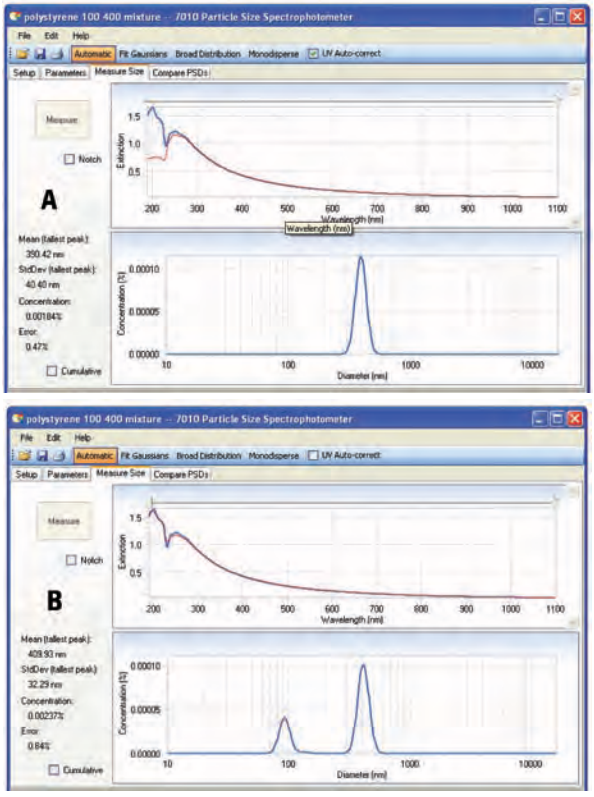



**Figure 17.** *Particle size distributions from mixture of 100 and 400 nm polystyrene size standards. A) Incorrect PSD with UV Autocorrect selected. B) Correct PSD with UV Autocorrect deselected. C) Same as B, except cumulative PSD is displayed.*

## Conclusion

The Agilent 7010 Particle Size Analyzer provides accurate results for complex particle size distributions of polymer dispersions. The UV-Vis technology in the Agilent 7010 allows one to measure multimodal dispersions or mixtures of very small particles in the presence of very large particles, which are typically challenging for light scattering techniques (dynamic light scattering or laser diffraction). With its ease of use, ability to give concentration information as well as particle size, and fast measurement time (less than 10 seconds), the Agilent 7010 Particle Size Analyzer is an indispensable technology for characterizing polymer particles ranging in size from 50 nm to 15 µm.

## Authors

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Agilent Technologies

# Chemical and Specialty Gas

## Technical Overviews

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# ZORBAX Eclipse XDB HPLC Columns

## The "Perfect Fit" for Developing Better HPLC Methods

### Technical Overview

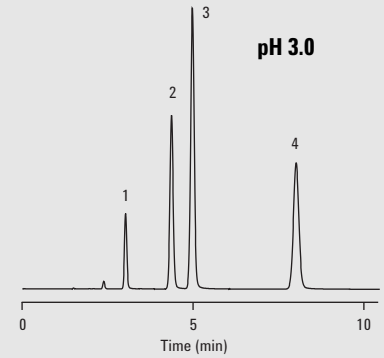
- Excellent peak shape for basic, acidic or neutral compounds
- High performance over a wide pH range
- Rugged, reproducible chromatography from column-to-column and lot-to-lot
- More selectivity options for method development

More and more chromatographers are developing their analytical and LC/MS separations on ZORBAX Eclipse XDB HPLC columns. Why? Because ZORBAX Eclipse XDB columns solve many of their separation challenges. In fact, Agilent Technologies includes a 4.6 x 150 mm, 5 µm ZORBAX Eclipse XDB-C8 column with every Agilent 1100 HPLC instrument it delivers. As Figure 1 shows, ZORBAX Eclipse XDB columns, specifically designed to extend column life and provide excellent peak shape for basic compounds in the pH range of 6 - 9, also deliver outstanding performance at low pH, as well.

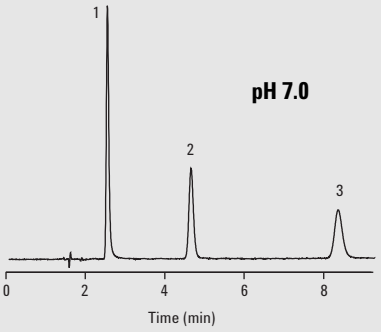
***More detailed information about the benefits of the Eclipse column family can be found in this brochure.***

Figure 1
**Good Peak Shape for Acids, Bases and Neutrals at Low and Intermediate pH**

**ZORBAX Eclipse XDB-C18, 4.6 x 150 mm, 5 µm**
**(Agilent Part No. 993967-902)**




| | |
|---|---|
| Mobile Phase: | 80% 25 mM $Na_2HPO_4$, pH 3.0<br>20% Methanol |
| Flow Rate: | 1.0 mL/min |
| Temperature: | 35°C |
| Sample: | 1. Theobromine<br>2. Theophylline<br>3. 1,7-dimethylxanthine<br>4. Caffeine |




| | |
|---|---|
| Mobile Phase: | 70% 25 mM $Na_2HPO_4$, pH 7.0<br>30% Methanol |
| Flow Rate: | 1 mL/min |
| Temperature: | RT |
| Detection: | UV 254 nm |
| Sample: | 1. Procainamide<br>2. N-acetylprocainamide<br>3. N-propionylprocainamide |

*Eclipse XDB HPLC Column Technology Provides:*

# Excellent Peak Shape

**eXtra Dense Bonding + High Purity Silica = Excellent Peak Shape**

eXtra Dense Bonding is key to the exceptional performance of ZORBAX Eclipse XDB columns at intermediate pH (Figure 2). This dense bonding is accomplished by adding an extra-dense monolayer of C18, C8 or Phenyl silane to the ultra-pure, fully-hydroxylated, ZORBAX Rx-silica surface. The packing is then endcapped not once, but twice, using two different and unique endcapping reagents. This combination of extra-dense surface coverage by the bonded phase and double endcapping produces a highly, deactivated stationary phase that virtually eliminates undesirable interactions between polar solutes and the silica surface. As a result, superior peak shape, high efficiency, and long-term chromatographic reproducibility are assured when using Eclipse XDB HPLC columns at both intermediate and low pH.

The exceptional and reproducible performance at low pH that you can expect from the Eclipse XDB is demonstrated in Figure 3. In this example, acetylsalicylic acid, and the base, dextromethorphan, are consistently separated with excellent peak shape at low pH on three different Eclipse XDB-C8 columns from three different lots of packing material.

Figure 2
**eXtra Dense Bonding (XDB) and Double Endcapping Improves Peak Shape for Polar Compounds at pH 7**

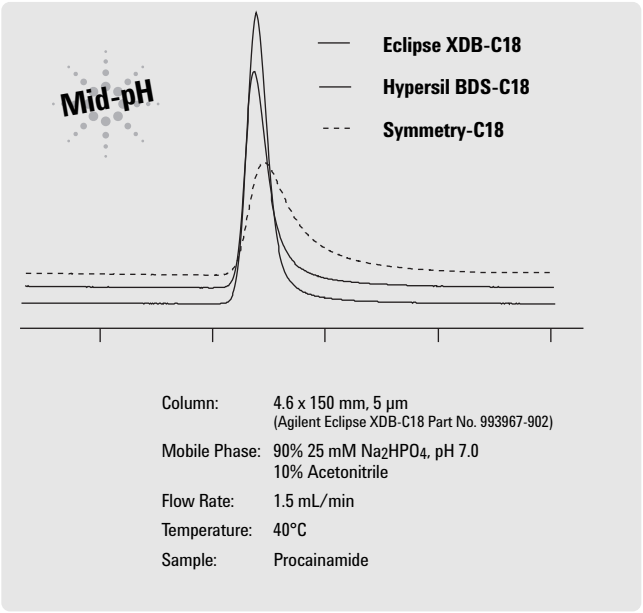
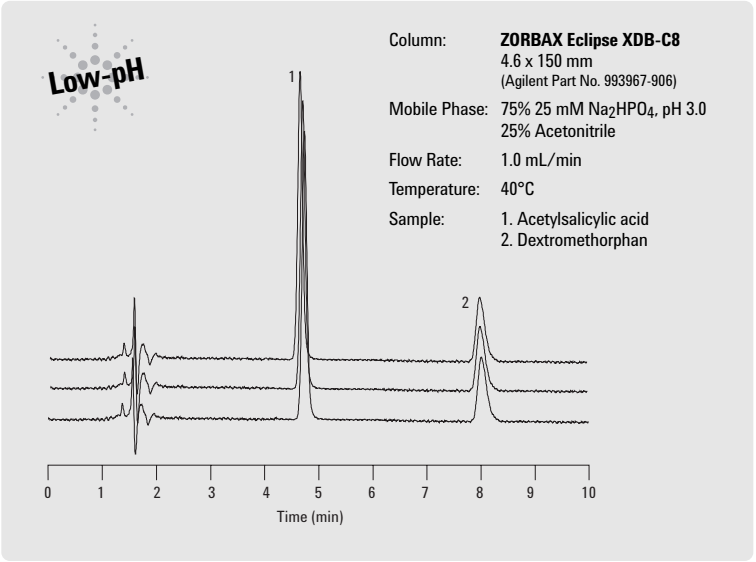



Figure 3
**eXtra Dense Bonding (XDB) and Double Endcapping Improves Peak Shape for Polar Compounds at pH 3**



***Eclipse XDB HPLC Column Technology Provides:***

# Long Column Life

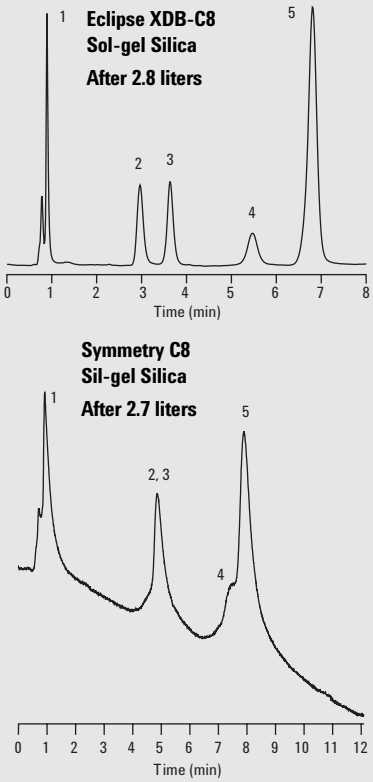
Eclipse XDB columns not only provide excellent peak shape but they are also exceptionally durable. In fact, the spherical ZORBAX Rx-SIL particles are the most durable, porous, 5 and 3.5 µm, silica particles commercially available. They are manufactured using a patented and proprietary process, forming thick, hard-walled silica, commonly referred to in the literature as "sol-gel" silica.

Because of the strength of the ZORBAX particle, all ZORBAX columns are consistently and reliably packed at pressures exceeding 8000 psi. The result is a durable column that can easily tolerate pressures up to 5000 psi in regular use without a loss in efficiency or a reduced lifetime.

## Long Column Life at Intermediate pH

This thick, hard-walled "sol-gel" silica resists dissolution at intermediate pH and when densely bonded, the resultant Eclipse XDB column provides excellent column performance and increased column lifetime, even under the stressed intermediate pH conditions described in Figure 4.

Figure 4
**Accelerated Column Aging Study Demonstrates the Durability of Eclipse XDB-C8 Over Waters' Symmetry C8**




Column: 4.6 x 150 mm

**Purge Conditions:**

Mobile Phase:
20% Acetonitrile
80% 250 mM phosphate buffer, pH 7

Flow Rate: 1.5 mL/min

Temperature: 60°C

**Test Conditions:**

Mobile Phase:
60% Acetonitrile
40% 10 mM phosphate buffer, pH 7

Flow Rate: 1.5 mL/min

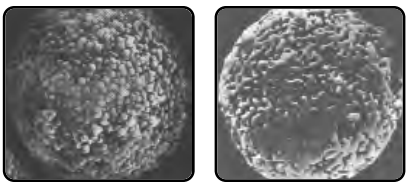
Temperature: 40°C

Sample: Tricyclic Antidepressants
1. Uracil 2. Nortriptyline 3. Doxepin
4. Amitriptyline 5. Trimipramine

Many commercial, base-deactivated, silica-based HPLC columns use manufacturing processes that produce a less robust "sil-gel" silica particle. The walls of these resulting high-surface area materials (typically 300 $m^2/g$ for an 80-100Å pore material) are thinner and less uniform and can easily crush under high pressure conditions. Moreover, in many cases, they fail to withstand the high pressures of high flow rate LC/MS and High-Throughput methods.

The Eclipse XDB thick, hard-walled "sol-gel" is compared to the thin-walled "sil-gel" silica, used to make most of today's base-deactivated products, in electron micrographs shown in Figure 5.

Figure 5
**Eclipse XDB is Based on Thick, Hard-Walled, Sol-gel Silica**



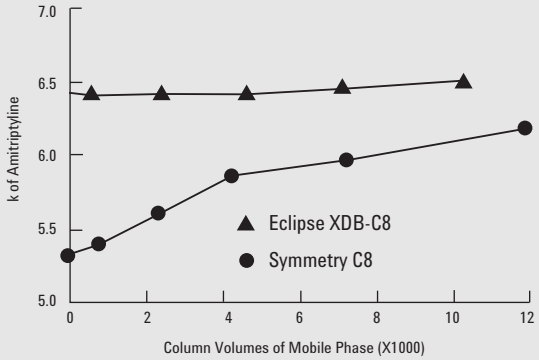
**Sol-gel** **Sil-gel**

*Eclipse XDB columns are made with patented "hard wall" sol-gel silica particles. The thick walls of this silica are more resistant to dissolution than the "thin wall" sil-gel silica that is used to make most base-deactivated columns.*

## Long Column Life at Low pH

At low pH, Eclipse XDB columns provide better column life than most commercially available reversed-phase HPLC columns. Figure 6 summarizes the results from a low-pH accelerated aging study where loss in column performance is measured by a loss in bonded phase, indirectly measured by the change in retention of amitriptyline. The results show that less than 3% of the Eclipse XDB column performance is lost when exposed to 12,000 mL of a pH 3 mobile phase at 60°C. Under these same conditions more than 14% of column performance is lost on another popular "deactivated" reversed-phase HPLC column.

Figure 6
**Accelerated Column Aging Study Demonstrates the Durability of ZORBAX Eclipse XDB-C8 Over Waters' Symmetry**




Column: 4.6 x 150 mm

**Purge Conditions:**

Mobile Phase: 30% Acetonitrile
70% 50 mM NaOAc-HCl, pH 3

Flow Rate: 1.5 mL/min

Temperature: 60°C

**Retention Test Conditions:**

Mobile Phase: 30% Acetonitrile
70% 50 mM NaOAc-HCl, pH 3

Flow Rate: 1.0 mL/min

Temperature: 60°C

Sample: Amitriptyline

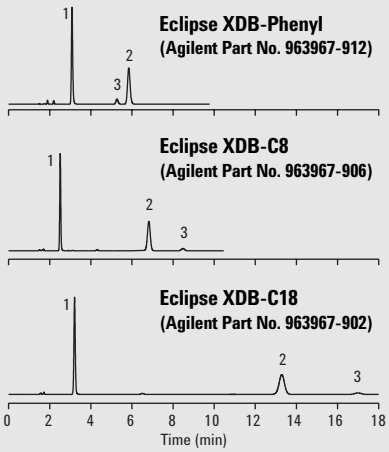
***Eclipse XDB HPLC Column Technology Provides:***

# More Selectivity Options C18, C8 and Phenyl

Eclipse XDB HPLC columns are available as C18, C8 and Phenyl bonded phases. The Eclipse XDB-Phenyl phase complements both the most retentive Eclipse XDB-C18 and the moderately retentive Eclipse XDB-C8. The Eclipse XDB-Phenyl offers unique selectivity as well as reduced retention of non-polar and moderately polar compounds while maintaining retention of polar analytes.

These benefits are illustrated in Figure 7. Sunscreen components are well retained on the Eclipse XDB-C18, although the analysis time is long. Analysis time is reduced with more than acceptable resolution when using the Eclipse XDB-C8 or Eclipse XDB-Phenyl column, where analysis time is shortened by 50 or 61 percent, respectively.

Figure 7
**Eclipse XDB-Phenyl Columns Offer Unique Selectivity and Short Analysis Times**




Column: **ZORBAX Eclipse XDB**
4.6 x 150 mm, 3.5 µm

Mobile Phase: 85% Methanol
15% Water

Flow Rate: 1.0 mL/min

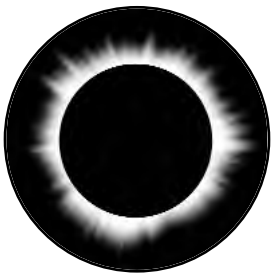
Temperature: 30°C

Detection: UV 310 nm

Sample: 1. Oxybenzone
2. Padimate O
3. Ethylhexyl Salicylate

## Eclipse XDB HPLC Column Technology Provides:

# Rapid Resolution

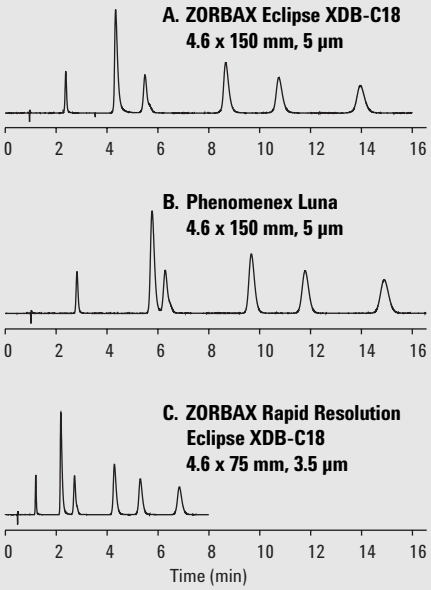


Eclipse XDB columns, available in 5 and 3.5 µm particle size packings, are highly efficient. In Figure 8A, six basic antidepressant compounds are well separated on a 5 µm, 4.6 x 150 mm, Eclipse XDB-C18 column using a methanol-phosphate mobile phase at pH 7. Peaks elute in sharp bands having average peak widths at half-height of 0.19 minutes. When the same sample was run on the Phenomenex Luna column, resolution between nortriptyline and doxepin ($R_{2,3}$) decreased significantly, with average peak widths at half-height being 47% wider, averaging 0.28 minutes for this assay.

For faster analysis, shorter Rapid Resolution Eclipse XDB columns, packed with 3.5 µm particles, provide equally efficient separations with reduced analysis times. This is demonstrated in Figure 8C, where analysis time is decreased by 50% — as retention decreases from 15.6 to 6.8 minutes — while resolution is maintained for this highly basic antidepressant sample.

***If you have any questions about this or other applications in this bulletin, call 800-227-9770 select option 4 and ask for HPLC column technical support.***

Figure 8
**Eclipse XDB Provides High Efficiency and Rapid Resolution**




Mobile Phase: 73% Methanol
27% 50 mM Phosphate, pH 7
Flow Rate: 1.5 mL/min.
Temperature: 40°C
Sample: Antidepressants
1. Imipramine
2. Nortriptyline
3. Doxepin
4. Doxylamine succinate
5. Amitriptyline
6. Cloripramine

Developing reliable reversed-phase methods for basic, acidic and neutral compounds just got easier . . .

Order Your ZORBAX Eclipse XDB HPLC Columns today!

### ZORBAX Eclipse XDB Column Specifications

| Bonded Phase | Pore Size | Surface Area | Temp. Limits | pH Range | Endcapped | Carbon Load |
|---|---|---|---|---|---|---|
| ZORBAX Eclipse XDB-C18 | 80Å | 180 $m^2/g$ | 60°C | 2.0 - 9.0 | Double | 10% |
| ZORBAX Eclipse XDB-C8 | 80Å | 180 $m^2/g$ | 60°C | 2.0 - 9.0 | Double | 7.6% |
| ZORBAX Eclipse XDB-Phenyl | 80Å | 180 $m^2/g$ | 60°C | 2.0 - 9.0 | Double | 7.2% |

## ZORBAX Eclipse XDB Column Ordering Information

| Column Description | Size (mm) | Particle Size (µm) | XDB-C18 USP L1 | XDB-C8 USP L7 | XDB-Phenyl USP L11 |
|---|---|---|---|---|---|
| **Standard Columns and Bulk Packings** | | | | | |
| Semi-Prep | 9.4 x 250 | 5 | 990967-202 | 990967-206 | |
| Analytical | 4.6 x 250 | 5 | 990967-902 | 990967-906 | 990967-912 |
| Analytical | 4.6 x 150 | 5 | 993967-902 | 993967-906 | 993967-912 |
| Analytical | 4.6 x 50 | 5 | 946975-902 | 946975-906 | |
| Rapid Resolution | 4.6 x 150 | 3.5 | 963967-902 | 963967-906 | 963967-912 |
| Rapid Resolution | 4.6 x 100 | 3.5 | 961967-902 | 961967-906 | |
| Rapid Resolution | 4.6 x 75 | 3.5 | 966967-902 | 966967-906 | 966967-912 |
| Rapid Resolution | 4.6 x 50 | 3.5 | 935967-902 | 935967-906 | 935967-912 |
| Solvent Saver | 3.0 x 250 | 5 | 990967-302 | 990967-306 | 990967-312 |
| Solvent Saver | 3.0 x 150 | 5 | 993967-302 | 993967-306 | 993967-312 |
| Solvent Saver Plus | 3.0 x 150 | 3.5 | 963954-302 | 963954-306 | 963954-312 |
| Solvent Saver Plus | 3.0 x 100 | 3.5 | 961967-302 | 961967-306 | 961967-312 |
| Solvent Saver Plus | 3.0 x 75 | 3.5 | 966954-302 | | |
| Narrow Bore | 2.1 x 150 | 5 | 993700-902 | 993700-906 | 993700-912 |
| Narrow Bore | 2.1 x 50 | 5 | 960967-902 | 960967-906 | 960967-912 |
| Narrow Bore RR* | 2.1 x 150 | 3.5 | 930990-902 | 930990-906 | |
| Narrow Bore RR | 2.1 x 100 | 3.5 | 961753-902 | 961753-906 | |
| Narrow Bore RR | 2.1 x 75 | 3.5 | 966735-902 | | |
| Narrow Bore RR | 2.1 x 50 | 3.5 | 971700-902 | 971700-906 | |
| MicroBore RR | 1.0 x 150 | 3.5 | 963600-902 | 963600-906 | |
| MicroBore RR | 1.0 x 50 | 3.5 | 965600-902 | 965600-906 | |
| MicroBore RR | 1.0 x 30 | 3.5 | 961600-902 | 961600-906 | |
| Bulk Packing, 2 grams | | 5 | 920966-902 | | |
| Guard Cartridges, 4/pk | 4.6 x12.5 | 5 | 820950-925 | 820950-926 | 820950-927 |
| Guard Cartridges, 4/pk | 2.1 x12.5 | 5 | 821125-926 | 821125-926 | 821125-926 |
| Guard Hardware Kit | | | 820777-901 | 820777-901 | 820777-901 |
| **Agilent Cartridge Columns** | | | | | |
| Analytical | 4.6 x 250 | 5 | 7995118-585 | 7995108-585 | |
| Analytical | 4.6 x 150 | 5 | 7995118-595 | 7995108-595 | |
| Rapid Resolution | 4.6 x 75 | 3.5 | 7995118-344 | 7995108-344 | |
| Solvent Saver | 3.0 x 75 | 3.5 | 7995230-344 | | |
| Guard Cartridges, 10/pk | 4.0 x 4 | 5 | 7995118-504 | 7995118-504 | |
| Cartridge Holder | | | 5021-1845 | 5021-1845 | |
| **High Throughput Cartridge Columns (requires Hardware Kit 820222-901)** | | | | | |
| Rapid Resolution Cartridge | 4.6 x 30 | 3.5 | 933975-902 | 933975-906 | |
| Rapid Resolution Cartridge, 3/pk | 4.6 x 30 | 3.5 | 933975-932 | 933975-936 | |
| Rapid Resolution Cartridge | 4.6 x 15 | 3.5 | 931975-902 | 931975-906 | |
| Rapid Resolution Cartridge, 3/pk | 4.6 x 15 | 3.5 | 931975-932 | 931975-936 | |
| Rapid Resolution Cartridge | 2.1 x 30 | 3.5 | 973700-902 | 973700-906 | |
| Rapid Resolution Cartridge, 3/pk | 2.1 x 30 | 3.5 | 973700-932 | 973700-936 | |
| Rapid Resolution Cartridge | 2.1 x 15 | 3.5 | 975700-902 | 975700-906 | |
| Rapid Resolution Cartridge, 3/pk | 2.1 x 15 | 3.5 | 975700-932 | 975700-936 | |
| Hardware Kit for High Throughput Columns | | | 820222-901 | 820222-901 | |
| **CombiHT Columns (end fittings required)** | | | | | |
| CombiHT | 21.2 x 150 | 5 | 970150-902 | 970150-906 | |
| CombiHT | 21.2 x 100 | 5 | 970100-902 | 970100-906 | |
| CombiHT | 21.2 x 50 | 5 | 970050-902 | 970050-906 | |
| CombiHT End Fittings (2) (required for use) | | | 820400-901 | 820400-901 | |
| **Capillary Glass-lined Columns** | | | | | |
| Capillary | 0.5 x 250 | 5 | 5064-8286 | | |
| Capillary | 0.5 x 150 | 5 | 5064-8287 | | |
| Capillary RR | 0.5 x 150 | 3.5 | 5064-8288 | | |
| Capillary RR | 0.5 x 35 | 3.5 | 5064-8298 | | |
| Capillary | 0.3 x 250 | 5 | 5064-8269 | | |
| Capillary | 0.3 x 150 | 5 | 5064-8291 | | |
| Capillary RR | 0.3 x 150 | 3.5 | 5064-8271 | | |
| Guard Cartridges | 0.5 x 35 | 5 | 5064-8296 | | |
| Guard Cartridges | 0.3 x 35 | 5 | 5064-8297 | | |

*RR: Rapid Resolution 3.5 µm columns.

For more information on these and other columns consult the Agilent web site at **www.agilent.com.**

**Configurations not shown are available upon request.**

**Agilent Technologies**

For the latest information on the complete line of Agilent Technologies columns and supplies for analytical instruments, see our online catalog at www.agilent.com/chem on the World Wide Web, or contact your local Agilent sales office. For all other areas contact Agilent or your local authorized distributor.

Information, descriptions and specifications in this publication are subject to change without notice.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# Polymer analysis by GPC-SEC

Technical Note

## Introduction

Gel Permeation Chromatography (GPC), also referred to as Size Exclusion Chromatography (SEC) is a mode of liquid chromatography in which the components of a mixture are separated on the basis of size. In GPC-SEC large molecules elute from the column first, followed by smaller molecules. It is an important tool for the analysis of polymers. The essential results are molecular weight data and molecular weight distribution curves which are needed to characterize a polymer with regard to differences in properties. GPC-SEC is mainly used for samples with a molecular weight above 2000 although it is also in use for oligomer separations. There is no upper limit in the molecular weight, even polymer analyses with molecular weights of several millions are possible. Demands on the instrumentation are very stringent due to a special calibration procedure using a linear elution volume on the x-axis versus a logarithmic molecular weight on the y-axis.

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## Mechanism

The column packing for GPC-SEC is a rigid or semi-rigid totally porous material with pores of known size. Figure 1 illustrates the mechanism. The pores are conical in shape, which is not necessarily the case in reality. The example shows a mixture which contains three components A, B and C with A being the largest and C being the smallest. As the components are carried through the column by the mobile phase, component A cannot diffuse into the pores, (that is, it is excluded), component B may diffuse approximately halfway into the pores, (that is, it partially permeates) and component C may diffuse all the way into the pores (that is, it permeates totally). Thus the order of elution from the column would be A, then B, and then C.

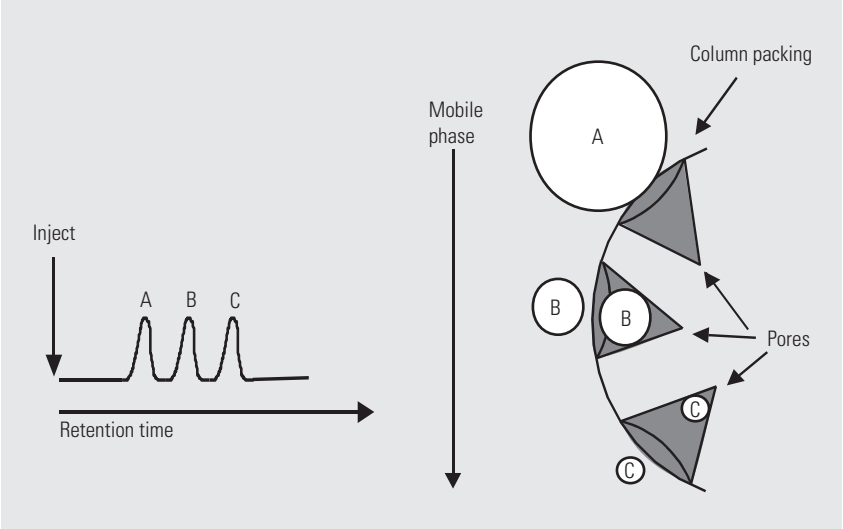


**Figure 1**
**GPC-SEC separation mechanism**

## Molecular weight correlation: calibration

The separation mechanism in GPC-SEC is based on the size of the molecule when solvated by the mobile phase. A correlation can be made between size and molecular weight. Figure 2 shows that a plot of logM against retention volume is linear for components that selectively permeate the column packing pores. From a calibration plot and the retention volume of the sample, its molecular weight or molecular weight range can be determined.

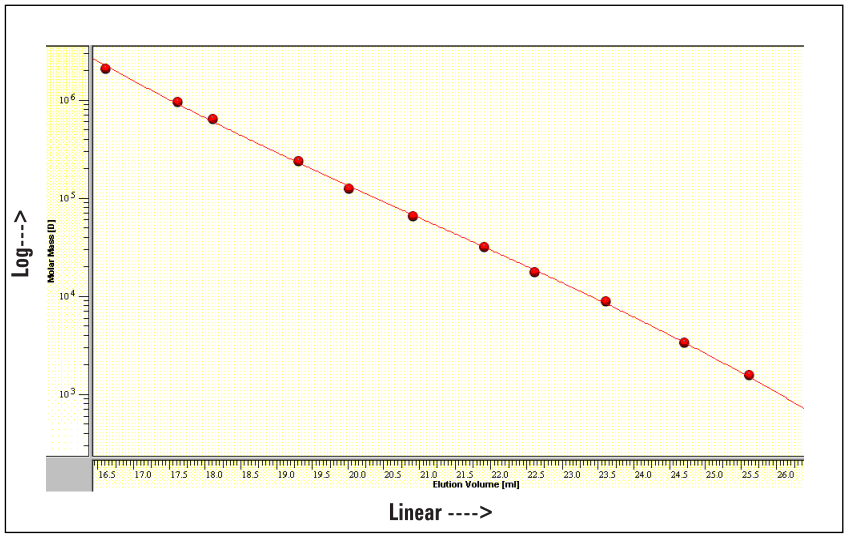


**Figure 2**
**Typical GPC-SEC calibration plot**

## Molecular weight averages and molar mass distributions

Simple transfer of the sample elution volume into the peak apex molecular weight $M_p$ is not sufficient because it characterizes the sample only in a single point. For better characterization the eluted peak is divided into several equidistant volume slices and the molecular weight averages are calculated, as shown in the equations on the right, where h(M) is the slice height at a molecular weight M. The most important averages are $M_n$ and $M_w$. $M_n$ provides information on the flexibility and $M_w$ on the strength of the material. The molecular weight averages describe the polymer at different points of the peak. This can also be achieved using traditional techniques such as membrane osmometry or light scattering. GPC-SEC, however, is the only technique which in addition yields the molecular weight distribution. This is a plot of the statistical frequency of molecular weights versus the log of the molecular weight. The molecular weight or molar mass distribution is most important to characterize polymers. The molecular weight averages describe only average properties of the sample. Figure 3 shows the molar mass distributions of three polymers with identical molecular weight averages. The completely different molar mass distributions indicate clearly that they have different properties.

Number average molecular weight: $$M_n = \frac{\sum h(M) \cdot M}{\sum h(M)} = \frac{\sum w(M)}{\sum w(M)/M}$$

Weight average molecular weight: $$M_w = \frac{\sum h(M) \cdot M^2}{\sum h(M) \cdot M} = \frac{\sum w(M) \cdot M}{\sum w(M)}$$

z- average molecular weight: $$M_z = \frac{\sum h(M) \cdot M^3}{\sum h(M) \cdot M^2} = \frac{\sum w(M) \cdot M^2}{\sum w(M) \cdot M}$$

Viscosity average molecular weight: $$M_v = \left( \frac{\sum w(M) \cdot M^a}{\sum w(M)} \right)^{1/a}$$

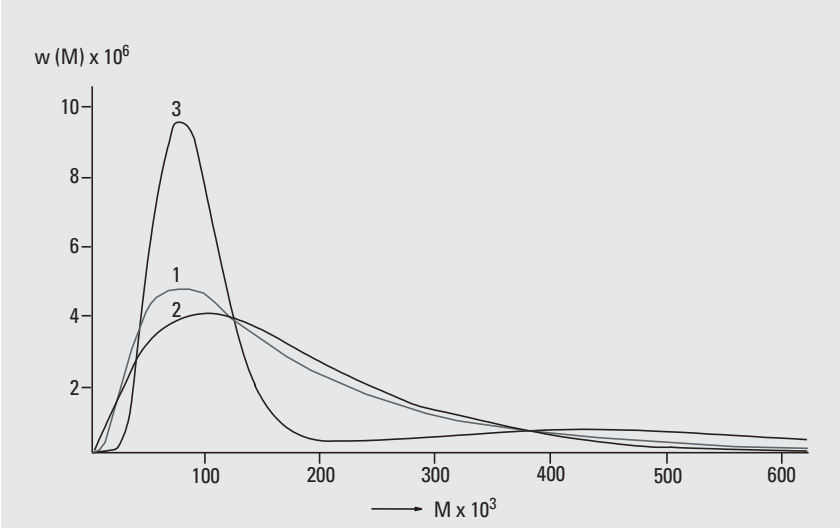


**Figure 3**
**Molar mass distributions of three polymers with the same molecular weight averages**

## Mobile phase selection

In theory, the mobile phase serves only to dissolve the sample and carry it through the column. In other modes of HPLC, such as partition, adsorption and ion-exchange, there is interaction between the mobile phase and the stationary phase on the column packing and retention can be varied by changing the strength of the mobile phase. In GPC-SEC a change in mobile phase may cause a relatively small change in retention due to a change in hydrodynamic volume of the sample in different mobile phases. Also, a change in mobile phase may cause a change in pore size of the gel packing due to swelling or shrinking of the gel. These changes in retention are very small compared to the changes seen in the other HPLC modes. In GPC-SEC the mobile phase serves only to dissolve the sample and carry it through the column and a change in solvent produces a relatively small change in retention. Therefore, gradient elution is not used.

The mobile phases can be roughly devided into organic and aqueous mobile phases. Tetrahydrofuran(THF) is the most frequently used organic solvent. It is used for a wide range of polymers as polystyrene, poly(methyl metacrylate), epoxy resins, polycarbonate, polyvinylchloride, and polystyreneacrylonitrile. Other solvents include toluene, dimethylacetamide and dimethylformamide. For more information on mobile phases and columns recommended for a wide selection of polymer, see reference 1.

## Column packings

Two general types of column packings are available: polymeric gels and silica gels. There are advantages and limitations to both types of packings. Polymeric gels are widely used. Adsorption effects are negligible, however, there are restrictions on solvents that can be used with these gels. Also, the gels can be damaged by pressure "shocks" since they are compressible. The silica packings are more stable physically and are compatible with a wide range of mobile phases. However, adsorption can be a problem with the silica packings unless the surface is deactivated. Highly-crosslinked polystyrene/divinylbenzene particles as packed in the Agilent PLgel columns are among the most widely used columns for polymer separations with organic mobile phases. They are available with different particle and pore sizes to cover a wide range of polymer molecular weight distributions (figure 4). For the analysis of broad distributed polymers one column alone is not sufficient. Such wide ranges usually require sets of several columns, typically between two to three (up to six). For more information on mobile phases and columns recommended for a wide selection of polymers, see reference 1.

An alternative to polystyrene/divinylbenzene based stationary phases are the ZORBAX PSM phases, which are available as small (5 µm) porous microspheres (PSM) in a deactivated and an untreated version. The deactivated version has been silanized for use with non-polar to relatively polar polymers in non-aqueous or partially aqueous solvents. The untreated version is for use with both non-aqueous and aqueous

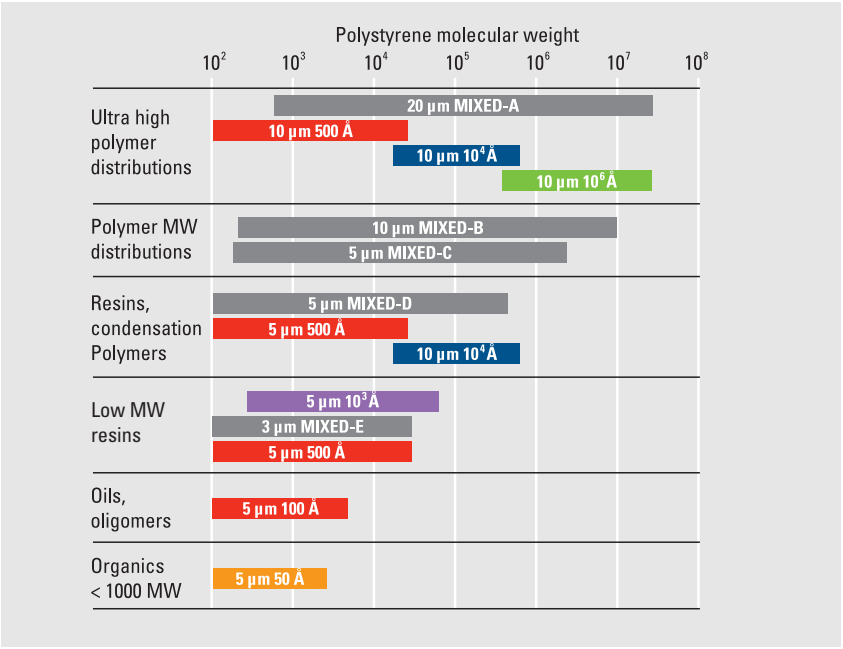


**Figure 4**
**Molecular weight application range of PLgel columns**

mobile phases. Dedicated to analyses with aqueous mobile phases are the Agilent PL aquagel-OH columns with their extremely hydrophilic polyhydroxyl surface. They can handle most neutral hydrophilic polymers, and the capability extends to the analysis of high molecular weight polymers (figure 5) including polyacrylamides and polyethylene oxides.

## Instrument requirements

Due to the special calibration procedure using a linear elution volume (retention time) on the x-axis versus a logarithmic molecular weight on the y-axis the requirements on hardware and software are very demanding. Accuracy and precision of molecular weight data depends on several hard- and software parameters as listed in table 1.

One of the most important parameters is flow precision. Table 2 shows the strong influence of flow deviations on the weight average molecular weight $M_w$ measured for a polystyrene sample.
The system was calibrated at a flow rate of 1.0 ml/min. When analyzed at exactly this flow rate the $M_w$ value is 35400. Table 2 shows that for a flow deviation of only +0.60 % or +1.30 % errors of 11.0 and even 23.6 % occur.

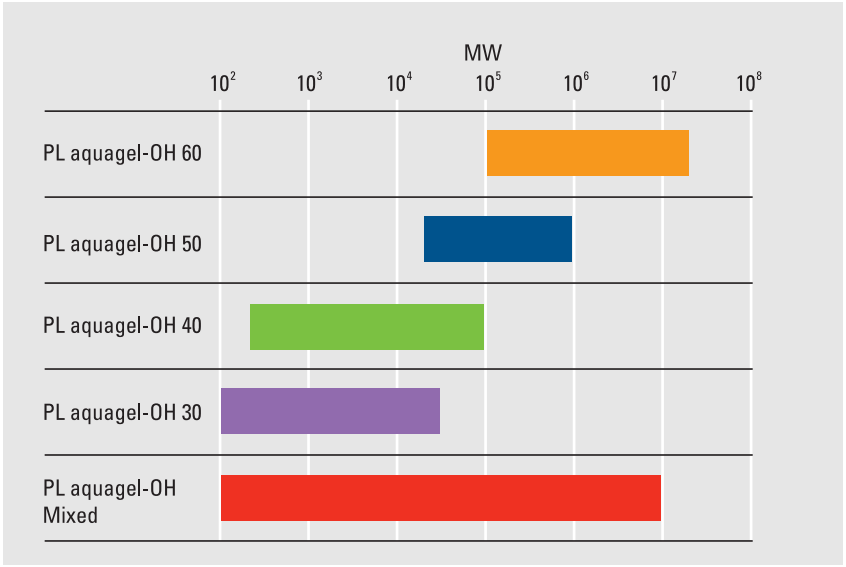


**Figure 5**
**Molecular weight application range of PL aquagel-OH columns**

| Hardware Parameters | Software Parameters |
|---|---|
| • Column stability<br>• Precise pump flow with retention time precision < 0.1 %<br>• Column temperature precision ± 0.15 °C<br>• Lowest short-term and long-term noise<br>• Autosampler with low maintenance | • Precision of calculation procedures<br>• Precision of baseline setting<br>• Precision of setting the calculation start and end marks<br>• Number of data points user selectable<br>• Various calibration routines<br>• Automated and interactive data analysis and reporting<br>• Possibility to use an internal standard correction for flow rate changes |

**Table 1**
**Hardware and software parameters influencing accuracy and precision of molecular weight data**

| Flow [ml/min] | Flow deviation [%] | $M_w$ | $M_w$ deviation [%] |
|---|---|---|---|
| 1.013 | +1.30 | 43400 | +23.6 |
| 1.006 | +0.60 | 39300 | +11.0 |
| 1.0 | 0 | 35400 | 0 |
| 0.992 | -0.80 | 31100 | -12.2 |
| 0.985 | -1.50 | 27700 | -21.80 |

**Table 2**
**Influence of flow variations on molecular weight**

Column temperature stability between calibration and sample run is also important. A 4 °C change, as it can easily occur if the column compartment is not thermostated, will create an error of 2.6 %.

On the software side it is important that the software is correctly installed and calculates correctly. State-of-the art GPC-SEC software therefore offers installation verification and system verification routines. The installation verification routine should be performed after installation and later on periodically to prove that all parts are correctly installed. System verification is used to prove that the software is calculating properly. A data file and a calibration file–provided as a protected part of the program–will be processed and a report will be generated as a printout. The GPC raw data from the known sample is processed in exactly the same way as data acquired by the Agilent ChemStation. This ensures that not only the final calculations are verified but also the complete data processing path. The results are then compared to the theoretical results and the system verification test is only passed if results differ less than a specified percentage. Hardware and software parameter effects on accuracy and precision of molecular weight data are discussed further in references 2 and 3.

Refractive index detection is most frequently used for polymer characterization by GPC-SEC. Some polymers, such as polyethyleneoxides, dextrans, celluloses, do not absorb in the UV-visible range.

On the other hand there are several polymers, that can be analyzed with UV-visible detection provided the eluent is transparent and the correct detection wavelength is selected. Examples are aromatic groups containing polymers as polystyrenes or poly(styreneacrylonitrile)s but also polymers without aromatic groups such as poly(methyl methacrylate)s, polybutadienes, polycarbonates, polyamides and polyacrylic acids. Figure 6 shows an overlay of a poly(methyl methacrylate) (PMMA) analysis obtained with refractive index and UV detection. One advantage of dual detection is that the operator receives more information about the sample. The PMMA chromatograms are very similar in the polymer region but show distinct differences in the oligomer region due to the better sensitivity of the UV detector.

If the UV detector is a diode array detector spectra can be acquired during the analysis and used for peak identification and peak purity control. For an example refer to reference 5. A further advantage of UV-visible detection is lower baseline noise and drift. This should have an influence on the accuracy and the precision of the molecular weight data.

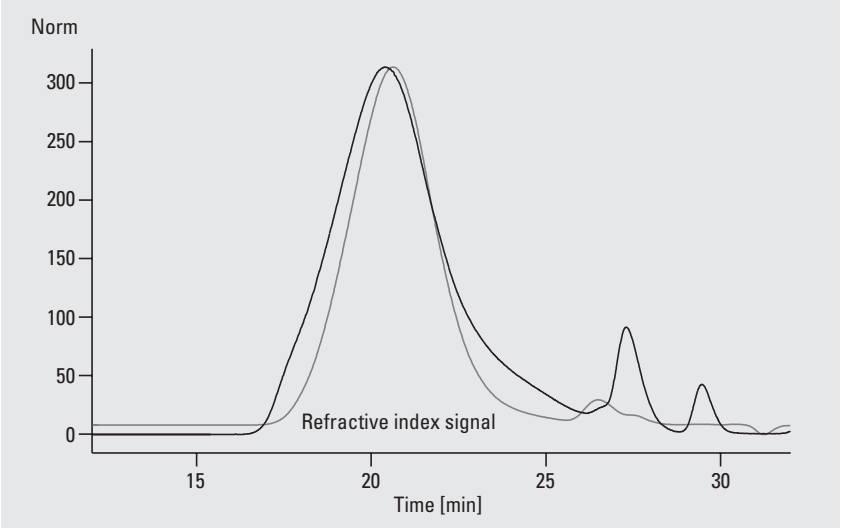


**Figure 6**
**Overlay of poly(methyl metacrylate) chromatograms obtained with UV and refractive index detection**

To study this we analyzed a technical polystyrene sample with UV-DAD-and refractive index detection in series. Table 3 shows the average $M_n$ and $M_w$ values and the respective relative standard deviations calculated from 10 automatic analyses.

State-of-the-art refractive detection has significantly improved in terms of baseline noise, wander, drift and automation capabilities. Therefore, the data in table 3 is very similar for the two detectors with some difference in the precision data. The precision data for UV-visible detection is typically better than the refractive index detection data by a factor of approximately two.

| | Average value | | Precision | |
|---|---|---|---|---|
| | $M_n$ | $M_w$ | $M_n$ | $M_w$ |
| Reference value | 86000 (GPC) | 246000 (light scattering) | - | - |
| UV-DAD | 90700 | 265000 | 0.69 | 0.33 |
| RID | 91530 | 265000 | 1.24 | 0.36 |

**Table 3**
**Comparison of accuracy and precision obtained with UV-DAD and refractive index detection**

## Conclusion

GPC-SEC is the most widely used technique for the analysis of polymers. It can be used for samples soluble in organic and aqueous eluents and molecular weights from approximately 100 to several million Dalton. In contrast to traditional techniques it yields all molecular weight averages and the molecular weight distribution. To obtain accurate and reliable results the demands on hardware and software are more stringent than for other HPLC modes.

## References


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2.
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4.
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**www.agilent.com/chem**



Printed 10/2000
Publication Number 5988-0110EN

**Agilent Technologies**
Innovating the HP Way

# LC-ICP-MS Connection Kit for Agilent 7500 Series

## Technology

- **Combining Agilent's expertise in LC and ICP-MS**
- **Easy switching between coupled and standalone configurations**
- **Optimized sample introduction compatible with standard and capillary LC applications**
- **Robust plasma capable of handling any organic mobile phase or gradient, including acetonitrile**
- **High ion transmission delivers high sensitivity even at capillary LC flow rates (20 mL/min)**
- **High stability electronics and mass analyzer for excellent long-term reproducibility**
- **Fully compatible with Agilent Plasma Chromatographic software for real-time data analysis**
- **Allows routine and overnight running of integrated LC-ICP-MS analyses**
- **Routine detection and quantification of elemental species**
- **Isotope analysis capability of ICP-MS enables isotope dilution and isotope tracer studies to be performed**

## Why LC-ICP-MS?

The measurement capability of existing liquid chromatography (LC) detectors may be limited in terms of sensitivity or specificity. Current and future applications are likely to require the analysis of inorganic species and organometallic compounds at ever lower concentrations, so alternative detection systems are necessary. Inductively coupled plasma mass spectrometry (ICP-MS) provides good selectivity (element specific analysis and even isotopic information) and ultra-trace detection limits for most elements.

Samples are introduced into a high-temperature argon plasma where they are decomposed, atomized, and ionized. Ions are introduced into the mass spectrometer for detection and identification. ICP-MS provides information regarding the total metal concentrations in a sample. When used in combination with a front-end separation technique such as LC, ICP-MS becomes a highly sensitive detector that can be used for a variety of speciation applications. LC-ICP-MS allows for the simultaneous separation and measurement of a variety of species/compounds in a single analytical run.

## The LC-ICP-MS Connection Kit

The Agilent LC-ICP-MS Connection Kit contains all the components required to easily combine the Agilent 1100 LC with the Agilent 7500 ICP-MS. It includes all the necessary fittings, tubing, and cables for complete synchronization of the LC and ICP-MS. An internal standard can be added post-column via the 7500 on-board pump. This provides additional flexibility and allows continuous point-by-point correction to provide the ultimate in data quality.

## Fully Integrated LC-ICP-MS Analysis

The Agilent 7500 Series sample introduction, robust plasma system, and interface can be configured to handle organic samples on a routine basis, without high plasma or interface loading. Typical mobile phases, such as methanol or 65% acetonitrile, can be introduced to the ICP-MS over extended periods. The column eluent is directed into the nebulizer/spray chamber via a connecting block. Using this configuration, the ICP-MS becomes a very sensitive elemental detector for the LC.

See Figure 1 for a schematic of the LC-ICP-MS system.

In a typical analysis, an ICP-MS sequence is created containing information on calibration standards, unknown samples, and any QC samples, such as those used for recalibration of retention times. The LC sequence controls sample injection and then sends a "start" signal to the ICP-MS. After data collection, the Plasma Chromatographic Software (Plasma Chrom) automatically locates and integrates the peaks and generates quantitative results for each compound identified in the sample, based upon a response curve generated from the standards analyzed. A quantitative analysis report can be printed automatically in real-time during the sequence, or the data can be manipulated (for example, using different integration parameters) and quantified offline at a later date.

## Ease of Use

Chromatographic data analysis is conducted via the optional Plasma Chrom module of the Agilent 7500 ChemStation software suite. The software enables, for the first time, the analysis of chromatographic data in real-time. Based on Agilent's renowned ChemStation chromatographic software, Plasma Chrom incorporates all of the

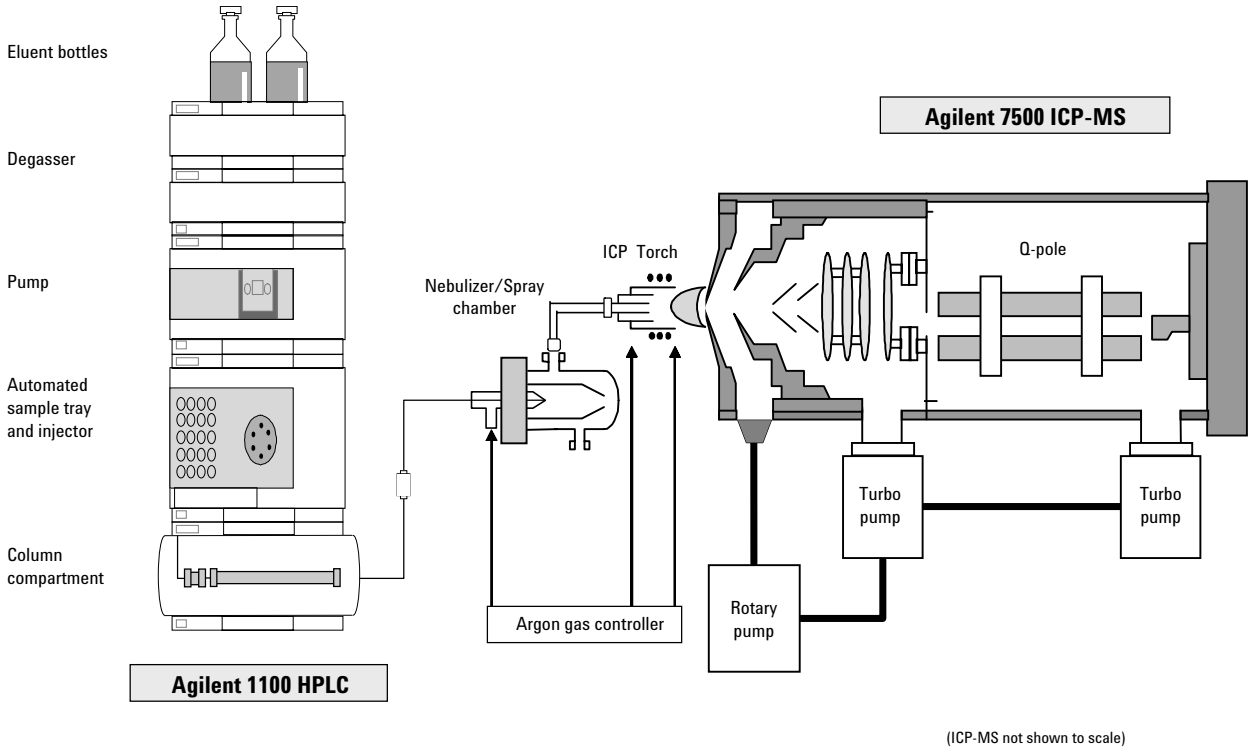


**Figure 1. Schematic of Agilent 1100 HPLC coupled to Agilent 7500 ICP-MS.**

features that chromatographers expect, such as real-time quality control (QC), advanced peak integration routines and confirmation of target analytes. Moreover, operation of the fully integrated Agilent LC-ICP-MS system is easy, making it suitable for both an R&D setting and for routine use.

## Applications

Agilent has developed the fully automated LC-ICP-MS interface in response to the demand for routine and overnight running of analyses in the environmental, clinical, nutritional, bio/pharmaceutical research, and quality control areas. LC-ICP-MS is applicable wherever the quantification of different species, forms, oxidation states, or biomolecules associated with trace elements is required. The ICP-MS adds the capacity to measure isotopic composition, so isotope ratio measurements, isotope dilution analysis, isotopic spike recovery, and tracer studies can be carried out.

Figure 2 displays a series of chromatograms obtained from a 12-hour long-term stability study (20 overlaid chromatograms, obtained from separate visits to sample vials during the 12 hours). The sample was a mixed organotin solution containing diphenyltin (DPhT), dibutyltin (DBT), triphenyltin (TPhT), and tributyltin (TBT), each at 2 ppb, running running with an acetonitrile (65%), acetic acid (10%) mobile phase (minor contaminants can be observed just before the tributyltin (TBT) peak). No reoptimization or retention time calibration was performed. The excellent stability and reproducibility of the system is clearly demonstrated.

## Conclusions

Agilent's LC-ICP-MS is opening up new possibilities for speciation measurement. The long-term reproducibility of the Agilent system will enable, for the first time, the study of species interconversion and equilibria within a given sample matrix. This has far reaching implications in terms of the development of new speciation standards and the validation of speciation measurement.

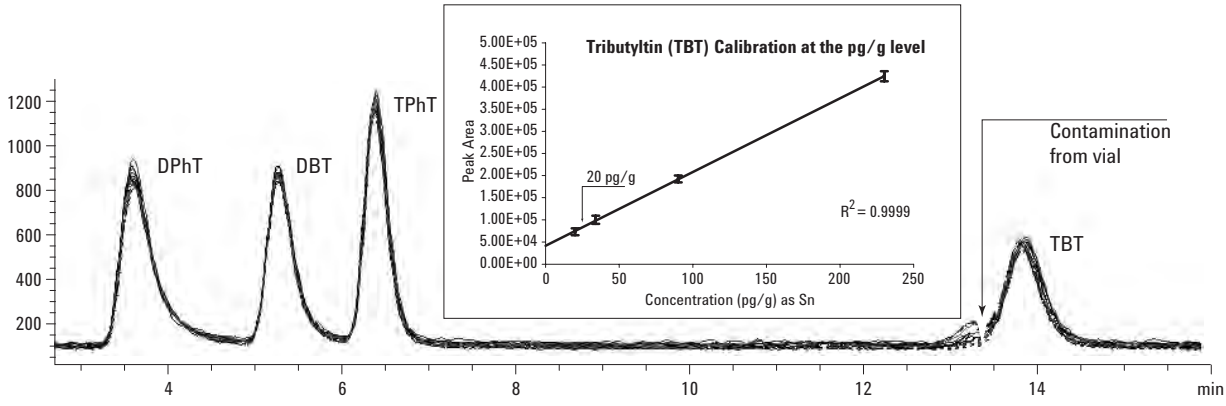


**Figure 2. Twenty overlaid chromatograms showing 12-hour long-term stability for a mixed organotin standard running acetonitrile/acetic acid mobile phase. Included is a low-level calibration for tributyltin. Data courtesy of LGC (Teddington) Ltd, UK.**

## Ordering Information for the Agilent LC-ICP-MS Connection Kit

| Description | Part no. |
|---|---|
| **LC-ICP-MS Connection Kit** | G1833-65200 |
| Kit contents: | |
| Sample tubing | |
| Union joint | |
| Tee joint | |
| Connectors | |
| Ferrules | |
| APG remote cable | |

**Required 1100 Series LC Configuration for:**

***Automated analysis***

| Description | Order code |
|---|---|
| Agilent 1100 Series HPLC | |
| Iso pump | G1310A |
| Autosampler | G1313A |
| Control module | G1323B |

***Manual analysis***

| Description | Order code |
|---|---|
| Agilent 1100 Series HPLC | |
| Iso pump | G1310A |
| Manual injector assembly | G1328B |
| Control module | G1323B |

**Note 1:** If the 1100 LC is controlled by a standalone ChemStation PC, then it is not necessary to order the G1323B Control Module.

**Note 2:** Additional optional items, not included in the LC connection kit, are required for the analysis of organic mobile phases.

## For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.



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5988-4393EN

Agilent Technologies

# ZORBAX Eclipse XDB HPLC Columns

## The "Perfect Fit" for Developing Better HPLC Methods

### Technical Overview

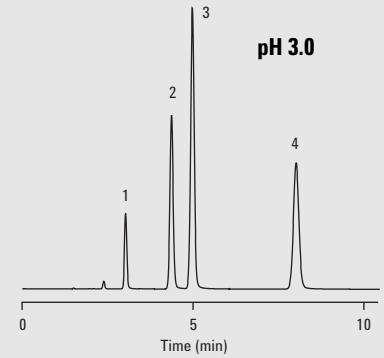
- Excellent peak shape for basic, acidic or neutral compounds
- High performance over a wide pH range
- Rugged, reproducible chromatography from column-to-column and lot-to-lot
- More selectivity options for method development

More and more chromatographers are developing their analytical and LC/MS separations on ZORBAX Eclipse XDB HPLC columns. Why? Because ZORBAX Eclipse XDB columns solve many of their separation challenges. In fact, Agilent Technologies includes a 4.6 x 150 mm, 5 µm ZORBAX Eclipse XDB-C8 column with every Agilent 1100 HPLC instrument it delivers. As Figure 1 shows, ZORBAX Eclipse XDB columns, specifically designed to extend column life and provide excellent peak shape for basic compounds in the pH range of 6 - 9, also deliver outstanding performance at low pH, as well.

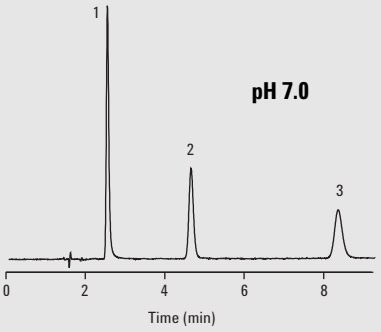
***More detailed information about the benefits of the Eclipse column family can be found in this brochure.***

Figure 1
**Good Peak Shape for Acids, Bases and Neutrals at Low and Intermediate pH**

**ZORBAX Eclipse XDB-C18, 4.6 x 150 mm, 5 µm**
**(Agilent Part No. 993967-902)**




| | |
|---|---|
| Mobile Phase: | 80% 25 mM $Na_2HPO_4$, pH 3.0<br>20% Methanol |
| Flow Rate: | 1.0 mL/min |
| Temperature: | 35°C |
| Sample: | 1. Theobromine<br>2. Theophylline<br>3. 1,7-dimethylxanthine<br>4. Caffeine |




| | |
|---|---|
| Mobile Phase: | 70% 25 mM $Na_2HPO_4$, pH 7.0<br>30% Methanol |
| Flow Rate: | 1 mL/min |
| Temperature: | RT |
| Detection: | UV 254 nm |
| Sample: | 1. Procainamide<br>2. N-acetylprocainamide<br>3. N-propionylprocainamide |

*Eclipse XDB HPLC Column Technology Provides:*

# Excellent Peak Shape

**eXtra Dense Bonding + High Purity Silica = Excellent Peak Shape**

eXtra Dense Bonding is key to the exceptional performance of ZORBAX Eclipse XDB columns at intermediate pH (Figure 2). This dense bonding is accomplished by adding an extra-dense monolayer of C18, C8 or Phenyl silane to the ultra-pure, fully-hydroxylated, ZORBAX Rx-silica surface. The packing is then endcapped not once, but twice, using two different and unique endcapping reagents. This combination of extra-dense surface coverage by the bonded phase and double endcapping produces a highly, deactivated stationary phase that virtually eliminates undesirable interactions between polar solutes and the silica surface. As a result, superior peak shape, high efficiency, and long-term chromatographic reproducibility are assured when using Eclipse XDB HPLC columns at both intermediate and low pH.

The exceptional and reproducible performance at low pH that you can expect from the Eclipse XDB is demonstrated in Figure 3. In this example, acetylsalicylic acid, and the base, dextromethorphan, are consistently separated with excellent peak shape at low pH on three different Eclipse XDB-C8 columns from three different lots of packing material.

Figure 2
**eXtra Dense Bonding (XDB) and Double Endcapping Improves Peak Shape for Polar Compounds at pH 7**

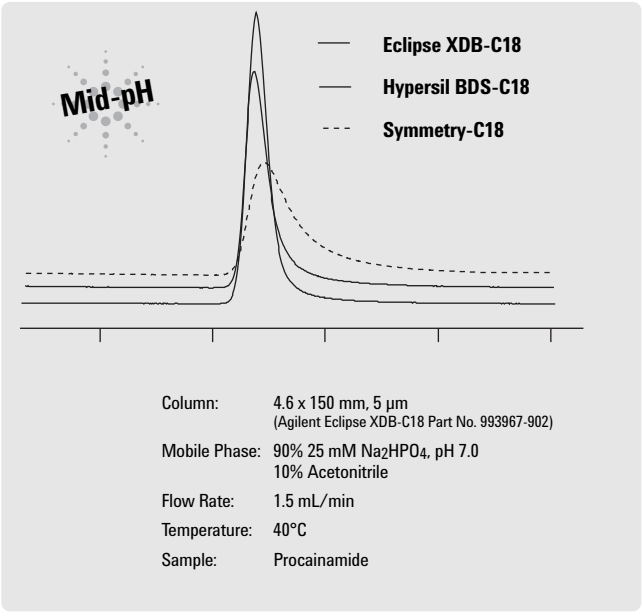
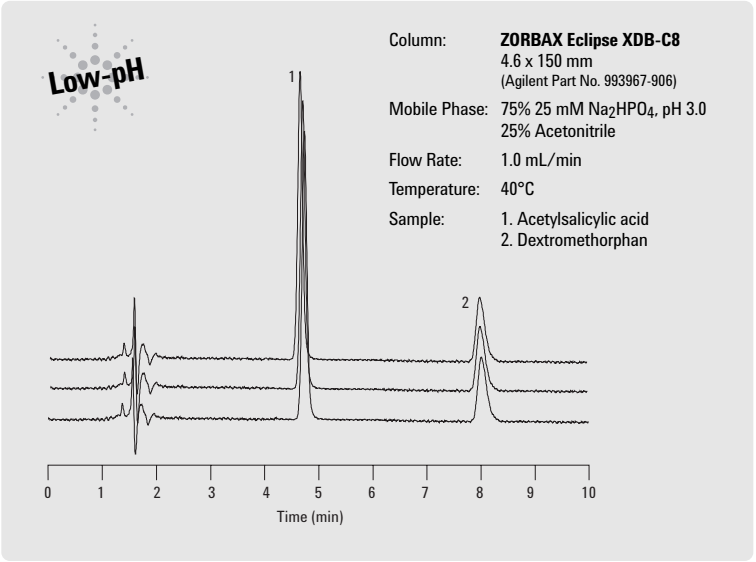



Figure 3
**eXtra Dense Bonding (XDB) and Double Endcapping Improves Peak Shape for Polar Compounds at pH 3**



***Eclipse XDB HPLC Column Technology Provides:***

# Long Column Life

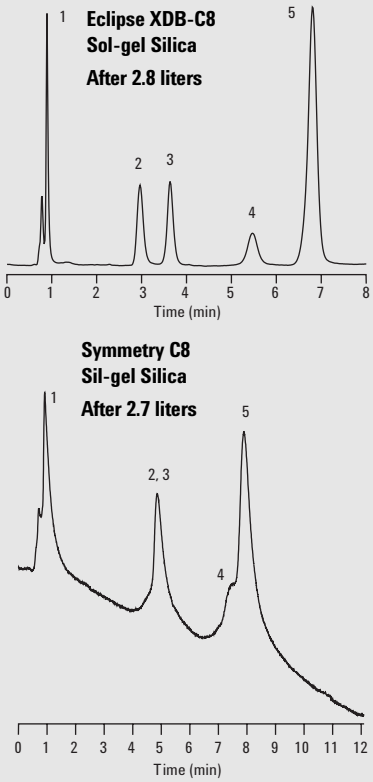
Eclipse XDB columns not only provide excellent peak shape but they are also exceptionally durable. In fact, the spherical ZORBAX Rx-SIL particles are the most durable, porous, 5 and 3.5 µm, silica particles commercially available. They are manufactured using a patented and proprietary process, forming thick, hard-walled silica, commonly referred to in the literature as "sol-gel" silica.

Because of the strength of the ZORBAX particle, all ZORBAX columns are consistently and reliably packed at pressures exceeding 8000 psi. The result is a durable column that can easily tolerate pressures up to 5000 psi in regular use without a loss in efficiency or a reduced lifetime.

## Long Column Life at Intermediate pH

This thick, hard-walled "sol-gel" silica resists dissolution at intermediate pH and when densely bonded, the resultant Eclipse XDB column provides excellent column performance and increased column lifetime, even under the stressed intermediate pH conditions described in Figure 4.

Figure 4
**Accelerated Column Aging Study Demonstrates the Durability of Eclipse XDB-C8 Over Waters' Symmetry C8**




Column: 4.6 x 150 mm

**Purge Conditions:**

Mobile Phase:
20% Acetonitrile
80% 250 mM phosphate buffer, pH 7

Flow Rate: 1.5 mL/min

Temperature: 60°C

**Test Conditions:**

Mobile Phase:
60% Acetonitrile
40% 10 mM phosphate buffer, pH 7

Flow Rate: 1.5 mL/min

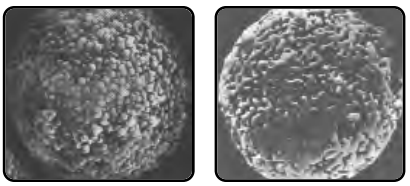
Temperature: 40°C

Sample: Tricyclic Antidepressants
1. Uracil 2. Nortriptyline 3. Doxepin
4. Amitriptyline 5. Trimipramine

Many commercial, base-deactivated, silica-based HPLC columns use manufacturing processes that produce a less robust "sil-gel" silica particle. The walls of these resulting high-surface area materials (typically 300 $m^2/g$ for an 80-100Å pore material) are thinner and less uniform and can easily crush under high pressure conditions. Moreover, in many cases, they fail to withstand the high pressures of high flow rate LC/MS and High-Throughput methods.

The Eclipse XDB thick, hard-walled "sol-gel" is compared to the thin-walled "sil-gel" silica, used to make most of today's base-deactivated products, in electron micrographs shown in Figure 5.

Figure 5
**Eclipse XDB is Based on Thick, Hard-Walled, Sol-gel Silica**



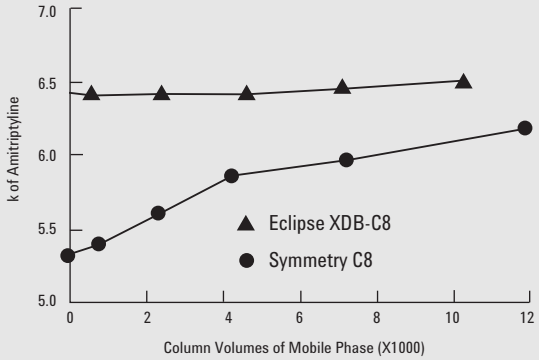
**Sol-gel** **Sil-gel**

*Eclipse XDB columns are made with patented "hard wall" sol-gel silica particles. The thick walls of this silica are more resistant to dissolution than the "thin wall" sil-gel silica that is used to make most base-deactivated columns.*

## Long Column Life at Low pH

At low pH, Eclipse XDB columns provide better column life than most commercially available reversed-phase HPLC columns. Figure 6 summarizes the results from a low-pH accelerated aging study where loss in column performance is measured by a loss in bonded phase, indirectly measured by the change in retention of amitriptyline. The results show that less than 3% of the Eclipse XDB column performance is lost when exposed to 12,000 mL of a pH 3 mobile phase at 60°C. Under these same conditions more than 14% of column performance is lost on another popular "deactivated" reversed-phase HPLC column.

Figure 6
**Accelerated Column Aging Study Demonstrates the Durability of ZORBAX Eclipse XDB-C8 Over Waters' Symmetry**




Column: 4.6 x 150 mm

**Purge Conditions:**

Mobile Phase: 30% Acetonitrile
70% 50 mM NaOAc-HCl, pH 3

Flow Rate: 1.5 mL/min

Temperature: 60°C

**Retention Test Conditions:**

Mobile Phase: 30% Acetonitrile
70% 50 mM NaOAc-HCl, pH 3

Flow Rate: 1.0 mL/min

Temperature: 60°C

Sample: Amitriptyline

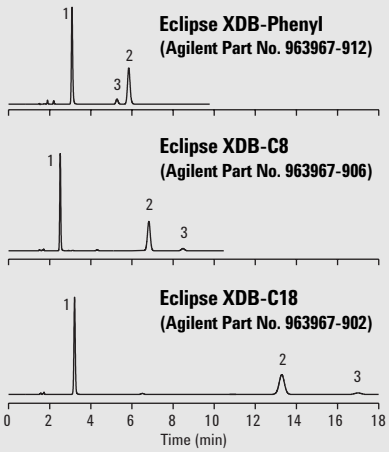
***Eclipse XDB HPLC Column Technology Provides:***

# More Selectivity Options C18, C8 and Phenyl

Eclipse XDB HPLC columns are available as C18, C8 and Phenyl bonded phases. The Eclipse XDB-Phenyl phase complements both the most retentive Eclipse XDB-C18 and the moderately retentive Eclipse XDB-C8. The Eclipse XDB-Phenyl offers unique selectivity as well as reduced retention of non-polar and moderately polar compounds while maintaining retention of polar analytes.

These benefits are illustrated in Figure 7. Sunscreen components are well retained on the Eclipse XDB-C18, although the analysis time is long. Analysis time is reduced with more than acceptable resolution when using the Eclipse XDB-C8 or Eclipse XDB-Phenyl column, where analysis time is shortened by 50 or 61 percent, respectively.

Figure 7
**Eclipse XDB-Phenyl Columns Offer Unique Selectivity and Short Analysis Times**




Column: **ZORBAX Eclipse XDB**
4.6 x 150 mm, 3.5 µm

Mobile Phase: 85% Methanol
15% Water

Flow Rate: 1.0 mL/min

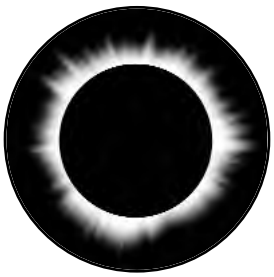
Temperature: 30°C

Detection: UV 310 nm

Sample: 1. Oxybenzone
2. Padimate O
3. Ethylhexyl Salicylate

## Eclipse XDB HPLC Column Technology Provides:

# Rapid Resolution

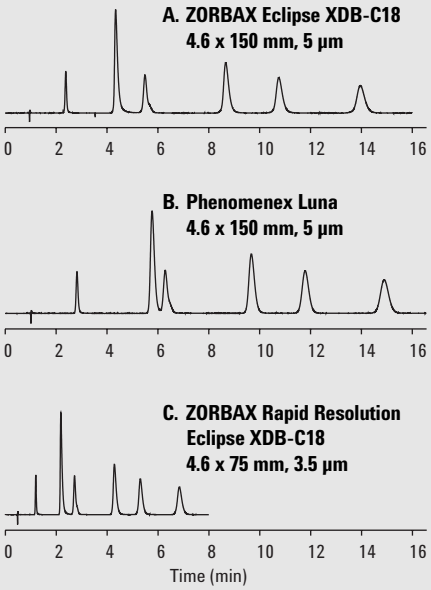


Eclipse XDB columns, available in 5 and 3.5 µm particle size packings, are highly efficient. In Figure 8A, six basic antidepressant compounds are well separated on a 5 µm, 4.6 x 150 mm, Eclipse XDB-C18 column using a methanol-phosphate mobile phase at pH 7. Peaks elute in sharp bands having average peak widths at half-height of 0.19 minutes. When the same sample was run on the Phenomenex Luna column, resolution between nortriptyline and doxepin ($R_{2,3}$) decreased significantly, with average peak widths at half-height being 47% wider, averaging 0.28 minutes for this assay.

For faster analysis, shorter Rapid Resolution Eclipse XDB columns, packed with 3.5 µm particles, provide equally efficient separations with reduced analysis times. This is demonstrated in Figure 8C, where analysis time is decreased by 50% — as retention decreases from 15.6 to 6.8 minutes — while resolution is maintained for this highly basic antidepressant sample.

***If you have any questions about this or other applications in this bulletin, call 800-227-9770 select option 4 and ask for HPLC column technical support.***

Figure 8
**Eclipse XDB Provides High Efficiency and Rapid Resolution**




Mobile Phase: 73% Methanol
27% 50 mM Phosphate, pH 7
Flow Rate: 1.5 mL/min.
Temperature: 40°C
Sample: Antidepressants
1. Imipramine
2. Nortriptyline
3. Doxepin
4. Doxylamine succinate
5. Amitriptyline
6. Cloripramine

Developing reliable reversed-phase methods for basic, acidic and neutral compounds just got easier . . .

Order Your ZORBAX Eclipse XDB HPLC Columns today!

### ZORBAX Eclipse XDB Column Specifications

| Bonded Phase | Pore Size | Surface Area | Temp. Limits | pH Range | Endcapped | Carbon Load |
|---|---|---|---|---|---|---|
| ZORBAX Eclipse XDB-C18 | 80Å | 180 $m^2/g$ | 60°C | 2.0 - 9.0 | Double | 10% |
| ZORBAX Eclipse XDB-C8 | 80Å | 180 $m^2/g$ | 60°C | 2.0 - 9.0 | Double | 7.6% |
| ZORBAX Eclipse XDB-Phenyl | 80Å | 180 $m^2/g$ | 60°C | 2.0 - 9.0 | Double | 7.2% |

## ZORBAX Eclipse XDB Column Ordering Information

| Column Description | Size (mm) | Particle Size (µm) | XDB-C18 USP L1 | XDB-C8 USP L7 | XDB-Phenyl USP L11 |
|---|---|---|---|---|---|
| **Standard Columns and Bulk Packings** | | | | | |
| Semi-Prep | 9.4 x 250 | 5 | 990967-202 | 990967-206 | |
| Analytical | 4.6 x 250 | 5 | 990967-902 | 990967-906 | 990967-912 |
| Analytical | 4.6 x 150 | 5 | 993967-902 | 993967-906 | 993967-912 |
| Analytical | 4.6 x 50 | 5 | 946975-902 | 946975-906 | |
| Rapid Resolution | 4.6 x 150 | 3.5 | 963967-902 | 963967-906 | 963967-912 |
| Rapid Resolution | 4.6 x 100 | 3.5 | 961967-902 | 961967-906 | |
| Rapid Resolution | 4.6 x 75 | 3.5 | 966967-902 | 966967-906 | 966967-912 |
| Rapid Resolution | 4.6 x 50 | 3.5 | 935967-902 | 935967-906 | 935967-912 |
| Solvent Saver | 3.0 x 250 | 5 | 990967-302 | 990967-306 | 990967-312 |
| Solvent Saver | 3.0 x 150 | 5 | 993967-302 | 993967-306 | 993967-312 |
| Solvent Saver Plus | 3.0 x 150 | 3.5 | 963954-302 | 963954-306 | 963954-312 |
| Solvent Saver Plus | 3.0 x 100 | 3.5 | 961967-302 | 961967-306 | 961967-312 |
| Solvent Saver Plus | 3.0 x 75 | 3.5 | 966954-302 | | |
| Narrow Bore | 2.1 x 150 | 5 | 993700-902 | 993700-906 | 993700-912 |
| Narrow Bore | 2.1 x 50 | 5 | 960967-902 | 960967-906 | 960967-912 |
| Narrow Bore RR* | 2.1 x 150 | 3.5 | 930990-902 | 930990-906 | |
| Narrow Bore RR | 2.1 x 100 | 3.5 | 961753-902 | 961753-906 | |
| Narrow Bore RR | 2.1 x 75 | 3.5 | 966735-902 | | |
| Narrow Bore RR | 2.1 x 50 | 3.5 | 971700-902 | 971700-906 | |
| MicroBore RR | 1.0 x 150 | 3.5 | 963600-902 | 963600-906 | |
| MicroBore RR | 1.0 x 50 | 3.5 | 965600-902 | 965600-906 | |
| MicroBore RR | 1.0 x 30 | 3.5 | 961600-902 | 961600-906 | |
| Bulk Packing, 2 grams | | 5 | 920966-902 | | |
| Guard Cartridges, 4/pk | 4.6 x12.5 | 5 | 820950-925 | 820950-926 | 820950-927 |
| Guard Cartridges, 4/pk | 2.1 x12.5 | 5 | 821125-926 | 821125-926 | 821125-926 |
| Guard Hardware Kit | | | 820777-901 | 820777-901 | 820777-901 |
| **Agilent Cartridge Columns** | | | | | |
| Analytical | 4.6 x 250 | 5 | 7995118-585 | 7995108-585 | |
| Analytical | 4.6 x 150 | 5 | 7995118-595 | 7995108-595 | |
| Rapid Resolution | 4.6 x 75 | 3.5 | 7995118-344 | 7995108-344 | |
| Solvent Saver | 3.0 x 75 | 3.5 | 7995230-344 | | |
| Guard Cartridges, 10/pk | 4.0 x 4 | 5 | 7995118-504 | 7995118-504 | |
| Cartridge Holder | | | 5021-1845 | 5021-1845 | |
| **High Throughput Cartridge Columns (requires Hardware Kit 820222-901)** | | | | | |
| Rapid Resolution Cartridge | 4.6 x 30 | 3.5 | 933975-902 | 933975-906 | |
| Rapid Resolution Cartridge, 3/pk | 4.6 x 30 | 3.5 | 933975-932 | 933975-936 | |
| Rapid Resolution Cartridge | 4.6 x 15 | 3.5 | 931975-902 | 931975-906 | |
| Rapid Resolution Cartridge, 3/pk | 4.6 x 15 | 3.5 | 931975-932 | 931975-936 | |
| Rapid Resolution Cartridge | 2.1 x 30 | 3.5 | 973700-902 | 973700-906 | |
| Rapid Resolution Cartridge, 3/pk | 2.1 x 30 | 3.5 | 973700-932 | 973700-936 | |
| Rapid Resolution Cartridge | 2.1 x 15 | 3.5 | 975700-902 | 975700-906 | |
| Rapid Resolution Cartridge, 3/pk | 2.1 x 15 | 3.5 | 975700-932 | 975700-936 | |
| Hardware Kit for High Throughput Columns | | | 820222-901 | 820222-901 | |
| **CombiHT Columns (end fittings required)** | | | | | |
| CombiHT | 21.2 x 150 | 5 | 970150-902 | 970150-906 | |
| CombiHT | 21.2 x 100 | 5 | 970100-902 | 970100-906 | |
| CombiHT | 21.2 x 50 | 5 | 970050-902 | 970050-906 | |
| CombiHT End Fittings (2) (required for use) | | | 820400-901 | 820400-901 | |
| **Capillary Glass-lined Columns** | | | | | |
| Capillary | 0.5 x 250 | 5 | 5064-8286 | | |
| Capillary | 0.5 x 150 | 5 | 5064-8287 | | |
| Capillary RR | 0.5 x 150 | 3.5 | 5064-8288 | | |
| Capillary RR | 0.5 x 35 | 3.5 | 5064-8298 | | |
| Capillary | 0.3 x 250 | 5 | 5064-8269 | | |
| Capillary | 0.3 x 150 | 5 | 5064-8291 | | |
| Capillary RR | 0.3 x 150 | 3.5 | 5064-8271 | | |
| Guard Cartridges | 0.5 x 35 | 5 | 5064-8296 | | |
| Guard Cartridges | 0.3 x 35 | 5 | 5064-8297 | | |

*RR: Rapid Resolution 3.5 µm columns.

For more information on these and other columns consult the Agilent web site at **www.agilent.com.**

**Configurations not shown are available upon request.**

**Agilent Technologies**

For the latest information on the complete line of Agilent Technologies columns and supplies for analytical instruments, see our online catalog at www.agilent.com/chem on the World Wide Web, or contact your local Agilent sales office. For all other areas contact Agilent or your local authorized distributor.

Information, descriptions and specifications in this publication are subject to change without notice.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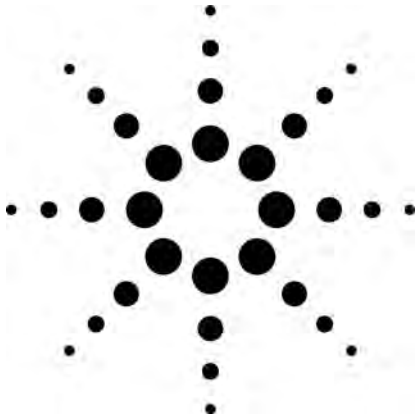
# GS-OxyPLOT: A PLOT Column for the GC Analysis of Oxygenated Hydrocarbons

## Technical Overview



Allen Vickers

## Introduction

GS-OxyPLOT is a porous layer open tubular (PLOT) column. The stationary phase is a proprietary, salt deactivated adsorbent with a high chromatographic selectivity for low molecular weight oxygenated hydrocarbons. It is designed for and ideally suited for application in the ASTM methods listed in Table 1. It is an appropriate replacement for Varian's CP-LowOx column, usually with little to no changes in analytical parameters. This column is particularly useful for the trace analysis of oxygenates such as those listed in Table 2. Other oxygenated hydrocarbons are also suitable for analysis with this column subject to limitations given below.

The column can be used as a single, primary analytical separation column for oxygenated compounds. In complex sample matrices that have high molecular weight species (ca. 300 mol. wt. and higher) and/or species with insufficiently high vapor pressure to migrate through the GS-OxyPLOT, this column can be used in multidimensional GC systems with other columns that have vastly different polarity and lower selectivity toward oxygenated hydrocarbons. For example, a nonpolar DB-1 column can be used as an injection precolumn to retain low volatility solutes, allowing the less retained, polar oxygenated solutes to move into the GS-OxyPLOT. Since the stationary phase of GS-OxyPLOT is an oxygenate adsorbent phase, the oxygenates that enter the column are trapped. As the GC oven temperature is increased, the oxygenates will begin to migrate and are separated in the column prior to detection.

When first installed, the GS-OxyPLOT should be conditioned at 300 °C for at least 3 hours. Experience has shown that this column has an infinite shelf life, but when the column has not been in use for extended periods of time, longer conditioning times of 8 hours or more may be required to obtain retention time stability. The column can be stored with septa placed over the ends of the column, returned to the original column box, and stored at normal ambient temperatures for future use.

GS-OxyPLOT has a minimum temperature limit of 0 °C, an isothermal maximum temperature limit of 300 °C, and an oven program maximum temperature of 350 °C. Because the stationary phase is a strong adsorbent for polar compounds, especially water, it is recommended that when the column is installed in a GC, but idle, that the GC oven be set to an isothermal temperature of 220 °C with normal carrier gas flow, so that the instrument can be brought back into operation quickly when samples are ready to be analyzed. Otherwise, if the column is left at low oven temperatures, it may require reconditioning at 300 °C for several hours to obtain stable retention times.

Saturated hydrocarbon solutes have virtually no interaction with the GS-OxyPLOT and elute from the column so long as the column temperature is hot enough to induce a high enough vapor pressure for the solute to move in the carrier gas. Normal alkanes up to $C_{18}$ will elute from GS-OxyPLOT within the program temperature maximum limit of the column. Because of the highly polar character of the GS-OxyPLOT phase, as would be

expected for oxygenate-selective PLOT column, the column has a relatively low sample load capacity for these nonpolar solutes. The low sample loading capacity is manifested chromatographically as a tailing peaking, indicative of phase overload in GS-OxyPLOT columns. Unsaturated hydrocarbons and aromatic hydrocarbons have relatively high retention. Injection of these organic compound classes should be limited to organic compounds with 11 carbons or less to prevent the column from fouling. As with the normal alkanes, the alkyl benzenes will show phase overloading at relatively low concentrations.

While GS-OxyPLOT is an ideal analytical solution for low molecular weight, oxygenated hydrocarbons, like all other similar oxygenate-selective PLOT columns,it is not recommended for higher molecular weight alkenals (e.g., 1-hexenal and 1-ocetenal). The combined interaction of the unsaturated and carbonyl functional groups can instigate tailing due to strong interactions and in some cases reaction between the phase and solutes.

**Table 1. ASTM Standardized Methods for Which GS-OxyPLOT Is Specifically Designed**

| | |
|---|---|
| ASTM Method D7059 | Determination of Methanol in Crude Oils by Gas Chromatography with Flame Ionization Detection |
| Proposed ASTM Method | Determination of $C_1$ to $C_5$ Oxygenates at Trace Levels in High Ethanol Content Gasoline Streams by Multidimensional Chromatography with Flame Ionization Detection* |
| Proposed ASTM Method | Determination of Oxygenates in Ethene, Propene, and $C_4$ and $C_5$ Hydrocarbon Matrices by Gas Chromatography and Flame Ionization Detection* |

*These are "proposed methods" (i.e., do not have method designation numbers) that are destined for approval by ASTM Committee D2. These methods have already been accepted by, and are being implemented in, petrochemical refineries around the world.

**Table 2. Examples of Oxygenated Compounds Suitable for GC Analysis Using the GS-OxyPLOT Column**

| | |
|---|---|
| 1. Dimethyl Ether | 13. Acetone |
| 2. Diethyl Ether | 14. Isovaleraldehyde |
| 3. Acetaldehyde | 15. Valeraldehyde |
| 4. Ethyl t-Butyl Ether | 16. Methyl Ethyl Ketone |
| 5. Methyl t-Butyl Ether | 17. Ethanol |
| 6. Diisopropyl Ether | 18. 1-Propanol |
| 7. Propionaldehyde | 19. Isopropyl Alcohol |
| 8. tert-Amyl Methyl Ether | 20. Allyl Alcohol |
| 9. Propyl Ether | 21. Isobutyl Alcohol |
| 10. Isobutraldehyde | 22. tert-Butyl Alcohol |
| 11. Butylaldehyde | 23. sec-Butyl Alcohol |
| 12. Methanol | 24. n-Butyl Alcohol |
| | 25. 2-Methyl-2-Pentanol |

## Ordering Information for the GS-OxyPLOT Column

| ID (mm) | Length (m) | Film Thickness (µm) | Temperature Limit (°C) | Cage Size | Part Number |
|---|---|---|---|---|---|
| 0.53 | 10 | 10 | 350 | 7″ | 115-4912 |
| 0.53 | 10 | 10 | 350 | 5″ | 115-4912E |

## References


1. A. K. Vickers, “A ‘Solid’ Alternative for Analyzing Oxygenated Hydrocarbons—Agilent’s New Capillary GC PLOT Column,” Agilent Technologies publication 5989-6323EN, Feb 2006.
2. A New Megabore GC Column for the Adsorption and Chromatographic Separation of Oxygenates in Hydrocarbon Matrices, poster, Pittcon07-27.
3. Analysis and Chromatographic Separation of Oxygenates in Hydrocarbon Matrices, Power Point presentation, Pittcon07-20.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5989-6447EN


Agilent Technologies

# Successful Detection Using the Agilent 255 Nitrogen Chemiluminescence Detector (255 NCD)

Technical Overview

## Introduction

The Agilent 255 Nitrogen Chemiluminescence Detector (255 NCD) can easily detect organic compounds containing nitrogen after conversion of the compounds to nitric oxide.

Frequently, chemists at Agilent are asked what nitrogen compounds are detected by the 255 NCD. Successful detection of nitrogen-containing compounds requires the conversion of these compounds to nitric oxide. The 255 NCD stainless steel burner converts nitrogen compounds to nitric oxide in a hydrogen and oxygen plasma at temperatures greater than 1800 °C.

The 255 NCD can easily detect organic compounds containing nitrogen after conversion of the compounds to nitric oxide. The stainless steel burner can also convert inorganic compounds such as ammonia and hydrazine to nitric oxide. The nitric oxide from the stainless steel burner reacts with ozone in the chemiluminescence reaction cell to produce a chemiluminescence reaction. A red optical filter allows transmission of the light from the chemiluminescence nitrogen reaction while suppressing chemiluminescence signals from other chemical species.

The selectivity of the 255 NCD results from the fact that not all compounds exhibit chemiluminescence when mixed with ozone. Also, the stainless burner cannot convert all compounds to nitric oxide.

Some compounds giving little or no response with the 255 NCD include carbon dioxide, water, nitrogen, oxygen, noble gases, and chlorinated hydrocarbons. These compounds represent the major constituents of many sample matrices. None of these compounds interfere significantly with the 255 NCD and determination of trace levels of the nitrogen-containing analytes.

#### Examples of Compounds Detected by the 255 NCD

- Amines
- Carbazoles
- Indoles
- Nitro-compounds
- Nitriles
- Nitrosamines
- Pyridines
- Quinolines
- Ammonia
- Hydrazine
- Hydrogen cyanide
- Nitric oxide, NO
- Nitrogen dioxide, $NO_2$
- $NO_X$

#### Compounds Not Detected by the 255 NCD

- Carbon dioxide
- Nitrogen gas
- Water
- Hydrocarbons

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Agilent Technologies

# Agilent Model 255 Nitrogen Chemiluminescence Detector (NCD) Analysis of Adhesive Samples Using the NCD

Technical Overview

## Introduction

The Agilent Model 255 NCD can easily replace a NPD for the analysis of 2-pyrrolidone and 1-vinyl-2-pyrrolidinone in adhesive samples.

A short-term evaluation was performed for the analysis of adhesive samples for two of the starting materials, 2-pyrrolidone and 1-vinyl-2-pyrrolidinone. According to government regulations, the concentration of 1-vinyl-2-pyrrolidinone cannot exceed 800 ppm in the final product.

The primary objective for the analysis of adhesive was to demonstrate the repeatability and stability of the Model 255 NCD. The secondary objective of the study was to prove the NCD could replace the nitrogen-phosphorus detector (NPD) being used for the application. Table 1 compares the NCD and NPD.

The results from the evaluation demonstrated the Model 255 NCD could easily replace a NPD to monitor 2-pyrrolidone and 1-vinyl-2-pyrrolidinone. The gas chromatograph and the Model 255 NCD were calibrated once and not recalibrated again during the 3-day demonstration. Representative precision data are shown in Tables 2 and 3. The gas chromatograph made over 160 injections of the adhesive samples during the 3-day evaluation with the percent relative standard deviation for the Model 255 NCD of less than 4%. The Model 255 was also linear from 20 to 3000 ppm. Figures 1 and 2 illustrate chromatographic response at high and low levels, respectively. Unlike an NPD, the sample matrix did not affect the detector performance.

For the 2-pyrrolidone and 1-vinyl-2-pyrrolidinone analysis, the NCD provides very good short-term and long-term precision. The NCD is unaffected by high levels of the sample matrix, and its use would require less day-to-day maintenance than an NPD. Use of the Model 255 NCD versus an NPD would result in more accurate and precise results and would reduce the level of instrument maintenance required.

**Table 1. Comparison of Agilent NCD to NPD**

| | Agilent 255 NCD | NPD |
|---|---|---|
| **Response** | Equimolar | Non-equimolar |
| **Quenching** | No | Yes |
| **Selectivity** | > 107 gN/gC | 105 gN/gC |
| **Sensitivity** | < 5 pg/sec | 0.4 pg/sec |
| **Ease of Use** | Straightforward | Daily maintenance required |

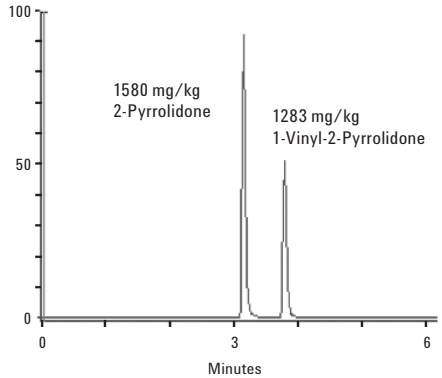


**Figure 1. Agilent Model 255 analysis of adhesive standard.**

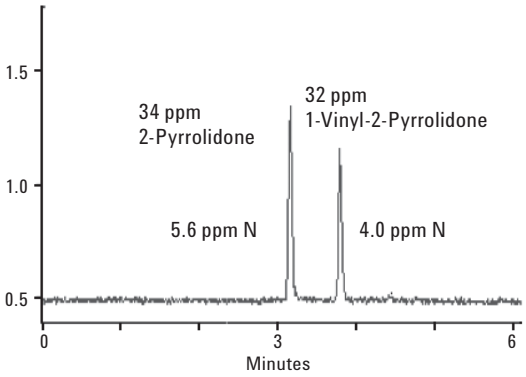


**Figure 2. Agilent Model 255 NCD analysis of adhesive sample diluted in tetrahydrofuran.**

**GC Operating Conditions**

(Agilent 6890 with EPC)

| | |
|---|---|
| Temperature: | 160 °C isothermal |
| Helium carrier: | 2.2 mL/min |
| Split injection: | 45.5:1 split |
| | 200 °C |
| | 1 µL injection volume |

**NCD Burner Conditions**

| | |
|---|---|
| Temperature: | 800 °C |
| Hydrogen flow rate: | 25 mL/min |
| Oxygen flow rate: | 10 mL/min |
| Column: | 20 Rtx-5, 0.32 mm id |
| | 3 µm film thickness |

**Sample Preparation**

Samples diluted in toluene
Dilution factors of 1:25 to 1:50

**Table 2. Summary of 2-Pyrrolidone in Adhesive Results**

| Sample number | Number of runs | Dilution factor | Diluted concentration (ppm) | Sample concentration (ppm) | RSD (%) |
|---|---|---|---|---|---|
| Adhesive 1 | 43 | 1:44 | 25.0 | 1094 | 2.2 |
| Adhesive 2 | 43 | 1:41 | 28.1 | 1163 | 2.2 |
| Adhesive 3 | 43 | 1:28 | 34.0 | 1405 | 2.2 |
| Adhesive 4 | 43 | 1:45 | 20.3 | 838 | 1.7 |

**Table 3. Summary of 1-Vinyl-2-Pyrrolidinone in Adhesive Results**

| Sample number | Number of runs | Dilution factor | Diluted concentration (ppm) | Sample concentration (ppm) | RSD (%) |
|---|---|---|---|---|---|
| Adhesive 1 | 43 | 1:44 | 27.1 | 1188 | 2.2 |
| Adhesive 2 | 43 | 1:41 | 15.1 | 624 | 2.2 |
| Adhesive 3 | 43 | 1:28 | 32.5 | 1342 | 2.2 |
| Adhesive 4 | 43 | 1:45 | Not detected | Not detected | |

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Agilent Technologies

# Agilent Model 255 Nitrogen Chemiluminescence Detector (NCD) Simultaneous Hydrocarbon Analysis with the NCD and an FID

Technical Overview

## Introduction

The nitrogen specificity of the Agilent Model 255 NCD and the universal detection of the flame ionization detector (FID) can provide a detailed analysis of a sample matrix. Chemiluminescence detection enables isolation of nitrogen-containing compounds, while the FID provides universal response for major components in many sample matrices.

Agilent has developed a detector interface to allow simultaneous universal and nitrogen specific detection for gas chromatography. An FID is used for universal detection and the Model 255 NCD is used for the specific detection of nitrogen compounds.

To perform simultaneous NCD and FID analysis, the capillary column is connected directly to the FID following the gas chromatograph manufacturer's installation instruction. The column effluent flows into the FID and then immediately continues through to the stainless steel burner of the NCD. The FID uses oxygen instead of air and the makeup gas is helium rather than nitrogen. Use of oxygen and helium avoids the formation of background nitric oxide in the flame of the detector.

The simultaneous mode is useful when the concentration of nitrogen in individual compounds is greater than 1 ppm. The detection scheme is also useful when the matrix of interest is unknown and there is a need for hydrocarbon data on the sample.

When necessary, the stainless steel burner is easily converted to Direct Analysis mode for better nitrogen sensitivity. The stainless steel burner was designed for use for either simultaneous NCD and FID analysis or specific nitrogen analysis only.

Figure 1 shows a chromatogram with nitrobenzene, 3-methylindole, and 9-methylcarbazole in toluene that demonstrates both the equimolar response and specificity of the NCD. The concentration of nitrogen is approximately 25 ppm for each compound. Also notice the lack of a solvent peak at the beginning of the NCD analysis. A benefit of the NCD is that non-nitrogen containing hydrocarbons in the sample are transparent to the NCD. The sample compounds flow from the column into the FID and the FID measures the hydrocarbon response. A portion of the FID effluent flows directly into the burner of the NCD.

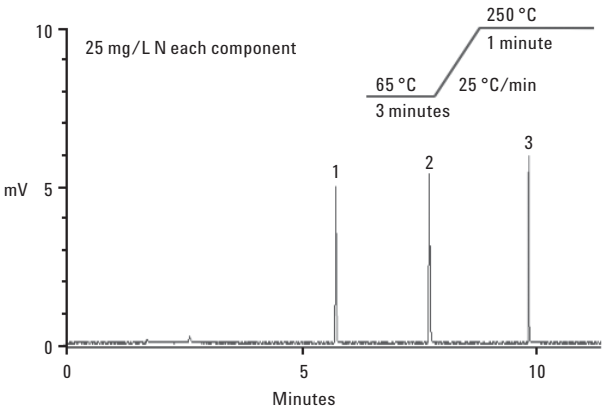


**Figure 1. NCD analysis.**

**Table 1. Precision of Simultaneous NCD and FID Analysis**

| Number of runs | Compound concentration (ppm) | N concentration (ppm) | Model 255 NCD (% RSD) | FID (% RSD) |
|---|---|---|---|---|
| Nitrobenzene | 218 | 25 | 2.3 | 1.5 |
| 3-methylindole | 234 | 25 | 2.2 | 1.3 |
| 9-methylcarbazole | 326 | 25 | 2.5 | 1.5 |

Notice the number of other small impurity peaks present in the FID chromatogram (Figure 2). The NCD did not detect these peaks since the NCD is specific only for nitrogen. If any of the small compounds contained nitrogen, the NCD would have detected them. Also, with the equimolar response of the NCD, it is possible to determine the concentration of nitrogen impurities in the sample.

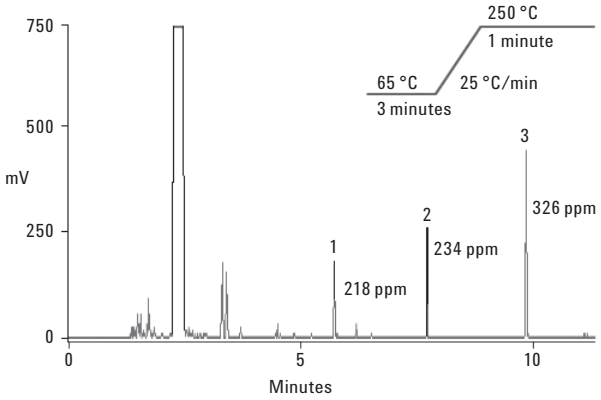


**Figure 2. FID analysis.**

**GC Operating Conditions**
(Agilent 6890 with EPC)

| | |
|---|---|
| Initial temperature: | 65 °C for 3 min |
| Temperature ramp: | 25 °C/min |
| Final temperature: | 250 °C for 1 min |
| Helium carrier: | 2.2 mL/min |
| Split injection: | 50:1 split |
| | 250 °C |
| | 2 µL injection volume |

**NCD Burner Condition**

| | |
|---|---|
| Temperature: | 800 °C |
| Hydrogen flow rate: | 25 mL/min |
| Oxygen flow rate: | 10 mL/min |
| Column: | 30 m HP-5, 0.32 mm id |
| | 0.25 µm film thickness |

**Components**

| | |
|---|---|
| Peak 1: | Nitrobenzene |
| Peak 2: | Methylindole |
| Peak 3: | 9-Methylcarbazole |

The toluene sample with nitrobenzene, 3-methylindole, and 9-methylcarbazole was analyzed 143 times over a 3-day period to demonstrate the stability of the simultaneous NCD and FID analysis. The results of 2.5% relative standard deviation and less demonstrate the stability of the NCD when operated in tandem with the FID (see Table 1). The results also demonstrate that the tandem NCD/FID operation does not affect the performance of the FID. Furthermore, the results also demonstrate the consistency in transferring a fraction of the FID exhaust gases to the NCD.

The nitrogen specificity of the NCD and the universal detection of the FID can provide a detailed analysis. Chemiluminescence detection enables isolation of nitrogen-containing compounds in the sample, while the FID provides universal response for the major compounds of many sample matrices.

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# Sulfur Compounds in Air – Agilent Model 355 SCD

Technical Overview

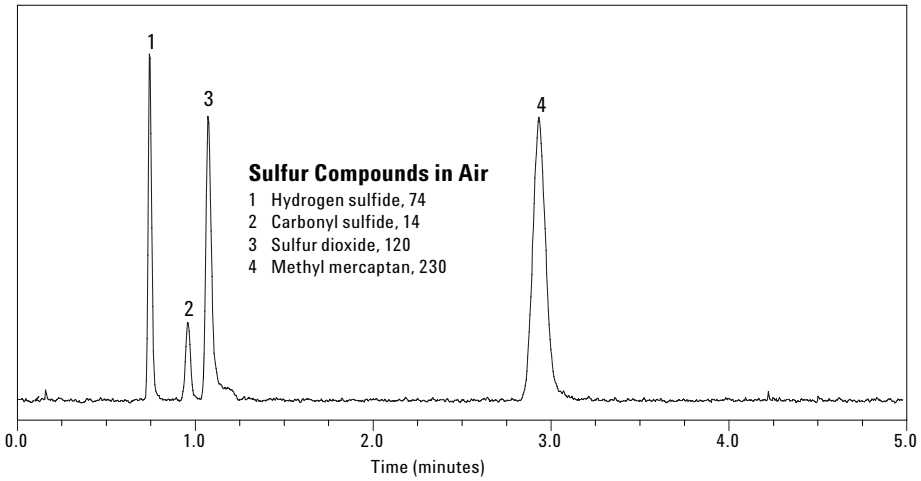
## Introduction

The reliable measurement of sulfur gases in air is extremely important. Many sulfur compounds are toxic and notorious for their obnoxious odors even when present at only parts per billion levels. Gaseous sulfur compounds may be generated and emitted by various industrial processes, such as petroleum refining, ore smelting, and kraft paper pulping. Measurement of gaseous sulfur compounds aids in protection of the environment and human health. There are numerous natural sources of sulfur gases–vegetation, animals, soils, volcanoes, etc.–and measurement of sulfur gases is also of great importance in understanding atmospheric chemistry.

Gas chromatography with sulfur chemiluminescence detection (SCD) provides a rapid means to identify and quantify various sulfur compounds that may be present in air. Unlike other sulfur selective detectors, such as the flame photometric detector (FPD), the SCD produces a linear and equimolar response to sulfur compounds without significant hydrocarbon quenching or interferences. Furthermore, the Model 355 SCD is at least 10 times more sensitive and 100 times more selective than the FPD.

The following chromatogram illustrates the ability of the SCD to speciate and quantitate sulfur compounds at levels less than 1 ppm in an air sample without any sample preconcentration.

Conditions are as follows: Model 355 SCD operated according to standard conditions; 1 mL sample size; column: 30 m, 0.32 mm id, 4 µm methyl silicone WCOT fused silica; temperature program: –25 °C isothermal. The gas chromatograph was a Agilent Technologies Model 5890 Series II equipped with electronic pressure programming for compressing the initial bandwidth.

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Agilent Technologies

# Agilent Model 355 Sulfur Chemiluminescence Detector (SCD): Thiophene in Benzene

Technical Overview

## Introduction

This overview discusses the analysis of benzene for sulfur contamination. The sensitivity, selectivity, and linear response of the Agilent 355 Sulfur Chemiluminescence Detector (SCD) in the analysis of trace levels of thiophene in benzene illustrates that the Model 355 is well-suited for low-level sulfur analysis.

Benzene is the basic unit of the aromatic class of compounds. The primary sources of benzene are from extraction of hydrocarbon crude distillates, refinery catalytic reforming, carbonization of coal, and the hydrodealkylation of a toluene charge stock. [1] The hydrodealkylation reaction results in the conversion of about 90% of the aromatics in the feed with a selectivity factor of about 95%. Thiophene, which also occurs in the light hydrocarbon fractions distilled from crude stocks and coal tar, is present in levels from 0.4 to 1.4 wt. %. [2] Traditionally, thiophene has been extracted by washing with $H_2SO_4$ to produce a sweeter product. However, this and other processes of thiophene removal still have difficulty reaching the level of purity required by many chemical markets. Consequently, it is often important to monitor trace levels of thiophene in benzene. The three main applications for benzene are production of ethylbenzene, cumene, and cyclohexane. These three products account for 80% of the benzene consumed as a chemical feedstock. [2]

These species can be classified as intermediates for a wide range of final products, including dyes, resins, solvents, and polymers, including nylon. The purity requirements for synthetic applications continue to become more confining, thereby increasing the need to monitor sulfur removal efficiency and to verify the purity of starting materials.

The data in Figure 1 illustrate the sensitivity of the 355 SCD for trace level analysis of sulfur in a hydrocarbon matrix without interference. Figure 2 displays the linear response of the SCD at trace levels. Correlation coefficients for five orders of magnitude were better than $R^2 = 0.999$. The selectivity of the 355 SCD for sulfur over hydrocarbon is shown in Figures 1 and 3, where sulfur chromatograms show no hydrocarbon interference from the eluting benzene.

The data in Figures 1 and 2 were collected on a Agilent 6890 gas chromatograph with a Agilent 355 SCD directly attached. The chromatograms in Figure 3 were collected simultaneously without column splitting, using the flame ionization detector attachment to the SCD. The chromatographic conditions for the trace analysis are summarized in Table 1.

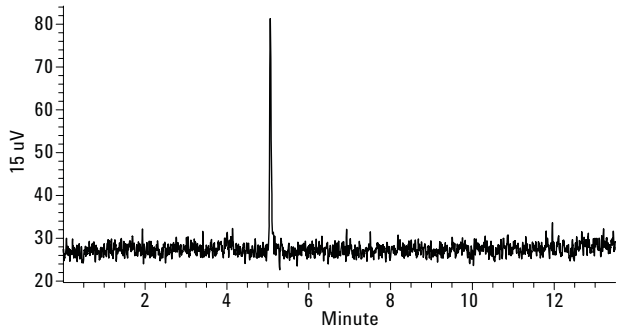


**Figure 1. Chromatogram illustrating the analysis of 15 ppb thiophene (as sulfur, split 1:10).**

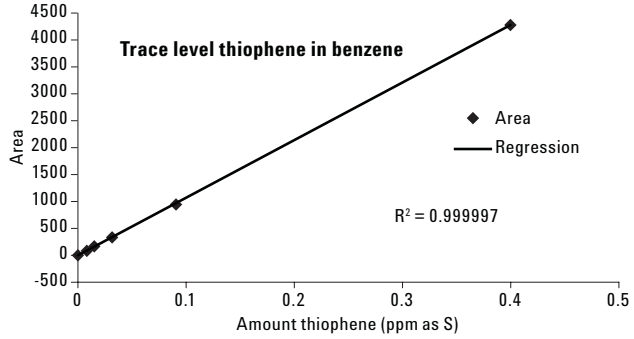


**Figure 2. Linearity of trace level analysis of thiophene in benzene.**

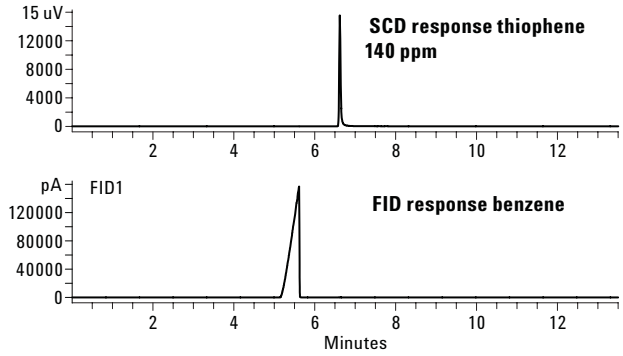


**Figure 3. Simultaneous FID-SCD chromatogram on SUPELCOWAX-10.**



**Table 1. Chromatographic Conditions**

| | |
|---|---|
| Injection temperature | 120 °C |
| Injection volume | 1 µL |
| Initial temperature | 30 °C |
| Initial time | 2 min |
| Rate | 10 °C/min |
| Final temperature | 125 °C |
| Final time | 2 min |
| Split ratio | 1:10 |
| Flow mode | Constant flow |
| Column flow | 2 mL/min |
| Column type | SUPELCOWAX-10 |
| Length | 30 m |
| Internal diameter | 0.32 mm |
| Film thickness | 1 µm |

## References

1. James H. Gary and Glenn E. Handwerk, "Petroleum Refining Technology and Economics," Marcel Dekker Inc., New York, NY, 1984, Chapter 14.

2. Wolfgang Y. Gerhartz, Stephen Yamamoto, et. al. eds., "Ullmann's Encyclopedia of Industrial Chemistry," VCH Publisher, Deerfield Beach, FL, 1985, vol. A3.

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# Agilent 355 Sulfur Chemiluminescence Detector (355 SCD): Sulfur Compounds in Ethylene and Propylene

Technical Overview

## Introduction

This technical overview briefly describes the analysis of ethylene and propylene gases for trace amounts of hydrogen sulfide and carbonyl sulfide as well as other volatile sulfur compounds using gas chromatography and sulfur selective detection. The method provides for the determination of individual volatile sulfur-containing compounds, as well as the determination of total sulfur content in chemical feedstocks.

The measurement of trace amounts of volatile sulfur compounds in ethylene and proplyene is important because of the contaminant nature of these compounds in hydrocarbon feedstocks. Accurate gas chromatographic determinations of trace volatile sulfur compounds involve unique analytical difficulties due to the chemical nature of these compounds. Volatile sulfur compounds are particularly reactive and adsorptive in nature, making trace level analysis reliant on exceptionally good chromatographic technique, using inert sample handling systems and valving, and selective detection that is minimally affected by matrix interference. Because of their respective boiling point ranges, the measurement of hydrogen sulfide in ethylene and carbonyl sulfide in propylene is generally of great concern.

This analysis is especially difficult using detectors such as the flame photometric detectors, where coelution of the analyte and solvent contribute to hydrocarbon quenching and interference, which may result in erroneous results. The following chromatograms illustrate the ability of the SCD to selectively detect trace levels of volatile sulfur compounds in hydrocarbon gas samples without suffering from any quenching or interference from the hydrocarbon matrix.

The analyses presented here were performed on an Agilent 5890 Series II gas chromatograph equipped with a split/splitless injector. The Agilent Model 355 Sulfur Chemiluminescence Detector (SCD) was directly connected to an Astec Gaspro capillary column and operated according to standard conditions.

Figure 1 illustrates the power of the 355 SCD for the analysis of COS in propylene. A 1-mL propylene sample containing 60 ppb wt sulfur as COS was introduced to the GC with no pretreatment. The injector was operated with a split ratio of 1:6, and the linear velocity was approximately 38 cm $sec^{-1}$. Temperature programming for this analysis was as follows: 50 °C for 1 min to 100 °C at 10 °C/min. This chromatogram verifies the selectivity of the Agilent 355 SCD for sulfur over carbon, with no hydrocarbon response or anomalies visible in the baseline. Also evident is the sensitivity of the SCD to sulfur species, making it ideal for trace analysis.

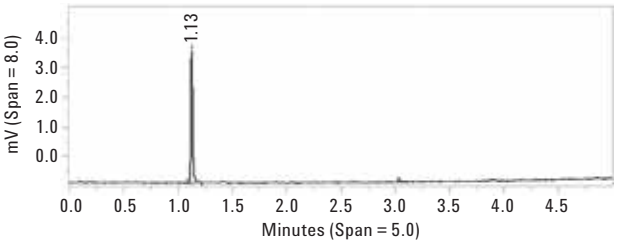


**Figure 1. 60 ppb carbonyl sulfide in propylene.**

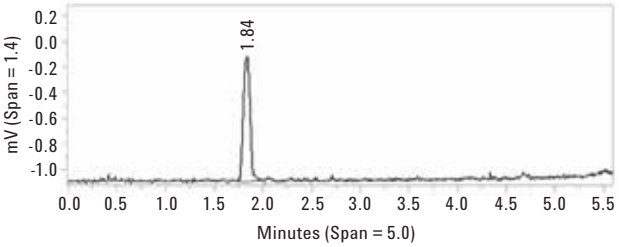


**Figure 2. 100 ppb hydrogen sulfide in ethylene.**

Figure 2 illustrates the analysis of 100 ppb hydrogen sulfide in ethylene using the GasPro column and SCD. As above, a 1-mL sample (gas) volume was introduced with a split 1:6. The oven temperature program started at 40 °C for 1 min and raised at 10 °C/min to the final temperature of 100 °C. In this case the temperature ramp for the analysis was deliberately set so that there would be a simultaneous elution of the ethylene and the hydrogen sulfide. As expected, this resulted in the exhibited band broadening; however, there was no evident quenching of the sulfur response and no hydrocarbon response or baseline anomalies. Although the SCD works well under these conditions, it is always recommended to separate the analyte from the matrix if at all possible to reduce solvent effects.

Recent developments in chromatographic column technology allow the ambient separation of hydrogen sulfide and carbonyl sulfide in hydrocarbon matrices. For ambient separation of $H_2S$ and COS as well as light mercaptans and sulfides, capillary columns such as the Chrompack CP-SilicaPLOT (30 m 0.32 mm id) or the Astec Gaspro (15 m 0.32 mm id) are ideal. The retention characteristics of these columns are unique and seem to be best suited for light applications.

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