A compilation of Application Notes from the
Agilent Information Pipeline eNewsletter

TOOLS AND TECHNIQUES THAT KEEP YOU PRODUCTIVE, PROFITABLE, AND COMPLIANT

The Measure of Confidence

Agilent Technologies

INTRODUCTION

Overcome today's challenges – and prepare for what lies ahead

Regulatory requirements, efficiency improvements dictated by cost containment, and good environmental stewardship impose tough demands on your industry… and your lab.

No matter where you are in the energy and chemical supply chain, Agilent can help you stay compliant, increase productivity, and ensure quality.

Agilent is your single-source for instruments, applications, supplies, services, data handling, and information management technologies. Our standard and custom analyzers are configured for your specific applications – whether you need to perform detailed speciation of complex hydrocarbon streams, calculate gas calorific values, assess the efficiency of your fuel cell stack, or analyze new biofuel formulations. And as always, our product and application experts are available to help you maximize productivity and profitability, while maintaining stringent industry standards.

In this compendium, you'll find a compilation of hand-selected Application Notes from past Agilent Information Pipeline eNewsletters – ranging from crude oil, natural gas, and refining… to specialty chemicals and alternative fuels.

AGILENT'S INFORMATION PIPELINE

Keep informed of what's happening in the energy and chemical industries. Subscribe to Agilent Information Pipeline at **agilent.com/chem/pipeline-contactus**

Learn more about solutions for the energy and chemical industry at **agilent.com/chem/energy**

TABLE OF CONTENTS

Click the text headers to jump to a specific page in this compendium.

ASTM

HYDRAULIC FRACKING

HYDRAULIC FRACKING (CONTINUED)

BIOFUELS

SIMULATED DISTILLATION

POLYMERS

PLOT COLUMNS

BACKFLUSH

AGILENT 7890B GC

Search for words or phrases used in any of the enclosed Applications Notes by clicking on the **Search** button below.

SEARCH

ASTM AND AGILENT

Creating the standards we all rely on

Since 1898, ASTM has developed more than 12,000 international voluntary consensus standards and testing methods. Today, ASTM is the recognized arbiter of analytical methods used by the energy and chemical industry to improve product quality, enhance safety, build consumer confidence, and determine market value.

Agilent scientists have spent more than 40 years – or a combined total of 200 analyst years – working with ASTM to build the material specifications and analytical methods upon which the energy and chemical industry depend.

Our employees serve as members, committee chairs, validation study participants, method developers, and technical presenters – while seeking intelligence about emerging needs that helps Agilent remain on the cutting edge of science.

As a result, Agilent instruments not only meet or exceed ASTM standards… but they are often the instruments on which these standards are developed.

Back to table of contents ▶

Learn more about solutions for the energy and chemical industry at **agilent.com/chem/energy**

Parallel GC for Complete RGA Analysis

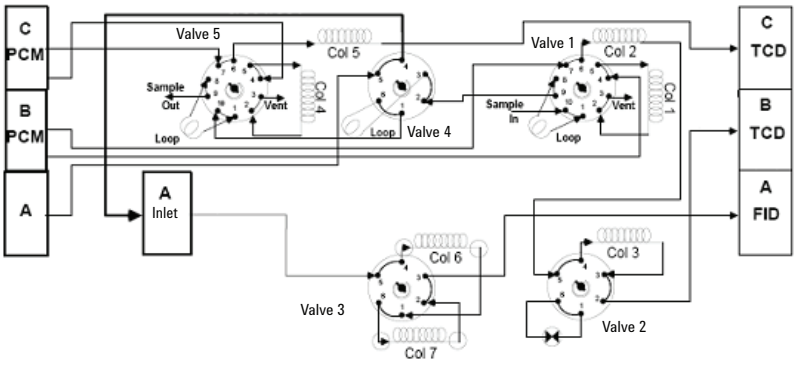
Application Brief

Chunxiao Wang

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

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

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



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

Figure1. RGA valve system.

Highlights

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

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

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

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

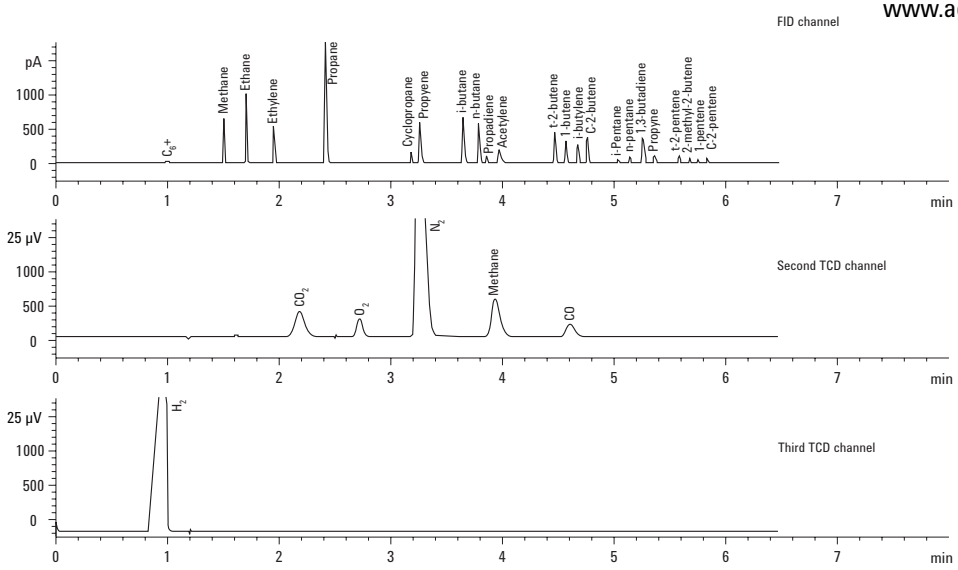


Figure 2. Refinery gas calibration standards analysis.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Reference

1. Chunxiao Wang, "Parallel GC for Complete RGA Analysis,"Agilent application brief, 5989-6103EN, January 19, 2007
2. ASTM D1945-03, "Standard Test Method for Analysis of Natural Gas by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
3. ASTM D1946-90 (2006), "Standard Practice for Analysis of Reformed Gas by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
4. UOP Method 539, "Refinery Gas Analysis by Gas Chromatography,"ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428, USA.

Published in the USA
December 12, 2008
5989-7438EN

Dual Channel Simulated Distillation of Carbon and Sulfur with the Agilent 7890A GC and 355 Sulfur Chemiluminescence Detector

Application Note

Hydrocarbon Processing

Authors

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

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

Abstract

Two-channel simulated distillation by gas chromatography (GC) for both hydrocarbons and sulfur is described. The method utilizes a 7890A GC configured with a high-temperature programmable temperature vaporizer (HT-PTV) inlet and a sulfur chemiluminescence detector (SCD) mounted in series with a flame ionization detector (FID) by use of a special mounting adapter. A simulated distillation (SimDis) software program provides an easy-to-use solution for sulfur and hydrocarbon simulated distillation. The data show that observed boiling point (BP) values agree with the ASTM D2887 consensus BP values within the allowable differences. The system also demonstrates very good repeatability for both hydrocarbon and sulfur SimDis. An example of a light cycle oil (LCO) analyzed according to D2887 is also included.

Agilent Technologies

Introduction

Sulfur and hydrocarbon simulated distillation results provide meaningful information to optimize refining processes and ensure compliance with petroleum product specifications. A previous application note [1] describes a 6890 GC based system for hydrocarbon simulated distillation by ASTM D2887 [2]. Now with the highly selective Agilent Sulfur Chemiluminescence Detector (SCD), sulfur simulated distillation is possible. This 7890A GC based simulated distillation system consists of acquiring and analyzing simultaneously the specific detector data for hydrocarbon (FID) and sulfur (SCD).

Experimental

This two-channel SimDis application uses the Agilent 7890A GC configured with a high-temperature programmable temperature vaporizer (HT-PTV) inlet, and an SCD mounted onto an FID using a special adapter. Detailed GC conditions used are listed in Table 1.

Table 1. 7890A Gas Chromatographic Conditions (1) D2887, (2) D7213

HT-PTV inlet typical temperature programs	(1) 225 to 350 °C (hold 15 min) at 200 °C/ min to 225 °C at 100 °C /min (2) 50 to 420 °C (hold 15 min) at 200 °C /min to 50 °C at 100 °C /min
Split ratio	(1) 4:1 for diluted sample, 20:1 for nondiluted sample (2) 1:1
Injection volume	(1) 0.1 µL (2) 0.5 to 1 µL
Column	(1) HP-1 10 m × 530 mm × 0.88 µm (19095z-021) (2) DB-HT-SimDis 5 m × 530 mm × 0.15 µm (145-1001)
Column flow (He)	(1) 13 mL/min, constant flow mode (2) 16 mL/min, constant flow mode
FID temperatures	(1) 350 °C (2) 400 °C
H_2 flow	40 mL/min
Air flow	400 mL/min
Make up (N_2)	40mL/min
SCD	
Burner temperature	800 °C
Vacuum of burner	324 torr
Vacuum of reaction cell	11.6 torr
H_2	40 SCCM
Air	8.3 SCCM
Oven programs	(1) 35 °C (hold 0.5 min) to 350 °C at 20 °C/min , hold 10 min (2) 40 to 420 °C at 20 °C/min , hold 6 min
Data acquisition rate	5 Hz typical

SimDis Software

The processes of SimDis analysis include: blank analysis for baseline subtraction, calibration for establishing the relationship between boiling point and retention time (RT), validation for verifying both the chromatographic conditions and calculations in the method, and sample analysis. The Agilent SimDis software divides these functions under separate tabs that make navigation and data processing straightforward. The software is based on four modules: Browse, Setup, SimDis, and Report. For example, the Setup module allows you to configure the files to use for BP calibration, blank selection, and QC reference. Partial integration with the GC ChemStation sequence makes automated data analysis possible.

Processing Two Signals

The software can process one or two channels of signal data (FID and SCD for example) from GC ChemStation data files. When working with dual channels, the SimDis software requires that each channel be labeled by the detector type rather than the defaults used by the GC ChemStation. Since the SCD operates off the analog input board (AIB), its signal begins with "AIB." For this reason, the post-run command macro SCDnamer.mac must be run to rename the signal file. The macro renames the AIB2B.ch channel as SCD1.ch. If the channel name is not corrected, the software will switch the FID and SCD channels during analysis, giving faulty results. The macro code to do this is shown below. It assumes the AIB is in the rear position (B).

```
!=======================================
! SCDNamer call this as a post run command when an SCD is installed
! it renames the dual channel AIB2B.ch to SCD1.ch to allow simdis to
! properly calibrate
!=======================================
NAME SCDNamer
! This macro renames the SCD files named as AIB2B.ch to SCD1.ch
if filestat(mode,dadatapath$+dadatafile$+"\AIB2B.CH")=1
rename dadatapath$+dadatafile$+"\AIB2B.ch",dadatapath$+dadatafile$+"\SCD1.ch"
print "File Renamed"
else
print "No AIB2B File found"
endif
RETURN
ENDMACRO
```

Results and Discussion

Calibration

A calibration mixture containing a series of known n-alkanes can be used for establishing the relationship between BP and RT. C5 to C40 is used for ASTM D2887, and Polywax 500 dissolved in toluene is used to calibrate ASTM D7213 [3]. Since both are too viscous or waxy at ambient temperature to sample with a syringe, they need to be heated manually to approximately 80 °C before injection. RT repeatability is key for consistent correlation of BP and RT. Figure 1 and Figure 2 show overlays of consecutive runs of C5 to C40 and Polywax 500, respectively. Tables 2 and 3 show repeatability for both RT and area.

Polywax 500 Sample Preparation

Place approximately 80 mg of Polywax 500 in a 2-mL vial. Add about 1.5 mL toluene followed by the addition of a suitable mixture of n-paraffins from C5 to C18 (Agilent SimDis calibration No.2). The final concentration should be approximately one part of (C5–C18) to 20 parts of toluene. Initially heat the solution to 80 °C to dissolve the Polywax 500.

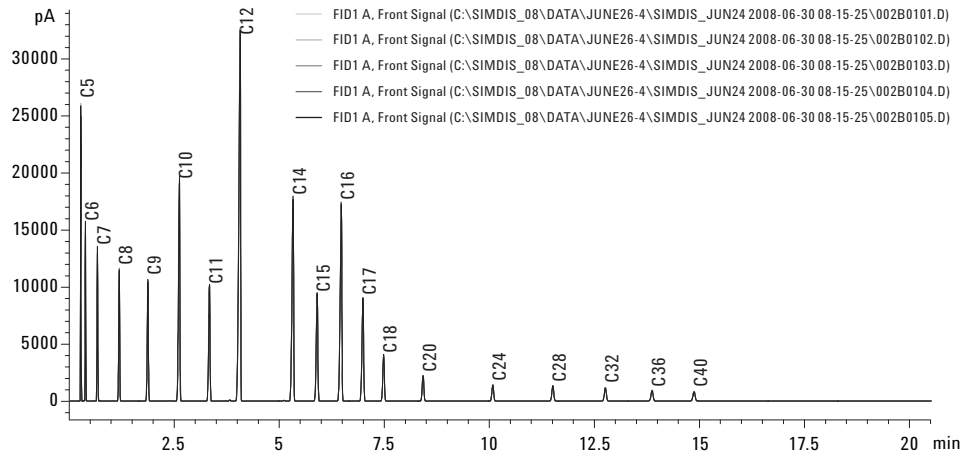


Figure 1. Overlay of five consecutive runs of C5 to C40 calibration mix, vial heated to 80 °C for 3 min prior to injection. GC conditions are listed in Table 1, items (1).

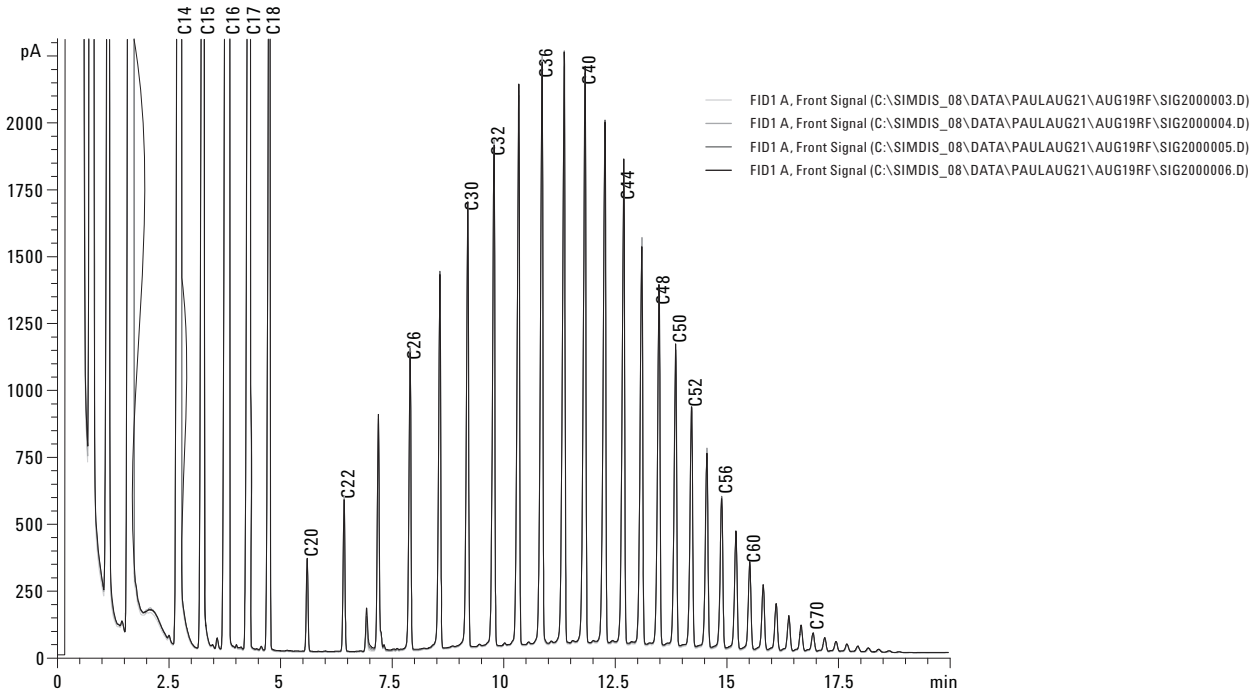


Figure 2. Overlay of four consecutive runs of Polywax 500 plus C5–C18. GC conditions are listed in Table 1, items (2).

Table 2. Repeatability for C5 to C40, n = 10

	Retention Time			Area		
	Average	STDEV	RSD%	Average	STDEV	RSD%
C5	0.275	0.000	0.06	19870	126	0.64
C6	0.388	0.000	0.09	14020	83	0.60
C7	0.673	0.001	0.17	16527	108	0.65
C8	1.192	0.002	0.16	18693	81	0.43
C9	1.874	0.002	0.12	20383	107	0.53
C10	2.622	0.003	0.10	43561	280	0.64
C11	3.338	0.002	0.07	22730	158	0.69
C12	4.068	0.002	0.05	94289	714	0.76
C14	5.327	0.002	0.03	48149	393	0.82
C15	5.902	0.002	0.03	24268	199	0.82
C16	6.477	0.001	0.02	49175	408	0.83
C17	6.991	0.001	0.02	24448	201	0.82
C18	7.485	0.000	0.00	10552	84	0.80
C20	8.424	0.001	0.01	6187	53	0.86
C24	10.083	0.000	0.00	4293	17	0.40
C28	11.512	0.001	0.01	4288	45	1.06
C32	12.762	0.002	0.01	3988	66	1.66
C36	13.874	0.001	0.01	3407	66	1.94
C40	14.874	0.002	0.01	3238	69	2.14

Table3. Repeatability of Polywax 500 Plus C5 to C18, n = 10

	Retention Time			Area		
	Average	STDEV	RSD%	Average	STDEV	RSD%
C14	2.769	0.002	0.07	49126	953	1.94
C15	3.278	0.002	0.05	24337	469	1.93
C16	3.847	0.002	0.05	49304	948	1.92
C17	4.311	0.002	0.05	24597	470	1.91
C18	4.753	0.001	0.03	11374	218	1.92
C20	5.596	0.001	0.01	952	17	1.80
C22	6.424	0.001	0.01	1635	30	1.81
C26	7.904	0.001	0.01	3615	62	1.71
C32	9.783	0.001	0.01	6856	105	1.53
C36	10.858	0.001	0.01	8418	137	1.63
C40	11.823	0.001	0.01	8432	128	1.52
C44	12.690	0.002	0.01	7037	137	1.95
C48	13.480	0.001	0.01	5288	104	1.98
C52	14.208	0.001	0.01	3677	67	1.83
C60	15.512	0.001	0.01	1353	19	1.40
C70	16.931	0.002	0.01	273	5	1.92

QC Reference

A QC reference sample is the basis for quantifying total sulfur and allows the direct entry of response factors for calculation based on total area and user-entered concentrations of sulfur. In this application, a diesel sample (SDF-1X-4, AccuStandard, Inc., New Haven, CT) with a sulfur concentration of 100 µg/g is used as the QC external reference for calibration of response factors for the SCD channel. This is needed for calculation of total sulfur in the sample. Figure 3 shows the graphic pane from the SimDis software for of the QC reference.

Reference Gas Oil Analysis

To meet the requirements of ASTM D2887, the reference gas oil (RGO) sample analysis must be performed to verify both the chromatographic performance and the calculation algo-

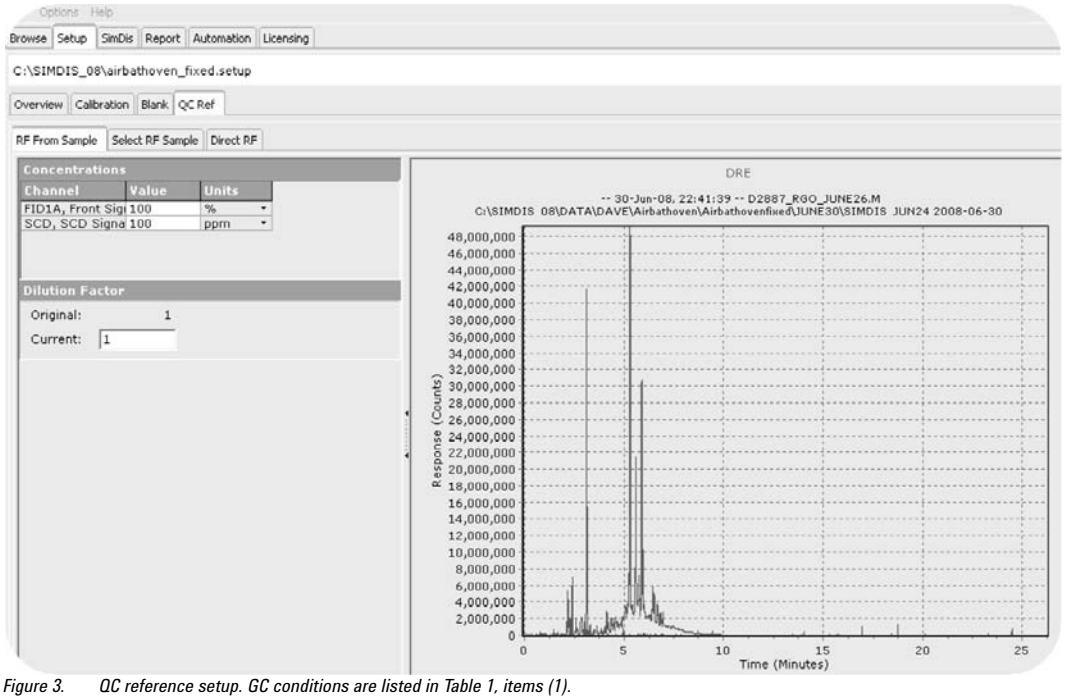


Figure 3. QC reference setup. GC conditions are listed in Table 1, items (1).

rithms involved in this test method. Figure 4 shows the chromatograms of RGO for both the hydrocarbon and sulfur channels. Tables 4 and 5 show the results for six runs of RGO analysis. The data show that observed BP values agree with the ASTM D2887 consensus BP values within the allowable differences and with good repeatability.

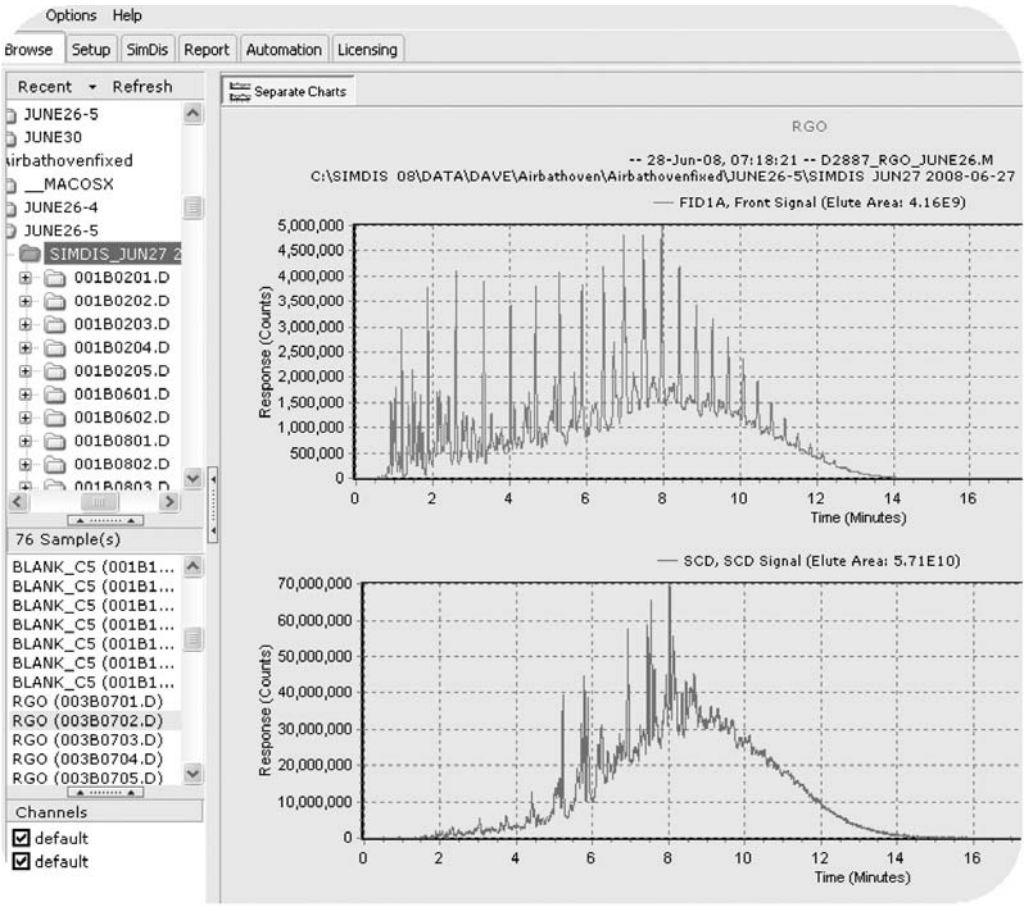


Figure 4, Chromatograms of RGO for hydrocarbon and sulfur channels. GC conditions are listed in Table 1, items (1).

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

	ASTM D2887 Values										
OFF %	BP, °C	Allowable Difference	1	2	3	4	5	6	Average	Difference	RSD%
IBP	115	7.6	114	114	114	114	114	114	114	1	0.00
10%	176	4.1	174	174	174	174	174	174	174	2	0.00
20%	224	4.9	223	223	223	223	223	223	223	1	0.00
30%	259	4.7	258	258	258	258	258	258	258	1	0.00
40%	289	4.3	287	287	287	287	287	287	287	2	0.00
50%	312	4.3	311	311	311	311	311	311	311	1	0.00
60%	332	4.3	330	330	330	330	330	330	330	2	0.00
70%	354	4.3	352	352	351	352	352	352	352	2	0.12
80%	378	4.3	376	376	376	376	376	376	376	2	0.00
90%	407	4.3	405	405	405	405	405	405	405	2	0.00
FBP	475	11.8	471	471	471	471	471	471	471	4	0.00

Table 5. Sulfur SimDis Results for Reference Gas Oil, BP in °C

OFF%	1	2	3	4	5	6	Average	STDEV	RSD%
IBP	168	169	169	167	165	169	168	1.60	0.95
10%	265	265	265	265	265	265	265	0.00	0.00
20%	293	293	293	293	293	293	293	0.00	0.00
30%	314	314	314	314	314	314	314	0.00	0.00
40%	329	330	330	330	330	330	330	0.41	0.12
50%	344	344	344	344	344	345	344	0.41	0.12
60%	359	359	359	360	360	360	360	0.55	0.15
70%	376	376	377	377	377	377	377	0.52	0.14
80%	396	396	396	397	397	398	397	0.82	0.21
85%	408	408	408	409	409	409	409	0.55	0.13
90%	422	422	423	423	424	424	423	0.89	0.21
FBP	495	495	495	499	499	501	497	2.66	0.53

Light Cycle Oil Analysis

To illustrate repeatability, chromatographic overlays are shown in Figures 5a and 5b for an LCO sample. Tables 6 and 7 list the results for hydrocarbon and sulfur SimDis, respectively. The average total sulfur content calculated is 248 ppm with 3.5% RSD.

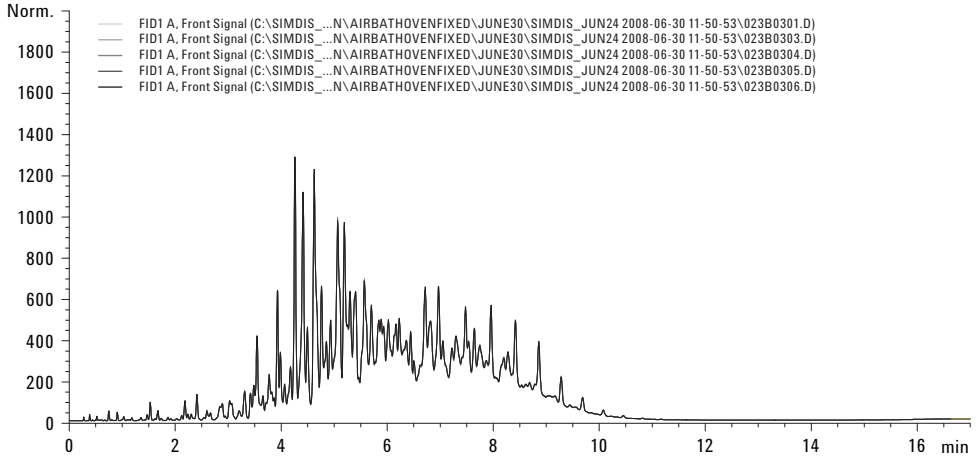


Figure 5a. Carbon SimDis of LCO. Five-run overlay.

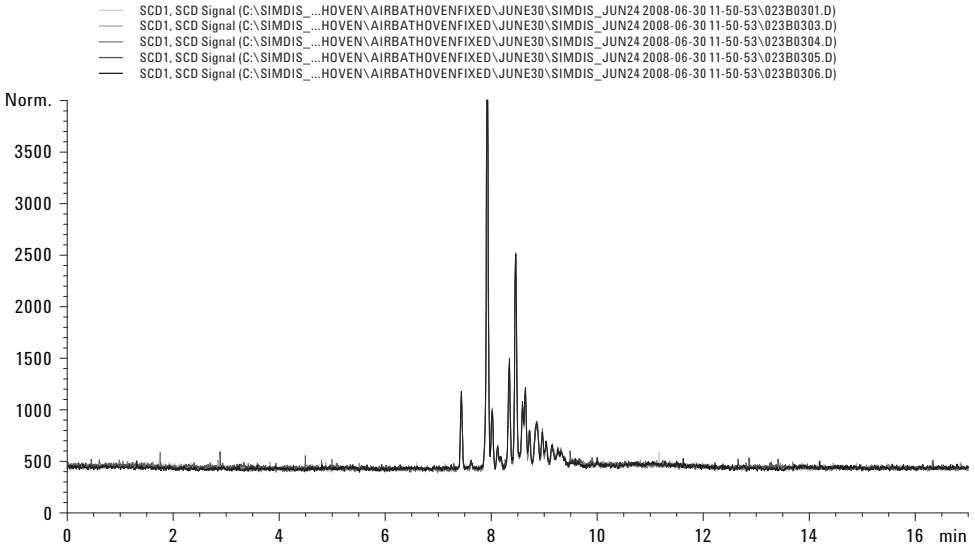


Figure 5b. Sulfur SimDis of LCO. Five-run overlay.

Table 6. Carbon SimDis Results for LCO, BP in °C

OFF%	1	2	3	4	5	Average	SD	RSD%
IBP	141	140	140	140	139	140	0.71	0.51
10%	221	221	221	221	221	221	0.00	0.00
20%	233	233	233	233	234	233	0.45	0.19
30%	247	247	247	247	247	247	0.00	0.00
40%	260	260	261	260	261	260	0.55	0.21
50%	274	275	275	275	275	275	0.45	0.16
60%	291	292	292	292	292	292	0.45	0.15
70%	306	307	307	307	307	307	0.45	0.15
80%	324	324	324	324	324	324	0.00	0.00
90%	344	344	344	344	344	344	0.00	0.00
FBP	391	391	391	391	392	391	0.45	0.11

Table 7. Sulfur SimDis Results for LCO, BP in °C

OFF%	1	2	3	4	5	Average	SD	RSD%
IBP	314	314	314	314	314	314	0.00	0.00
10%	328	329	328	328	328	328	0.45	0.14
20%	329	329	329	329	329	329	0.00	0.00
30%	329	329	329	329	329	329	0.00	0.00
40%	332	332	332	332	332	332	0.00	0.00
50%	342	342	342	342	342	342	0.00	0.00
60%	345	345	345	345	345	345	0.00	0.00
70%	347	347	346	346	347	347	0.55	0.16
80%	351	351	350	350	351	351	0.55	0.16
90%	359	359	357	359	358	358	0.89	0.25
FBP	375	375	371	374	371	373	2.05	0.55
Sulfur, ppm	254	250	240	238	258	248	8.62	3.48

Conclusions

This new SimDis procedure utilizes a 7890A GC configured with the HT-PTV inlet, and an SCD mounted in series with an FID. The Agilent SimDis software is capable of processing both FID and SCD data channels, providing a solution for hydrocarbon and sulfur simulated distillation.

Sulfur simulation distillation has been demonstrated using the Agilent 355 sulfur chemiluminescence detector. With a selectivity over carbon of approximately 10^6, reliable boiling point distributions of sulfur in petroleum fractions can be obtained.

References

1. C. Wang and R. Firor, "Simulated Distillation System for ASTM D2887," Agilent Technologies, publication 5989-2726EN
2. ASTM D2887-06 a,"Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography," Annual Book of Standards, Volume 05.01, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA
3. ASTM D 7213-05, "Standard Test Method for Boiling Point Distribution of Petroleum Distillates from 100 °C to 615 °C by Gas Chromatography," Annual Book of Standards, Volume 05.04, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Published in the USA
December 5, 2008
5990-3237EN

Agilent Technologies

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

Chunxiao Wang and Wenmin Liu

Application Brief

HPI

Knowledge of impurities in benzene provides critical quality control information where benzene is either produced or used in a manufacturing process. ASTM D4492 [1] was used for analyzing these impurities, including nonaromatics containing up to nine carbon atoms, toluene, C8 aromatics, and 1,4-dioxane. The Agilent 7820A gas chromatograph offers an efficient and easy-to-use platform for the analysis of benzene and may other aromatic solvents. For this application, an Agilent 7820A GC is configured with a split/splitless capillary inlet and a flame ionization detector (FID). Agilent EZChrom Elite Compact software is used to control the 7820A GC and provide data acquisition/data analysis. The Agilent 7820A GC supports an automatic liquid sampler (ALS), allowing fully unattended operation – from injection all the way through final reporting.

Experimental

Table 1. Typical GC Conditions

Inlet settings	250 °C, Split ratio: 100:1 to 30:1
Injection volume	0.5 µL
Column	HP-INNOWax 60 m × 0.32 µm × 0.5 µm
Column flow (He)	2.6 mL/min (21.8 at 75 °C), constant flow mode
Oven temperature program	For impurities in benzene: 75 °C (10 min); 3 °C/min to 100 °C For aromatic solvent: 75 °C (10 min); 3 °C/min to 100 °C 10 °C/min to 145 °C
FID setting	
Temperature	250 °C
H2 flow	40 mL/min
Air flow	400 mL/min
Make up (N2)	25 mL/min
Data acquisition rate:	20 Hz

Highlights

- An easy-to-use, single-column method for benzene as well as a wide range of aromatic solvent purity analyses meets the chromatographic requirements of 10 separate ASTM methods. Therefore fewer GCs, stock columns, and supplies are required to analyze many different types of samples.
- EPC control and automatic injection ensures excellent repeatability for both retention time and peak area.
- The wide dynamic response range of the FID enables a quantitative analysis of samples containing both very high and very low concentrations in a single run.

Agilent Technologies

Discussion

The Agilent 7820A GC with full electronic pneumatics control (EPC) on all inlets and detectors ensures good repeatability and also makes it fast and easy to set and to save the pressures and flows. Figure 1 shows the chromatograms of the D4492 calibration standard. Excellent repeatability for retention time with RSD of approximately 0.03 to 0.01% and peak area with RSD of about 1.6% are shown in Table 2.

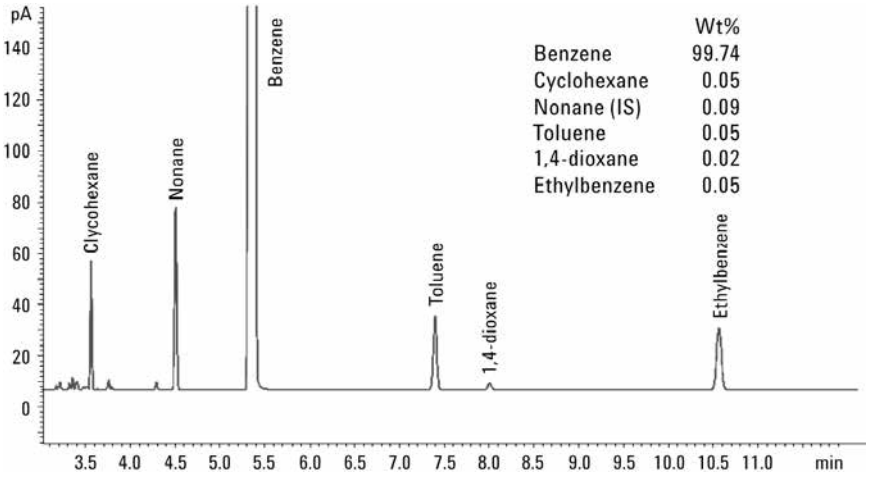


Figure 1. ASTM D4492 benzene calibration standard. *Oven temperature program: 75 °C (10 min); 3 °C/min to 100 °C. Sample size: 0.5 µL, Split ratio: 100:1.*

Table 2. Repeatability–ASTM D4492 Benzene Calibration Standard (11 runs) with First Run Included

	Cyclohexane	Nonane	Bezene	Toluene	1,4-dioxane	Ethylbenzene
			Peak Area			
1	430130	861450	900088289	590385	56288	689141
2	425791	848159	888131170	581775	55693	677502
3	437496	874885	915251703	599534	57071	698269
4	439204	879141	918796665	601857	57355	701225
5	438646	876346	917995860	601138	57056	700462
6	436941	876809	914994185	599823	57743	699919
7	423567	844923	885230656	580241	55487	675473
8	420259	843030	878870585	577475	55392	673593
9	422665	844761	883243038	579572	55419	675665
10	430741	865226	901189833	591633	56211	691217
11	431032	865007	901921807	592037	56118	691200
Mean:	430588	861794	900519436	590497	56348	688515
Std Dev:	6852	14298	14909746	9406	837	11061
%RSD:	1.59	1.66	1.66	1.59	1.49	1.61

Table 2. ***Repeatability–ASTM D4492 Benzene Calibration Standard (11 runs) with First Run Included*** *(Continued)*

	Cyclohexane	Nonane	Bezene	Toluene	1,4-dioxane	Ethylbenzene
			Retention Time			
1	3.562	4.503	5.369	7.397	8.003	10.561
2	3.562	4.504	5.371	7.398	8.005	10.563
3	3.562	4.504	5.371	7.398	8.007	10.565
4	3.561	4.503	5.370	7.398	8.006	10.563
5	3.561	4.503	5.370	7.398	8.006	10.563
6	3.561	4.503	5.369	7.398	8.007	10.563
7	3.561	4.503	5.369	7.398	8.006	10.563
8	3.561	4.503	5.369	7.398	8.006	10.563
9	3.561	4.504	5.370	7.398	8.006	10.563
10	3.563	4.506	5.372	7.400	8.007	10.567
11	3.563	4.506	5.372	7.400	8.009	10.565
Mean:	3.562	4.504	5.370	7.398	8.006	10.564
Std Dev:	0.0008	0.0012	0.0012	0.0009	0.0015	0.0016
%RSD:	0.02	0.03	0.02	0.01	0.02	0.01

The FID has a very wide dynamic response range due to its full digital path. This enables a quantitative analysis of samples containing very high and very low concentrations in a single run. Figure 2 shows that trace impurities spiked in benzene, trace level (10 ppm) ethyl benzene, and > 99% benzene can be quantitative analyzed in a single run.

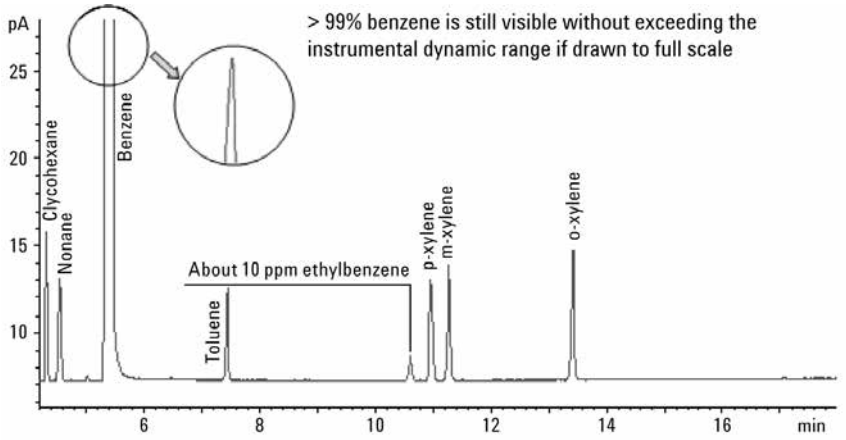
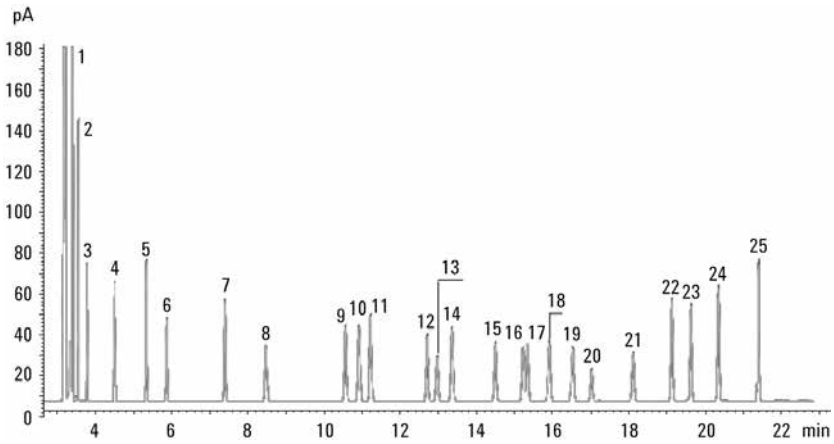


Figure 2. ***Analysis of trace impurities spiked in benzene.*** *Oven temperature program: 75 °C (10 min); 3 °C/min to 100 °C. Sample size: 0.5 µL, Split ratio: 30:1.*

This system is also chromatographically suitable for a wide range of aromatic solvent samples according to 10 different ASTM aromatics methods as mentioned in reference 2. An n-hexane solution was prepared containing 0.1 wt% of aromatic solvents and impurities specified by the 10 ASTM methods for the analysis; the chromatographic overlay of 11 runs demonstrates outstanding repeatability as shown in Figure 3.



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

Figure 3. Chromatographic overlay of 11 runs of aromatic solvent specified by 10 ASTM methods. *Oven temperature program: 75 °C (10 min); 3 °C/min to 100 °C, 10 °C/min to 145 °C. Sample size: 0.5 µL, Split ratio: 100:1.*

References

1. ASTM D4492-98, "Standard Test Method for Analysis of Benzene by Gas Chromatography," Annual Book of Standards, Volume 06.04, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA
2. James D. McCurry, “A Unified Gas Chromatography Method for Aromatic Solvent Analysis,” Agilent Technologies publication 5988-3741EN

Chunxiao Wang and Wenmin Liu and are application chemist based at Agilent Technologies (Shanghai), Co. Ltd., 412 Ying Lung Road, Waigaoqiao Free Trade Zone, Shanghai, 200131 China

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
February 9, 2009
5990-3548EN

Agilent Technologies

Parallel GC for Complete Refinery Gas Analysis

Application

Hydrocarbon Processing

Author

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

Abstract

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

Introduction

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

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

Experimental

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

The FID channel is for light hydrocarbon analysis. The sample from valve 4 is injected via the capillary injector into valve 3 to permit an early back-

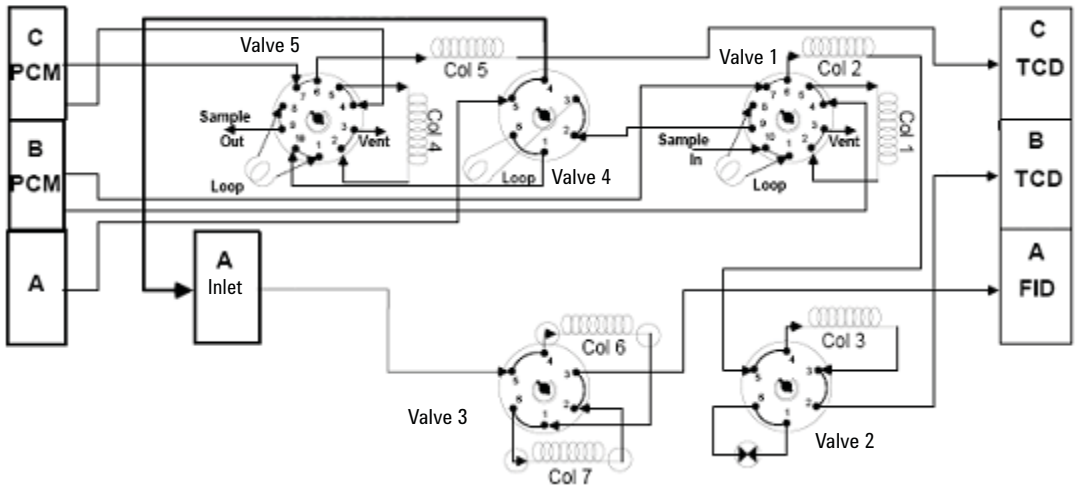
flush of the grouped heavier hydrocarbons (normally C_6+). Valve 3 is a sequence reversal with a short DB1 (column 6) for separating the hexane plus fraction (C_6+) from the lighter components. C_1 through C_5 hydrocarbons are separated on a PLOT alumina column. As soon as the light components C_1 through C_5 pass through the DB1column, valve 3 is switched to reverse the sequence of the DB1 and PLOT aluminum column so that components heavier than nC_6, including nC_6, are backflushed early. As a result, group C_6+ is followed by the individual hydrocarbons from the PLOT alumina column.

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

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

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

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



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

Figure 1. RGA valve system.

Table 1. Typical GC Conditions for Fast Refinery Gas Analysis

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

Table 2. RGA Calibration Gas Standards

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

Results and Discussion

Enhance Gas Analysis with Union Connector

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

Fast Refinery Gas Analysis (RGA)

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

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

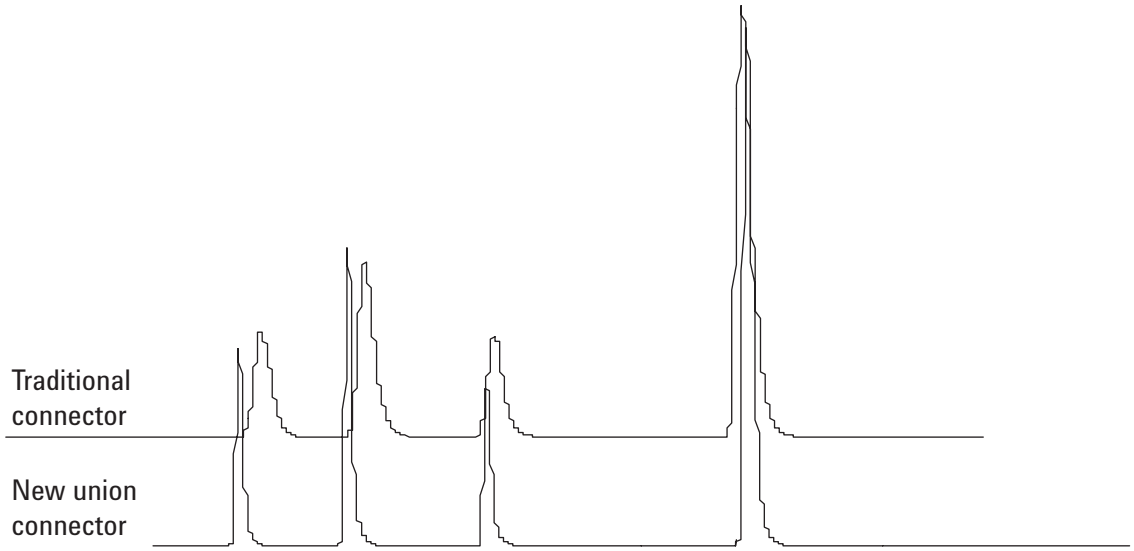


Figure 2. Hydrocarbon peaks obtained from traditional tube connector and new union connector.

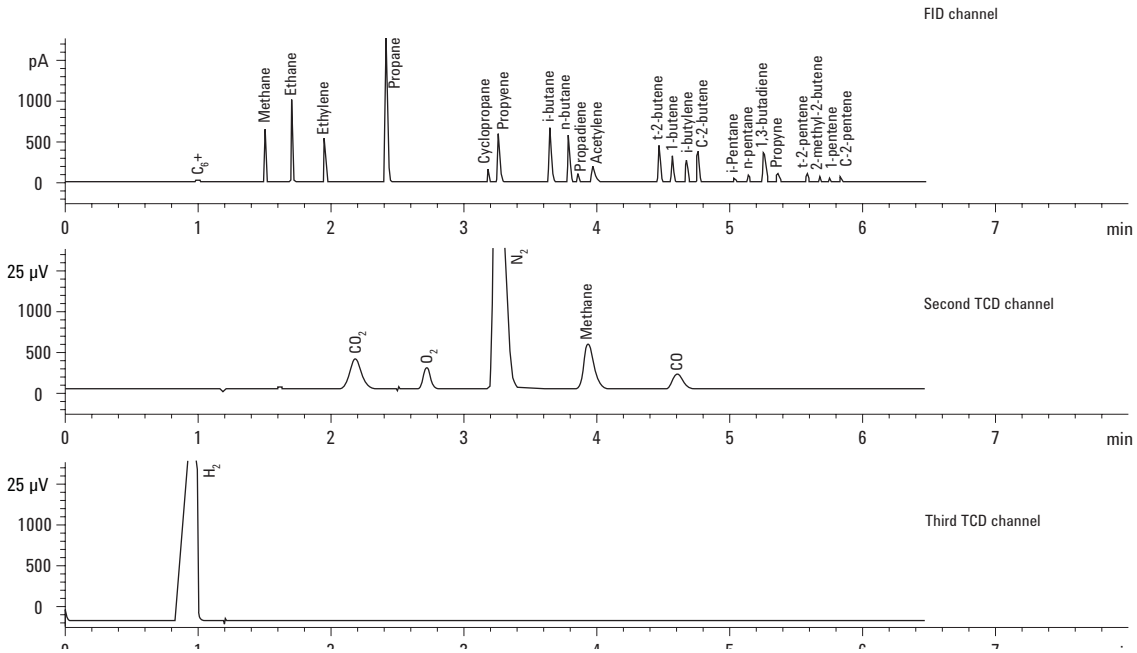


Figure 3. Refinery gas calibration standards analysis. The concentrations for each compound are shown in Table 2.

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

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

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

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

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

Flexibility for Hydrocarbon Analysis

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

H_2S and COS Analysis

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

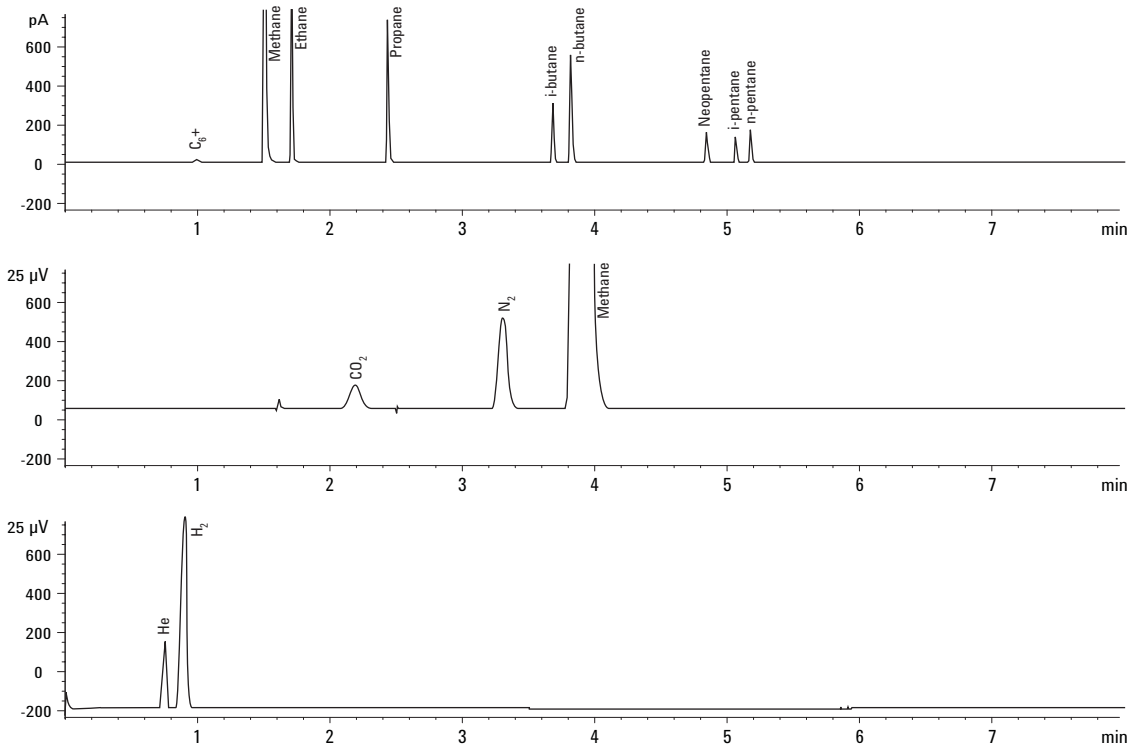


Figure 4. Natural gas analysis of a calibration gas.

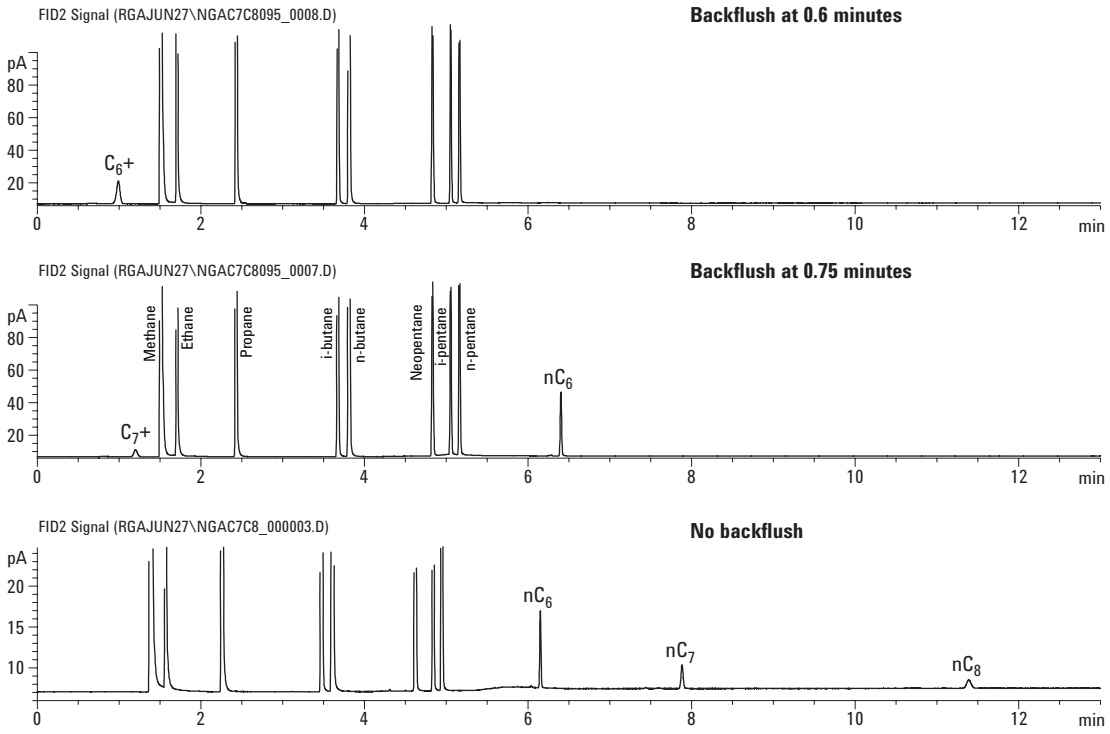


Figure 5. Chromatograms of light hydrocarbons on FID channel with different backflush times .

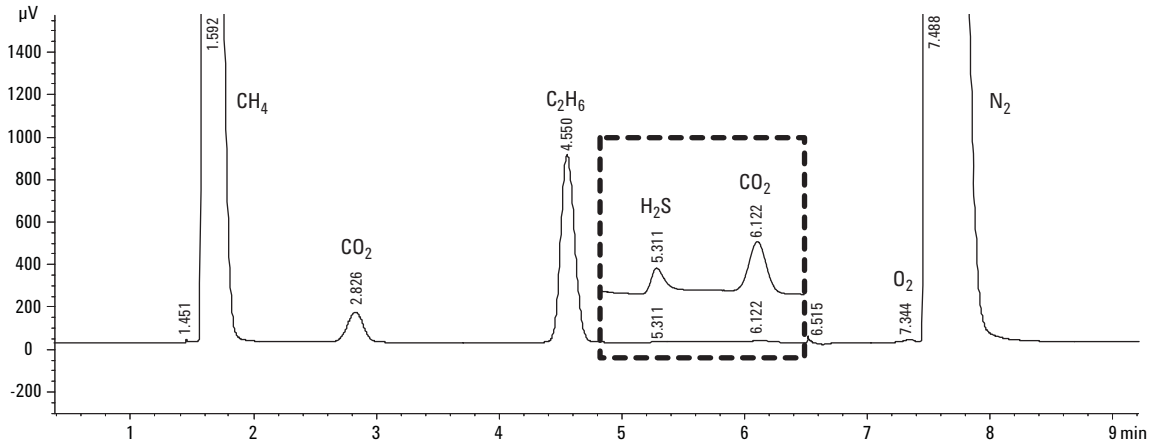


Figure 6. H_2S at approximately 500 ppm and COS 300 ppm on second TCD channel.

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

Reporting

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

Conclusions

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

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

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

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

www.agilent.com/chem

References

1. ASTM D1945-03, “Standard Test Method for Analysis of Natural Gas by Gas Chromatography,” ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
2. ASTM D1946-90 (2006), “Standard Practice for Analysis of Reformed Gas by Gas Chromatography,” ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
3. UOP Method 539, “Refinery Gas Analysis by Gas Chromatography,” ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428, USA.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
September 26, 2007
5989-7437EN

Agilent Technologies

Automated Preparation of Simulated Distillation Samples for ASTM Methods D2887, D7213, D7398 and D6352 using a Dual Tower 7693A and Tray System

Application Note

Hydrocarbon Processing

Authors

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

Abstract

A dual tower 7693A and tray system installed on the 7890A Gas Chromatograph was used for preparation of hydrocarbon calibration standards, solvent blanks, and actual petroleum samples for the purpose of analysis by simulated distillation (SimDis). The front tower is equipped with a 5 or 10 µL syringe while the back tower is equipped with a 250 or 500 µL syringe. A 150 sample tray with heater and mixer/barcode reader is also used. Procedures are described for sample preparation for ASTM D2887, D7213, D7398 and D6352. The Multimode Inlet, G3510, operated in a temperature programmed split mode was used for all samples.

Agilent Technologies

Introduction

Sample and calibration standard preparation for various simulated distillation methods is normally a manual process requiring dilution, mixing, and heating. Many procedures use volatile toxic solvents such as carbon disulfide. ASTM method D2887 commonly uses CS_2 for sample dilution while D6352 may use CS_2 or toluene for polywax calibration standard prepration. Sample heating is required for many of these procedures. Using the automation capabilities of the 7693A tower and tray system improves lab safety as well when working with CS_2 and other solvents by avoiding manual handling and uncontrolled heating of mixtures.

Experimental

For all experiments, the 7890A GC was equipped with dual 7693A towers and tray. The front tower used a standard 5 or 10 µl syringe and the rear tower was equipped with the optional large syringe carriage with either a 250 or 500 µL syringe. Sample prep procedures were done on the rear tower and sample injection occurred on the front tower. The 7890A was configured with the multimode inlet operated in temperature programmed split mode. Detection was with FID. In addition, two 7890A oven systems were used. The first configuration used the conventional air bath oven and the second used the Low Thermal Mass (LTM) system. Instrumental parameters for various configurations are listed in Table 1.

Table 1. 7890A SimDis parameters

LTM System for D2887	
LTM module	5M × 0.32 mm × 0.50 µm DB1, 5 inch format
7890A oven	300 °C isothermal
Inlet	Multimode, 270 °C (0 min) to 355 °C at 200 °C/min
Liner	Single taper with glass wool, 5183-4647
Split ratio	20:1
Pressure program (Inlet)	8 psi (0 min) – 42 psi (0.9 min) at 14 psi/min
LTM program	40 °C (0 sec) to 350 °C (30 sec) at 100 °C/min
Standard System for D2887	
Column	10M × 0.53 mm × 3.0 µm D2887
Oven	40 °C (0 min) to 350 °C (5 min) at 15 °C/min
Inlet	Multimode, G3510, 50 °C (0 min) to 330 °C (4 min) at 200 °C/min
Liner	Single taper with glass wool, 5183-4647
Split	4 to 1
Flow	3.2 psig at 40 °C, constant flow mode
7890A system for D7213 and D7398 (Polywax 500 calibration)	
LTM	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis 5-inch LTM format
Oven	LTM configuration, 7890A oven 325 °C isothermal, module 40 °C (0 min) to 400 °C (30 sec) at 50 °C/min
Inlet	Multimode, 270 °C (0 min) to 400 °C (3 min) at 300 °C/min
Split ratio	4 to 1 and 10 to 1
Pressure program	2.5 psi (0 min) to 9.5 psi (1.0 min) at 1 psi/min
Standard Air Bath Oven	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis
Oven program	40 °C (0 min) to 400 °C (5 min) at 15 °C/min
Inlet	Multimode, 210 °C (0 min) to 400 °C (10 min) at 200 °C/min
Split ratio	4 to 1
Flow	15 mL/min, constant flow mode
7890A system for D6352 (Polywax 655 calibration)	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis
Oven program	40 °C (0 min) to 430 °C (5 min) at 15 °C/min
Inlet	Multimode, 250 °C (0 min) to 430 °C (hold until end of run) at 200 °C/min
Split ratio	4 to 1
Flow	16 mL/min, constant flow mode
7693A System	
Front tower	5 or 10 µL syringe, G4513A
Back tower	250 or 500 µL syringe, G4521A syringe carriage
Tray	150 sample capacity with heater and mixer/barcode reader, G4520A
Inlet	G3510 Multimode, CO_2 cooled
ChemStation	B.04.01
7890A firmware	A.01.10 or greater

Discussion

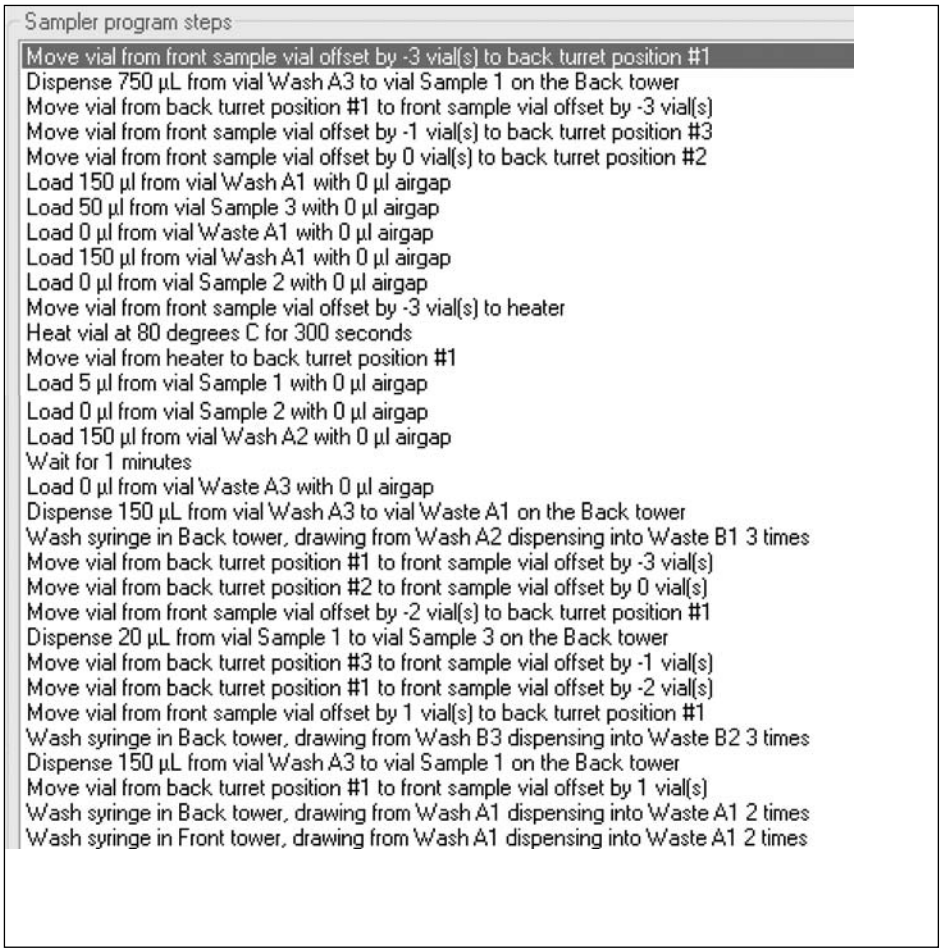
A typical sample preparation program for D2887 setup is shown in Table 2. This illustrates just one way to program preparation of the calibration standard, reference gas oil (RGO), and blank that are necessary to set up a system for routine analyses. The commands can be assembled in other ways to produce the same end result. The following vials and tray locations are used with this program.

Tray position 1	Calibration mix, 0.5 µL of C5 to C40, Agilent part number 5080-8716
Tray position 2	1 mL RGO, Agilent part number 5060-9086
Tray position 3 to 5	Empty vials with 100 µL inserts, Agilent part number 5188-6592

When the procedure is complete, vial 3 will be the prepared RGO for injection, vial 4 will be the prepared calibration mix for injection, and vial 5 will be a CS_2 blank. Next, a three-line sequence is set up that starts with vial 4 (calibration mix). Vial 4 is run with the ChemStation method set with this procedure active, then vial 3 (RGO) and vial 5 (CS2 blank) are run using the same method but with the prep procedure inactive (unchecked in ChemStation's 7890A Injector Program pane under edit 7890A Parameters parameters menu because these samples are already prepared from the method in the first line of the sequence table). For all three samples, the core ChemStation method performs a sample preheat at 80 °C and a sample mix at 500 rpm for 20 seconds before injection. Lastly, the calibration, prepared RGO, and blank vials are fitted with 100 µL inserts so that the solvent amounts used for the procedure are minimized. Please note that when these inserts are used, mixing should be limited to speeds of approximately 500 rpm to avoid "spilling" liquid over the top of the insert into the bottom of the 2-mL vial.

Preparation of polywax standards for the higher temperature SimDis method is always challenging due to their low solubility. Solvents such as CS_2 and toluene are commonly used, and

Table 2. Sample prep procedure for D2887



heating of the solvent/polywax vial is required just prior to injection. This entire procedure can be automated with the 7693A tower and tray system. The basic procedure for Polywax 500 is as follows:

- Place approximately 80–100 mg of Polywax 500 in a 2-mL vial and seal
- Add 125 µL of a C20/toluene solution to the polywax vial
- Add 1.25 mL of toluene to the polywax-C20 vial
- Mix the vial
- Heat the vial at 80 °C for 4 min
- Return to tray
- Heat one final time (3 min. typical) just prior to injection

Table 3 shows the basic prep procedure using a dual tower/tray system automating the steps shown above. The only manual step is adding the solid polywax to Vial 1. Vial 2 contains a C20/toluene mixture. Preparation of this sample could be automated as well. This procedure is applicable to D7213 SimDis and D7398 (Boiling Range Distribution of Fatty Acid Methyl Esters).

A resulting chromatogram from injection of the prepared Polywax 500 vial (vial 1) is shown in Figure 1. A symmetric distribution of the polywax fragments with good resolution to C80 can be seen.

Table 3. Preparation of Polywax 500

Sampler program steps
Wash syringe in Back tower, drawing from Wash A1 dispensing into Waste A1 2 times
Move vial from tray vial #1 to back turret position #1
Move vial from tray vial #2 to back turret position #2
Dispense 1000 µL from vial Wash A2 to vial Sample 1 on the Back tower
Dispense 5 µL from vial Sample 2 to vial Sample 1 on the Back tower
Move vial from back turret position #1 to mixer
Move vial from back turret position #2 to tray vial #2
Mix at 2000 rpm 2 times for 10 seconds
Move vial from mixer to heater
Heat vial at 80 degrees C for 240 seconds
Move vial from heater to tray vial #1
Wash syringe in Back tower, drawing from Wash A2 dispensing into Waste B1 3 times

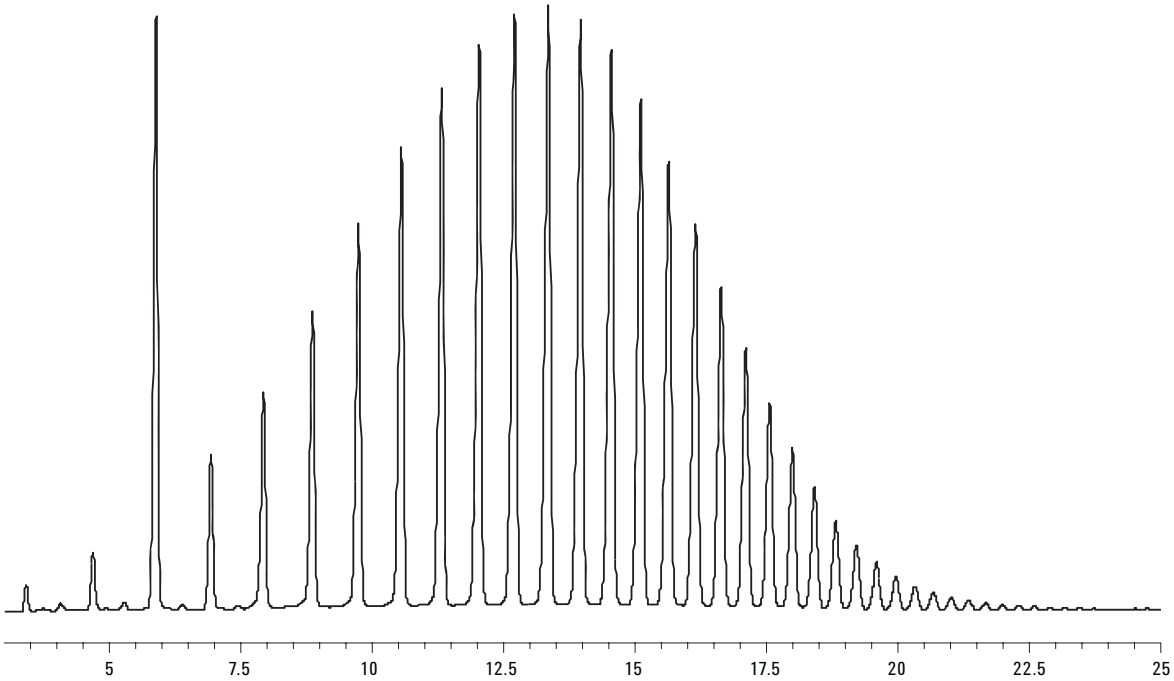


Figure 1. Polywax 500 with C20 marker. Multimode inlet with 7890A oven.

The preparation program for Polywax 655 is essentially the same as shown above for Polywax 500 except that heating is extended to 6 minutes, for better dissolution. Then just prior to injection, the prepared vial is heated for another 3 minutes. In the chromatogram shown below in Figure 2, a small amount (5 µL) of C5-C18 mix was added to the Polywax 655/ toluene solution as part of the automated procedure.

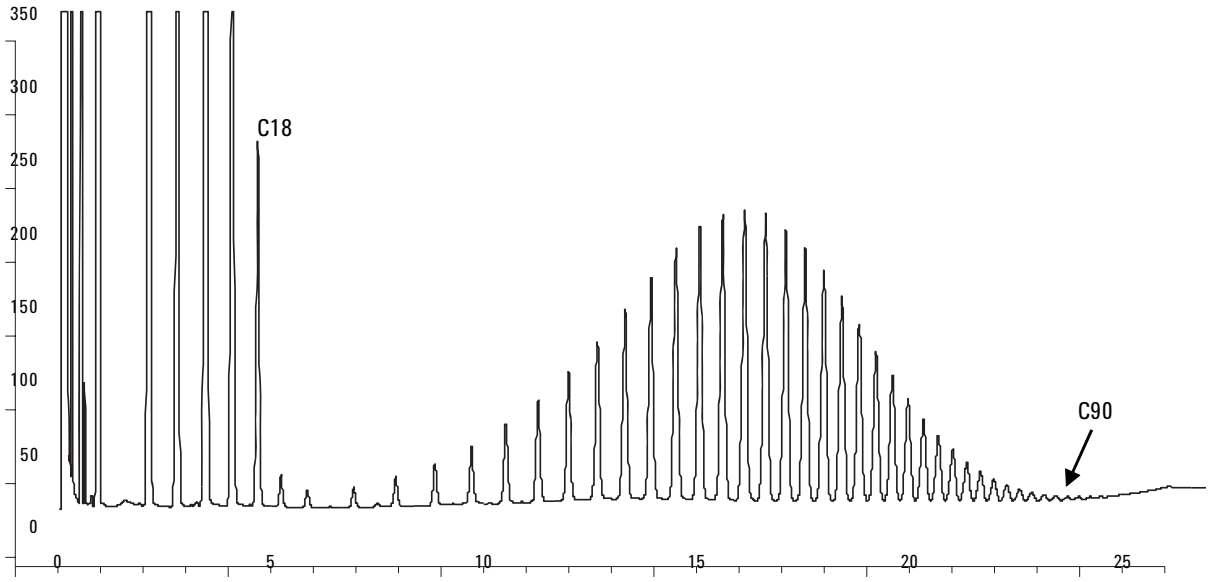


Figure 2. Chromatogram of Polywax 655.

The chromatogram was produced with the multimode inlet used in temperature-programmed split mode. Good definition of polyethylene fragmented to C110 is shown in Figure 3 where the last 5 minutes of the chromatogram are enlarged to show detail. Producing this detail out to C110 is extremely difficult for most chromatographic systems. The 7890A/7693A system produces excellent results with this sample.

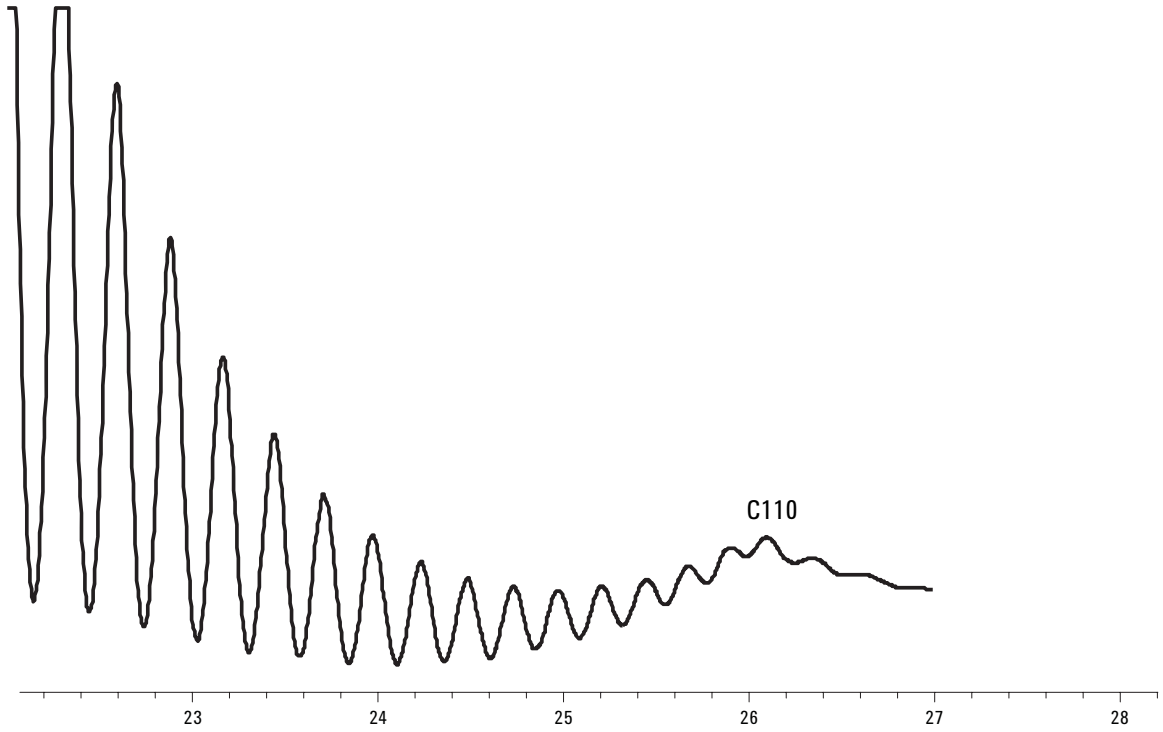


Figure 3. Polywax 655 to C110. Multimode inlet program: 150 °C (0 min) to 430 °C (hold until end of run) at 200 °C/min. 7890A oven: 40 °C (0 min) to 430 °C (5 min) at 15 °C/min. 3 µL injection. Solvent is toluene.

Reproducibility of the sample preparation steps is excellent as seen in Figure 4, for the dilution of a heavy vacuum gas oil sample (HVGO). The program steps that were followed to produce these chromatograms are given in Table 4. The back tower equipped with a 500-µL syringe, was used for sample preparation and the front tower with a 5-µL syringe was used for sample injection. Carbon disulfide was used for sample dilution. This program assumes a sequence is run using vial 2. Vial 1 is the stock HVGO sample that is first prepared by adding 0.5 g of the oil to a 2-mL vial. This material is extremely viscous and cannot be drawn into a syringe. Therefore the program performs a fully automated two-stage dilution prior to injection.

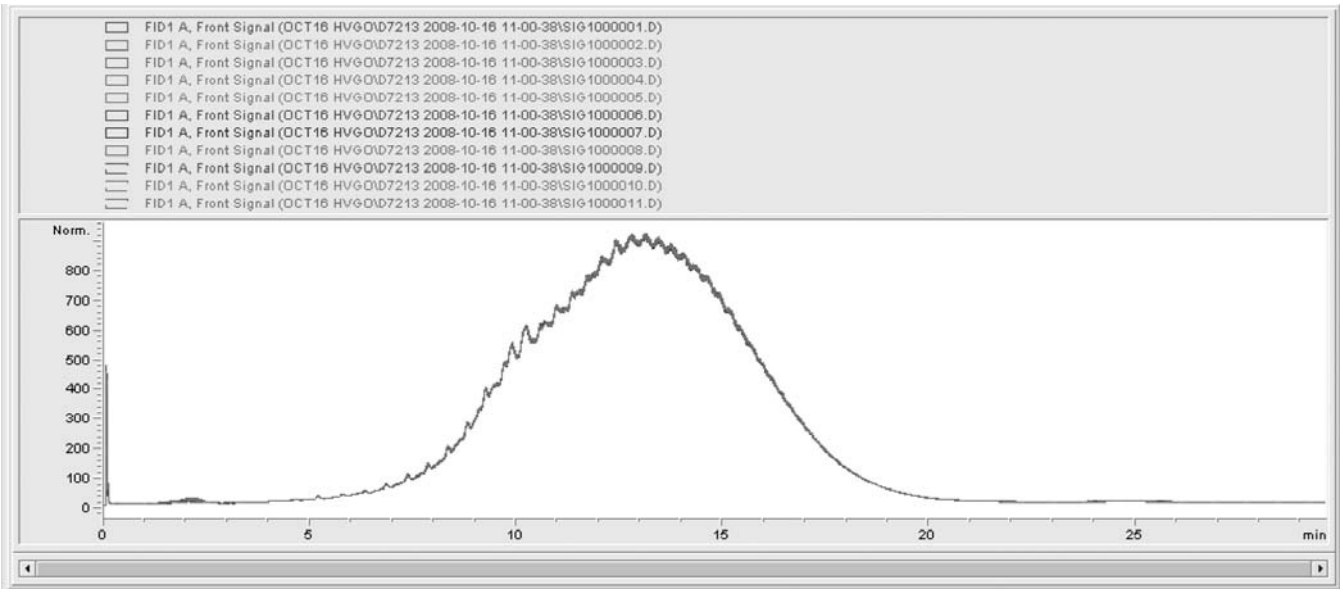


Figure 4. Overlay of 11 runs of HVGO, each prepared using 7693A towers and tray.

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

Sampler program steps
Move vial from front sample vial offset by -1 vial(s) to back turret position #1
Dispense 600 µL from vial Wash A3 to vial Sample 1 on the Back tower
Move vial from back turret position #1 to heater
Move vial from front sample vial offset by 0 vial(s) to back turret position #1
Heat vial at 60 degrees C for 180 seconds
Mix at 3000 rpm 3 times for 20 seconds
Move vial from heater to back turret position #2
Dispense 250 µL from vial Sample 2 to vial Sample 1 on the Back tower
Wash syringe in Back tower, drawing from Wash A3 dispensing into Waste A1 3 times
Dispense 1000 µL from vial Wash A1 to vial Sample 1 on the Back tower
Move vial from back turret position #2 to front sample vial offset by -1 vial(s)
Move vial from back turret position #1 to mixer
Mix at 3000 rpm 4 times for 20 seconds
Move vial from mixer to front sample vial offset by 0 vial(s)

Conclusions

Difficult sample preparation procedures that are commonly used for petroleum and fuel samples can be easily automated with the 7693A tower and tray system for the 7890A and the 6890A. The system is particularly well suited for preparation of polywax calibration samples that are used for higher temperature methods. Tasks such as mixing, solid dissolution, dilution, heating, and internal standard addition are easily accomplished.

Chromatographic performance is enhanced through use of the multimode inlet. Using standard split injection liners, good sample capacity without carryover and with minimal discrimination of wide boiling samples is seen. The inlet was used in the temperature-programmed split mode for this work. Cryo cooling was not used, however, cryo can be used optionally to shorten inlet cool down between runs if desired.

For samples that fall within the boiling point range of D2887, D7213, and D7398, the Low Thermal Mass (LTM) system can be used to shorten typical analysis cycle times by 30 to 50% [1]. The high temperature method D6352 requires the standard 7890A oven.

The sample prep procedures listed here represent just one way of accomplishing a given task. Given the commands available with the system, there are many variants that will lead to the same end result.

Reference

1. C. Wang, R. Firor, and P. Tripp, "Fast Hydrocarbon and Sulfur Simulated Distillation Using the Agilent Low Thermal Mass (LTM) System on the 7890A GC and 355 Sulfur Chemiluminescence Detector," November 2008, Agilent Technologies publication 5990-3174EN.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
March 26, 2009
5990-3778EN

Agilent Technologies

Analysis of Denatured Fuel Ethanol using ASTM Method D5501-09

Application Note

HPI/Energy/Renewable Fuels

Author

James D. McCurry, Ph.D.
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Abstract

Denatured fuel ethanol is the feedstock used to make different types of high ethanol content motor fuels. Before it can be used, the amount of ethanol and methanol must be measured to assure product quality. ASTM method D5501-09 uses high resolution gas chromatography to perform this analysis. In this paper, the Agilent 7890A GC system was configured to run D5501-09. Excellent system performance and precision were demonstrated using the 7890A GC. Combined with the Agilent MultiTechnique ChemStation, this system offers a complete, automated solution for denatured fuel ethanol analysis.

Agilent Technologies

Introduction

Ethanol is a key additive in gasoline, serving both as a smog reducer as well as a fuel supplement to reduce the overall use of petroleum. It is relatively easy to produce by fermenting sugars obtained from food crops such as corn and sugar cane. However, the future of ethanol fuel cannot rely on food. To solve this problem, researchers are investigating ways to convert polymeric biomass carbohydrates, such as cellulose, to fermentable sugars. These sugars can then be used as an ethanol fermentation feedstock into the existing production infrastructure.

Whether ethanol comes from food sugars or converted biomass, it is first denatured before use as a motor fuel. Hydrocarbons are common denaturants and ASTM Standard D4806 specifies the types of hydrocarbons that can be used as denaturants [1]. Once the hydrocarbons are added, the product is called denatured fuel ethanol. Commercial fuels are then made by blending denatured fuel ethanol with gasoline. To assure product quality, ASTM has published method D5501-09, which uses gas chromatography to measure the ethanol and methanol content in ethanol fuels [2]. This paper describes the configuration and performance of the Agilent 7890A GC System when running ASTM D5501-09 for the analysis of denatured fuel ethanol.

Experimental

An Agilent 7890A GC System was configured according to D5501-09 and is shown in Table 1. The operating conditions for this method are shown in Table 2. Prior to sample analysis, the GC inlet splitter linearity was checked to assure there was no sample discrimination. A splitter linearity mix was prepared using the procedure described in ASTM Practice D4307 [3]. Ten hydrocarbons ranging from C_5 to C_{11} were gravimetrically blended and the final weight percent of each hydrocarbon in the mix was recorded. This mix was run using the GC conditions shown in Table 2. Calibrations for ethanol, methanol and hydrocarbons were performed using standards obtained from Spectrum Quality Standards, Sugarland, TX USA. After calibration, a commercial denatured fuel ethanol sample was analyzed to determine the ethanol and methanol content.

Table 1. The Agilent 7890A GC System Instrument Configuration for ASTM Method D5501

Standard Agilent 7890A GC System Hardware	
G3440A	Agilent 7890A Series GC System
Option 113	150 psi Split/Splitless Inlet with EPC control
Option 211	Capillary FID with EPC control
G4513A	Agilent 7693 Automatic Liquid Sampler
GC Capillary Column	
Analytical Column	PDMS, 150 m × 0.25 mm id × 1.0 µm film
Data System	
G2070BA	Agilent MultiTechnique ChemStation rev B.04.01
Consumables	
5181-1273	5 µL autoinjector syringe
5183-4647	Single taper split liner with glass wool
5183-4759	Advanced green inlet septa
Calibration Standards	
ETOH5501CAL	D5501 Calibration Set
Spectrum Quality Standards PO Box 2346 Sugarland, TX 77487-2346 USA	

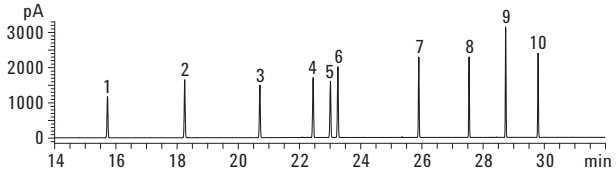
Table 2. GC Operating Conditions for ASTM Method D5501

Split/Splitless Inlet	
Temperature	300 °C
Pressure	Helium at 66 psi
Split ratio	200:1
Septum Purge	3 mL/min
Sample Size	0.5 µL injection
Initial column flow	2.34 mL/min, constant flow mode (24 cm/sec average linear velocity)
FID temperature	300 °C
Oven temperature program	60 °C for 15 min 30 °C/min to 250 °C, hold for 23 min

Results

The splitter linearity test was performed to assure quantitative transfer of all compounds from the inlet to the column without any boiling point discrimination. The test sample contained saturated hydrocarbons between C_5 and C_{11}, which covers the boiling range typically found in denatured fuel ethanol. Using a relative mass response factor of 1, each hydrocarbon in the splitter linearity mix was quantified using a normalized percent calculation. The D5501-09 method specifies that the measured mass percent of each hydrocarbon must match the known mass percent within ±3% relative difference. Figure 1 shows the chromatogram of the splitter linearity mix and the results that meet the ASTM D5501-09 specification. This shows that optimal split injection, with no discrimination, can be easily achieved using the Agilent 7693A ALS fast injection and the Agilent split optimized inlet liner.

System calibration for methanol, ethanol and hydrocarbons was done by running seven calibration standards using the GC conditions listed in Table 2. Methanol was calibrated between 0.05 and 0.6 wt% while ethanol was calibrated between 93 and 98 wt%. The calibration for the hydrocarbon



	Compound	Known wt%	Calc wt%	Relative difference (%)
1	n-pentane	6.9	7.0	**2**
2	2,4-dimethylbutane	9.5	9.6	**1**
3	2,4-dimethylpentane	8.5	8.6	**1**
4	3-methylhexane	10.1	10.1	**1**
5	2,2,4-trimethylpentane	9.5	9.7	**1**
6	n-heptane	11.4	11.4	**0**
7	n-octane	10.9	10.8	**1**
8	Nonane	9.6	9.6	**1**
9	Decane	13.3	13.3	**1**
10	Undecane	10.3	10.2	**1**

Figure 1. Analysis of the splitter linearity test mix containing saturated hydrocarbons from C_5 to C_{11}. These results meet the D5501-09 criteria for splitter linearity.

response was done using n-heptane between 1.95 and 7.4 wt%. After the calibration data was collected and the peak integration optimized, the individual response factors (R) for methanol, ethanol and n-heptane were calculated at each calibration level. Using the response factor of n-heptane, the relative response factors (RR) for methanol and ethanol were then determined at each level using the formulas described in ASTM Practice D4626 [4].

The D5501-09 method allows a single level calibration using a standard containing methanol and ethanol amounts expected in the users' samples in order to save time and resources. For this paper, the amount of alcohols in the sample was not known, therefore average RRs were calculated from all seven calibration standards and are shown in Table 3. These average RRs were then used to quantify the alcohols found in the sample of denatured fuel ethanol.

Table 3. Calibration Data for Denatured Fuel Ethanol Analysis

n-Heptane	Methanol	Ethanol
Average RR (1.95 – 7.4 wt%)	**Average RR (0.05 – 0.6 wt%)**	**Average RR (93 – 98 wt%)**
1.00	2.97	2.06

A sample of commercial denatured fuel ethanol was obtained from a producer and analyzed using the Agilent 7890A GC System running ASTM method D5501-09. Five aliquots of the sample were each measured two times for a total of ten runs. An example chromatogram is shown in Figure 2. It is important to optimize the peak integration in order to correctly measure the methanol peak area. Failure to do so could add peak response from nearby C_4 hydrocarbons to the methanol peak resulting in results that are too high. An example of optimized methanol peak integration is shown in Figure 3.

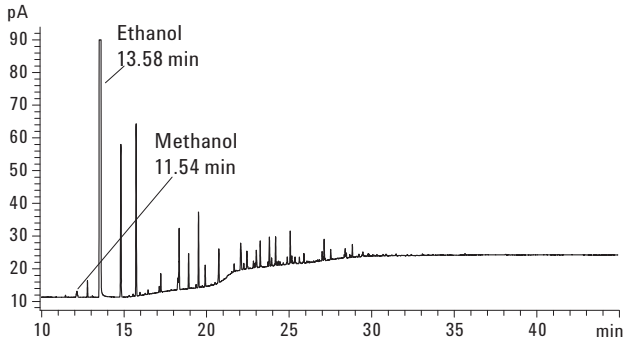


Figure 2. Analysis of a commercial denatured fuel ethanol sample using ASTM method D5501-09.

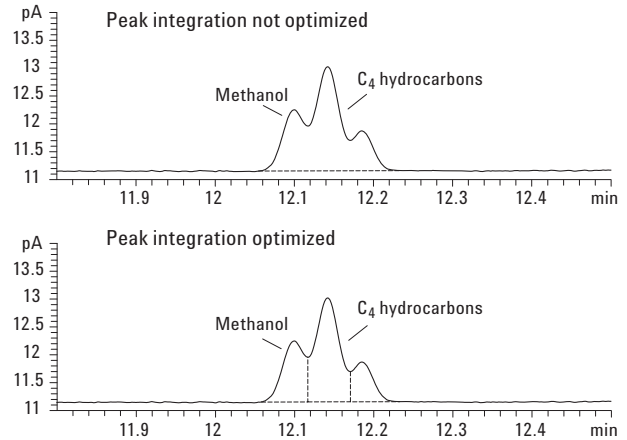


Figure 3. Optimizing the methanol peak integration is important for obtaining correct results.

Quantification of the alcohols in this sample was done using the average RRs calculated in Table 3. For all other peaks in the chromatogram, the n-heptane RR of 1 was used to measure the mass percent. Final reporting of all components was done using a normalized percent calculation as described in the D5501-09 method. The Agilent MultiTechnique ChemStation software can automatically perform both the average response factor calibration as well as the required normalized percent reporting. These results are shown in Table 4. Excellent system measurement precision was obtained for both the low level ethanol content as well as the very high level ethanol content.

Table 4. Results and Precision for the Analysis of Methanol and Ethanol in Denatured Fuel Ethanol.

Run	Methanol	Ethanol
1	0.02	97.81
2	0.02	97.83
3	0.02	97.81
4	0.02	97.82
5	0.02	97.79
6	0.02	97.81
7	0.02	97.78
8	0.02	97.76
9	0.02	97.77
10	0.02	97.74
Avg	**0.02**	**97.79**
Std Dev	**2.18e-4**	**0.03**
RSD	**1.16%**	**0.03%**

Conclusion

The measurement of methanol and ethanol in denatured fuel ethanol can be quite challenging due to the complexity of the hydrocarbon denaturant and the need to quantify near 100% ethanol as well as low level components in the sample. ASTM method D5501-09 uses high resolution gas chromatography to perform this measurement. In this paper, the Agilent 7890A GC Service was configured to run method D5501-09. The system showed no inlet discrimination so that quantitative sample transfer to the column could be made for the wide boiling range components found in denatured fuel ethanol. This was a key factor in the excellent precision shown in this paper. Calibration of a large ethanol concentration as well as a low-level methanol and hydrocarbon concentrations were done using the Agilent MultiTechnique ChemStation. The ChemStation was also able to automate the final calculations and reporting.

References

1. "D4806 - Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
2. "D5501-09 Standard Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
3. "D4307 - Standard Practice for Preparation of Liquid Blends for Use as Analytical Standards"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
4. "D4626 – Standard Practice for Calculation of Gas Chromatographic Response Factors"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
October 20, 2010
5990-6650EN

Agilent Technologies

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

Application

Hydrocarbon Processing

Authors

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

Mario Morales
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Abstract

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

Introduction

Many sources of natural gas and petroleum gases contain varying amounts and types of sulfur compounds. The analysis of gaseous sulfur compounds is difficult because they are polar, reactive, and present at trace levels. Sulfur compounds pose problems both in sampling and analysis. Analysis of sulfur compounds many times requires special treatment to sample pathways to ensure inertness to the reactive sulfur species. Sampling must be done using containers proven to be nonreactive. Laboratory equipment must also be inert and well conditioned to ensure reliable results. Frequent calibration using stable standards is required in sulfur analysis [1].

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

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

Experimental

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

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

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

Table 1. Sulfur Standards in Helium

1.	Hydrogen sulfide	H_2S
2.	Carbonyl sulfide	COS
3.	Methyl mercaptan	CH_3SH
4.	Ethyl mercaptan	CH_4CH_3SH
5.	Dimethyl sulfide	CH_3SCH_3
6.	Carbon disulfide	CS_2
7.	2-propanethiol	$CH_3SHC_2H_5$
8.	Tert-butyl mercaptan	$(CH_3)_3CSH$
9.	1-propanethiol	$CH_3(CH_2)_2SH$
10.	Thiophene	C_4H_4S
11.	n-butanethiol	$CH_3(CH_2)_3SH$
12.	Diethyl sulfide	$CH_3CH_2SCH_2CH_3$
13.	Methyl ethyl sulfide	$CH_3SCH_2CH_3$
14.	2-methyl-1-propanethiol	$(CH_3)_2CHCH_2SH$
15.	1-methyl-1-propanethiol	$CH_3CH_2CHSHCH_3$

Experimental Conditions

GC Conditions

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

SCD Conditions

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

Results and Discussion

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

Figure 2 is the chromatogram of low-level sulfur compounds at 1.35 ppb (H_2S), which is prepared by the point-of-use gas blending system. Table 2 is the calculated signal to noise (S/N) of each compound, from the achieved data. It can be seen that DP SCD can detect low-level sulfur compounds.

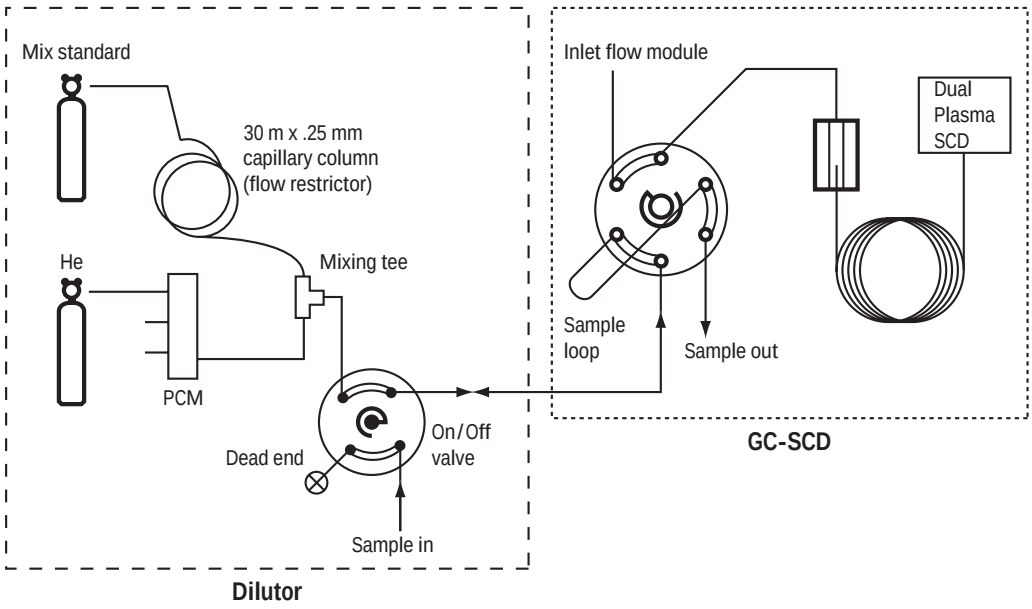


Figure 1. Diagram of online dilutor GC-DP SCD.

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

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

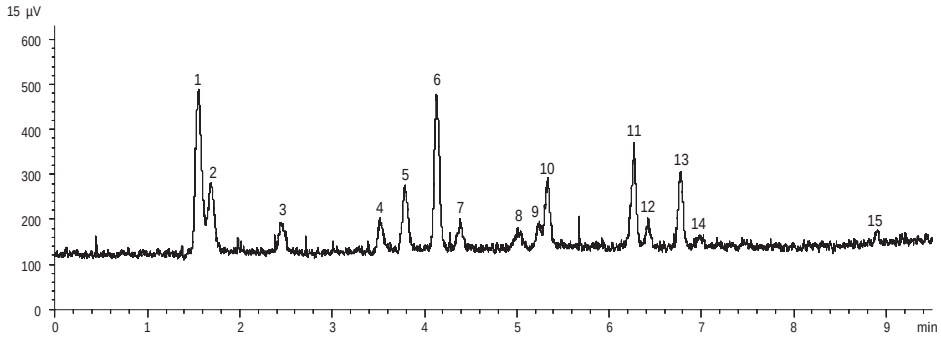


Figure 2. Chromatogram of sulfur compounds in helium at 1.35 ppb. (Refer to Table 1 for peak identification.)

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

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

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

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

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

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

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

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

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

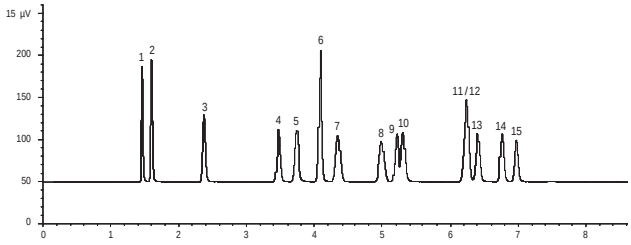


Figure 3. Chromatogram of sulfurs in natural gas. (Refer to Table 1 for peak identification.)

Natural Gas Sample Analysis

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

Table 5. Result of the Three Real Samples

Samples		H_2S	COS	Methyl Mercaptan
BLEND AL	Conc. (ppm, v/v)	2.3	2.0	2.0
	RSD (%, n = 5)	2.3	0.3	1.4
BLEND 6	Conc. (ppm, v/v)	27.1	21.9	17.3
	RSD (%, n = 5)	1.2	0.4	2.3
BLEND 12	Conc. (ppm, v/v)	15.0	9.2	10.1
	RSD (%, n = 5)	0.7	0.6	0.6
Standard	Conc. (ppm, v/v)	2.0	0.8	0.9
natural gas	RSD (%, n = 5)	1.7	2.5	1.7

Conclusions

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

References

1. ASTM D5504-98: Standard test method for determination of sulfur compounds in natural gas and gaseous fuels by gas chromatography and chemiluminescence
2. Roger L. Firor, “Volatile Sulfur in Natural Gas, Refinery Gas, and Liquified Petroleum Gas,” Agilent Technologies publication 5988-2791EN
3. Roger L. Firor and Bruce D. Quimby, “A Comparison of Sulfur Selective Detectors for Low-Level Analysis in Gaseous Streams,” Agilent Technologies publication 5988-2426EN

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
August 12, 2008
5989-9234EN

Agilent Technologies

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

Application

Hydrocarbon Processing

Authors

Chun-Xiao Wang and Wei Luan
Agilent Technologies (Shanghai) Co. Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
P.R. China

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

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

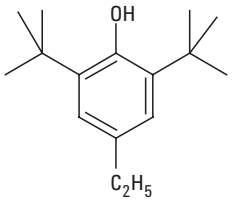
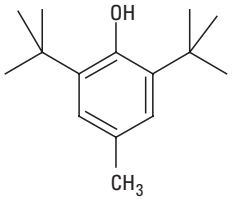
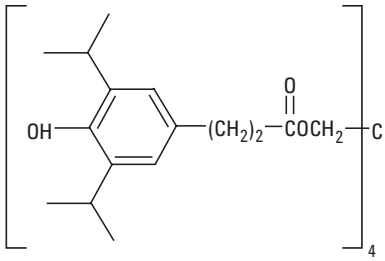
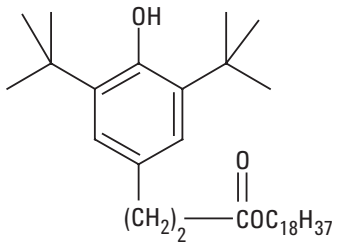
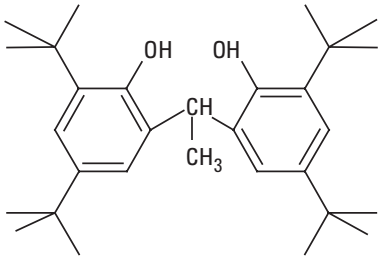
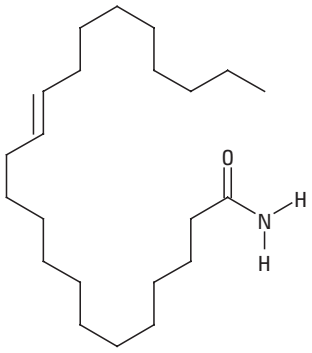
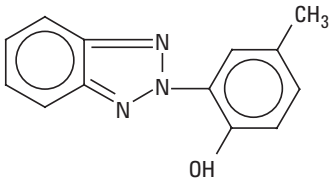
Registered trade name	CAS no.	Chemical name	Chemical structure
BHEB	4310-42-1	2,6-di-tert-butyl-4-ethyl-phenol or butylated hydroxyethyl benzene	
BHT	128-37-0	2,6-di-t-butyl-cresol or butylated hydroxy toluene	
Irganox 1010	6683-19-8	Tetrakis[methylene(3,5-di-t-butyl-4-hydroxy hydrocinnamate)] methane	
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 B: acetonitrile (ACN)
Gradient slope:	See individual chromatograms for flow rate and gradient time
Column temperature:	See individual chromatograms

Samples

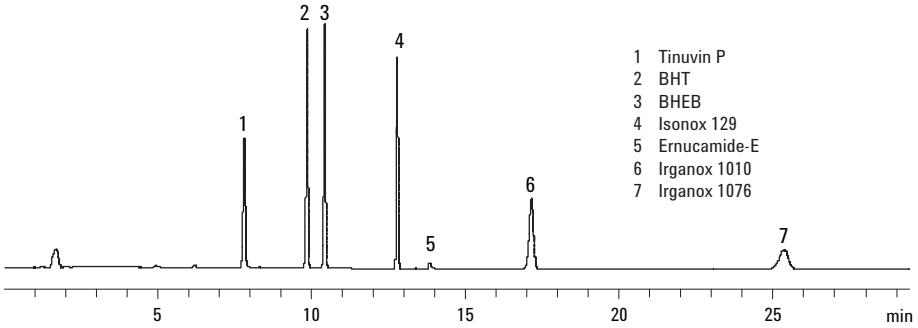
1. Standard mixture described in ASTM D5815 and D1996, 50 µg/mL, 200 µg/mL in isopropanol
2. Linear low-density polyethylene from customer, ground to 20 mesh, extracted by ultrasonic or reflux method

Results and Discussion

Fast Method Conversion

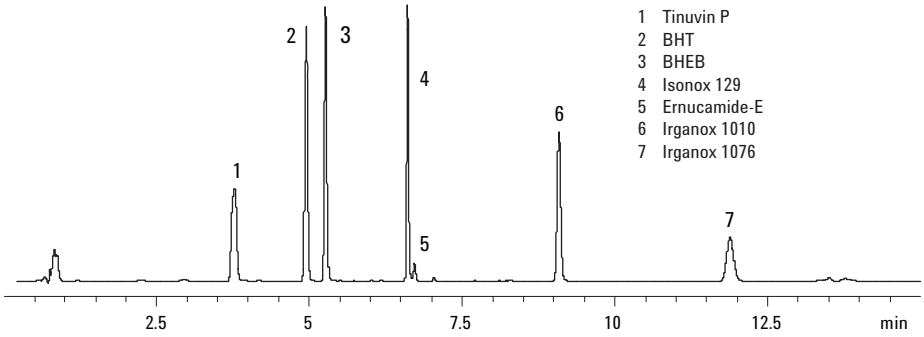
The separation was initially performed on a standard 4.6 mm × 150 mm, 5-µm ZORBAX Eclipse XDB-C18 column thermostatted to 60 °C (Figure 1) following the conditions in ASTM D5815 (or D1996). The method was then scaled in flow and time for exact translation to a 2.1 mm × 50 mm, 1.8-µm column (Figure 2).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



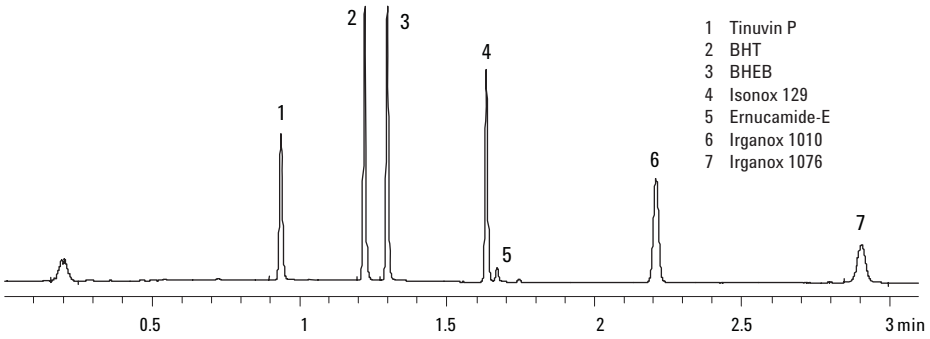
		Gradient	
Conventional method:	Follow ASTM D5815 (or D1996) method with		
	ZORBAX Eclipse XDB-C18,		%B
	4.6 mm × 150 mm, 5 µm	0	50
Sample:	Standard 50 µg/mL	11	100
Sample size:	10 µL	28	100
Detector:	UV 200 nm	28.1	50
Column temperature:	60 °C		
Mobile phase:	A: water		
	B: acetonitrile		
Flow rate: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

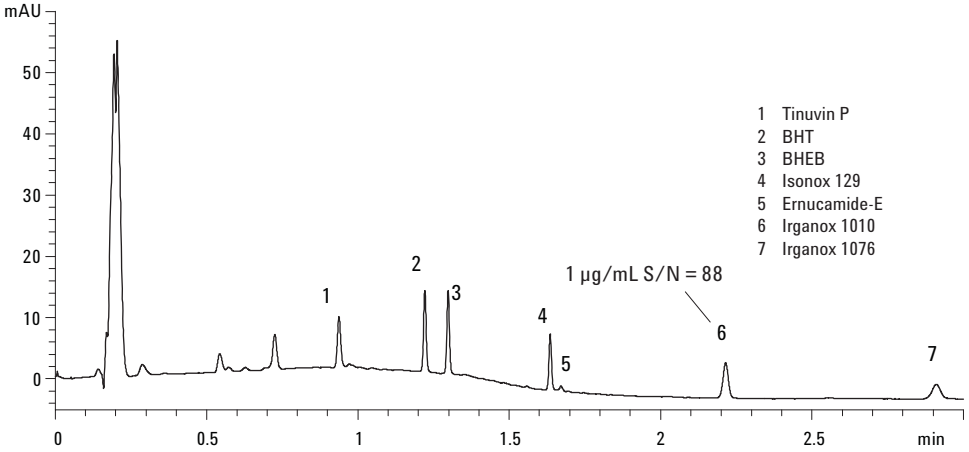


		Gradient	
Speed-optimized:	Optimize the conventional method for speed with		%B
	ZORBAX Eclipse XDB-C18,		
	2.1 mm × 50 mm, 1.8 µm	0	50
Sample:	Standard 50 µg/mL	1.3	100
Sample size:	2 µL	3	100
Detector:	UV 200 nm	3.1	50
Column temperature:	60 °C	3.5	50
Mobile phase:	A: water		
	B: acetonitrile		
Flow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

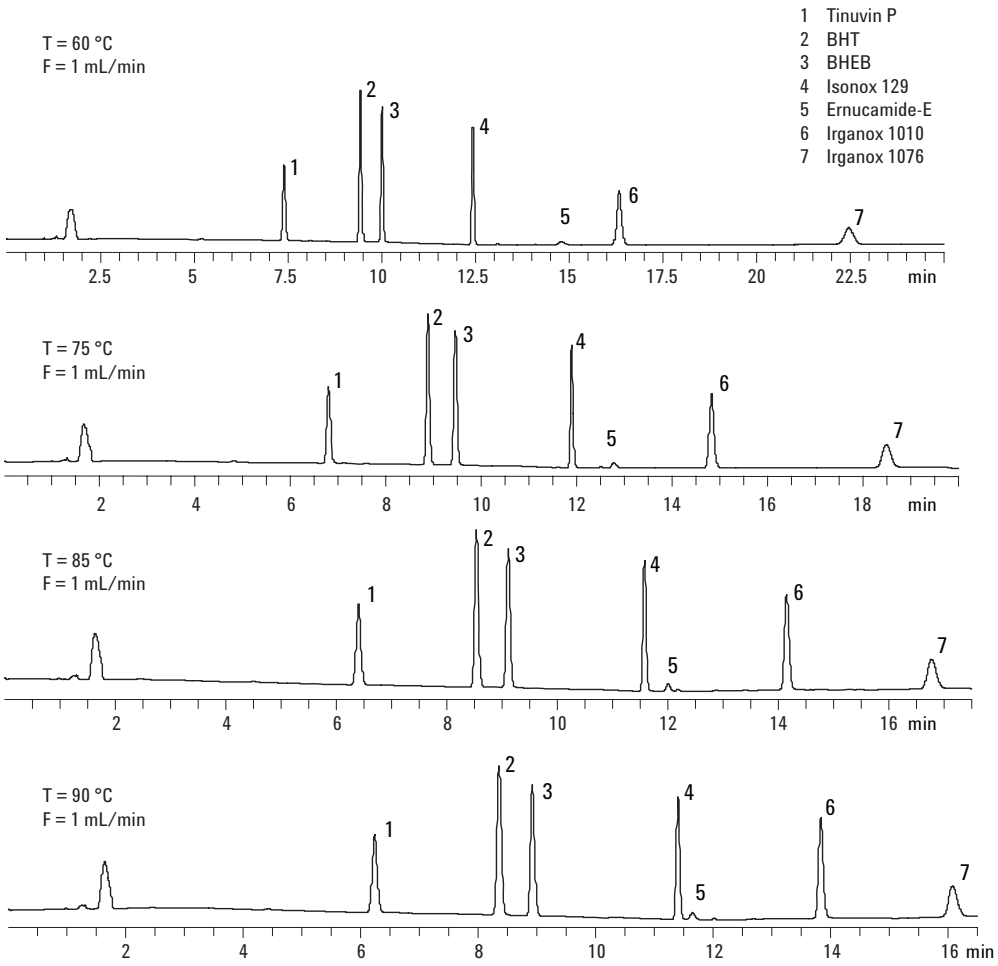
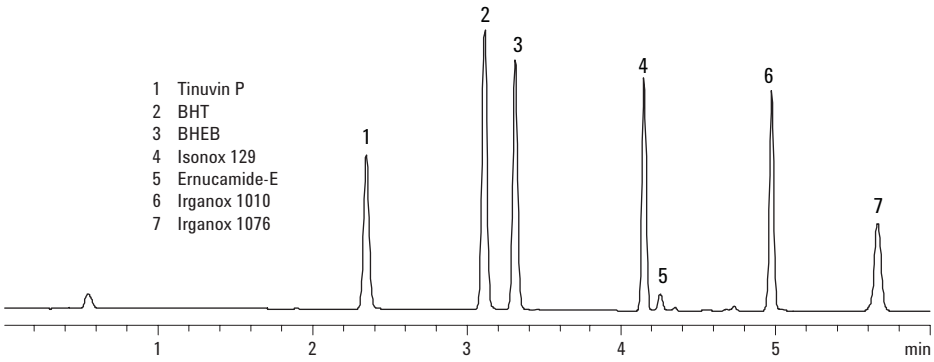
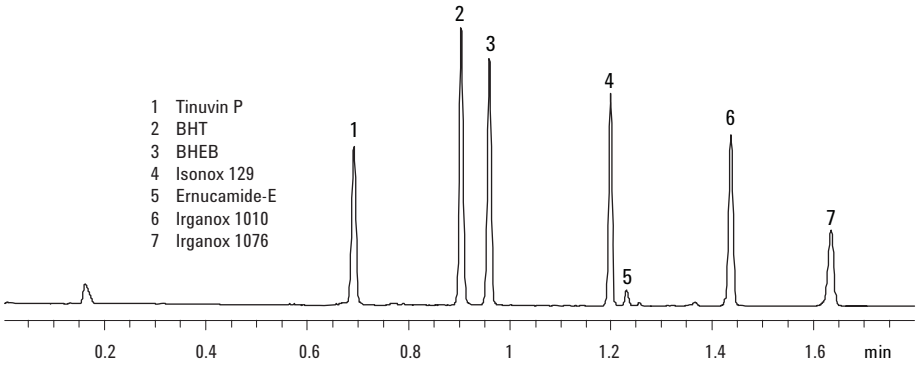


Figure 5. Separation of additives standards on ZORBAX StableBond RRHT SB-C18, 4.6 mm × 150 mm, 1.8 µm.



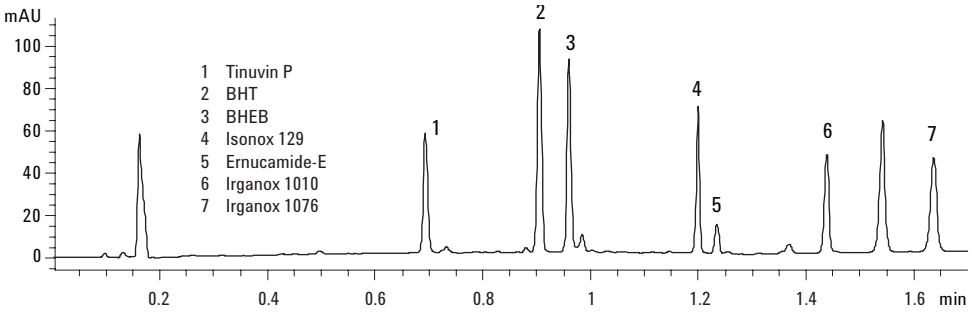
Sample:	Standard 200 mg/mL
Sample size:	2 µL
Detector:	UV 200 nm
Mobile phase:	A: water
	B: acetonitrile
Gradient slope:	6.8%
Flow rate:	1mL/min

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.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

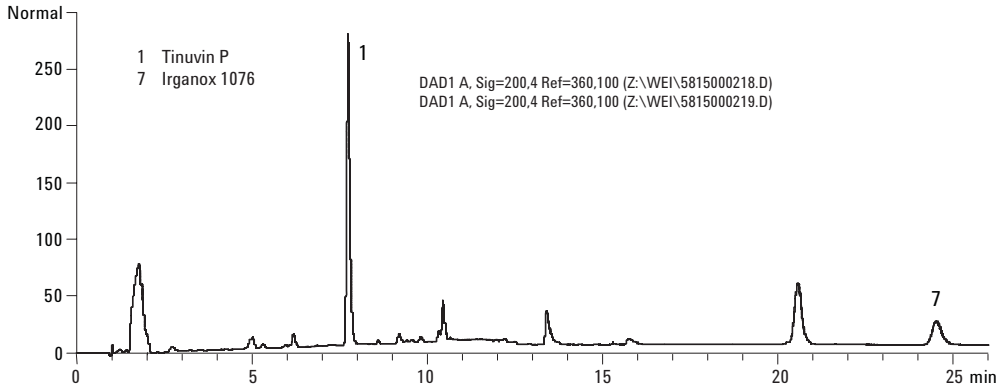


Figure 9. Chromatogram Overlays of extractions by reflux and ultrasonic extraction methods for LLDPE.

Printed in the USA
January 17, 2007
5989-5850EN

Agilent Technologies

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.

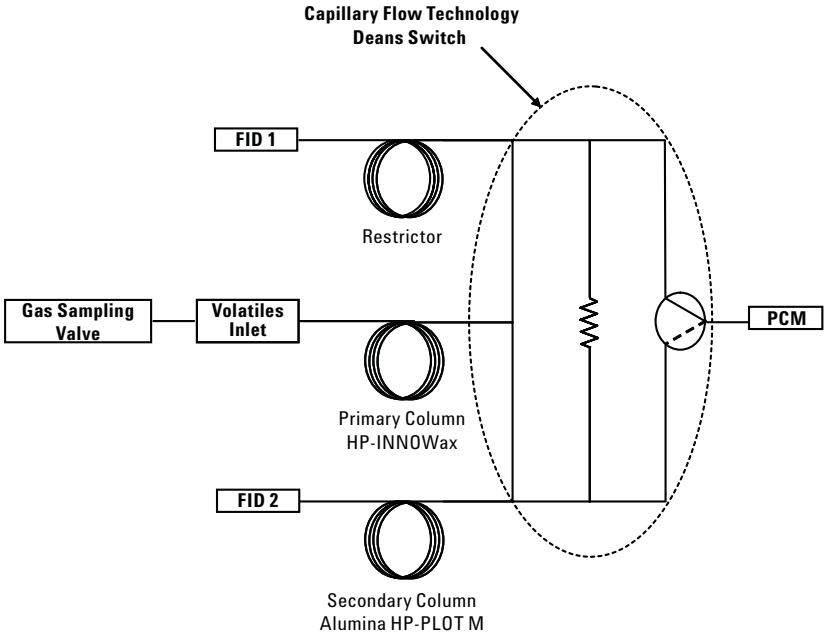


Figure 1. Configuration of Agilent 7890A for the 2-D GC analysis of trace oxygenates and hydrocarbons in ethylene.

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.

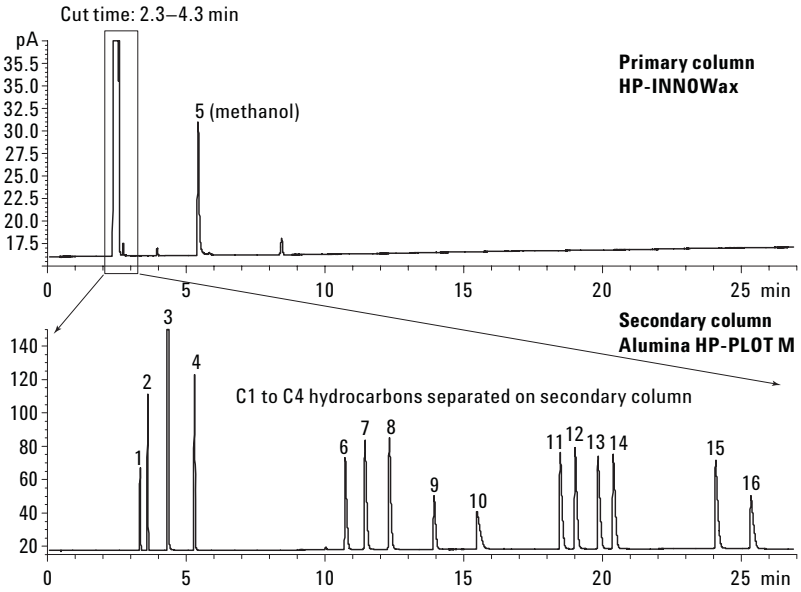


Figure 2. Capillary Flow Technology Deans switch used to separate 100 ppmV oxygenate and hydrocarbon impurities in ethylene.

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

1. Annual Book of ASTM Standards, Vol. 05.03, “Petroleum Products and Lubricants (III), D5303 - D6553,” ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA.
2. J. D. McCurry, “Fast Determination of Denatured Fuel Ethanol Purity by Two-Dimensional Gas Chromatography,” Agilent Technologies publication 5988-9460EN, April 2003.
3. R. L. Firor and B. D. Quimby, “Automated Dynamic Blending System for the Agilent 6890 Gas Chromatograph: Low Sulfur Detection,” Agilent Technologies publication 5988-2465EN, April 2001.

James McCurry is a senior applications chemist based at Agilent Technologies, Wilmington, Delaware.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
January 5, 2007
5989-6082EN

Agilent Technologies

Meeting the requirements of ASTM D 6591-06 (IP548/06) Using Agilent 1200 Series HPLC Systems

Application

Hydrocarbons

Abstract

The performance of diesel fuel is predominantly determined by its ignition quality. This parameter is known as the Cetane number. The Cetane number describes the volume % Cetane (aliphatic hexadecane) present in a mixture of Cetane and (aromatic) 1-Methyl-naphthalene. Generally, in order to provide the best performance and maximize the lifetime of an engine, the amount of aromatics in diesel should be as low as possible. For the analysis of non-aromatics and aromatics in diesel fuel and petroleum distillates boiling in the range of 150 °C to 400 °C, there exists an ASTM Method (D 6591-06), and identical method IP548/06 that uses HPLC with refractive index detection. The two compound classes (aromatics and non-aromatics) are separated using normal phase HPLC and a column that has little affinity for non-aromatic but has pronounced selectivity for aromatic hydrocarbon classes [1]. The refractive index detector is used because this detector responds to both non-aromatic and aromatic hydrocarbons.

Authors

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

Malgorzata Sierocinska
Agilent Technologies
European Field Support Centre
Waldbronn
Germany

Agilent Technologies

About Standard Method ASTM D 6591-06

"This test method covers a high performance liquid chromatographic test method for the determination of monoaromatic, di-aromatic, tri+-aromatic, and polycyclic aromatic hydrocarbon contents in diesel fuels and petroleum distillates boiling in the range of 150 to 400 °C. The total aromatic content in % m/m is calculated from the sum of the corresponding individual aromatic hydrocarbon types.

NOTE 1—Aviation fuels and petroleum distillates with boiling points that range from 50 to 300 °C are not determined by this test method and should be analyzed by Test Method, D 6379 or another suitable equivalent test method.

- 1.2 The precision of this test method has been established for diesel fuels and their blending components, containing from 4 to 40 % (m/m) mono-aromatic hydrocarbons, 0 to 20 % (m/m) di-aromatic hydrocarbons, 0 to 6 % (m/m) tri+-aromatic hydrocarbons, 0 to 26 % (m/m) polycyclic aromatic hydrocarbons, and 4 to 65 % (m/m) total aromatic hydrocarbons.
- 1.3 Compounds containing sulfur, nitrogen, and oxygen are possible interferents. Mono-alkenes do not interfere, but conjugated di- and poly-alkenes, if present, are possible interferents.
- 1.4 By convention, this standard defines the aromatic hydrocarbon types on the basis of their elution characteristics from the specified liquid chromatography column relative to model aromatic compounds. Quantification is by external calibration using a single aromatic compound, which may or may not be representative of the aromatics in the sample, for each aromatic hydrocarbon type. Alternative techniques and methods may classify and quantify individual aromatic hydrocarbon types differently.
- 1.5 Fatty Acid Methyl Esters (FAME), if present, interfere with tri+-aromatic hydrocarbons. If this method is used for diesel containing FAME, the amount of tri+-aromatics will be overestimated."[2]

This method, also known as IP548/06, is an official method of the American Society of Testing Methods (United States, www.astm.org). The method requires a column backflush-capable instrument configuration and analysis scheme, and is similar to other hydrocarbon group analysis methods. Because of this similarity, with respect to mobile phase and detection strategy, the instrument configuration is readily adaptable to those other methods.

The various methods associated with middle distillate fuel analysis are shown in Table 1.

Equipment and Conditions

LC:	Agilent 1200 Series LC
Binary pump:	G1312B used isocratically with pump head seals for normal phase, Agilent p/n 0905–1420
Autosampler:	G1367C with needle wash
Therm. Column Compartment:	G1316C with 6 port 2 position switching valve
Refractive Index Detector:	G1362A
Software:	Agilent ChemStation with version B.04.02 software
Columns:	Agilent ZORBAX NH_2 4.6 × 250 mm, 5 µm (p/n 880952-708)
Mobile Phase:	n-heptane, HPLC grade
Flow Rate:	1 ml/min
Injection Volume:	10 µl
Oven Temperature:	20 °C
Detection:	Refractive index

Sample preparation

Samples and standards were prepared according to guidance published in the method, using heptane as the diluent. System qualification and final quantitative results were reported using Agilent ASTM D 6591-06 standard mixtures (p/n 5190-0483 system performance solution SPS, and p/n 5190-0482 quantitative calibrant solutions A-D, respectively).

Table 1. Fuel Analysis Methods

IP Method and Revision	Method Overview	Special Parameters	ASTM Method	Comments
IP391/07	150-400 °C diesel fuel petro/bio blends up to B-5	no backflush, amino and/or cyano column	No current equivalent available	same as method EN12916:2006 *MAH, DAH, Tri+AH are reported
IP436/01	50-300 °C aviation fuel, kerosene	no backflush, amino and/or cyano column	D-6379-04	MAH and DAH reported not for samples with Tri+AH
IP548/06	150-400 °C diesel fuel	backflush required, amino and/or cyano column	D-6591-06	MAH, DAH, Tri+AH reported FAME interferes with result

*MAH – monoaromatic hydrocarbon, DAH – diaromatic hydrocarbon, Tri+AH – tri and higher ring aromatic hydrocarbons

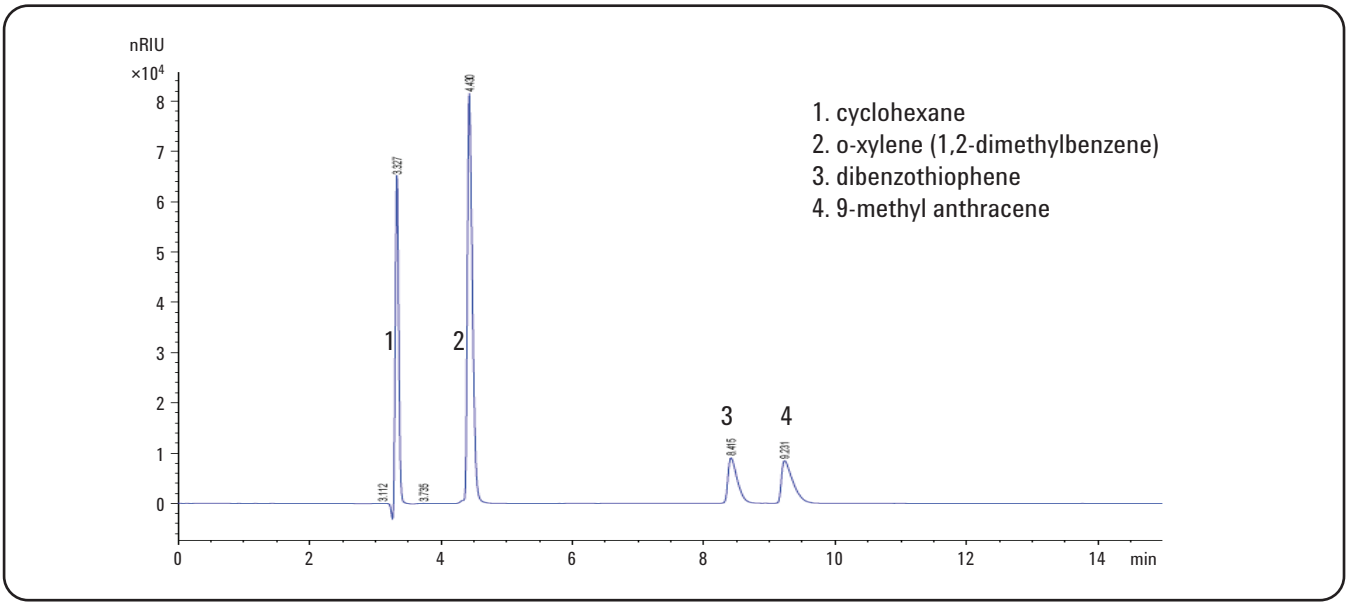


Figure 1. Standard chromatogram of system performance solution (SPS).

Results and Discussion

The first steps in method implementation are to analyze a system performance solution (SPS) that establishes overall separation selectivity and resolution, and to establish the event time table for column backflushing during the analysis. (Sections 9.4 and 9.6 of the method). Figure 1 illustrates the results of running the performance solution on the Agilent system without a backflush event.

The SPS is used to determine selectivity and retention data for the saturate and aromatic markers that are used for method acceptance criteria. It is also used to determine the backflush time for eluting tri+aromatics as a single peak.

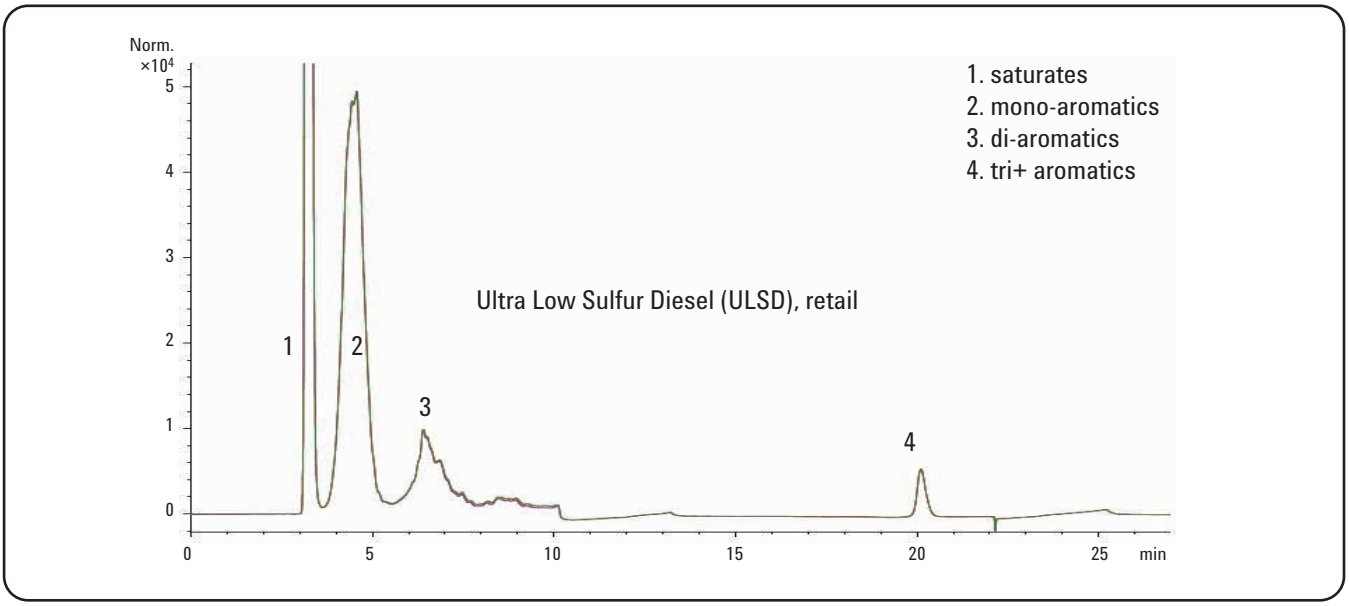


Figure 2. Petroleum diesel sample, n=3 overlay, showing cutpoints for the various compound groups typically present in these samples.

Resolution between cyclohexane and o-xylene (1,2-dimethylbenzene) is part of the method specification and must attain a minimum value of 5.

With a genuine fuel sample, in this case retail quality petrodiesel, greater complexity and overlapping of the various compound class regions are evident. Within the method definitions there are specific "cutpoints" defining the grouping to be performed in the quantitative reports. Manual peak integration is specified in the method for setting the baseline, and inserting valley drop points.

Results and Discussion

Method Performance

As with most official methods, there are specific performance criteria that allow qualification of the separation system and its subsequent use for reporting quantitative results of diesel fuel analysis.

- 6.4 Column System—Any stainless steel HPLC column(s) packed with an approved amino-bonded (or polar amino/cyano-bonded) silica stationary phase is suitable, provided it meets the resolution requirements laid down in 9.4.3. [2]
- 9.4.1 Ensure that baseline separation is obtained between all components of the SPS.
- 8.9 Ensure that the resolution between cyclohexane and 1,2 dimethylbenzene is at least 5 as described in 9.4.3.
- 9.4.3.1 Column Resolution
  Calculate the resolution, R, between cyclohexane and 1,2 dimethylbenzene using the following equation.

$$R = \frac{2(t2-t1)}{1.699(y1+y2)}$$

difference in retention time

averaging of peak widths

- 10.1.5: R = >0.999, Intercept <0.01 g / 100 ml)

Table 2.

Name	R. Time [min]	width (hh)	Resolution
1. cyclohexane	3.307	0.059	
2. 1,2-dimethylbenzene)	4.477	0.097	8.79
3. dibenzothiophene	8.907	0.186	
4. 9-methyl anthracene (r.t. with backflush)	18.905	0.282	

In Figure 1 there is distinct separation between the markers specified in sections 9.4 and 9.6 of the method. Table 2 confirms the minimum resolution requirement of section 9.4 and shows retention time data obtained with the programmed backflush calculated as defined in section 9.6. With this information, it is possible evaluate calibration standards.

An overlay of calibrant solutions A-D is shown in Figure 3. The backflush time was determined from injections of SPS at the beginning of the analysis sequence.

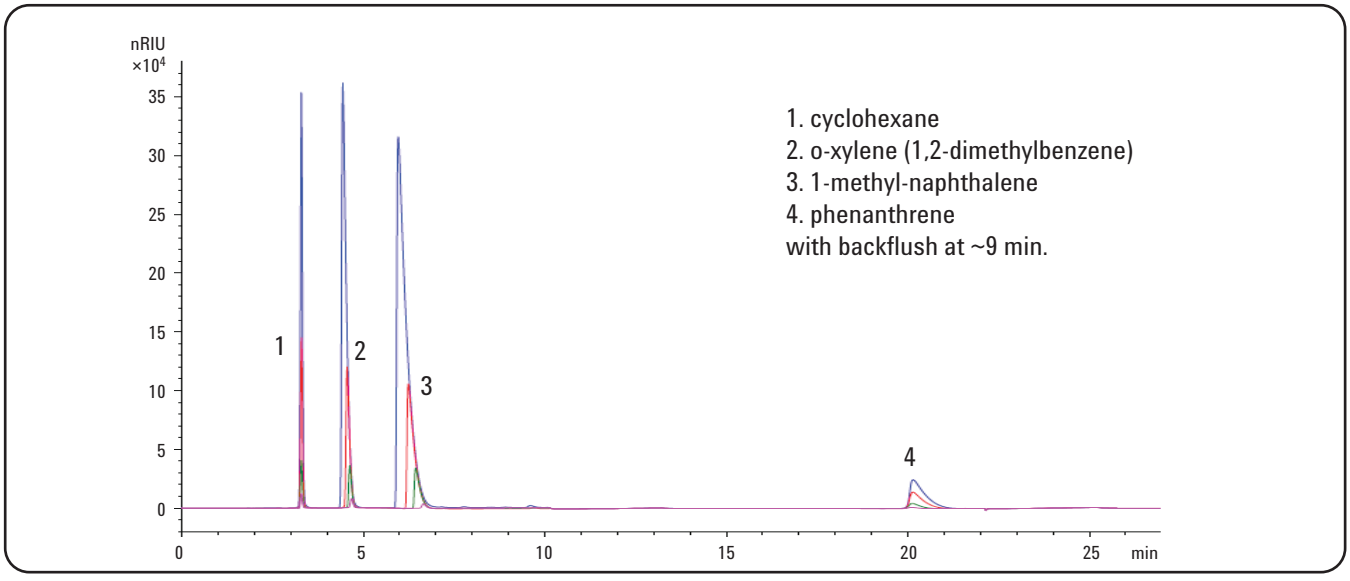


Figure 3. Overlay of calibrant solutions A-D.

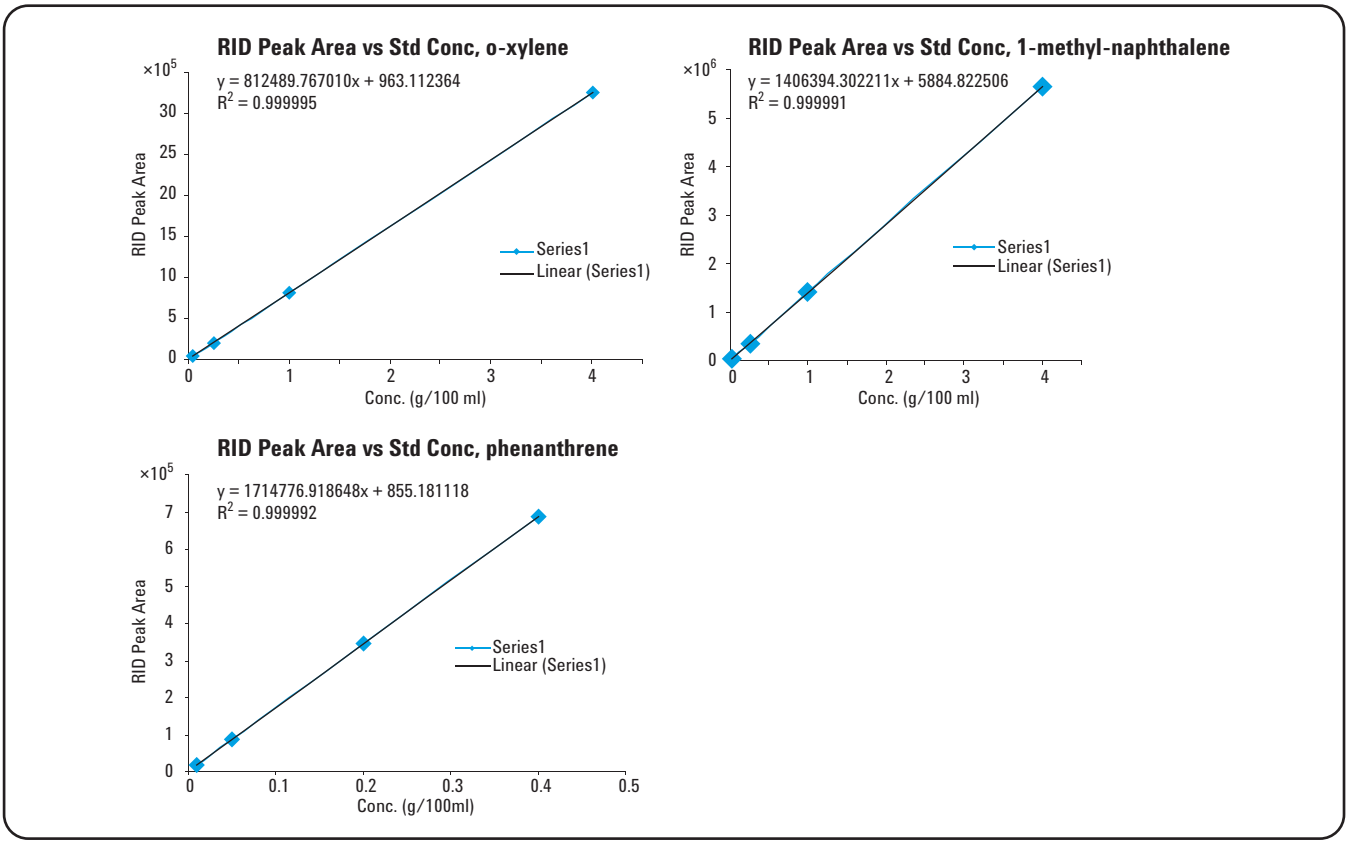


Figure 4. Calibration plots for o-xylene,1-methyl-naphthalene, and phenanthrene which, are the three components of the four calibration levels specified in the method.

In the calculated results, all calibration plots exceed linearity of 0.9999 and have calculated intercepts well below 0.01 g/100 mL, which are the method specifications of section 10.1.5.

Retention time and peak area precision can be found in Table 3, illustrating that the overall performance of the calibration method is excellent.

Table 3. Calibration Precision

Calibrant A

Analyte	RT, Avg, n=3	RT, Stdev	RT, RSD%	Area Avg, n=3	Area Stdev	Area RSD%
xylene	4.44	0.0005	0.01%	3.29E+06	755.9	0.02%
1-Methyl-naphthalene	5.96	0.001	0.02%	5.76E+06	2299.2	0.04%
phenanthrene	20.14	0.0020	0.01%	7.12E+05	8351.8	1.17%

Calibrant B

Analyte	RT, Avg, n=3	RT Stdev	RT, RSD%	Area Avg, n=3	Area Stdev	Area RSD%
xylene	4.55	0.0020	0.05%	8.33E+05	5263.9	0.63%
1-Methyl-naphthalene	6.24	0.0041	0.07%	1.46E+06	14197.7	0.97%
phenanthrene	20.13	0.0023	0.01%	3.55E+05	849.5	0.24%

Calibrant C

Analyte	RT, Avg, n=3	RT Stdev	RT, RSD%	Area Avg, n=3	Area Stdev	Area RSD%
xylene	4.63	0.0017	0.04%	2.06E+05	536.3	0.26%
1-Methyl-naphthalene	6.44	0.0036	0.06%	3.66E+05	1830.7	0.50%
phenanthrene	20.12	0.0040	0.02%	8.87E+04	139.0	0.16%

Calibrant D

Analyte	RT Avg, n=3	RT Stdev	RT, RSD%	Area Avg, n=3	Area Stdev	Area RSD%
xylene	4.67	0.0005	0.01%	4.03E+04	214.7	0.53%
1-Methyl-naphthalene	6.65	0.0020	0.03%	2.96E+04	334.1	1.13%
phenanthrene	20.10	0.0025	0.01%	1.76E+04	176.5	1.00%
Average RSD% All Runs			**0.028%**			**0.555%**

Results for specific petrodiesel and petro/biodiesel blends

Various samples were collected from local commercial and retail fuel delivery points. An overlay of three samples is shown in Figure 5.

Despite some apparent compositional differences among the samples, the general resolution and valley points are consistent. This should ensure relatively straightforward data reduction.

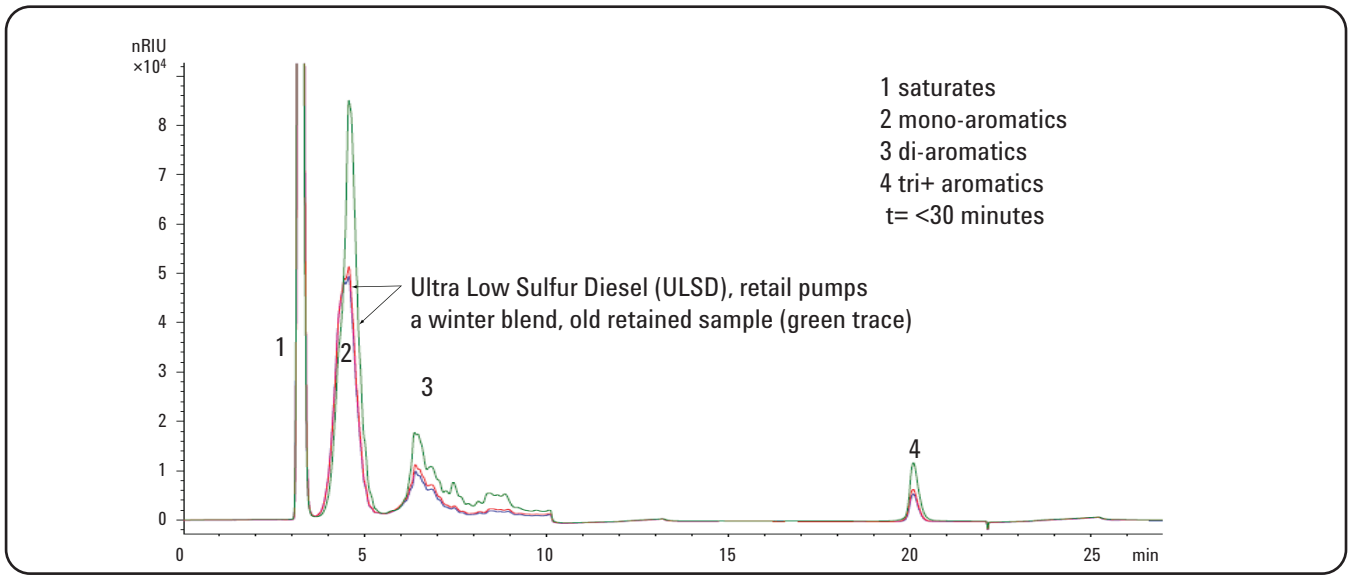


Figure 5. Overlay of three samples.

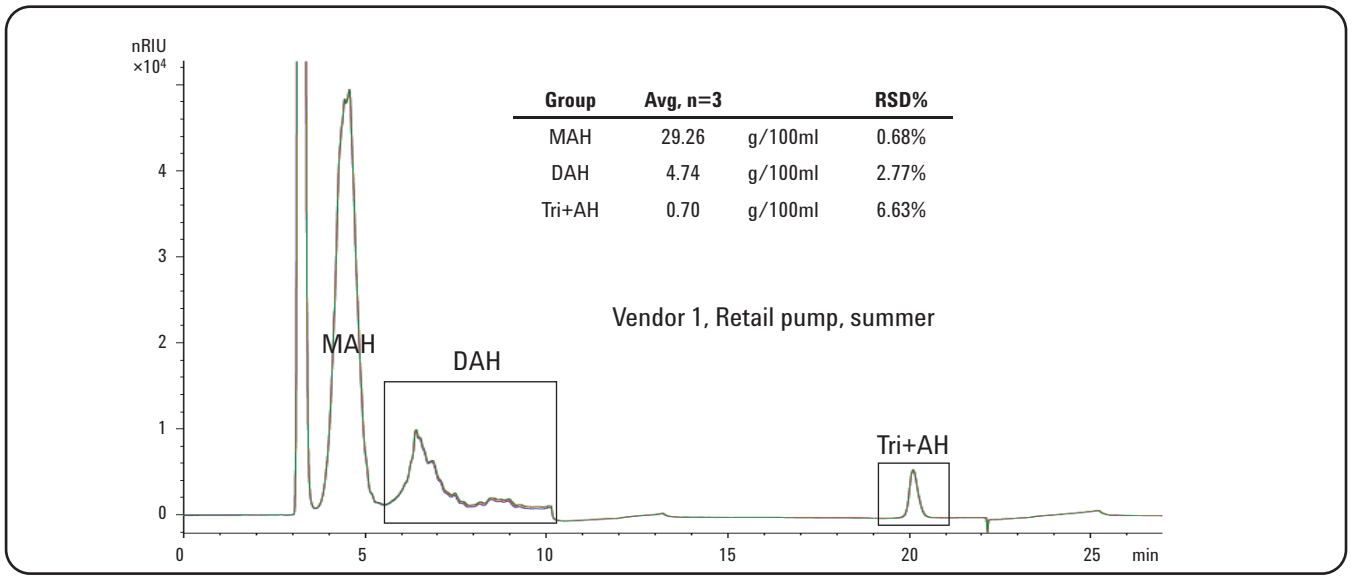


Figure 6. Results and precision for sample designated "Vendor 1".

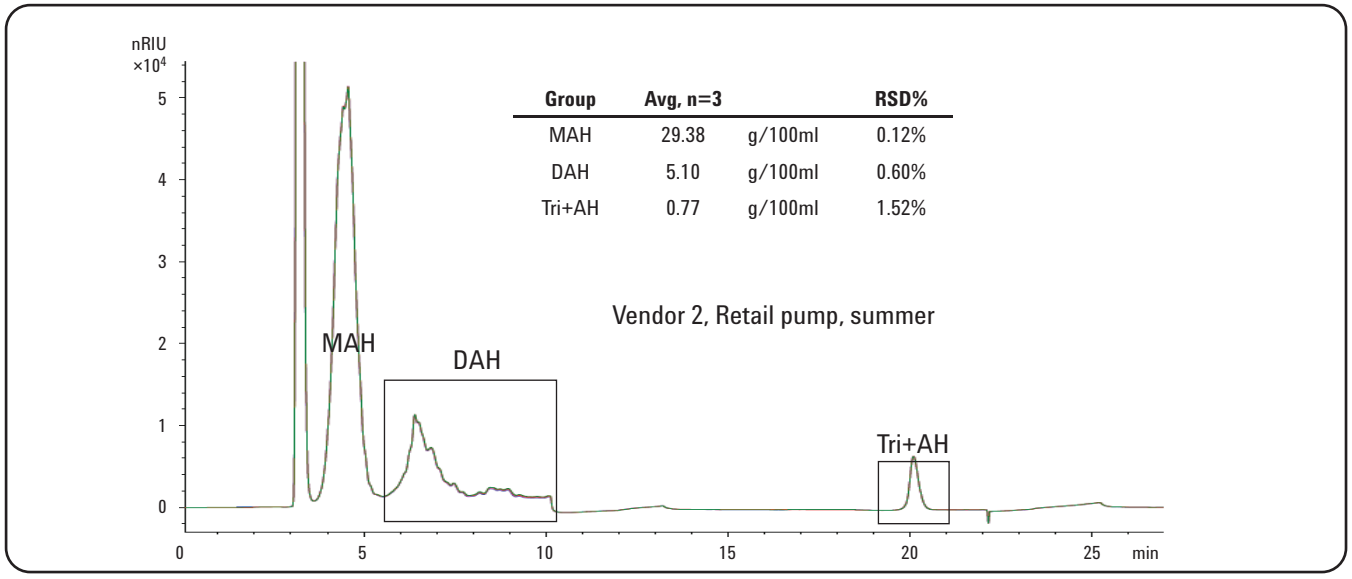


Figure 7. Results and precision for sample designated "Vendor 2".

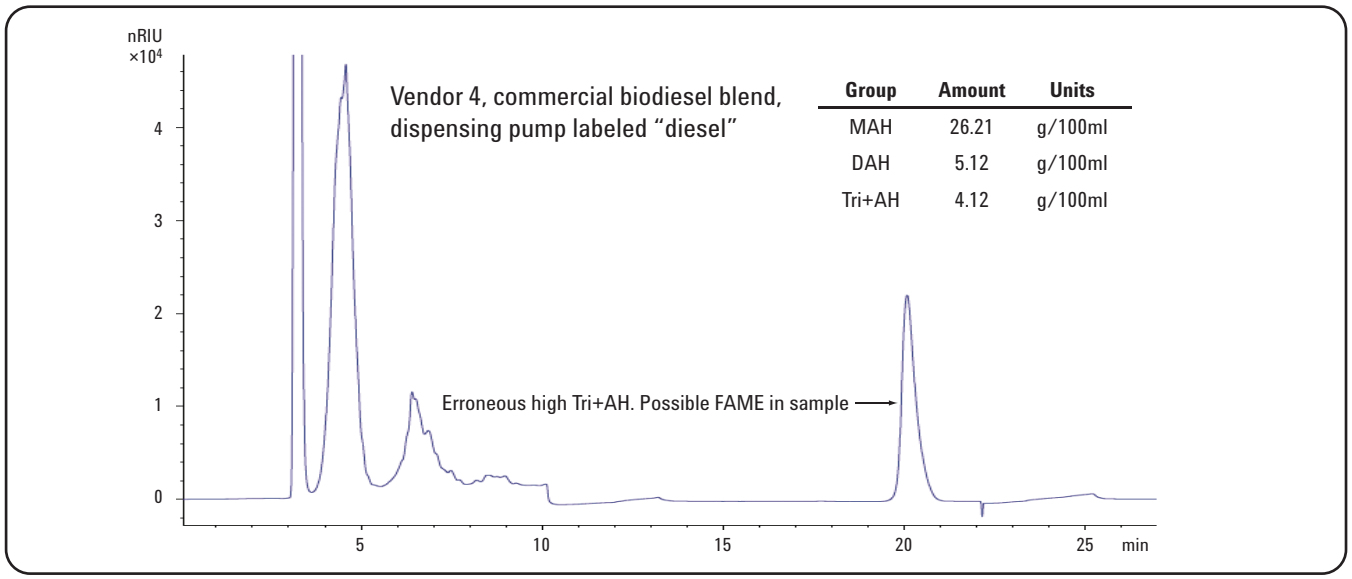


Figure 8. This sample was represented as diesel and was analyzed by the method. Suspiciously high tri+aromatic values compelled an analysis by the alternate, biodiesel approved, method IP391/07.

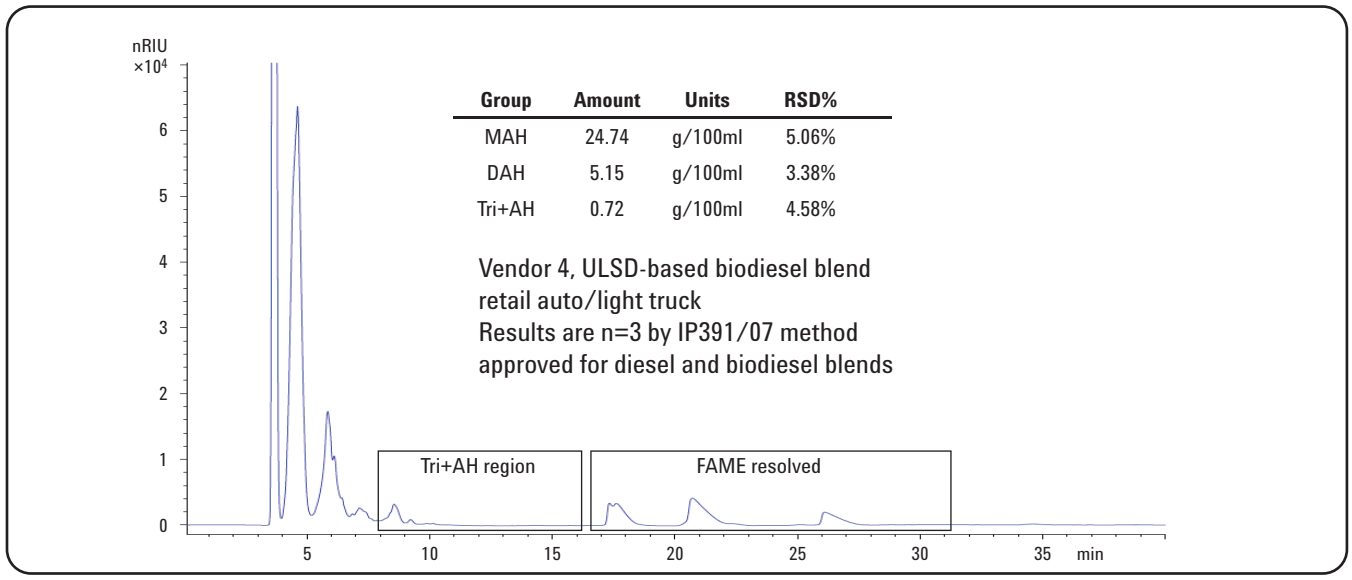


Figure 9. Analysis of suspect biodiesel sample by IP391/07 conditions confirms the contamination or dispensing pump mislabeling and yields a more expected result for typical diesel motor fuel. For further details on the performance and utility of this method, please refer to Agilent application note 5990-4789EN. [3]

Ruggedness and Stability of the ASTM D 6591-06 method

As with most normal phase methods the column is susceptible to adsorption of highly polar components that can affect overall separation performance. Water present in samples or mobile phase also adsorb to the column and somewhat predictably cause reduced elution times for all sample components. Using a high quality anhydrous HPLC grade mobile phase is essential, and the user may consider using a drying agent such as molecular sieve to dehydrate the mobile phase. While this is often done by adding molecular sieve to the solvent container, it is also possible and preferable to prepare a high pressure compatible column with prewashed drying agent and placing it inline between the pump and injector.

Conclusion

The performance of the Agilent 1200 Series High Performance LC system with normal phase separation and refractive index detection meets or exceeds the requirements of ASTM D 6591-06 within the range of samples defined in the method. The user should take care to identify samples of petrodiesel containing biodiesel components to ensure adequate analysis modifications are made to prevent erroneous high tri+aromatic values. IP391/07 (EN12916:2006) is required for samples found to contain biodiesel FAME components, and any results showing suspiciously high Tri+aromatics values with ASTM D 6591-06 should be re-analyzed by IP391/07.

References

1. Angelika Gratzfeld-Huesgen, “Analysis of Aromatic Hydrocarbons in Middle Distillates with HPLC using IP Standard Method 391/95”, Agilent Application Note, 5965-9044E, 1997.
2. ASTM D 6591-06 “Standard Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection”.
3. Michael Woodman and Malgorzata Sierocinska, “Meeting the Requirements of EN12916:2006 (IP391/07) Using Agilent 1200 Series HPLC Systems”, Agilent Application Note 5990-4789EN, 2009.

www.agilent.com/chem

Printed in the USA
May 28, 2010
5990-5867EN

Agilent Technologies

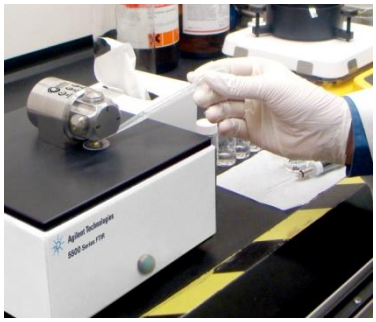
Portable measurement of biodiesel in diesel fuels by ASTM D7371-07 (FTIR-ATR-PLS method) with the Agilent 5500t FTIR spectrometer

Application Note

Author

Frank Higgins

Agilent Technologies
Connecticut, USA



Background

Biodiesel blending with current ultra low sulfur diesel (ULSD) fuels is increasing in popularity for both large scale fleet use and individual small scale consumers. The test method detailed in this application brief can be used for quality control purposes in the production and distribution of diesel fuel and biodiesel blends. The ASTM D7371 method is applicable to 1-100 volume % biodiesel (FAME) concentrations in diesel fuel oils; it applies to all common 5 % (B5), 10 % (B10), and 20 % (B20) biodiesel blends. The ASTM D7371 method coupled with the Agilent 5500t FTIR spectrometer provides an easy, accurate, and portable means for measuring the biodiesel content of a blended fuel with petroleum diesel fuel.

Agilent Technologies

Experiment

Following the ASTM D7371 procedures, three different diesel fuels are used to create the calibration standards. The cetane index in diesel fuels is varied by changing the relative percentage of aromatic to aliphatic hydrocarbons; higher cetane index fuels have less aromatic compounds. Cetane index is typically lower during cold months. The ASTM D7371 is designed to account for these seasonal differences in the diesel fuels. The ASTM certified B100 Biodiesel was mixed with diesel fuel blended at three different cetane indexes, referred to in the D7371 as diesel cetane check fuel low, high and ultra high. As specified in the method, a total of 70 standards were produced with biodiesel concentrations ranging from 0-100%. In addition to the calibration standards, 21 qualification standards were created with different concentrations than the calibration standards. The qualification standards were used to determine the method's accuracy and robustness.

All standards were measured using the Agilent 5500 Series FTIR spectrometers with an integrated 9 reflection diamond attenuated total reflectance (ATR) sample interface. The spectra were collected using 64 scans at 4cm-1 resolution yielding a 30 second sample measurement time. A partial least squares (PLS) model was developed using Thermo Galactic PLS/IQ software. The model concentrates on the ester carbonyl and other absorbance bands specific to fatty acid methyl esters (FAME). The PLS models were incorporated into Microlab software for an easy end-user biodiesel in diesel fuel application.

Results

A series of spectra from the calibration set are shown in Figure 1. Bands due to biodiesel can be seen both at 1741cm^{-1} and between 1170-1245cm^{-1}; these areas are correlated to the concentration of biodiesel in the D7371 method. The absorbance increases linearly with the concentration throughout the whole range from 0-100 %.

This provides a very accurate and precise measurement using the 5500 Series FTIR spectrometers.

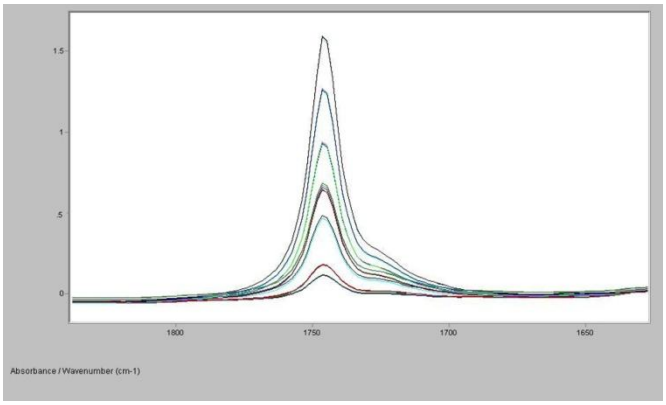


Figure 1. FTIR spectra overlaid of ASTM D7371 standards with biodiesel in diesel at 0, 2.5, 5, 10, 15, 20, 30, 50, 70, and 100 % biodiesel (v/v)

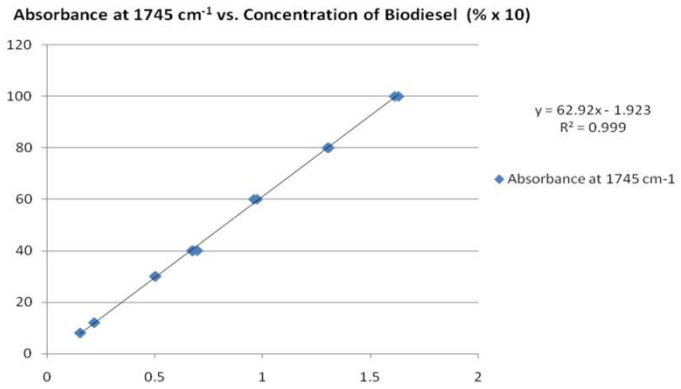


Figure 2. The PLS model's actual vs. predicted plot of biodiesel in diesel, low calibration set (0-10 % biodiesel)

ASTM D7371 specifies individual calibration models for the concentration ranges 0 -10 %, 10 - 30 % and 30 -100 %; each calibration model contains standards from each of the three cetane index diesel fuel stocks (ultra high, high and low). The 0-10 % calibration model results are plotted in Figure 2 as the actual (x-axis) vs. predicted (y-axis) biodiesel concentrations. The correlation coefficient for this model is R_2= 0.999. Results for the 10 - 30 % and 30 - 100 % models were similar. Each model uses 3 - 4 factors on mean centered data.

The three models based on the ASTM D7371 method were incorporated into a single method within the Microlab software. A screen shot showing one of the calibration definitions definition is shown in Figure 3.

The Microlab software also contains logic to report only the result from the correct model.

Using the "Component Reporting" feature, shown in Figure 4, which result will be shown to the user based on the predicted result. Using this feature, a single, correct result is present to the user even though results from three methods are calculated. This reduces confusion and allows samples to be measured by untrained users.

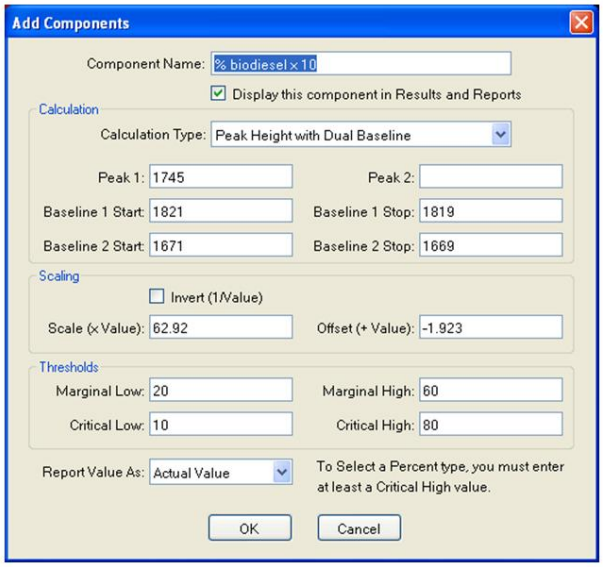


Figure 3. The Microlab methods editing feature where the 1-10 % biodiesel model is assigned

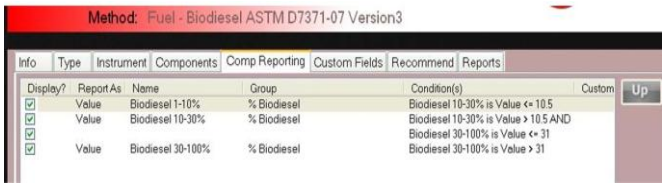


Figure 4. The conditional reporting setup window from the Microlab PC software, which determines the model results to be displayed when running a sample

The Microlab ASTM D7371 method was used to predict the concentrations of a separate qualification set. The qualification set covers the entire 0-100 % range of biodiesel in diesel, and the different cetane index diesel fuels were also used to make the qualification samples. The average relative error (1-100 % range) is 0.47 % and the maximum relative error is 1.56 %. The results of the separate validation are shown in Table 1. It should be noted that the standard error of qualification calculated for these tests is less than half the acceptable standard error of qualification listed in the ASTM method. A screen shot showing the software display for a 2.5 % biodiesel validation sample is shown in Figure 5.

Figure 5. Microlab results screen for a 2.50 vol % sample of biodiesel in diesel

Table 1. The results from the qualification set samples measured with the ASTM 7371 method in the Microlab software

Qualification Sample	Predicted Biodiesel (Vol %)	Actual Biodiesel (Vol %)	Error (%)
Q1	0.77	0.71	8.61
Q2	5.98	5.95	0.55
Q3	13.14	13.14	0.01
Q4	26.50	26.44	0.24
Q5	59.05	58.73	0.54
Q6	92.12	92.07	0.05
Q7	97.73	97.77	0.04
Q8	0.36	0.36	0.77
Q9	1.64	1.66	1.56
Q10	5.91	5.94	0.49
Q11	38.51	38.69	0.47
Q12	84.16	84.39	0.27
Q13	95.74	95.88	0.14
Q14	99.11	99.30	0.20
Q15	0.35	0.36	1.09
Q16	3.60	3.55	1.28
Q17	8.35	8.31	0.43
Q18	13.15	13.10	0.39
Q19	21.17	21.49	1.50
Q20	73.70	73.65	0.06
Q21	95.66	95.49	0.18
		Average Error Total (%)*:	0.47
		Maximum error (%*):	1.56
		Standard Error of Qualification (SEQ):**	0.08
		ASTM D7371 SEQ Limit (PSEQ):	0.21

Conclusions

This set of experiments show the ability of Agilent 5500 Series FTIR spectrometers with 9 reflection diamond ATR sample interface to meet the ASTM D7371 method. The method file which calculates the concentration in all ranges from 1 % to 100 % biodiesel and selectively reports the correct concentration is standard with all 5500 FTIR and 4500 FTIR systems. The results from a separate validation show that the instrument and method are very accurate while being very simple to use.

www.agilent.com/chem

Published May 1, 2011
Publication Number 5990-7807EN

Agilent Technologies

HYDRAULIC FRACTURING

Meet exacting standards for shale gas analysis

If you work in the natural gas industry, no one has to tell you that hydraulic fracturing (fracking) is big news. To date, 1,000 trillion cubic feet of natural gas from shale are being developed in North America, plus another 200 trillion cubic feet in Europe.

As worldwide demand for this fuel source grows, you face increased pressure to ensure its safety and heating/calorific value. And *that's* where Agilent can help.

The **Agilent 490 Micro GC Natural Gas Analyzer** and **490 Micro GC for Mud Logging** are preconfigured for reliable shale gas analysis in seconds, and are small enough to take virtually anywhere. Back at the lab, you can count on **Agilent's 7890B Natural Gas Analyzer** – based on our industry-leading GC platform – for turnkey operation and outstanding results.

Back to table of contents ►

Learn more about solutions for the energy and chemical industry at **agilent.com/chem/energy**

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

Application

Hydrocarbon Processing

Authors

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

Mario Morales
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Abstract

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

Introduction

Many sources of natural gas and petroleum gases contain varying amounts and types of sulfur compounds. The analysis of gaseous sulfur compounds is difficult because they are polar, reactive, and present at trace levels. Sulfur compounds pose problems both in sampling and analysis. Analysis of sulfur compounds many times requires special treatment to sample pathways to ensure inertness to the reactive sulfur species. Sampling must be done using containers proven to be nonreactive. Laboratory equipment must also be inert and well conditioned to ensure reliable results. Frequent calibration using stable standards is required in sulfur analysis [1].

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

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

Experimental

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

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

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

Table 1. Sulfur Standards in Helium

1.	Hydrogen sulfide	H_2S
2.	Carbonyl sulfide	COS
3.	Methyl mercaptan	CH_3SH
4.	Ethyl mercaptan	CH_4CH_3SH
5.	Dimethyl sulfide	CH_3SCH_3
6.	Carbon disulfide	CS_2
7.	2-propanethiol	$CH_3SHC_2H_5$
8.	Tert-butyl mercaptan	$(CH_3)_3CSH$
9.	1-propanethiol	$CH_3(CH_2)_2SH$
10.	Thiophene	C_4H_4S
11.	n-butanethiol	$CH_3(CH_2)_3SH$
12.	Diethyl sulfide	$CH_3CH_2SCH_2CH_3$
13.	Methyl ethyl sulfide	$CH_3SCH_2CH_3$
14.	2-methyl-1-propanethiol	$(CH_3)_2CHCH_2SH$
15.	1-methyl-1-propanethiol	$CH_3CH_2CHSHCH_3$

Experimental Conditions

GC Conditions

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

SCD Conditions

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

Results and Discussion

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

Figure 2 is the chromatogram of low-level sulfur compounds at 1.35 ppb (H_2S), which is prepared by the point-of-use gas blending system. Table 2 is the calculated signal to noise (S/N) of each compound, from the achieved data. It can be seen that DP SCD can detect low-level sulfur compounds.

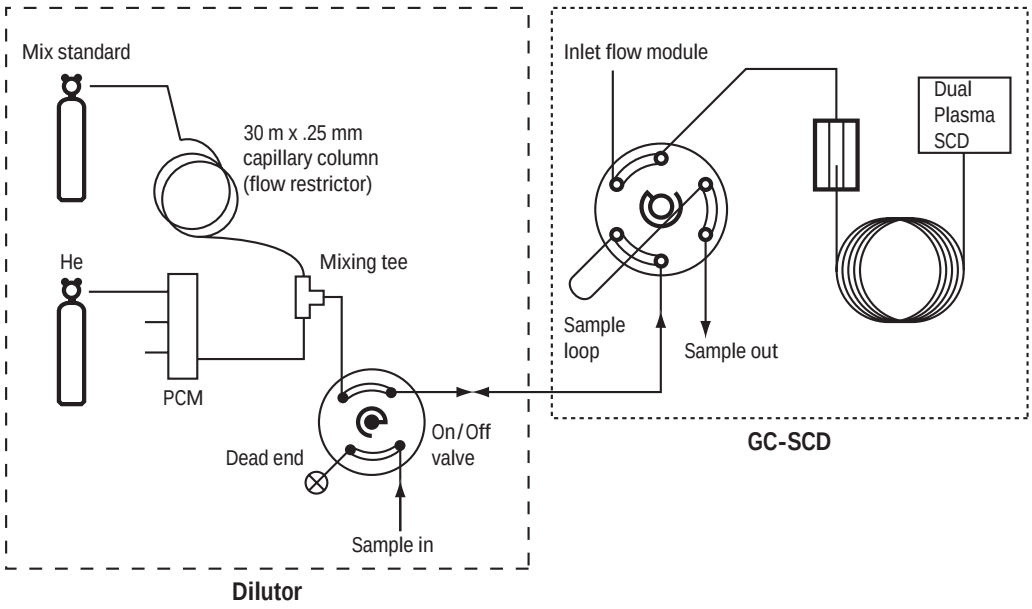


Figure 1. Diagram of online dilutor GC-DP SCD.

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

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

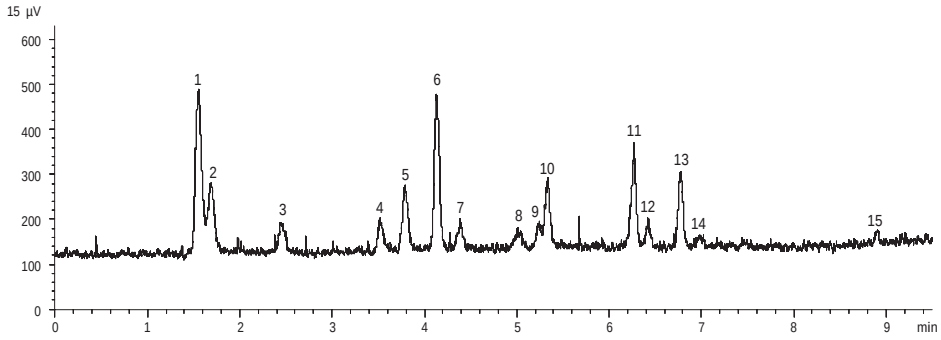


Figure 2. Chromatogram of sulfur compounds in helium at 1.35 ppb. (Refer to Table 1 for peak identification.)

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

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

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

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

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

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

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

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

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

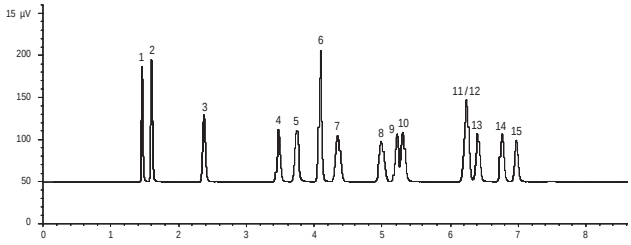


Figure 3. Chromatogram of sulfurs in natural gas. (Refer to Table 1 for peak identification.)

Natural Gas Sample Analysis

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

Table 5. Result of the Three Real Samples

Samples		H_2S	COS	Methyl Mercaptan
BLEND AL	Conc. (ppm, v/v)	2.3	2.0	2.0
	RSD (%, n = 5)	2.3	0.3	1.4
BLEND 6	Conc. (ppm, v/v)	27.1	21.9	17.3
	RSD (%, n = 5)	1.2	0.4	2.3
BLEND 12	Conc. (ppm, v/v)	15.0	9.2	10.1
	RSD (%, n = 5)	0.7	0.6	0.6
Standard	Conc. (ppm, v/v)	2.0	0.8	0.9
natural gas	RSD (%, n = 5)	1.7	2.5	1.7

Conclusions

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

References

1. ASTM D5504-98: Standard test method for determination of sulfur compounds in natural gas and gaseous fuels by gas chromatography and chemiluminescence
2. Roger L. Firor, “Volatile Sulfur in Natural Gas, Refinery Gas, and Liquified Petroleum Gas,” Agilent Technologies publication 5988-2791EN
3. Roger L. Firor and Bruce D. Quimby, “A Comparison of Sulfur Selective Detectors for Low-Level Analysis in Gaseous Streams,” Agilent Technologies publication 5988-2426EN

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
August 12, 2008
5989-9234EN

Agilent Technologies

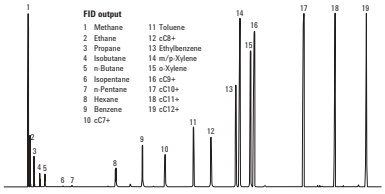
Application 125-00
Agilent Fast Natural Gas Analyzer
Technical Overview

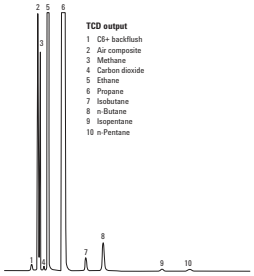
Application Highlights

- A thermal conductivity detector (TCD) to identify air composite (oxygen, nitrogen, and carbon monoxide), methane, carbon dioxide, ethane, propane, isobutane, n-butane, neopentane, isopentane, and n-pentane with an initial C6+ composite backflush to detector.
- 200 ppm lower detection limit for all components except those eluting on the tail of a major preceding constituent.
- System compliant with Gas Processors Association methods 2177 and/or 2261.
- Analysis time is approximately 15 minutes.

Optional Configurations

- Detailed hydrocarbon analysis of extended natural gas
- TCD/FID/FPD for extended natural gas with trace sulfur analysis
- TCD/FID for extended natural gas with helium or hydrogen



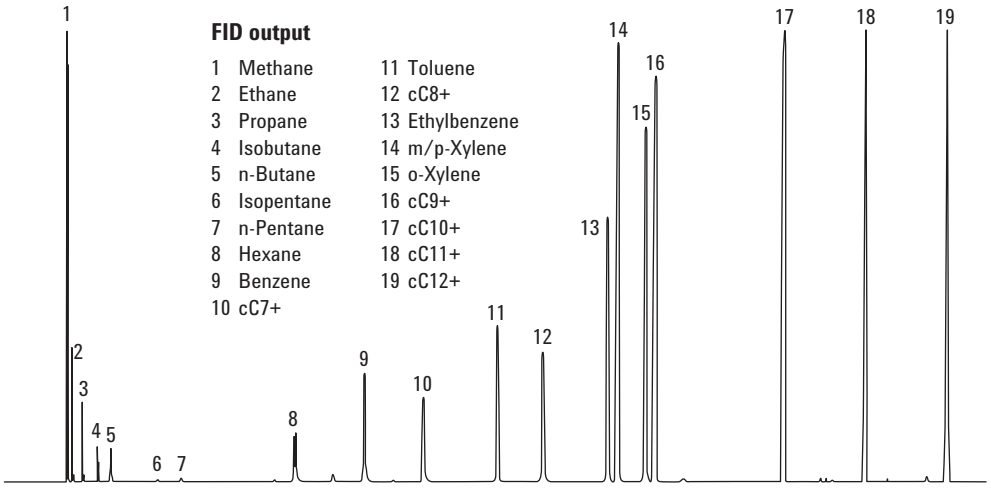


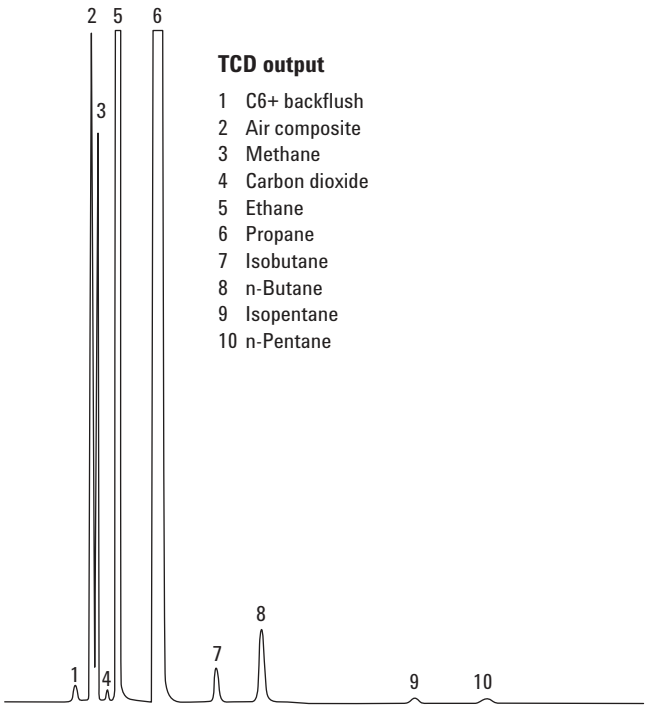
For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Agilent Technologies

WASSON·ECE INSTRUMENTATION





FID and TCD output from Agilent Fast Natural Gas Analyzer.

Printed in the USA
December 3, 2002
5988-6725EN

Agilent Technologies

WASSON·ECE INSTRUMENTATION

Parallel GC for Complete RGA Analysis

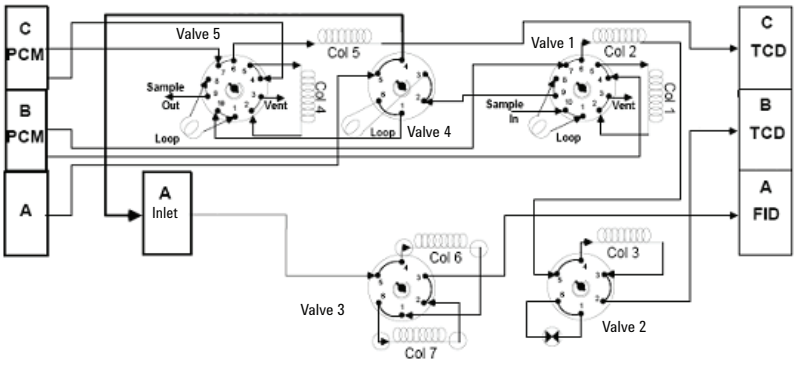
Application Brief

Chunxiao Wang

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

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

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



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

Figure1. RGA valve system.

Highlights

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

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

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

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

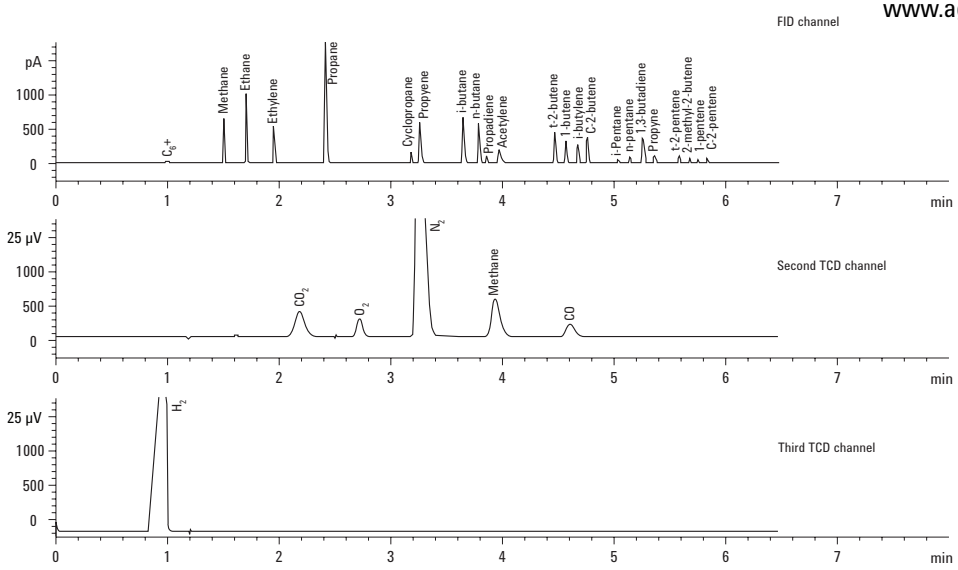


Figure 2. Refinery gas calibration standards analysis.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Reference

1. Chunxiao Wang, "Parallel GC for Complete RGA Analysis,"Agilent application brief, 5989-6103EN, January 19, 2007
2. ASTM D1945-03, "Standard Test Method for Analysis of Natural Gas by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
3. ASTM D1946-90 (2006), "Standard Practice for Analysis of Reformed Gas by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
4. UOP Method 539, "Refinery Gas Analysis by Gas Chromatography,"ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428, USA.

Published in the USA
December 12, 2008
5989-7438EN

Analysis of Volatile Organic Compounds in Water Using Static Headspace-GC/MS

Application Note

Environmental

Authors

Karine Jacq, Frank David, Pat Sandra
Research Institute for Chromatography
Pres. Kennedypark 26, B-8500 Kortrijk
Belgium

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

Abstract

A static headspace (SHS) method was optimized for the determination of volatile organic compounds (VOCs) in water. Analysis was performed by GC/MS in simultaneous scan/SIM mode. Using the trace ion detection mode on a 5975C MSD equipped with triple axis detection, "purge and trap" sensitivities can be obtained, combined with the robustness and ease-of-use of static headspace.

Agilent Technologies

Introduction

The determination of volatile organic compounds (VOCs) in environmental samples is mostly performed using either static headspace (SHS) or purge and trap (P&T) extraction. Both combine separation by gas chromatography (GC) with detection by mass spectrometry (MS). P&T (also called dynamic headspace) is based on an exhaustive extraction process where, ideally, all solutes present in the sample are extracted completely, concentrated in an adsorbent trap, and then thermally desorbed from the trap to introduce sample to the GC/MS for analysis. In contrast, SHS establishes an equilibrium between the solid or liquid sample and the gas or headspace phase above it in a sealed vial. A portion of the headspace is transferred to the GC/MS for analysis via a valve with a sample loop. In principle, because of exhaustive sampling, P&T is more sensitive than SHS and is preferred for analysis of sub-ppb (ng/L) VOCs in drinking water and surface water. However, P&T autosamplers are more complicated to run and maintain than are SHS autosamplers. SHS offers higher robustness and fewer problems related to carryover, cross-contamination, foam formation (due to the presence of detergents), and water management (trapping problems). In many routine laboratories, there is high interest in efforts to improve instrumentation to the point where SHS analyzes VOCs at the necessary regulatory limits.

Recent developments in GC/MS hardware have resulted in higher sensitivity and lower detection limits, thereby allowing SHS to be considered for drinking and surface water analyses. In addition, faster electronics allow the use of simultaneous scan/SIM methods and fast GC separation, while maintaining enough data points for accurate peak detection and quantification.

In this application note it is shown that by using a state-of-the-art GC/MS system and optimized SHS conditions, P&T sensitivities can be obtained, while maintaining all of the classic advantages of static headspace in terms of ease of use and robustness.

Experimental Conditions

Sample Preparation

Analyses were performed using 10-mL water samples. Samples were placed in a 20-mL headspace vial (P/N 5182-0837) containing 7 g sodium sulfate. The samples were spiked with an internal standard solution. The vials were tightly closed with an aluminum crimp cap with PTFE/silicone septum (P/N 5183-4477) using an electronic crimper (P/N 5184-3572).

An internal standard mixture of three deuterated VOCs was used. The mixture was made from three individual solutions of 1,2-dichloroethane-d4, toluene-d8, and chlorobenzene-d5 (all from Supelco [Bellefonte, PA, USA], 2,000 ppm in methanol). The individual solutions were mixed and diluted in methanol to 800 ng/mL. From this working solution, 10 µL was spiked into each 10-mL sample aliquot, corresponding to an internal standard concentration of 800 ng/L (800 ppt).

In total, 60 target analytes were analyzed and are listed in Table 1. The target list corresponds to EPA Method 524.2 and is also typical of several EU methods.

Calibration was done by analyzing reference water blanks spiked with internal standards and mixtures of the target analytes. Standard mixtures containing all 60 analytes are available from Supelco or Dr Ehrenstorfer (Augsburg, Germany). For reference water, bottled drinking water (Evian) was used with the same salt and internal standards addition as used for the samples. Bottled drinking water often offers better blank values than does HPLC grade water or Milli-Q water.

Calibration levels were between 45 and 1,250 ng/L. These were obtained by spiking 10 µL of VOC standard solutions at 45 to 1,250 ng/mL in methanol.

Instrumental Conditions

The analyses were performed on an Agilent 7890A GC/5975C MSD system. SHS was performed with an Agilent G1888 HS autosampler, equipped with a 1-mL sample loop. The SHS was coupled to a split/splitless injection port. The carrier gas line entering the SSL inlet port was cut close to the inlet and the long leg connected to the carrier gas inlet port on the G1888. The transfer line from the G1888 was connected with a stainless steel zero dead volume union on the tubing end close to the SSL inlet.

The 5975C MSD was operated in simultaneous SIM/SCAN mode with the trace ion detection mode switched on. The MSD was also equipped with the triple axis detector (TAD) option.

The experimental conditions can be summarized as follows:

SHS

Pressurization:	0.15 min, 20 kPa
Loop:	1 mL, 120 °C, 0.5 min fill time, 0.1 min equilibration time transfer line 120 °C, 0.5 min injection time

GC

Inlet:	Split/splitless, 250 °C, split 1/10, headspace liner (P/N 5183-4709)
Column:	DB-624, 20 m × 0.18 mm × 1 µm (J & W 121-1324)
Gas:	He, constant pressure (95 kPa)
Oven:	40 °C (5 min) → 180 °C @ 8 °C/min → 250 °C (0.17 min) @ 30 °C/min
Run time:	25-min run

MS (5975C Inert, Agilent)

Transfer line:	300 °C
Scan:	0 to 2 min: 45 to 300 *m/z*, 2 to 25 min: 33 to 300 *m/z*
SIM:	See Table 1

Triple Axis Detector (G3392A upgrade kit)

The method was locked on toluene at 10.42 min. All the data shown correspond to the SIM chromatograms.

Table 1. SIM Windows, Retention Times, and Ions for Quantification

Peak no	Name	CAS	RT (min)	Start time window	Dwell time (ms)	IS	Target ion	Qualifiers	
1	Dichlorodifluoromethane	75-71-8	1.31	0.00	70	1	85	87	50
2	Chloromethane	74-87-3	1.45			1	50	52	
3	Vinylchloride	75-01-4	1.55			1	62	64	
4	Bromomethane	74-83-9	1.80	1.80	100	1	94	96	
5	Chloroethane	75-00-3	1.89			1	64	49	
6	Fluorotrichloromethane	75-69-4	2.12	2.10	100	1	101	103	66
7	1,1-dichloroethene	75-35-4	2.62	2.55	100	1	96	61	98
8	Dichloromethane	75-09-2	3.17	3.10	100	1	49	84	86
9	1,2-dichloroethene Z	156-60-5	3.50	3.45	100	1	61	96	98
10	1,1-dichloroethane	75-34-3	4.11	4.00	100	1	63	83	98
11	2,2-dichloropropane	594-20-7	5.07	4.60	70	1	77	41	
12	1,2-dichloroethene E	156-59-2	5.13			1	61	96	98
13	Bromochloromethane	74-97-5	5.55	5.50	70	1	49	130	
14	Trichloromethane	67-66-3	5.75			1	83	47	
15	1,1,1-trichloroethane	71-55-6	6.02			1	97	61	
16	Tetrachloromethane	56-23-5	6.32	6.25	70	1	119	117	82
17	1,1-dichloro-1-propene	563-58-6	6.35			1	75	39	110
IS1	**1,2-dichloroethane d_4**		6.72			IS1	65	102	
18	Benzene	71-43-2	6.73	6.55	70	2	78	52	
19	1,2-dichloroethane	107-06-2	6.79			1	98	62	
20	Trichloroethene	79-01-6	7.98	7.40	100	1	132	95	130
21	1,2-dichloropropane	78-87-5	8.40	8.30	100	1	63	76	112
22	Dibromomethane	74-95-3	8.61			1	174	93	79
23	Bromodichloromethane	75-27-4	8.97	8.85	100	1	83	47	129
24	1,3-dichloropropene Z	542-75-6	9.82	9.50	100	1	75	39	110
IS2	**Toluene d_8**		10.30	10.10	70	IS2	98	100	70
25	Toluene	108-88-3	10.42			2	91	92	65
26	1,3-dichloropropene E	542-75-6	10.93	10.68	100	1	75	39	110

Table 1. SIM Windows, Retention Times, and Ions for Quantification (continued)

Peak no	Name	CAS	RT (min)	Start time window	Dwell time (ms)	IS	Target ion	Qualifiers	
27	1,1,2-trichloroethane	79-00-5	11.25	11.10	100	1	97	83	61
28	Tetrachloroethene	127-18-4	11.44	11.36	70	1	166	131	94
29	1,3-dichloropropane	142-28-9	11.55			1	76	41	78
30	Dibromochloromethane	124-48-1	11.96	11.75	70	1	129	127	79
31	1,2-dibromoethane	106-93-4	12.12			1	107	109	27
IS3	**Chlorobenzene d_5**		13.00	12.50	70	IS3	117	82	54
32	Chlorobenzene	108-90-7	13.09			3	112	51	77
33	1,1,1,2-tetrachloroethane	630-20-6	13.29	13.21	70	1	131	117	95
34	Ethylbenzene	100-41-4	13.35			2	91	106	51
35	m-xylene	108-38-3	13.59			2	91	106	51
36	p-xylene	106-42-3	13.59	13.47	100	2	91	106	51
37	o-xylene	95-47-6	14.34	14.00	80	2	91	106	51
38	Styrene	100-42-5	14.38			2	104	78	
39	Tribromomethane	75-25-2	14.70	14.54	100	1	173	252	91
40	Cumene	98-82-8	15.08	14.88	100	2	105	120	77
41	Bromobenzene	108-86-1	15.59	15.35	50	3	77	156	
42	1,1,2,2-tetrachloroethane	79-34-5	15.72			1	83	85	
43	1,2,3-trichloropropane	96-18-4	15.76			1	75	77	110
44	n-propylbenzene	103-65-1	15.89			2	120	91	
45	2-chlorotoluene	95-49-8	16.01			3	91	126	
46	4-chlorotoluene	106-43-4	16.23	16.12	80	3	126	91	63
47	1,2,4-trimethylbenzene	95-63-6	16.26			2	105	120	
48	*tert*-butylbenzene	98-06-6	16.88	16.60	80	2	134	119	91
49	1,3,5-trimethylbenzene	108-67-8	16.98			2	105	120	
50	*sec*-butylbenzene	135-98-8	17.31	17.15	70	2	105	134	91
51	1,3-dichlorobenzene	541-73-1	17.46			3	146	111	75
52	Cymene	99-87-0	17.62	17.55	80	2	119	134	
53	1,4-dichlorobenzene	106-46-7	17.65			3	146	111	75
54	1,2-dichlorobenzene	95-50-1	18.36	18.00	70	3	146	111	75
55	n-butylbenzene	104-51-8	18.43			2	91	134	92
56	1,2-dibromo-3-chloropropane	96-12-8	19.93	19.00	100	1	157	75	153
57	1,2,4-trichlorobenzene	120-82-1	21.55	20.80	100	3	180	145	109
58	Hexachloro-1,3-butadiene	87-68-3	21.93	21.75	80	1	225	190	260
59	Naphthalene	91-20-3	22.01			2	128	102	
60	1,2,3-trichlorobenzene	87-61-6	22.49	22.28	100	3	180	145	109

Method Development

Column Selection and Chromatographic Conditions

For the analysis of VOCs, a column with low phase ratio (relatively thick film) is normally used. In this work, a 20 m × 180 µm id column coated with 1 µm DB-624 was used. This column (or a 0.25 mm id version) has recently become preferred for EPA Methods 524 or 624 compared to larger diameter columns used when the methods were originally developed. The narrow id allows one to speed up the analysis while maintaining resolution. Most of the target analytes were well separated using the temperature program indicated above. In cases of coelution, solutes could be effectively quantified using unique MS ions. Only p-xylene and m-xylene were not separated at all. In addition, the quantification ion may need to be changed if both 1,2-dichloroethene (E) and 2,2-dichloropropane (t_R = 5.1 minutes) or 1,1,2,2-tetrachloroethane and 1,2,3-trichloropropane (t_R = 15.7 minutes) are found to be present in samples.

Another critical aspect in the analysis of VOCs by SHS or P&T coupled to GC/MS is the focusing of the most volatile

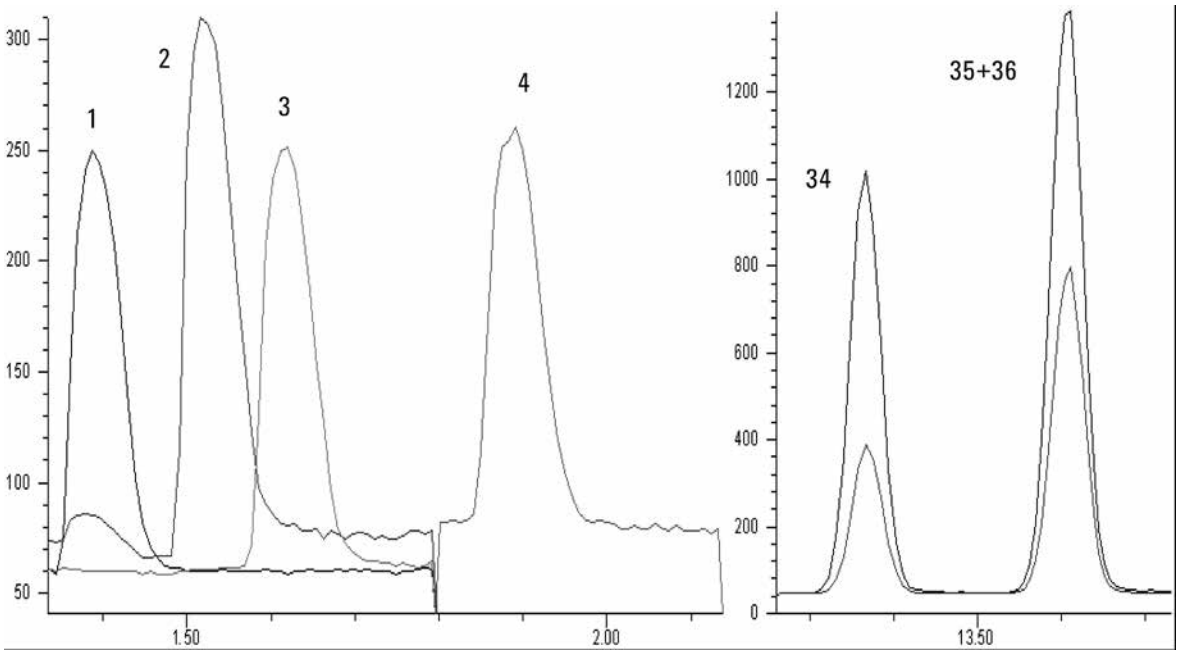


Figure 1. Peak shape of very volatile compounds compared to less volatile compounds – Extracted Ion Chromatograms at m/e 85 (1. CCL_2F_2), m/e 50 (2. chloromethane), m/e 62 (3. vinylchloride), m/e 94 (4. bromomethane), and ions at m/e 91 and 106 (34. ethylbenzene and 35/36. m/p xylene).

(gaseous) solutes (first six eluters). If the transfer from the sampler (SHS or P&T) is too slow, their bandwidths are large or distorted. Transfer and injection speeds can be increased by increasing the split ratio, but the sensitivity decreases as a consequence. A good compromise was found using a 1:10 split ratio. The resulting peak widths obtained for a water sample spiked at the 300 ppt level are shown in Figure 1. The peaks for early peaks difluorodichloromethane, chloromethane, vinylchloride, and bromomethane are broader than for the later-eluting (focused) analytes, such as ethylbenzene and xylenes, but were still acceptable for good quantification at the required detection limits.

Effect of Salt Addition

The sensitivity of an SHS method is limited by the concentration of the VOC in the headspace. This concentration depends on the initial concentration in the water, the phase ratio between liquid phase and gas phase, and the water/air distribution constant. The last depends on solute characteristics (vapor pressure, water solubility), temperature, pressure, pH, and salt concentration.

To normalize the salt concentration (same concentration in calibration solutions and samples), a high concentration of salt (sodium chloride, sodium sulfate) is typically added to saturate the sample.

The effect of salt addition is demonstrated in Figure 2 by comparing the responses of the VOCs obtained by analyzing a water sample spiked at 300 ppt level with and without salt addition. An average gain in sensitivity by a factor 2.2 was obtained by addition of salt. The "salting-out effect" drives the VOCs into the headspace. For some solutes, such as 1,2-bromo-3-chloropropane, which has a lower response in MS, the gain was almost a factor of 4.

Figure 2 shows overlaid SIM chromatograms for some early-eluting (highly volatile) solutes (Figure 2a) and mideluting ones (Figure 2b). The gain factor for the most volatile solutes (gases: chloromethane to vinylchloride) is small for some (= 1.5), but is larger for the mideluters (gain is a factor < 2.5).

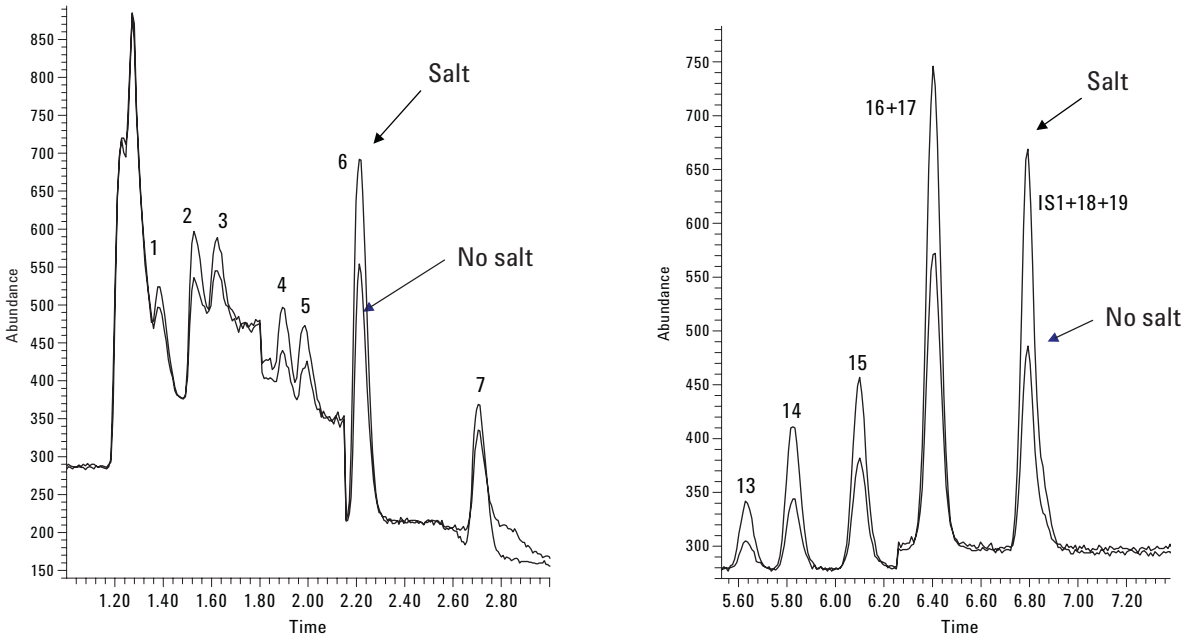


Figure 2. Effect of salt addition on response, water spiked at 300 ppt. See Tables 1 and 2 for peak identification.

SHS Conditions

Incubation Time

Since SHS is an equilibrium technique, the equilibration time plays an important role. Maximum sensitivity is obtained if equilibrium is reached between the concentration of the solutes in the sample and in the headspace gas phase. Tests were made using a 10-mL water sample spiked at 300 ppt level. Headspace injections were performed after equilibration times between 10 and 60 minutes (using 80 °C equilibration temperature, high shaking).

No significant difference in peak areas was observed for the different VOCs, indicating that equilibrium is reached for the 10-mL sample using the high-shaking mode on the G1888 in less than 10 minutes. Therefore, an equilibration time of 10 minutes was selected for further work.

Incubation Temperature

The sample-headspace equilibrium is also influenced by the temperature. Seven experiments with increasing incubation temperature from 40 to 100 °C in 10 °C increments were performed (10-minute equilibration time, vial pressure: 48 kPa).

In general it is expected that a higher temperature will increase the concentration of the solutes in the headspace and consequently will increase the response in GC/MS analysis.

From the experiments, however, some interesting observations can be made. The responses (peak areas) for some selected solutes are plotted versus equilibration temperature in Figure 3. Vinylchloride was selected as representative for the high-volatility (early-eluting) VOCs, benzene was selected as representative for a medium-volatility (mideluting) VOC, and 1,2,3-trichlorobenzene as a representative for the late-eluting, low-volatility VOCs.

As can be seen from the plots, the high-volatility solutes behave slightly differently from the others. Between 40 and 70 °C, the response obtained for vinylchloride is nearly constant. At temperatures higher than 70 °C, the response drops. The same behavior was observed for the other early-eluting solutes (for example, dichlorodifluoromethane, chloromethane, bromomethane, chloroethane and fluorotrichloromethane). For these solutes, static headspace extraction at low equilibration temperatures is already efficient.

For medium- and low-volatility solutes, the analytical sensitivity maximized at 70 °C. For all solutes, including the high-volatility analytes, responses decreased by 50 to 60 percent as the equilibrium temperature increased from 70 to 100 °C. This is probably caused by increased vial pressure leading to higher dilution during sample loading (decompression) in the headspace sampler.

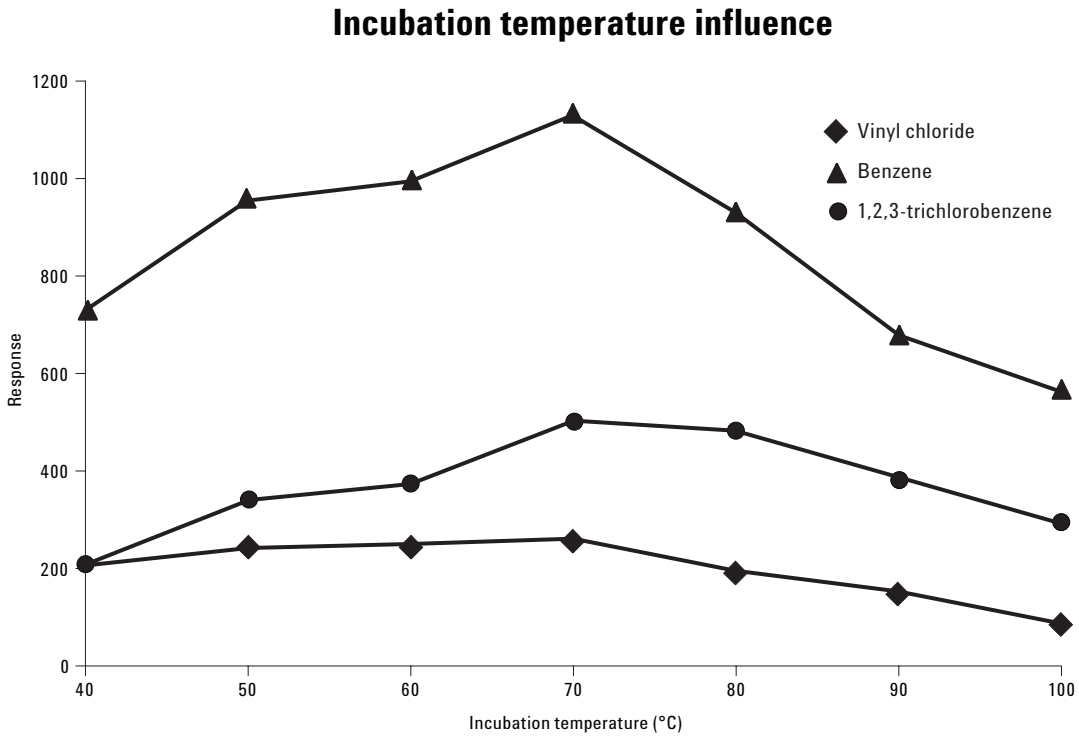


Figure 3. Influence of SHS incubation temperature on response for vinylchloride (early eluter), benzene (mideluter), and 1,2,3-trichlorobenzene (late eluter).

The higher response obtained at 70 °C in comparison to equilibration at 40 °C is illustrated for the solutes eluting in the 2.5- to 9-minute elution window (eluting between dichloroethene and bromodichloromethane) in Figure 4a. In Figure 4b, the chromatograms obtained at 70 and 100 °C (similar elution window as in Figure 4a) are compared. The decrease in response at 100 °C is clear and, moreover, an increase in background level is observed. This is probably due to the introduction of a higher amount of water (as vapor) during headspace injection.

For these reasons, 70 °C was selected as the optimum equilibration temperature.

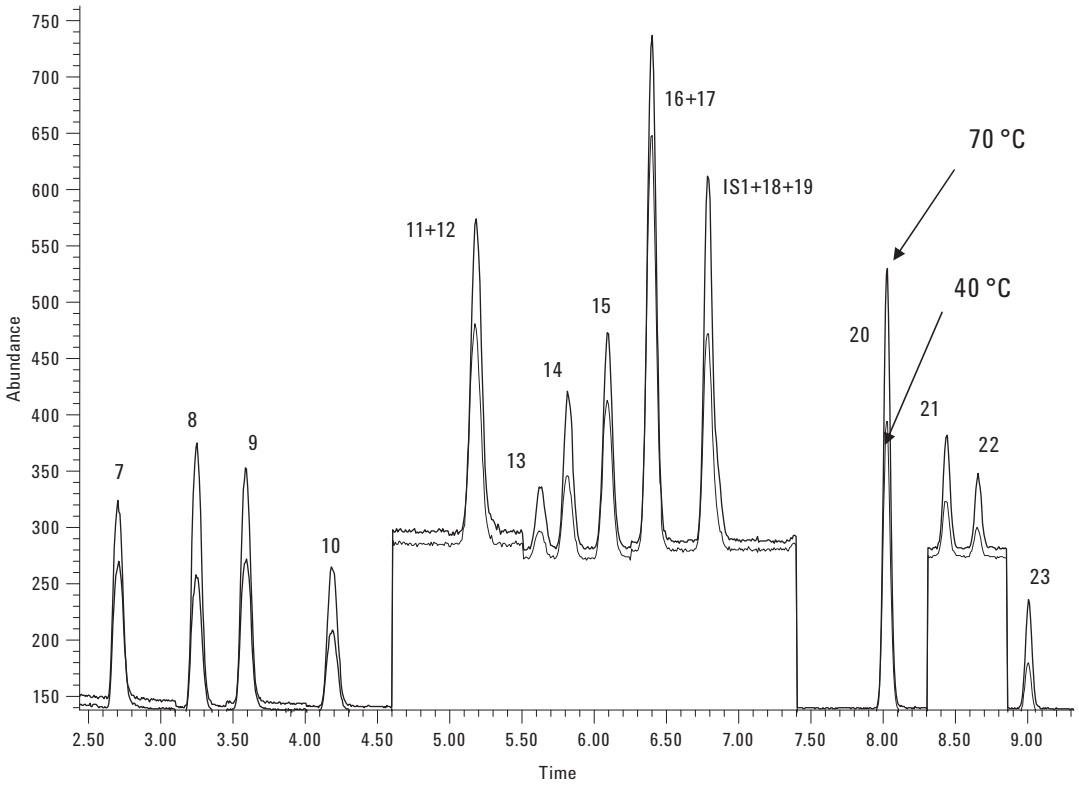


Figure 4a. Overlay of SIM chromatograms obtained by SHS GC/MS using incubation temperatures of 40 and 70 °C. See Tables 1 and 2 for peak identification.

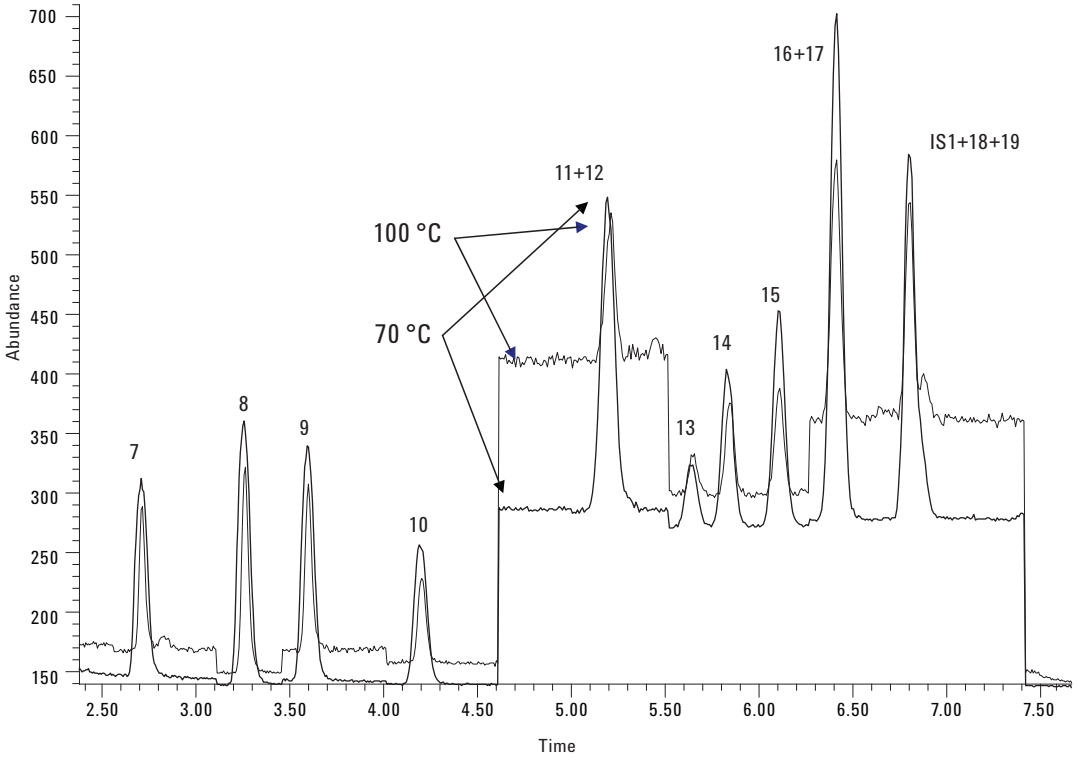


Figure 4b. Overlay of SIM chromatograms obtained by SHS GC/MS using incubation temperatures of 70 and 100 °C. See Tables 1 and 2 for peak identification.

Vial Pressure

After equilibrium, the vial is pressurized with carrier gas. The pressurized headspace is vented to a gas sampling valve with sample loop for subsequent injection into the GC/MS for analysis. The pressure provides a reproducible driving force to move sample to the loop. Too little pressure will prevent a representative sample from filling the sample loop. Too much pressure will result in excessive dilution of headspace, lowering the concentration of analytes and reducing analytical sensitivity. Since the optimal vial pressure is a function of several variables, such as vial size, sample temperature, and sample loop volume, it should be optimized.

Six experiments were performed at 70 °C equilibrium temperature and 10-minute equilibrium time with increasing vial pressures from 0 to 100 kPa in 20-kPa increments. No significant difference in analyte sensitivity was observed for vial pressure settings between 0 and 40 kPa. At higher vial pressures, however, the response of all analytes dropped (response at 100 kPa was 30 percent lower than at 20 kPa vial pressure). A vial pressure of 20 kPa was selected as optimum.

Final Chromatogram

An example of a blank water sample spiked at 1,250 ppt level with all 60 solutes and the three internal standards (at 800 ppt) is shown in Figure 5.

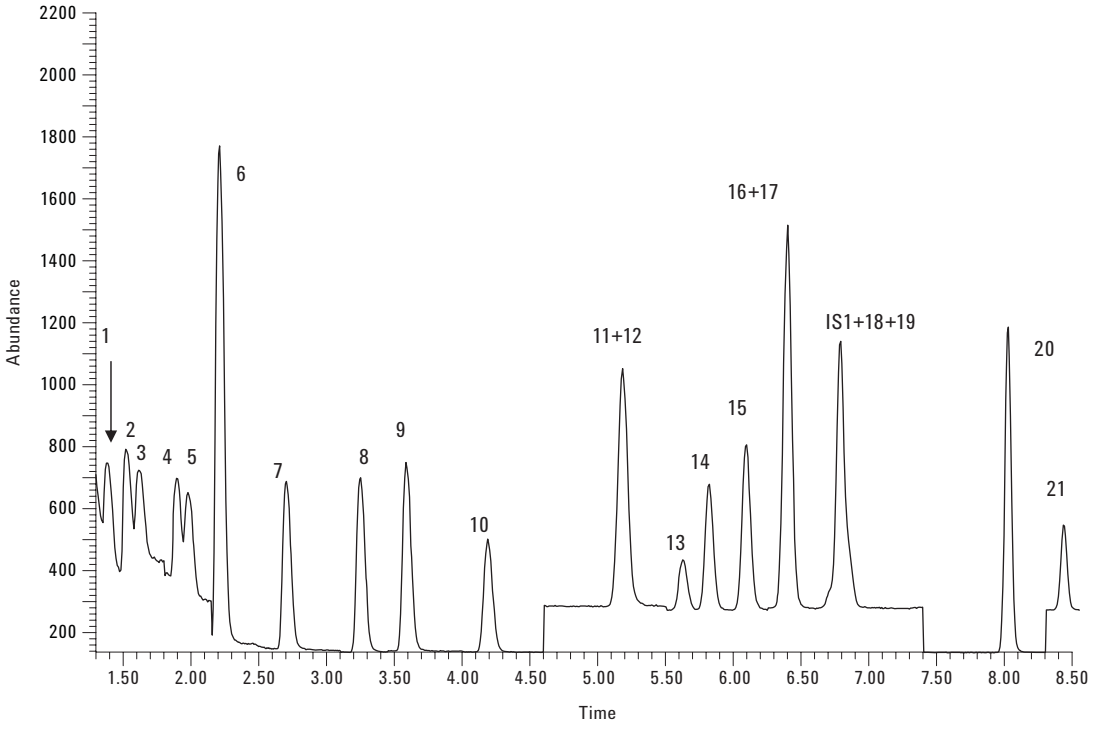


Figure 5a. SIM chromatogram obtained by SHS GC/MS of water sample spiked at 1.25 ppb with VOCs. See Tables 1 and 2 for peak identification.

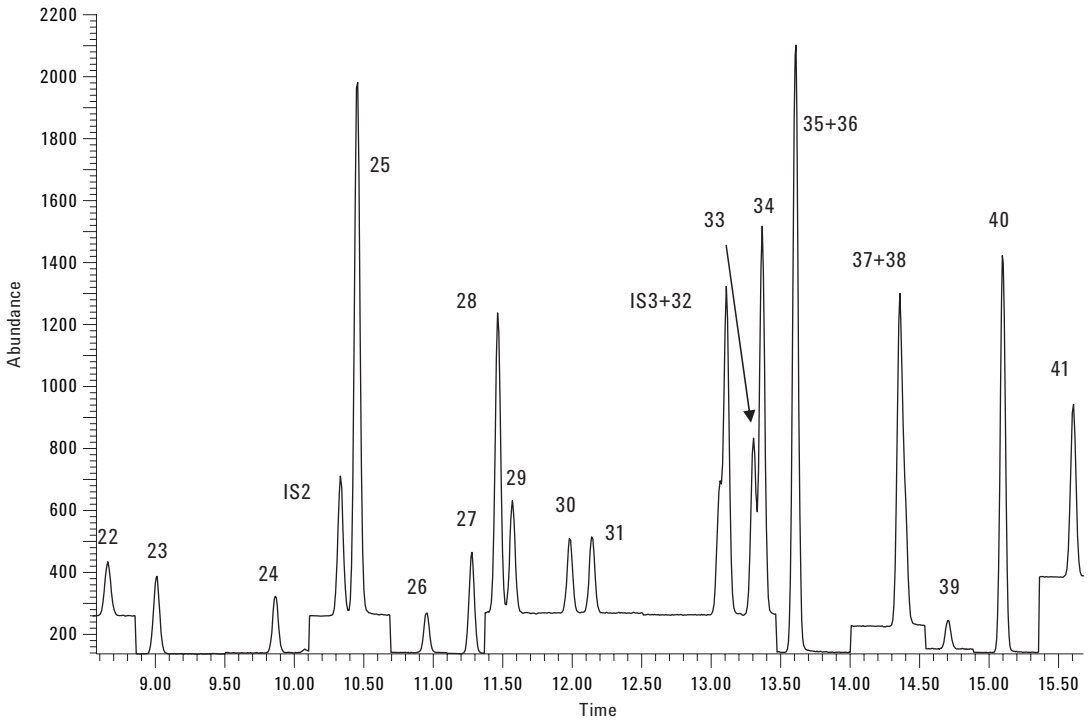


Figure 5b. SIM chromatogram obtained by SHS GC/MS of water sample spiked at 1.25 ppb with VOCs. See Tables 1 and 2 for peak identification.

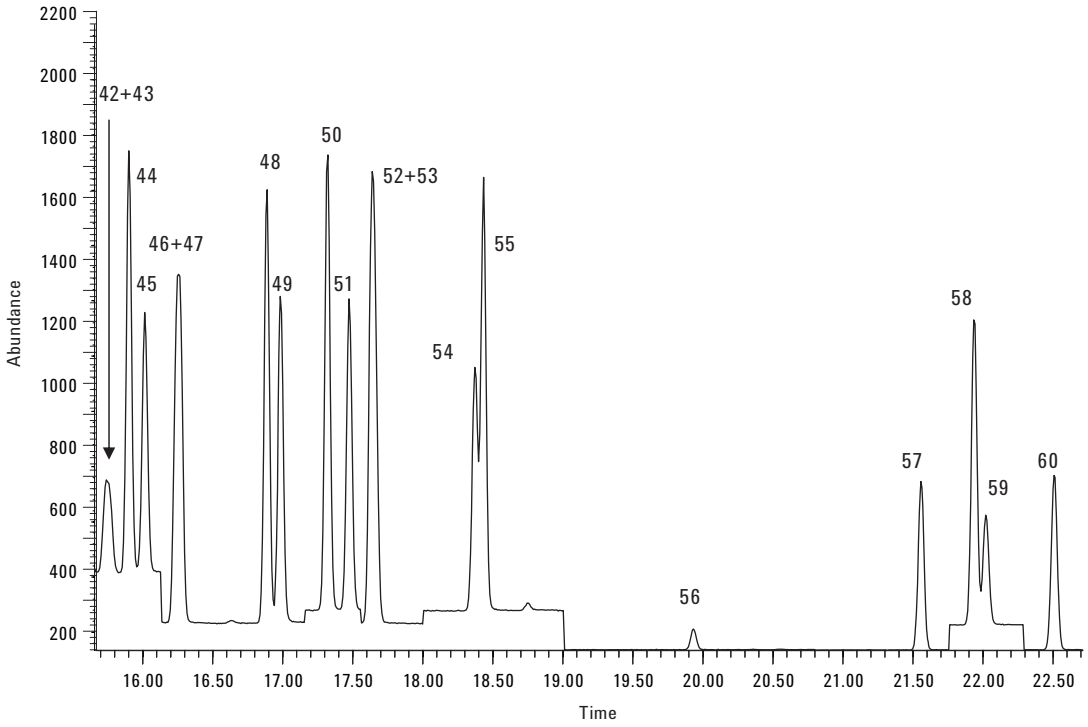


Figure 5c. SIM chromatogram obtained by SHS GC/MS of water sample spiked at 1.25 ppb with VOCs. See Tables 1 and 2 for peak identification.

Validation

Linearity

Linearity was tested on five levels (+ blank) between 45 and 1,250 ppt. The correlation coefficients of the external standard calibration curve were 0.99 on average. The correlation coefficients for the internal standard method (plot of relative areas versus relative concentration) for all solutes are given in Table 2.

The linearity was better than 0.990 in all cases (average 0.996), except for 1,2-dibromo-3-chloropropane ($r^2 = 0.966$), which gives a lower response in MS.

The linearity was also calculated as %RSD in relative response factors over the entire calibration range. The RSD values obtained in this range are also listed in Table 2. For three solutes, namely dichloromethane, trichloromethane (chloroform), and toluene, the lowest calibration points were not taken into account, since in the blank analyses also some traces of these solutes were present (due to lab contamination).

On average, the RSDs are around 10 to 15 percent (mean = 13.6 percent), well below the 20 percent requirements specified in EPA Method 524.2 (for P&T GC/MS).

Repeatability

Repeatability (n = 6) was tested at the 150-ppt level. The average %RSD was 5.4 percent. For most solutes, even for the high-volatility analytes, the RSDs at this level were well below 10 percent. For some haloalkanes, which have lower MS responses, higher values were observed, but still meet method requirements and are close to those achieved with P&T. For low-volatility solutes, such as aromatics (BTEX) and chloroaromatics, RSDs were excellent.

Limits of Detection (LODs)

Using trace ion detection (TID) mode (selected in method setup) in combination with a triple-axis detector (hardware upgrade), improved signal-to noise values can be obtained as illustrated in Figure 6. A subset of the chromatogram is shown for a blank water sample spiked at 45 ppt, comparing standard mode (Figure 6a) and TID ON (Figure 6b). Using TID, noise is reduced, resulting in better S/N ratio.

LODs were calculated for each compound at the 45-ppt level. Results are listed in Table 2. Typically, the LODs were ≤ 20 ppt. For most aromatics and chloroaromatics, LODs were ≤ 10 ppt. For some haloalkanes and haloalkenes, the LOD was between 20 and 50 ppt. 1,2-dichloroethane had the highest value at 136 ppt.

Regulatory limits, as included in EU Directive 98/83/EC on drinking water, are 1 µg/L (1 ppb) for benzene, 10 µg/L (10 ppb) for trichloroethylene, and 0.5 µg/L (500 ppt) for vinylchloride. It is clear that the LODs obtained by this SHS GC/MS method are more than adequate to meet the EU method requirements (we achieved one to two orders of magnitude better LODs).

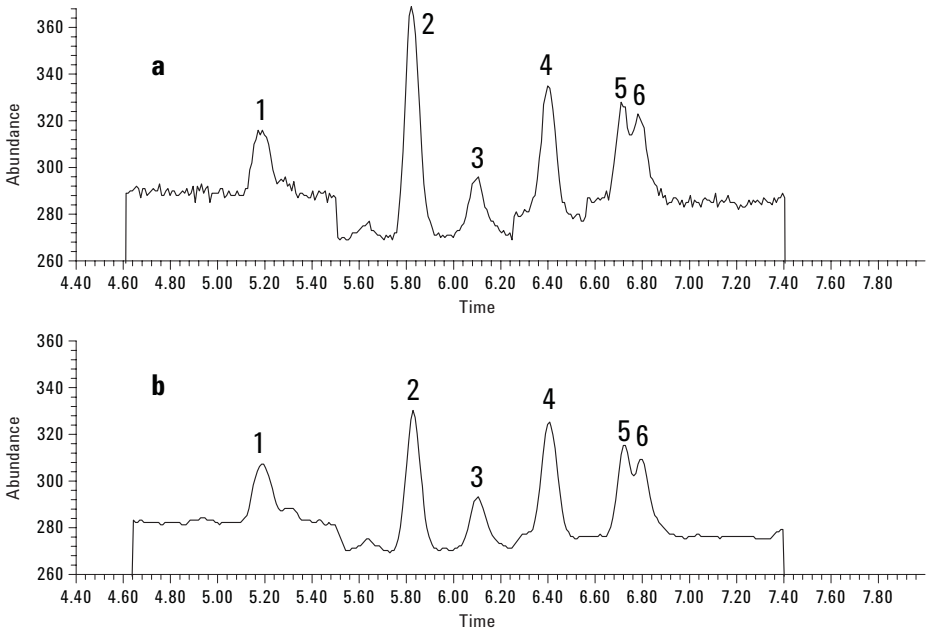


Figure 6. SIM chromatogram with MS in normal mode (top) or in TID ON mode (bottom) (water sample spiked at 45 ppt level). Peaks: 1. 2,2-dichloropropane+1,2-dichloroethene; 2. trichloromethane, 3. trichloroethane (1,1,1); 4. tetrachloromethane+1,1-dichloropropene; 5. benzene; and 6. dichloroethane.

Table. 2 Figures of Merit for VOC Analysis Using the New SHS GC/MS Method

Peak no	Compounds	RT	Q Ion	r^2 45 – 1250	RSD 150 ppt (n = 6)	RSD 45-1250	LOD (ppt)
IS1	**1,2-dichloroethane d_4**	6.72	65	/	3.3	/	/
1	Dichlorodifluoromethane	1.31	85	0.996	2.6	13.5	**24**
2	Chloromethane	1.45	50	0.995	3.8	10.7	**45**
3	Vinyl chloride	1.55	62	0.998	5.7	6.4	15
4	Bromomethane	1.80	94	0.999	6.8	6.2	**45**
5	Chloroethane	1.89	64	0.999	2.4	5.7	**27**
6	Fluorotrichloromethane	2.12	101	0.998	1.8	18.5	6.3
7	1,1-dichloroethene	2.62	96	0.999	7.2	3.5	18
8	Dichloromethane	3.17	49	0.996	5.6	**10.7***	20
9	1,2-dichloroethene trans	3.50	61	0.999	2.9	12.5	14
10	1,1-dichloroethane	4.11	63	0.999	0.7	9.5	12
11	2,2-dichloropropane	5.07	77	0.998	4.1	14.1	15
12	1,2-dichloroethene cis	5.13	61	1.000	4.2	8.4	**23**
13	Bromochloromethane	5.55	49	0.997	**15.0**	4.0	**38**
14	Trichloromethane	5.75	83	0.994	3.8	16.2*	10
15	1,1,1-trichloroethane	6.02	97	0.997	3.5	15.1	9.0
16	Tetrachloromethane	6.32	119	0.997	1.6	14.6	9.0
17	1,1-dichloro-1-propene	6.34	75	0.999	2.8	5.3	15
19	1,2-dichloroethane	6.79	98	0.992	**11.2**	5.2	**136**
20	Trichloroethene	7.98	132	0.997	5.0	6.9	10
21	1,2-dichloropropane	8.40	63	0.998	4.4	9.9	20
22	Dibromomethane	8.61	174	0.996	**11.3**	8.2	20
23	Bromodichloromethane	8.97	83	0.999	6.7	4.9	**21**
24	1,3-dichloropropene cis	9.82	75	0.999	3.6	8.3	**23**
26	1,3-dichloropropene trans	10.93	75	0.999	**19.3**	13.4	**28**
27	1,1,2-trichloroethane	11.25	97	0.995	9.0	13.5	15
28	Tetrachloroethene	11.44	166	0.998	0.8	11.5	5.9
29	1,3-dichloropropane	11.55	76	0.994	5.1	13.5	11
30	Dibromochloromethane	11.96	129	0.998	9.0	6.5	17
31	1,2-dibromoethane	12.12	107	0.994	7.6	12.0	20
33	1,1,1,2-tetrachloroethane	13.29	131	1.000	7.9	10.9	14
34	Tribromomethane	14.70	173	0.997	9.9	13.8	**23**
42	1,1,2,2-tetrachloroethane	15.72	83	0.992	9.3	12.9	14
43	1,2,3-trichloropropane	15.76	75	0.990	**14.7**	12.5	14
56	1,2-dibromo-3-chloropropane	19.93	157	**0.966**	**19.4**	9.5	**47**
58	Hexachloro-1,3-butadiene	21.93	225	0.993	3.7	16.7	5.9
IS2	**Toluene d_8**	10.30	98	/	2.9	/	/
18	Benzene	6.73	78	0.995	1.1	10.8	4.7
25	Toluene	10.42	91	0.991	2.5	**8.8***	3.8
34	Ethylbenzene	13.35	91	0.999	2.8	7.5	4.5
35+36	p-xylene + m-xylene	13.59	91	0.998	2.3	16.4	3.0
37	o-xylene	14.34	106	0.999	7.9	13.1	13
38	Styrene	14.38	104	0.997	6.7	12.1	12
40	Cumene	15.08	105	0.999	3.2	15.4	4.2
44	n-propylbenzene	15.89	120	0.999	3.9	14.0	15
47	1,2,4-trimethylbenzene	16.26	105	0.999	3.8	10.1	7.9

Table 2. Figures of Merit for VOC Analysis Using the New SHS GC/MS Method (continued)

Peak no	Compounds	RT	Q Ion	r^2 45 – 1250	RSD 150 ppt (n = 6)	RSD 45-1250	LOD (ppt)
48	*tert*-butylbenzene	16.88	134	0.998	3.8	10.7	14
49	1,3,5-trimethylbenzene	16.98	105	0.998	4.1	10.8	7.6
50	*sec*-butylbenzene	17.31	105	0.997	4.2	6.1	4.1
52	Cymene	17.62	119	0.997	4.3	17.9	5.3
55	n-butylbenzene	18.43	91	0.998	3.8	16.5	5.8
59	Naphthalene	22.01	128	0.993	4.5	11.2	14
IS3	**Chlorobenzene d_5**	13.00	117	/	2.5	/	/
32	Chlorobenzene	13.09	112	0.995	1.5	16.2	6.4
41	Bromobenzene	15.59	77	0.995	6.8	13.5	17
45	2-chlorotoluene	16.01	91	0.999	4.5	17.7	7.6
46	4-chlorotoluene	16.23	126	0.999	2.5	14.3	9.4
51	1,3-dichlorobenzene	17.46	146	0.998	2.9	15.2	7.1
53	1,4-dichlorobenzene	17.65	146	0.999	3.3	9.8	7.9
54	1,2-dichlorobenzene	18.36	146	0.997	1.1	14.6	9.0
57	1,2,4-trichlorobenzene	21.55	180	0.998	6.1	13.2	11
60	1,2,3-trichlorobenzene	22.49	180	0.997	5.3	11.3	10
	AVERAGE			**0.996**	**5.4**	**13.6**	

*Contamination at lowest (45 ppt) level. RSDs listed are in the range of 150 to 1,250 ppt.

Simultaneous Scan/SIM Mode

In the proposed method, the MS was operated in simultaneous scan/SIM mode. The SIM mode resulted in high sensitivity, while the scan mode can be used for confirmation of solute identity at 1-ppb or higher concentration levels (for some solutes even at the 0.1-ppb level).

If needed, the scan data can also be used for identification of nontarget sample components at levels above 1 ppb.

For SIM, dwell times of 50 to 100 ms were used and for scan mode, the sample rate was set at 2^1. This corresponds to about 9 scans/s. In this way, more than five spectra are collected across the peak. This is illustrated in Figures 7a and 7b, showing the data points obtained for three late-eluting (focused) peaks (sec. butylbenzene, 1,3-dichlorobenzene, and cymene+1,4-dichlorobenzene) for a scan trace at 1-ppb level and a SIM trace at 45-ppt level, respectively. (AMDIS was used to highlight the data points).

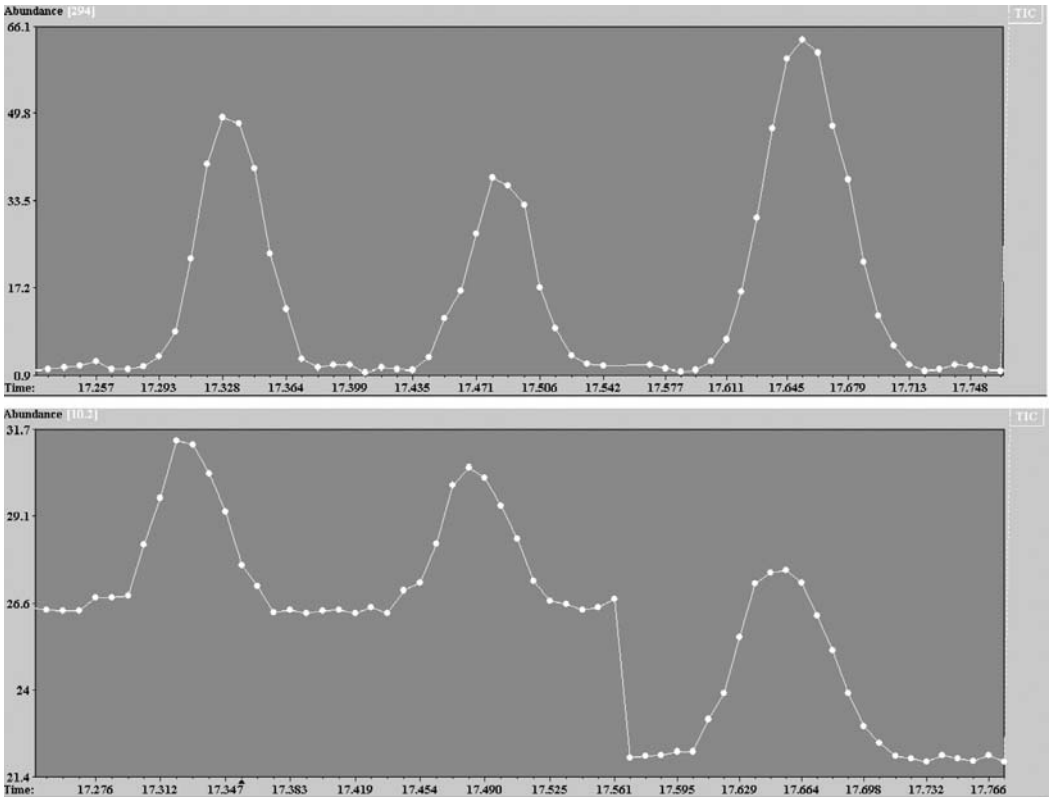


Figure 7. Demonstration of number of data points per peak for scan chromatogram at 1.25-ppb level (top) and SIM chromatogram at 45-ppt level (bottom) using 5075C in scan/SIM mode (scan: 2^1 sampling).

Examples

An example of an SHS GC/MS analysis of tap water sample is shown in Figure 8. In the chromatogram, several solutes are detected. Most of these solutes are identified as chlorinated hydrocarbons, originating from the chlorination process. It is interesting to note that in this sample, trichloromethane (peak 2) is only present at trace level, while in other tap-water samples, it is often present as the most abundant peak. Here the brominated halocarbons are more abundant, probably indicating a different water treatment procedure.

The concentrations of the detected VOCs were determined using the internal standard method. The following concentrations were found:

1. 1,2-cis-dichloroethene (3 ppb)
2. Trichloromethane (0.1 ppb)
3. 1,1,1-trichloroethane (0.4 ppb)
4. Trichloroethylene (0.8 ppb)
5. Bromodichloromethane (1 ppb), IS2 (d8-toluene)
6. Toluene (49 ppt)
7. Tetrachloroethylene (0.3 ppb)
8. Dibromochloromethane (6.4 ppb), IS3 (d5-chlorobenzene)
9. Tribromomethane (14 ppb)

A river-water sample was also analyzed. In this sample, chlorinated hydrocarbons were not detected. However, it was interesting to observe that some aromatic hydrocarbons were present. These aromatic hydrocarbons could originate from gasoline spillage.

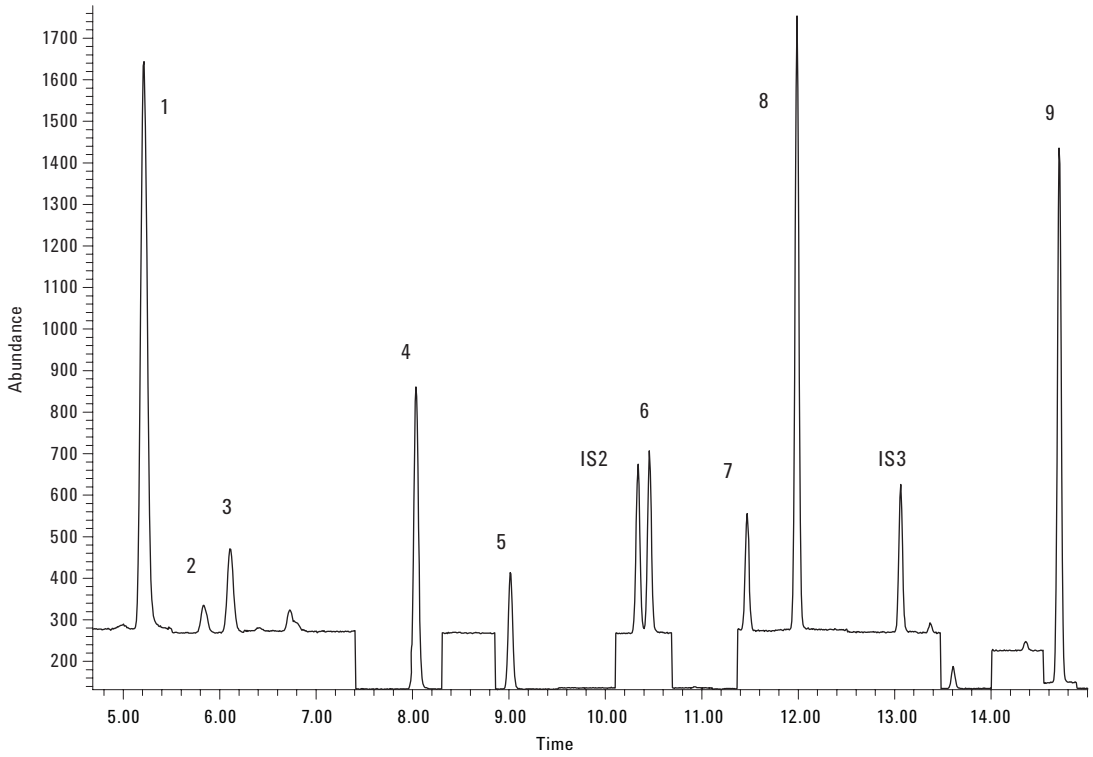


Figure 8. Analysis of tap water using SHS GC/MS. Peaks: 1. 1,2-cis-dichloroethene (3 ppb); 2. 1,1,1-trichloroethane (0.4 ppb); 3. trichloromethane (0.1 ppb); 4. trichloroethylene (0.8 ppb); 5. bromodichloromethane (1 ppb), IS2 (d8-toluene); 6. toluene (49 ppt); 7. tetrachloroethylene (0.3 ppb); 8. dibromochloromethane (6.4 ppb), IS3 (d5-chlorobenzene); and 9. tribromomethane (14 ppb).

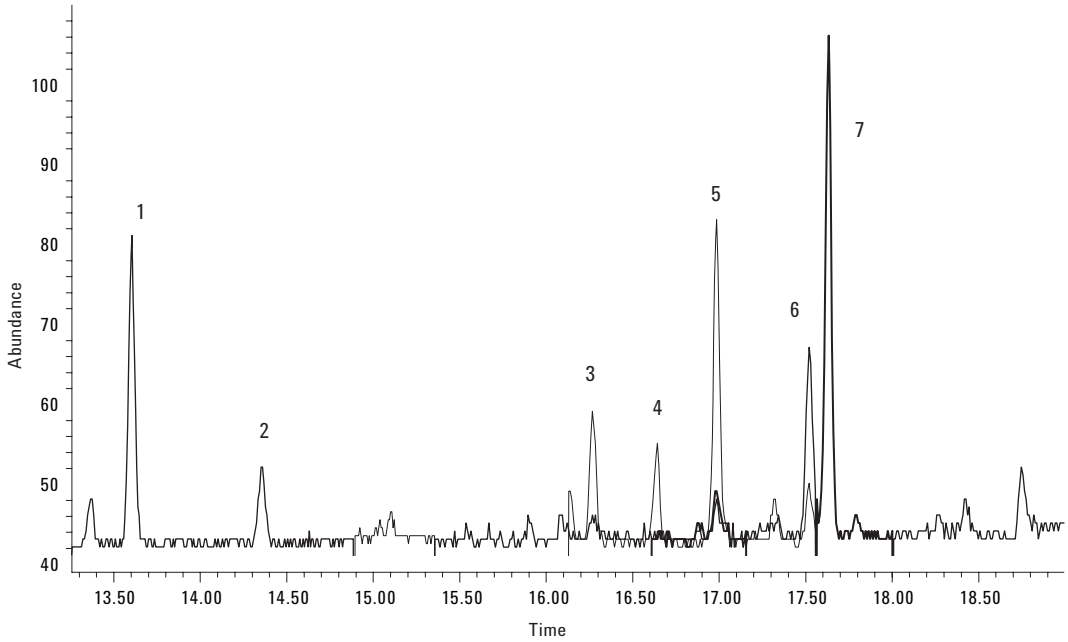


Figure 9. Extracted ion chromatograms obtained on river-water sample analyzed by SHS GC/MS. Peaks: 1. m/p xylene (13 ppt); 2. o. xylene (4 ppt); 3. 1,2,4-trimethylbenzene (39 ppt); 4. t.butylbenzene (5 ppt); 5. 1,3,5-trimethylbenzene (81 ppt); 6. C3-benzene isomer; and 7. cumene (88 ppt).

Conclusions

A fast SHS GC/MS method was developed and validated for analysis of low-level VOCs in water. Using the 5975C MSD with triple-axis detector, trace ion detection mode, and simultaneous SIM/scan mode, LODs were one to two orders of magnitude better than required by U.S. EPA and EU directives. Excellent repeatability and robustness can be obtained.

www.agilent.com/chem

Published in the USA
December 9, 2008
5990-3285EN

Agilent Technologies

Fast Analysis of Natural Gas Using the Agilent 490 Micro GC Natural Gas Analyzer

Application Note

Micro Gas Chromatography, Hydrocarbon Processing, Natural Gas Analysis

Author

Remko van Loon,
Agilent Technologies,
Middelburg, the Netherlands

Abstract

During production and distribution of natural gas it is of high importance to determine its composition and calorific value because natural gas is bought and sold on its energy content. This application note shows the use of the Agilent 490 Micro GC Natural Gas Analyzer for the analysis of natural gas and the calculation of its heating value. With the 490 Micro GC, Agilent provides ideal solutions for laboratory, on-line and field use.

Agilent Technologies

Introduction

Natural gas mainly consists of methane and variable levels of other hydrocarbons and permanent gases such as oxygen, nitrogen, and carbon dioxide. Different sources of natural gas usually have similar composition but vary in concentration.

Natural gas is traded on its energy content and therefore the analysis of the chemical composition and calorific value is of high importance for all stakeholders. That is where the 490 Micro GC based Natural Gas Analyzer can play a significant role.

The 490 Micro GC Natural Gas Analyzers are shipped as a total solution; the analyzers are factory tuned, for optimal separation, and come with final test data, a complete method, a user manual, and a check-out sample. Easy-to-use software is available for the calculation of all required physical properties, such as heating value and Wobbe index, conform official methods from the American Society of Testing and Materials (ASTM), Gas Processors Association (GPA) and International Standards Organization (ISO).

Natural Gas Analyzer setup

Based on the 490 Micro GC, four Natural Gas Analyzers are available, depending on the composition of the natural gas and the compounds of interest. The configurations and analysis characteristics for all analyzers are shown in Table 1. Additional information for the configurations can be found in Natural Gas Analyzer Data Sheet [1].

The Natural Gas Analyzers are equipped with heated injectors and sample lines, both set to 110 °C in the analyzer method, to eliminate any cold spots and prevent possible condensation of moisture, and to ensure the integrity of the sample is maintained throughout the sample flow path.

Table 1 shows multiple column channels are equipped with a back flush to vent option. To protect the CP-Molsieve 5A stationary phase and maintain the separation efficiency of the molecular sieve column, it is necessary to back flush carbon dioxide, moisture, and higher hydrocarbons. Moisture and carbon dioxide tend to adsorb quickly to the molecular sieve stationary phase change its chromatographic properties. This can result in retention shifts and loss of separation. Higher hydrocarbons will eventually elute, but will cause higher detector noise levels and would lead to reduced sensitivity; the back flush to vent functionality on the Molsieve 5A column channel prevents this from happening. On the PoraPLOT U and HayeSep A channels, the higher hydrocarbons, C4 and higher, are back flushed to vent. This prevents these late eluting components from interfering in the next analysis.

Table 1. Agilent 490 Micro GC Natural Gas Analyzers Overview.

Analyzer characteristics	Natural Gas Analyzer A	Natural Gas Analyzer A Extended	Natural Gas Analyzer B	Natural Gas Analyzer B Extended
Micro GC cabinet	Dual with 2 channels	Quad with 3 channels	Dual with 2 channels	Quad with 3 channels
Column channels installed	HayeSep A 40 cm, without backflush	HayeSep A 40 cm, with backflush	PoraPLOT U 10 m, with backflush	CP-MolSieve 5A 10 m, with backflush and retention time stability option
	CP-Sil 5 CB 6 m, without backflush	CP-Sil 5 CB 4 m, with backflush	CP-Sil 5 CB 6 m, without backflush	PoraPLOT U 10 m, with backflush
		CP-Sil 5 CB 8 m, without backflush		CP-Sil 5 CB 6 m, without backflush
Analysis	Hydrocarbons C1-C9 Carbon dioxide, Air	Hydrocarbons C1-C12 Carbon dioxide, Air	Hydrocarbons C1-C9 Carbon dioxide, Air, Hydrogen sulfide	Hydrocarbons C1-C9 Carbon dioxide, Air, Hydrogen sulfide Permanent gases (N_2, O_2, He and H_2)

The CP-Molsieve 5A is equipped with the retention time stability (RTS) option. This RTS option consists of additional in-line filters between the electronic gas control and the column module to ensure moisture and carbon dioxide free carrier gas. The use of the RTS option enables a more efficient back flush of carbon dioxide. This enhances column lifetime and, most importantly, leads to more stable retention times.

The natural gas sample can be introduced to the 490 Micro GC either pressurized (maximum limit 1 bar), through a Tedlar sampling bag using the internal sampling pump, or by using continuous flow sampling mode. When you need to analyze multiple streams on a single analyzer or you want to connect multiple calibration samples for automated calibration, the use of a stream selector valve is recommended.

To expand the range of samples to Liquid Petroleum Gas (LPG) and Liquefied Natural Gas (LNG), the Micro-Gasifier provides controlled evaporation before the sample is introduced into the gas chromatographic injector for analysis. In addition, high-pressure gas samples can be reduced without creating cold spots, which prevents discrimination in the sample.

Fast Natural gas analysis using the Natural Gas Analyzer A

The first channel in the Natural Gas Analyzer A is equipped with a HaySep A column for separating methane from the composite air peak (nitrogen and oxygen). Carbon dioxide, ethane, and propane are analyzed on this column channel as well. Figure 1 shows an example chromatogram for these compounds.

For the analysis of the hydrocarbons from propane to n-nonane, a second column channel, equipped with a 6-meter CP-Sil 5 CB column, is used. Figure 2a shows a chromatogram on the 6-meter CP-Sil 5 CB for the separation until n-octane; n-hexane elutes in less than 60 seconds and n-octane in just over 3 minutes. Propane is analyzed on both HayeSep A and CP-Sil 5 CB column enabling the use of propane as a bridge component. The extended part of the chromatogram obtained with a 6-meter CP-Sil 5 CB column, displayed in Figure 2b, shows the analysis of hydrocarbons until n-nonane.

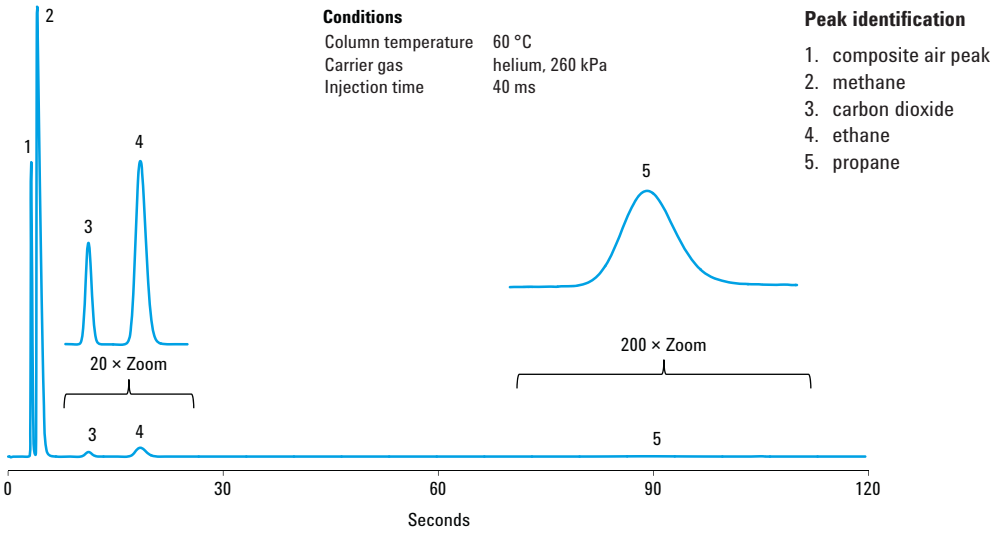


Figure 1. Chromatogram for nitrogen, carbon dioxide, and C1 – C3 hydrocarbons on a HayeSep A column.

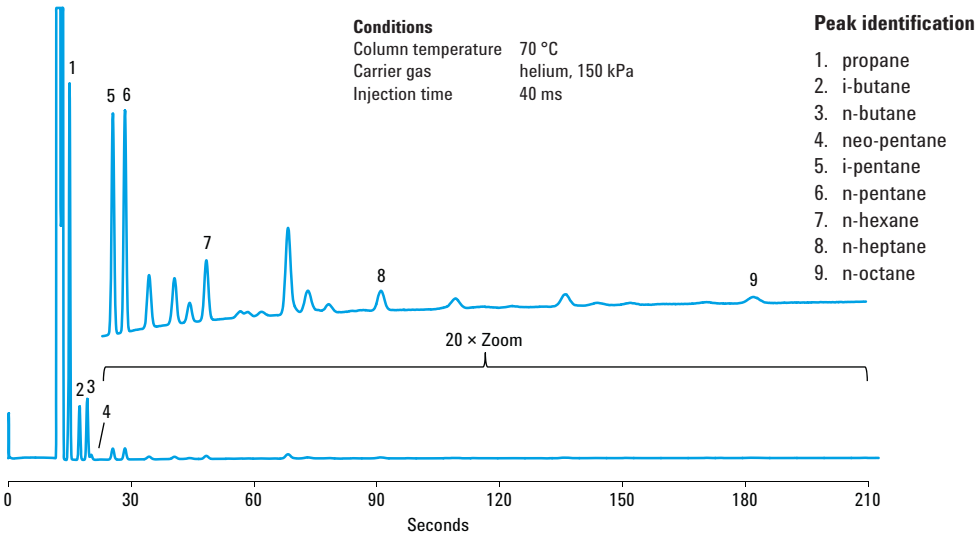


Figure 2a. Chromatogram for C3 – C8 hydrocarbon using a 6-meter CP-Sil 5 CB column.

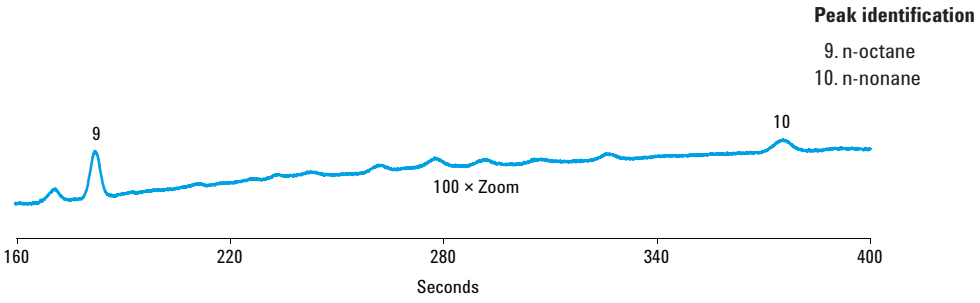


Figure 2b. Chromatogram for C8 – C9 hydrocarbons using a 6-meter CP-Sil 5 CB column.

Analysis up to n-dodecane with the Natural Gas Analyzer A Extended

The extended version of the Natural Gas Analyzer A is used for the analysis of natural gas until n-dodecane. This extended analyzer is equipped with three column channels. First, a HayeSep A column channel is used for separation of composite air peak from methane, carbon dioxide ethane, and propane. This channel is equipped with back flush functionality ensuring that butanes and later eluting hydrocarbons are back flushed to vent. Figure 3 shows an example for the HayeSep A channel, propane is eluting in less than 2 minutes.

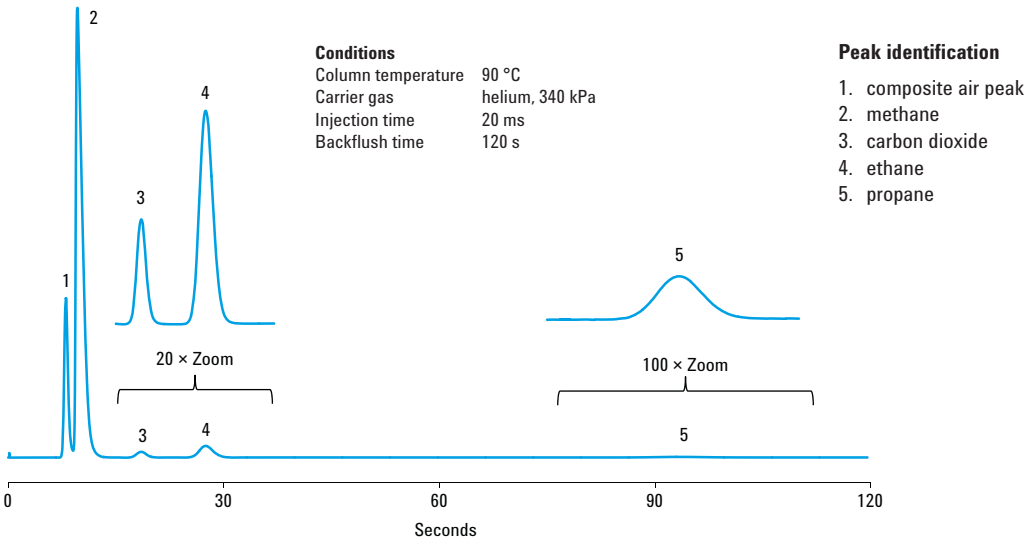


Figure 3. Chromatogram for HayeSep A column with backflush.

The second channel, equipped with a 4-meter CP-Sil 5 CB column with back flush functionality, is used to analyze C3 to C5 hydrocarbons; the chromatogram is shown in Figure 4. N-hexane and higher hydrocarbons are back flushed to vent.

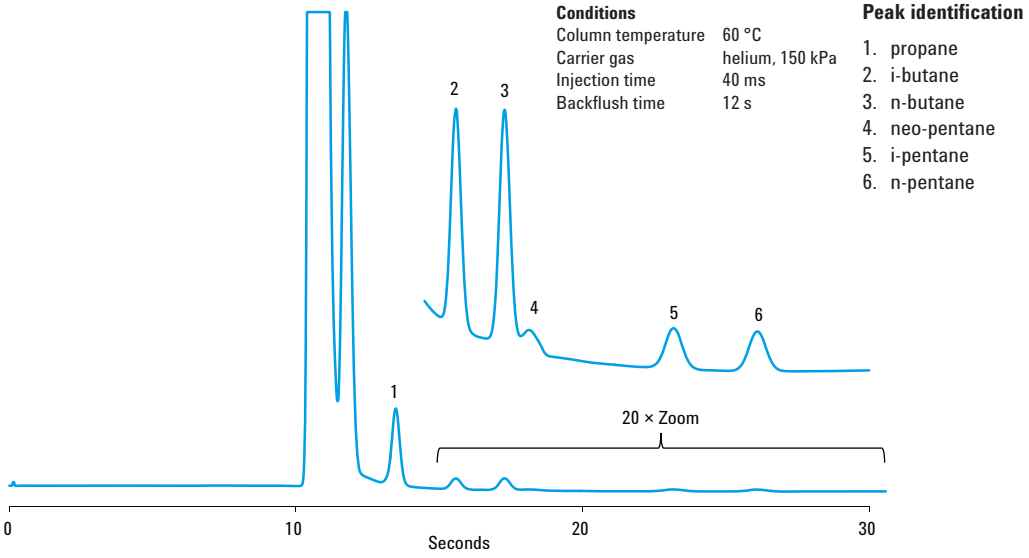


Figure 4. Chromatogram for C3 to C5 hydrocarbons on a 4-meter CP-Sil 5 CB.

A third column channel, equipped with a 8-meter CP-Sil 5 CB column, is used to analyze the higher hydrocarbons from n-hexane to dodecane; n-Dodecane elutes in approximately 240 seconds. A natural gas sample sample until n-decane, demonstrated in Figure 5a, is analyzed in less than 2 minutes. Figure 5b displays a hydrocarbon gas mixture from n-hexane until n-dodecane, typical analysis time is 240 seconds.

Analysis of natural gas including hydrogen sulfide using the Natural Gas Analyzer B

When your natural gas analysis needs to include hydrogen sulfide, the 490 Micro GC Natural Gas Analyzer B is the analyzer of choice. This analyzer uses a PoraPLOT U column channel for the separation of methane from the composite air peak (nitrogen and oxygen). This column is also used for the analysis of carbon dioxide, ethane, and propane. The chromatogram in Figure 6 shows an example of natural gas on the PoraPLOT U column; total analysis is done in approximately 60 seconds. For the analysis of hydrogen sulfide, the stainless steel tubing in the PoraPLOT U channel and the sample inlet of the Micro GC have an UltiMetal deactivation layer, which results in an inert sample flow path and excellent peak shape ensuring correct analysis of hydrogen sulfide even at ppm level.

Hydrocarbon analysis from propane until n-nonane for the Natural Gas Analyzer B is done with a second channel equipped with a 6-meter CP-Sil 5 CB. This column is identical to the one used for the Natural Gas Analyzer A.
The chromatograms for this channel are displayed in Figure 2a and 2b.

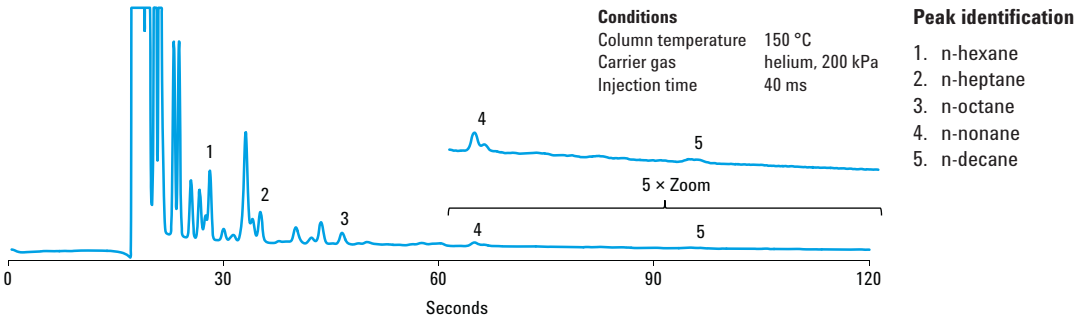


Figure 5a. Analysis of natural gas on an 8-meter CP-Sil 5 CB.

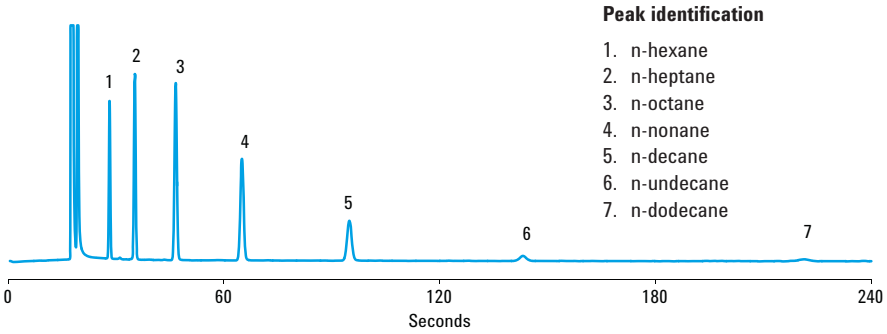


Figure 5b. Analysis C7 – C12 hydrocarbon mix on an 8-meter CP-Sil 5 CB.

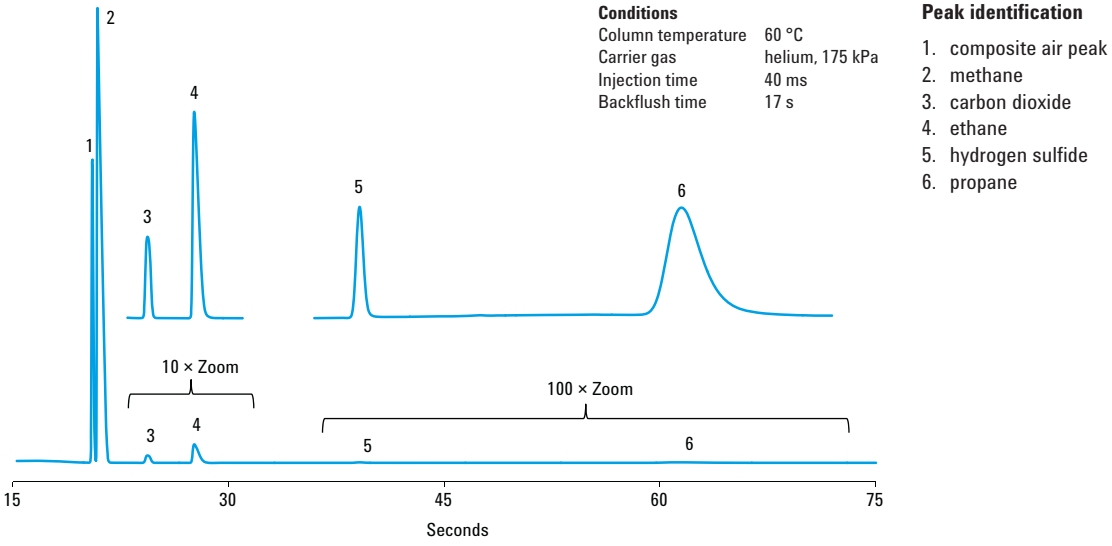


Figure 6. Chromatogram for natural gas on the PoraPLOT U column channel.

Permanent gas analysis using Natural Gas Analyzer B Extended

The Extended version of the 490 Micro GC Natural Gas Analyzer B is equipped with an additional CP-MolSieve 5A column channel for the analysis of permanent gases in your natural gas sample. Helium carrier gas on this channel enables the separation and quantification of oxygen and nitrogen, an example is shown in Figure 7 (top part).

When you need to analyze helium, neon, or hydrogen as well, the use of argon instead of helium as carrier gas is required. The bottom part of Figure 7 shows a chromatogram for the molecular sieve column running with argon as carrier gas. To have the flexibility to change the carrier gas for only the molecular sieve column to argon, this channel is connected to a separate carrier gas inlet at the rear of the micro GC.

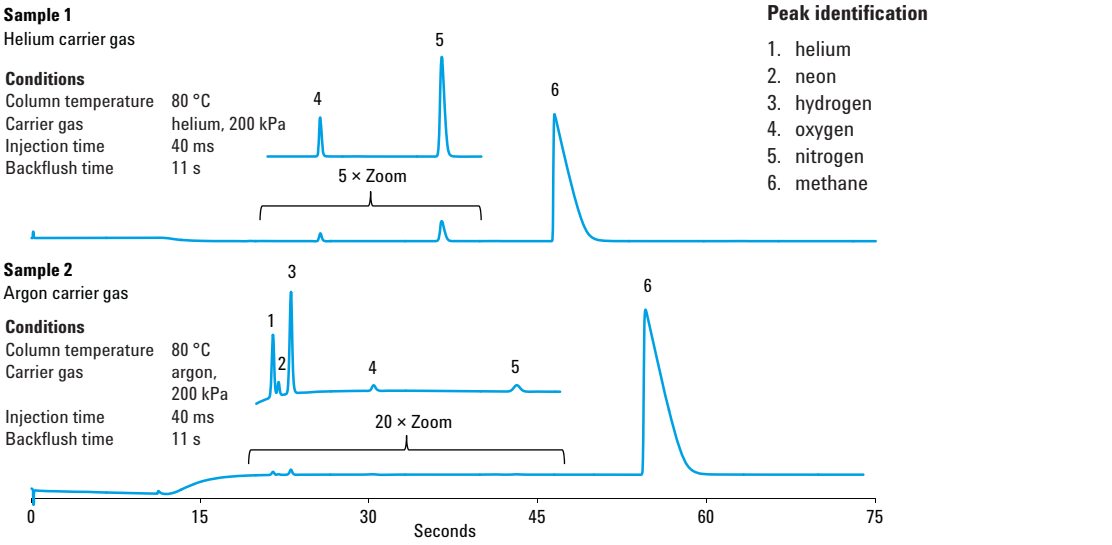


Figure 7. Chromatograms for the analysis of permanent gases on the CP-MolSieve 5A column channel.

Reporting tools for the physical properties of natural gas

The results for all individual components are sent from the chromatography data software of choice (EZChrom Elite, OpenLAB EZChrom, or OpenLAB Chemstation) to optional EZReporter software to calculate a wide range of physical properties like, calorific value, relative density, compressibility, and Wobbe index, see Figure 8 (left). These key parameters are important to determine the commercial value of the natural gas. EZReporter supports reports in accordance with official methods ASTM D3588, ISO 6976, and GPA 2172. The reports can be printed locally or exported to a file for further use in a laboratory information management system (LIMS).

The software includes functionality to select raw analysis amounts and calculated key parameters for monitoring and historical trend analysis. Upper and lower warning limits can be given to these monitor parameters to better visualize the results from your natural gas stream. Some examples are given in Figure 8 (middle and right).

Conclusion

Micro GC Natural Gas Analyzer is a genuinely better solution for analyzing your natural gas stream. Whether in the lab, on-line/at-line, or in the field, the "Measure Anywhere" Micro GC provides natural gas analysis in a matter of seconds.

The Natural Gas Analyzer A analyzer combined with a HayeSep A and 6-meter CP-Sil 5 CB column channel is used for the analysis of natural gas. This analyzer will separate methane from air and can analyze up to n-nonane. Carbon dioxide is also analyzed. Total analysis time depends on the hydrocarbons in the sample; up to n-heptane is done in approximately 90 seconds, n-nonane elutes just under 400 seconds.

When you want to analyze until n-dodecane in natural gas, the Natural Gas Analyzer A Extended is required. The 6-meter CP-Sil 5 CB column channel is replaced by two different CP-Sil 5 CB channels. A short CP-Sil 5 CB (4-meter) will analyze from propane to the pentanes; hexane and higher will be back flushed to vent. The second CP-Sil 5 CB channel, with an 8-meter column, is used for analysis of hexane up to n-dodecane.

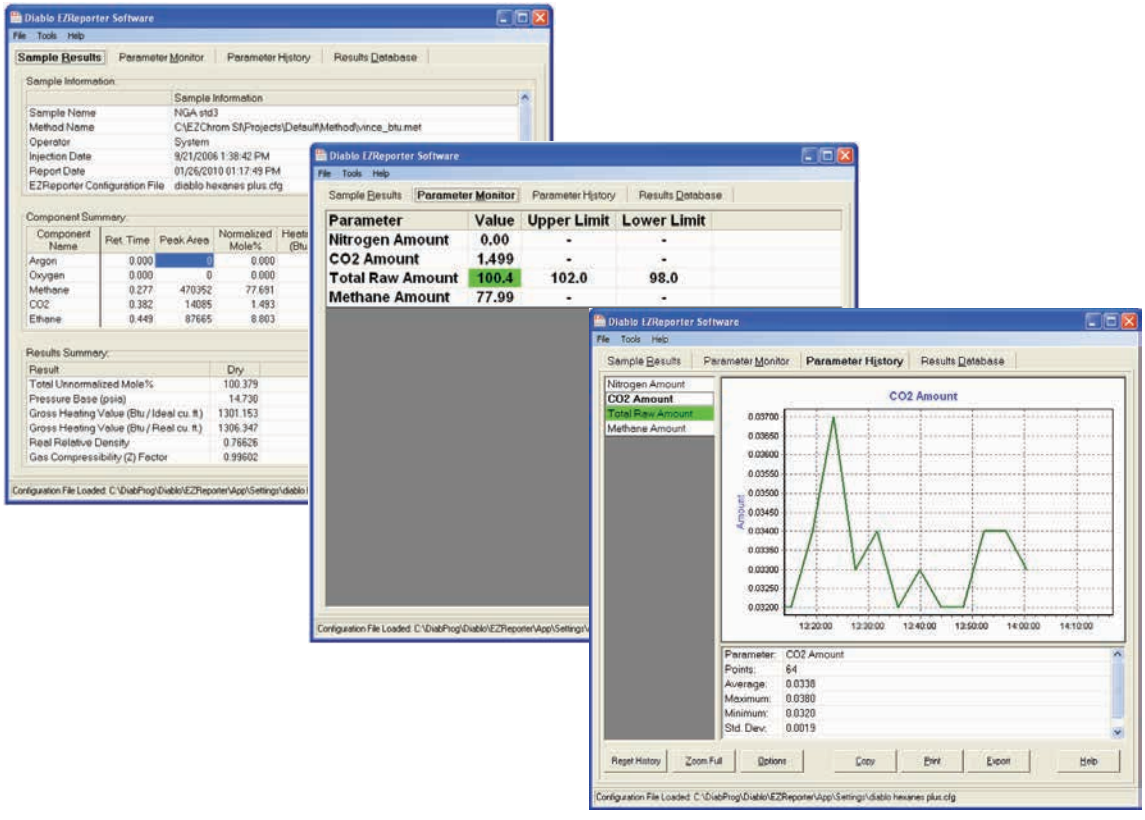


Figure 8. EZReporter, sample results with calculated physical properties (left), parameter monitoring (middle), and trend analysis (right).

The Natural Gas Analyzer B, equipped with a PoraPLOT U and a 6-meter CP-Sil 5 CB CB column channel, provides fast analysis of natural gas, from the separation of air and methane, carbon dioxide, and hydrocarbons up to n-nonane. This analyzer setup is designed for the analysis of hydrogen sulfide. The stainless steel sample inlet of the systsm is deactivated using an UltiMetal treatment resulting in excellent peak shape for hydrogen sulfide.

If more detailed analysis of the permanent gases in the natural gas sample is required, the extended version of the Natural Gas Analyzer B is the system of choice. This analyzer is equipped with an additional CP-MolSieve 5A column enabling the separation of oxygen and nitrogen, using helium as carrier gas. When this analyzer uses argon as carrier gas, helium and hydrogen can be detected as well.

The 490 Micro GC Natural Gas Analyzers are factory tuned, including the appropriate settings for the back flush times. The Agilent Natural Gas Analyzers are shipped with final test data, optimized analytical method, Natural Gas Analyzer User Manual, and a check out sample kit to have all information available upon installation.

The analyzer hardware together with your chromatography data system (CDS) of choice provides an easy-to-use and powerful system. The EZReporter software is linked to Agilent CDS, resulting in automatic calorific value/BTU calculations and reports according to American Society of Testing and Materials (ASTM D3588), Gas Processors Association (GPA 2172), and International Standards Organization (ISO 6976).

For more information about the 490 micro GC Natural Gas Analyzer or other Micro GC solutions, visit our website at www.agilent.com/chem/microgc.

References

1. 5991-0301EN; Agilent 490 Micro GC Natural Gas Analyzers; Data Sheet; April 2012.

For More Information

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

www.agilent.com/chem/microgc

Printed in the USA
April 16 2012
5991-0275EN

Agilent Technologies

BIOFUELS

Confirm the quality of nontraditional liquid fuels – and contribute to the future of energy

Biofuels are coming into their own as governments seek to increase energy independence, minimize the impact of global warming, and conserve nonrenewable petroleum reserves. That means your lab will face growing pressures to monitor conversion processes and certify quality.

You can depend on Agilent to provide the instruments, supplies, and expertise you need for feedstock quality, process control, and product certification. In the lab or in the field, our wide array of biodiesel analyzers, oxygenates analyzers, Micro GC-based biogas analyzers, and spectroscopy products help you meet the demands you face today… and in the future.

We are also monitoring emerging technologies in cellulosic ethanol, alga oil, biobutanol, and other potential fuels to ensure that we have the next-generation technologies ready when you need them.

Back to table of contents ►

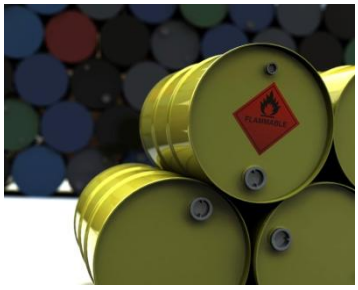
Test method for low level detection of biodiesel in diesel using the Agilent 5500t FTIR spectrometer

Application Note

Author

John Seelenbinder and Frank Higgins

Agilent Technologies, Connecticut, USA



Introduction

Agilent Technologies 4500t and 5500t FTIR spectrometers are gaining rapid acceptance for measuring biodiesel (%FAME) in diesel fuel for applications where low level contamination of diesel fuel by FAME is problematic. Diesel fuel containing up to 5 % biodiesel meets the ASTM D975 standard, which does not require disclosure of the biodiesel level, and this can be a significant issue for certain diesel fuel users. Agilent has now developed an enhanced method for determining contamination levels of FAME in diesel. This method combines the more sensitive transmission IR sampling interface specified in EN 14078 with the universal algorithm and sample set specified in ASTM D7371 to produce the most sensitive and accurate method available. This enables the 5500t FTIR systems to quickly and accurately predict the percentage of biodiesel in diesel fuel in the range from 0.025 % to 20 %. In round robin testing, the accuracy of this method has been found to be superior to the other methods, especially for measuring low levels of biodiesel.

Agilent Technologies

Instrumentation

The Agilent biodiesel test method was designed around the 5500t FTIR series of portable spectrometers, equipped with the innovative, patented sampling interface. This sampling system has been engineered to provide a highly reproducible 100 micron transmission pathlength, as called for in the EN 14078 method. The sample interface is one area where the ASTM method differs from the EN method. The ASTM method specifies an attenuated total reflectance (ATR) sample interface; the EN method specifies a transmission sample interface. The ASTM ATR method is easy to use, but does not provide the level of detection required for measuring biodiesel contamination; the EN transmission cell method provides the sensitivity required, but traditional IR transmission cells are not easy to use with respect to both filling and cleaning, particularly for viscous liquids like diesel fuel.

Agilent FTIR transmission sampling interface is unique in that it provides the sensitivity and limit of detection as required in EN14078, but at the same time is as easy to use as the ATR cell employed in ASTM D7371. In the sampling system, the upper window of the transmission cell is mounted in a precision rotating assembly. This opens by rotating this window into the upward position. Then, a single drop of fuel is placed on the bottom transmission window, the upper window is then rotated back into the closed position creating a path length of 100 micrometers. Clean-up is equally straightforward, since the sample is simply wiped from the windows when the FTIR instrument is in the open position. This patented sample interface gives the ease of use of the ATR measurement with the path length and sensitivity of a transmission measurement. Furthermore, the design provides a path length reproducibility of better than 0.2 micrometers. Representative spectra measured on the 5500t FTIR spectrometer of biodiesel in diesel are shown in Figure 1.

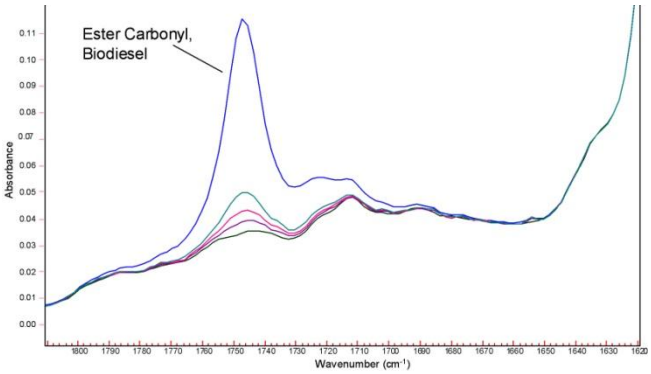


Figure 1. The overlaid IR spectra of diesel fuels with various ultra low concentrations of biodiesel, at 0.50 % (Blue), 0.10 % (Lt. Green), 0.05 % (Red), 0.025 % (Maroon), and 0.00 % (Dk. Green)

Calibration

In order to produce a quantitative measurement, the spectra generated from an infrared spectrometer must be calibrated with quantitative samples. The ASTM and EN methods specify different methods of quantitation. Both methods measure the carbonyl absorbance of the fatty acid methyl ester molecule; the EN method uses a simple linear fit to the band height while the ASTM method uses a multivariate, partial least squared (PLS) method. The univariate method specified in the EN method directly follows a Beers law calibration. As specified in the method, the absorbance of the carbonyl stretching frequency at 1745 cm^{-1} is measured with local baseline points at 1820 cm^{-1} and 1770 cm^{-1}. The absorbance intensity is then plotted against the concentration of 10 standards. A linear fit is used for the calibration curve.

ASTM D7371 specifies a more complicated multivariate PLS method. The method is still based on Beers Law; however, the full spectrum technique better accounts for baseline effects and interferents. In addition to the different algorithm, the ASTM method specifies a large collection of samples. The samples cover the entire calibration range and are made in three different diesel formulations: low, high, and ultra high Diesel Cetane Check Fuel (DCCF-Low, DCCF-High, and DCCF-Ultra High). The DCCF basestock fuels and biodiesel B100 used to create the biodiesel calibration and qualification

standards are in compliance with specifications described in Annex 2 (A2.1, A2.2.1, A2.2.2, and A2.2.3). Varying the aromatic content of the diesel fuel used in the calibration and qualification sets creates a more robust and accurate PLS model.

Agilent's transmission IR based method incorporates 3 calibration models similar to the ASTM 7371 method; the Microlab software automatically selects the result from the correct calibration to display without any user input. The calibration ranges are 0.025-1 %, 1-10 %, 10-25 % biodiesel in petroleum diesel. The PLS model for the low biodiesel range (0.025-1 %) consisted of 70 spectra preprocessed with mean centering, baseline correction, and thickness correction and uses a portion of ester carbonyl region of the mid IR spectrum (1950-1720 cm^{-1}) similar to the ASTM 7371 method.

The calibration for the second range (1-10% biodiesel) consists of 46 spectra preprocessed with mean centering and baseline correction. The model uses a portion of ester carbonyl region of the mid IR spectrum (1800-1720 cm^{-1}) similar to the ASTM 7371 method. The third calibration (10-25 % biodiesel) uses 40 spectra preprocessed with mean centering and baseline correction preprocessing. Three spectral regions are used : the ester carbonyl at 1846-1758 cm^{-1} and 1738-1719 cm^{-1}, and the ester C-O stretch at 1327-1119 cm^{-1}

Method Performance

Each calibration model was tested with both a cross validation (leave one out) and a separate validation set. The cross validation data was used to calculate the standard error of cross validation (SECV) and to prepare an actual versus predicted plot. The correlation of the actual versus predicted plot was also calculated. The results of each model are listed in Table 2. All models produced a correlation greater than R_2= 0.999 and an average relative error for the separate validation set of less than 1.5%.

The Agilent method was compared to the ASTM 7371 method by two other analytical labs in a blind round robin experiment initiated and conducted by a third party. Twenty samples were received with no identification of their composition and run with the 5500t FTIR. The Agilent method performed the best of all six biodiesel methods, including the ASTM 7371 methods. The total average relative error was only 2.1% (all samples, 2-20% range), the low level accuracy was much better than any other method at only 1.1% relative error.

Range	SECV	R^2	#Validation Samples	Avg. Relative Error
0.025 - 1 %	0.0016 %	0.9999	29	1.37 %
1% - 10 %	0.0164 %	0.9999	12	0.06 %
10% - 20%	0.04 %	0.9999	8	0.57 %

Conclusion

Two established standard techniques exist for measurement of biodiesel in fuel by infrared spectroscopy: ASTM D7371 and EN 14078. Unfortunately, both of those methods are focused on measurement of levels consistent with blended fuels; they do not address the needs of users who need to minimize the amount of biodiesel in their fuel supply. Agilent Technologies, employing its 5500t FTIR system, combines the transmission sample interface specified in the EN 14078 method with the algorithm and standards specified in ASTM E7371, yielding a method that accurately predicts the percentage of biodiesel in diesel fuel in the range from 0.025 % to 20 %. The accuracy of this method has been tested and found to be superior to other methods, especially for low levels of biodiesel. Thus, users who must quickly and accurately detect low level biodiesel contamination in their diesel fuel supply will find this new technology and methodology of great value.

www.agilent.com/chem

Published May 1, 2011
Publication Number 5990-7804EN

Agilent Technologies

Biodiesel in diesel fuel using the Agilent 5500t FTIR by EN14078 method

Application Note

Author

John Seelenbinder

Agilent Technologies,
Connecticut, USA

Objective

Determine concentration of biodiesel in diesel fuel from 1% to 6% (v/v) per EN14078 procedure.

Samples

Two stock solutions in the concentrations of 20% (v/v) and 4% (v/v) of biodiesel in standard U.S. automotive diesel were made. These solutions were diluted to yield solutions of 0.8, 1.2, 3, 4, 6, 8 and 10% (v/v) biodiesel in diesel.

Experiment

Each of the above concentrations of biodiesel in diesel was measured using an Agilent 5500t FTIR spectrometer with a 100 µm pathlength Tumbler transmission cell; 32 scans were collected at 4 cm^{-1} resolution yielding a 15 second sample measurement time. Measurements were made in triplicate. A calibration curve was made according to the EN14078 procedure "Liquid petroleum products — Determination of fatty acid methyl esters (FAME) in middle distillates — Infrared spectroscopy method". The maximum absorbance at 1745 cm^{-1} was plotted versus volume percent of biodiesel.

Agilent Technologies

Results

The average absorbance measured from the lowest concentration (0.8%) was 0.15 Abs. The highest concentration (10%) produced an absorbance of 1.6 Abs. The FAME absorbances at 1745 cm^{-1} for all concentrations are shown in Figure 1. Note that all three replicates are shown in that figure.

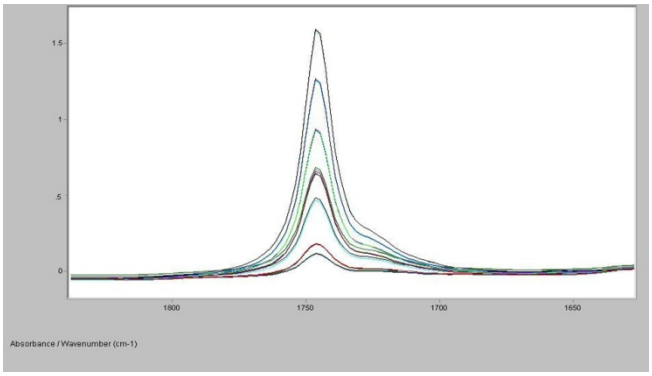


Figure 1. Absorbance at 1745 cm^{-1} of biodiesel in diesel fuel at 0.8, 1.2, 3, 4, 6, 8 and 10% (v/v)

The absorbance at 1745 cm^{-1} was measured on each of the samples using a two-point baseline at 1820 cm^{-1} and 1670 cm^{-1}. A calibration plot was drawn using two measurements at each concentration; it is shown in Figure 2. A simple linear regression yielded a correlation of 0.999.

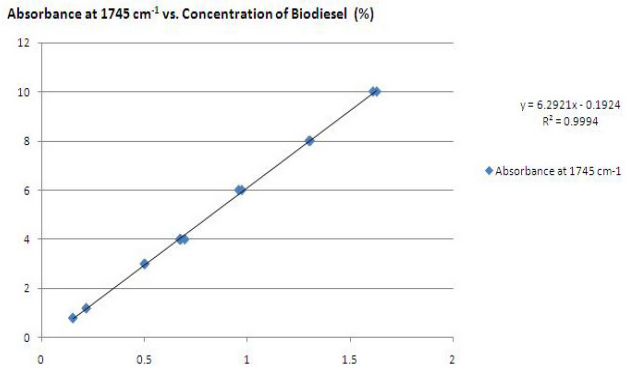


Figure 2. Calibration plot of biodiesel in diesel fuel showing linear fit of absorbance from 0.8 to 10% (v/v)

The data from the calibration was used to generate a method in the MicroLab software. Note that the concentrations are formatted at % x 10 in order to display the calculated value to 0.1%. The method is shown in Figure 3.

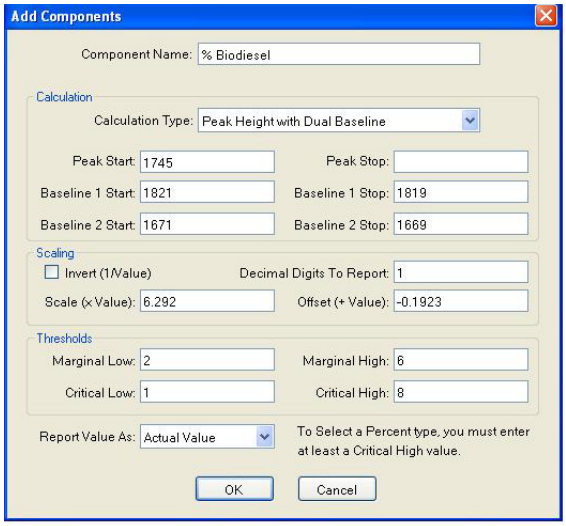


Figure 3. Biodiesel method in MicroLab software

This method was used in the MicroLab software to predict the concentration of the remaining samples. The average error was 0.129% (v/v) with a maximum error of 0.2% (v/v). The results are shown in Table 1, and an example of the MicroLab software results screen is shown in Figure 4.

Table 1. Results from samples measured with the biodiesel method in the MicroLab software

Actual %	Abs at 1745 cm^{-1}	Predicted %	Error (%)
0.8	0.154	0.8	0
1.2	0.219	1.1	0.1
3	0.504	2.90	0.1
4	0.696	3.9	0.1
6	0.971	5.8	0.2
8	1.3	7.8	0.2
10	1.631	9.8	0.2
		Average error:	0.13
		Maximum error:	0.20

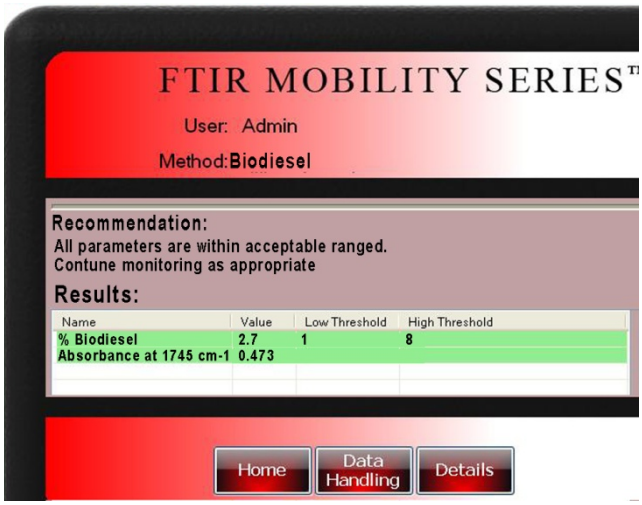


Figure 4. MicroLab results screen for a 3.0% sample of biodiesel in diesel

Conclusion

This experiment shows the ability of the Agilent 5500t FTIR spectrometer with the Tumbler transmission cell to quantify the amount of biodiesel in diesel fuel per the European Standard EN14078. The system using a 100 µm liquid cell produced ideal absorbances in the concentration range of interest (1.0 to 6.0% (v/v)). The MicroLab software can be easily configured to calculate the percent biodiesel in diesel fuel and presents the data in an easily understandable format.

www.agilent.com/chem

Published December 2, 2011
Publication Number 5990-7802EN

Low level detection of biodiesel in diesel fuel using the Agilent 5500t FTIR spectrometer

Application Note

Author

Frank Higgins

Agilent Technologies,
Connecticut, USA

Background

Recent increases in production of biodiesel along with the high cost of crude oil have encouraged some producers to mix biodiesel with regular diesel fuel. Although biodiesel provides some environmental advantages, problems have been reported in the use of mixed fuels in engines designed for petroleum based diesel. Additionally, biodiesel can promote biological growth in the diesel fuel when stored for a period of time. In response to these issues there is a need to determine if biodiesel is present in regular diesel fuel, especially for industries which store large amounts of diesel fuel. The European Union has recently released regulations requiring the measurement of biodiesel in diesel and has issued an analytical test method, EN 14078, for testing.

In the United States, a recent ASTM ruling (D-975) allows shipments of up to 5% biodiesel in fuel without notification to the customer. This notification requirement does not meet the needs of all industries. As an example, the U.S. Nuclear Regulatory Commission (NRC) suggests lower limits for biodiesel in fuel blend for stationary standby diesel engines at nuclear plants because of the potential for instability of the higher percent biodiesel blends resulting from the buildup of oxidation products. These conflicting rulings make it incumbent on the user to verify the level of biodiesel before being placed in long-term storage.

Agilent Technologies

The Agilent 5500t FTIR spectrometer provides an easy to use means of measuring biodiesel in diesel. The EN 14078 method comes pre-programmed on the 5500t FTIR spectrometer; this method can determine the amount of biodiesel in the range between 1 % and 10 %. The design is easy to use and provides nearly instant answers. In some cases, however, even lower levels of detection are required. To meet these needs, Agilent Technologies has modified the EN 14078 method to provide detection down to 0.025 % biodiesel in diesel. The Low Level Biodiesel in Diesel method can quantitatively determine the amount of biodiesel in the range from 0.025 % to 5 % with the same easy to use system.

Experiment

Six standards of biodiesel in diesel were made by successive dilution in the range from 0.0 to 1.5 %. Each concentration was measured using an Agilent 5500t FTIR spectrometer with a 100 µm path length Tumbler transmission cell; 32 scans were collected at 4 cm^{-1} resolution yielding a 15 second sample measurement time. Measurements were made in triplicate on two separate instruments. A calibration curve was made using the 1745 cm^{-1} carbonyl band specified in the EN 14078 method. The EN method specifies peak height but to achieve lower limits of detection the peak area was used in this method.

Results

Figure 1 shows the carbonyl region of the spectrum of the 6 samples tested plus a blank. The lowest concentration of 0.025 % is clearly visible with an absorbance which can be discerned over the blank. The absorbance increases linearly all the way to the highest concentration at 1.5 % biodiesel.

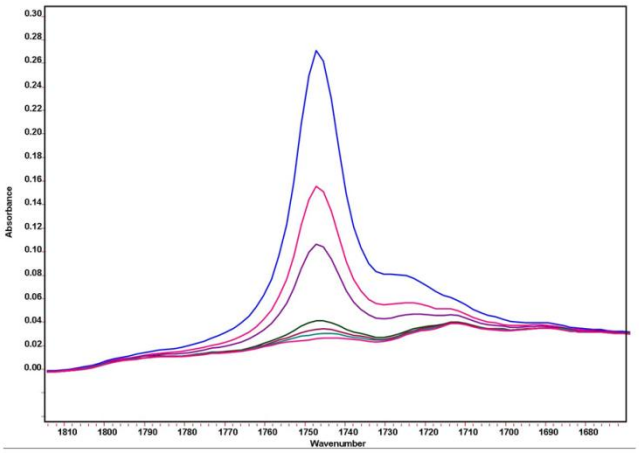


Figure 1. Absorbance at 1745 cm-1 of biodiesel in diesel fuel at 0.0, 0.025, 0.05, 0.1, 0.5, 0.8 and 1.5 % (v/v)

The calibration plot of the peak area of the 1745 cm^{-1} band is shown in figure 2. The plot shows an excellent correlation of R^2 = 0.9998.

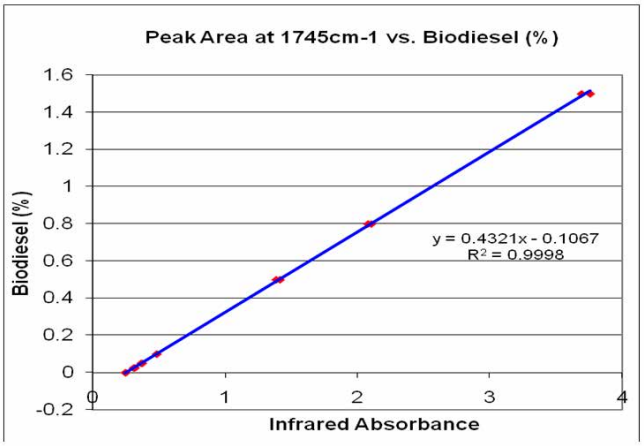


Figure 2. Calibration plot of biodiesel in diesel fuel showing linear fit of absorbance from 0 to 1.5 % (v/v)

The data from the calibration was used to generate a method in the MicroLab software. The method is shown in Figure 3.

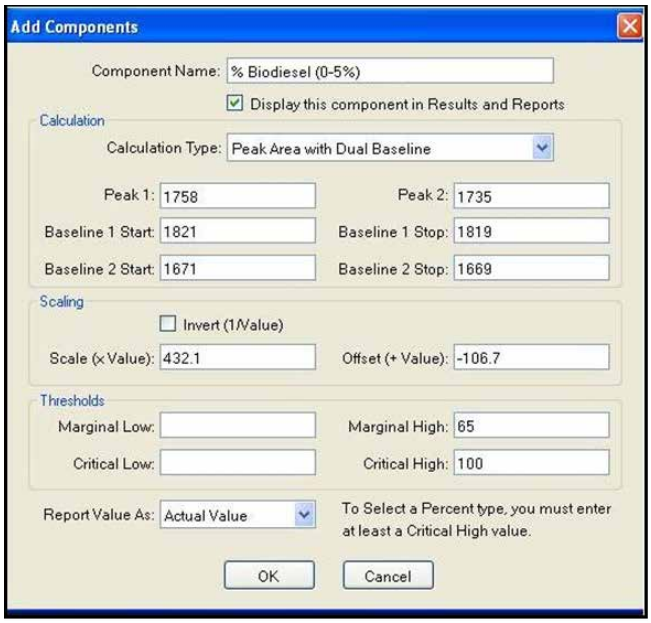


Figure 3. Biodiesel method in MicroLab software

This method was used in the MicroLab software to predict the concentration of a separate validation set. The validation set ranged from 0 to 5% biodiesel in diesel. The average relative error was 1% with a maximum relative error of 2%. These results indicate that the same method can be used to predict concentrations at least as high as 5%. The results are shown in Table 1, and an example of the MicroLab software results screen is shown in Figure 4.

Table 1. Results from samples measured with the biodiesel method in the MicroLab software

Actual %	Peak Area Abs at 1745	Predicted %	Error (%)
0	0.245	0	0.0
0.025	0.307	0.025	0.0
0.050	0.365	0.049	2.0
0.100	0.482	0.101	1.0
0.5	1.382	0.491	1.8
0.8	2.078	0.790	1.3
1.5	3.691	1.488	0.8
3.0	7.122	2.971	1.0
5.0	11.674	4.938	1.2
		Average error:	1.0
		Maximum error:	2.0

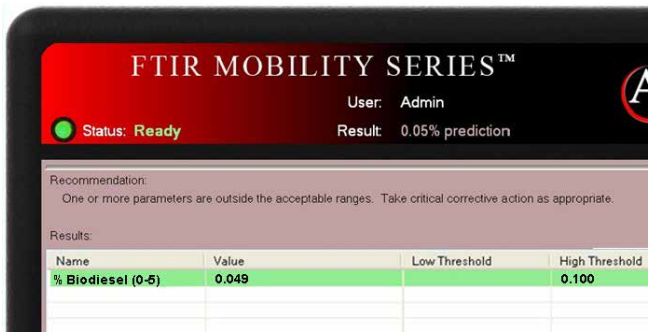


Figure 4. MicroLab results screen for a 0.05 % sample of biodiesel in diesel

www.agilent.com/chem

Published May 1, 2011
Publication Number 5990-7803EN

Agilent Technologies

Analysis of Glycerin and Glycerides in Biodiesel (B100) Using ASTM D6584 and EN14105

Application

HPI/Petrochemicals/Polymers

Author

James D. McCurry
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Chun-Xiao Wang
Agilent Technologies (Shanghai) Co., Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
Peoples Republic of China

Abstract

The analysis of free glycerin (glycerol) and total glycerides (mono-, di-, and triglycerides) in B100 biodiesel was performed according to ASTM method D6584 and CEN method EN14105. Method improvements were demonstrated through the use of a 530-µm id high-temperature fused-silica retention gap coupled to the analytical column. This was made possible with an Agilent Capillary Flow Technology Ultimate Union designed for inert, high-temperature GC oven operation. This configuration on the Agilent 7890A GC System showed calibration and precision performance that exceeded both D6584 and EN14105 specifications. This application provides complete system configuration as well as guidelines for successful analysis of free glycerin and total glycerides in biodiesel.

Introduction

Biodiesel is a motor or heating fuel produced from renewable vegetable oils or animal fats. With the high cost and limited availability of crude oil, renewable fuels like biodiesel are seen as a way to replace, supplement, or extend traditional petroleum fuels. Biodiesel is produced by a process called transesterification. The vegetable oil is reacted with methanol in the presence of a catalyst to produce a mixture of fatty acid methyl esters (FAME) and glycerin. After removal of the glycerin and other contaminants, the remaining FAME mixture is pure biodiesel. Depending on the oil source, a typical biodiesel contains FAME mixtures having both saturated and unsaturated carbon chains from C_8 to C_{24}. Table 1 shows the distribution and relative amounts of FAME found in biodiesel made from common plant oils.[1]

Pure biodiesel is generally not used as a fuel, but instead it is blended with petroleum diesel. Biodiesel is defined by the notation Bxx, where xx indicates the volume percent of FAME content in the liquid. Using this nomenclature, B100 is pure FAME, B50 contains 50 volume % FAME, B5 contains 5 volume % FAME, etc. Common commercial biodiesel blends are B2, B5, and B20.

Before biodiesel can be sold as a fuel or blending stock, it must first meet a defined standard. ASTM standard D6751 and European Committee of Standardization (CEN) standard EN14214 set similar specifications for biodiesel blending and motor fuels.[2,3] In each standard, an important specification is a limit on the amounts of free glycerin and glycerides in biodiesel. Free glycerin is a byproduct of biodiesel production. Mono-glycerides, diglycerides, and triglycerides are partially reacted oils that may be contaminants in the finished biodiesel. High amounts of free glycerin can cause problems due to separation. High amounts of glycerides and glycerin can result in increased engine deposits. Table 2 shows the limits set by each standard.

Table 1. Distribution and Relative Amounts of FAMEs Derived from Vegetable Oils

	Weight Percent FAMEs											
Oil type	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C20:0 C18:3	C20:1 C22:0	C22:1
Rapeseed					2–5	0.2	1–2	10–15	10–20	5–10	0.9	50–60
Soybean				0.3	7–11	0–1	3–6	22–34	50–60	2–10	5–10	
Palm				1–6	32–47		1–6	40–52	2–11			
Coconut	5–9	4–10	45–52	13–18	7–10		1–4	5–8	1–3			
Palm kernel	2–4	3–7	44–51	14–19	6–9	0–1	1–3	10–18	1–2		1–2	

Table 2. Free and Total Glycerin Specifications for Biodiesel

	EN14214		ASTM D6571	
	Limit (% m/m)	Test method	Limit (% m/m)	Test method
Free glycerin	0.02 max	EN14105	0.020 max	D6584
Monoglycerides	0.80 max	EN14105	NA	D6584
Diglycerides	0.20 max	EN14105	NA	D6584
Triglycerides	0.20 max	EN14105	NA	D6584
Total glycerin	0.25 max	EN14105	0.240 max	D6584

ASTM and CEN have defined several physical and chemical test methods to meet the standard specifications. An important chemical test measures the free glycerin and glyceride content in B100. Two gas chromatographic methods, EN14105 and D6584, were developed to make this measurement.[4,5] Both are nearly identical in sample preparation, instrument configuration, operating conditions, and reporting. Since glycerin and glycerides are polar and high boiling, they must first be derivatized to improve volatility and reduce activity before injection into the GC. A cool-on-column inlet (COC) and high-temperature capillary column are used to make the analysis of these compounds easier. Another important consideration when using these methods is the source of the biodiesel. Both methods were developed for B100 derived from vegetable oils such as rapeseed, soybean, sunflower, and palm. It is known that these methods are not suitable for B100 derived from lauric acid oils, such as coconut and palm kernel oils.

Experimental

Instrument Configuration

Table 3 lists the details of the GC configuration used for this work. A 530-µm id high-temperature retention gap was used between the on-column inlet and the analytical capillary column to improve sample vaporization and provide easy sample injection using a standard tapered needle syringe. An Agilent Capillary Flow Technology Ultimate Union was used to join the retention gap and the analytical column. Table 4 shows the GC operating conditions used for this analysis.

Standard and Sample Preparation

Commercially prepared stock standards were purchased containing glycerin, monoolein, diolein, triolein, butanetriol (internal standard #1), and tricaprin (internal standard #2) at concentrations specified in the ASTM and CEN methods. A list of these standards and other chemical reagents used for this analysis are shown in Table 3.

Five GC calibration standards were prepared by mixing aliquots of the individual stock standards in proportions specified by the ASTM and CEN methods. After mixing, 100 µL of the derivatization agent, N-Methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) was added to each calibration standard. After 20 minutes, 8 mL of reagent grade n-heptane was added to each calibration standard. These final reaction mixtures were directly injected into the gas chromatograph.

Sample preparation followed the procedure in the ASTM and CEN methods. Two samples of B100, from soybean oil and rapeseed oil, were used for this application. Each sample was run two times over four consecutive days with fresh calibration standards prepared and run for each analysis.

Table 3. System Configuration (SP1 7890-0294)

Standard 7890A GC hardware	
G3440A	Agilent 7890A Series GC
Option 122	Cool-on-column inlet with electronic pneumatics control (EPC)
Option 211	Capillary flame ionization detector (FID) with EPC control
G2613A	Agilent 7683 Autoinjector
Columns	
Analytical column	DB-5ht, 15 m x 0.32 mm id x 0.1-µm film (part no. 123-5711)
High-temperature retention gap	Deactivated fused-silica tubing, 1 m x 0.53 mm id (part no.160-2865-5 comes in 5-m lengths)
Union	Capillary Flow Technology Ultimate Union Kit (part no. G3182-61580)
Union ferrules	0.32-mm column Siltite ferrules (part no. 5188-5362) 0.53-mm column Siltite ferrules (part no. 5188-5363)
Data system	
	Agilent Multitechnique ChemStation
Consumables	
5181-1267	10-µL Teflon fixed autoinjector syringe
Standards and reagents*	
44892-U	Glycerin stock standard, 1 mL, 500 µg/mL in pyridine
44893-U	Monoolein stock standard, 3 mL, 5000 µg/mL in pyridine
44894-U	Diolein stock standard, 2 mL, 5000 µg/mL in pyridine
44895-U	Triolein stock standard, 2 mL, 5000 µg/mL in pyridine
44896-U	Butanetriol internal standard #1, 5 mL, 1000 µg/mL in pyridine
44897-U	Tricaprin internal standard #2, 5 mL, 8000 µg/mL in pyridine
394866-10X1ML	MSTFA derivatization grade reagent N-methyl-N-(trimethylsilyl)trifluoroacetamide
H2198	Reagent grade n-heptane

*Available from Sigma-Aldrich, PO Box 14508, St. Louis, MO 63178, USA

Table 4. Instrument Conditions

Cool-on-column inlet	
Mode	Ramped
Initial temperature	oven track, approx 50 °C
Pressure	7.6 psi helium
Injection amount	1 µL
Initial column flow	3.0 mL/min, constant pressure mode
FID temperature	380 °C
Oven temperature program	50 °C for 1 min, 15 °C/min to 180 °C, hold 0 min 7 °C/min to 230, hold 0 min 30 °C/min to 380, hold 10 min

Results and Discussion

After running the standards, Agilent ChemStation was used to calculate linear calibration curves for glycerin, monoolein, diolein, and triolein. The curves for each compound showed excellent linearity and y-intercepts near zero. These curves are shown in Figure 1. The correlation coefficients (r^2) for each compound exceeded the specification of 0.99 set forth in the ASTM and CEN methods.

Figure 2 shows the typical chromatograms obtained for samples of soybean B100 and rapeseed B100. The large peaks observed in each chromatogram are the FAMEs present in the samples. Figure 3 shows the selected regions of the rapeseed chromatogram where glycerin, monoglycerides, diglycerides, and triglycerides elute. Peak identification for each compound is made using the relative retention times published in the ASTM method (Table 5). The retention time of the first internal standard, 1,2,4-butanetriol, was used to identify glycerin. The retention time of the second internal standard, tricaprin, was used to identify the monoglycerides, diglycerides, and triglycerides.

Using the approach detailed in the ASTM and CEN methods, the amount of glycerin in each sample was calculated with the calibration functions derived from the glycerin calibration curve. Likewise, the amount of monoglycerides, diglycerides, and triglycerides was determined from the monoolein, diolein, and triolein calibration functions, respectively. Table 6 list the amounts of glycerin and glycerides found in each sample.

Precision of the analysis was measured using repeatability, which is the difference between two successive analyses of the same sample run on the same day by a single operator on the same instrument. This repeatability measurement was made for each sample over four consecutive days. Table 7 shows the results of the daily precision measurements compared to the specifications from the ASTM D6584 method. These results show excellent single-day precision as determined by repeatability.

ASTM D6584 and EN14105 are not easy methods to run for a number of reasons: the sample preparation is lengthy and difficult; the sample injection

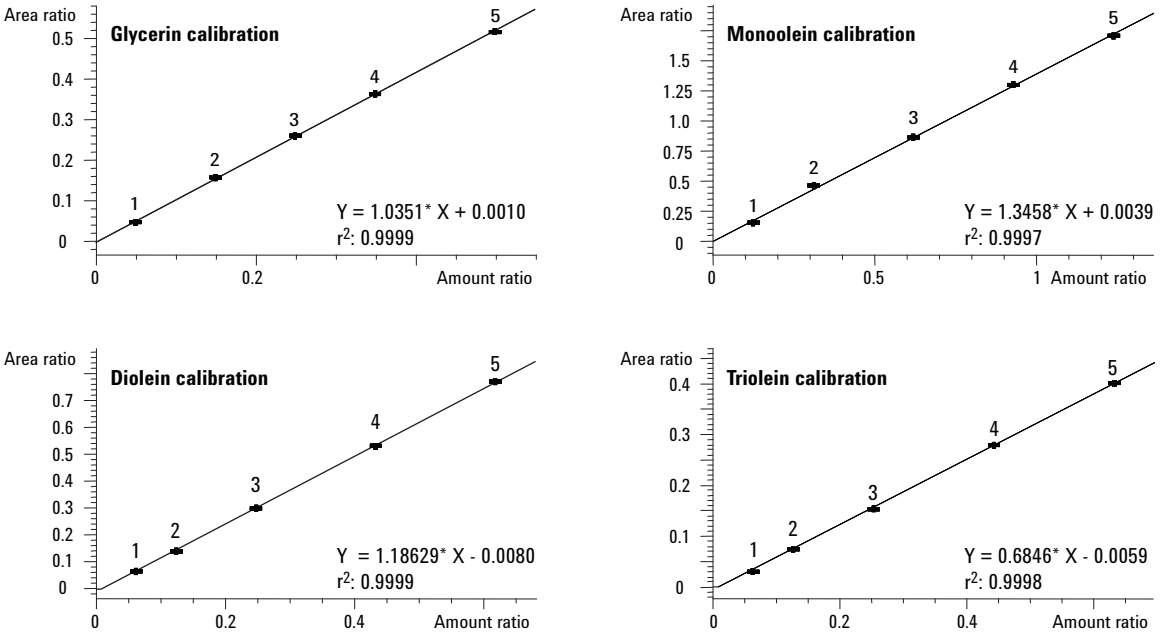


Figure 1. Calibration curves for glycerin, monoolein, diolein, and triolein.

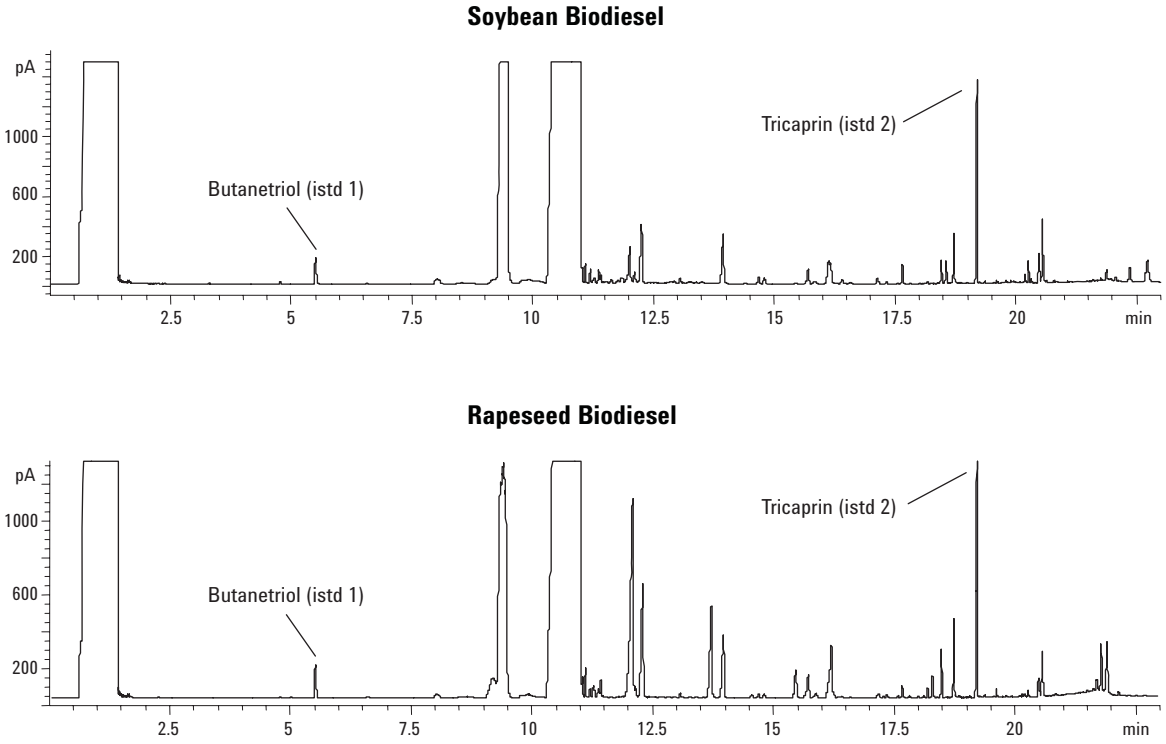


Figure 2. Chromatograms showing typical analysis of free and total glycerins in two B100 biodiesel samples.

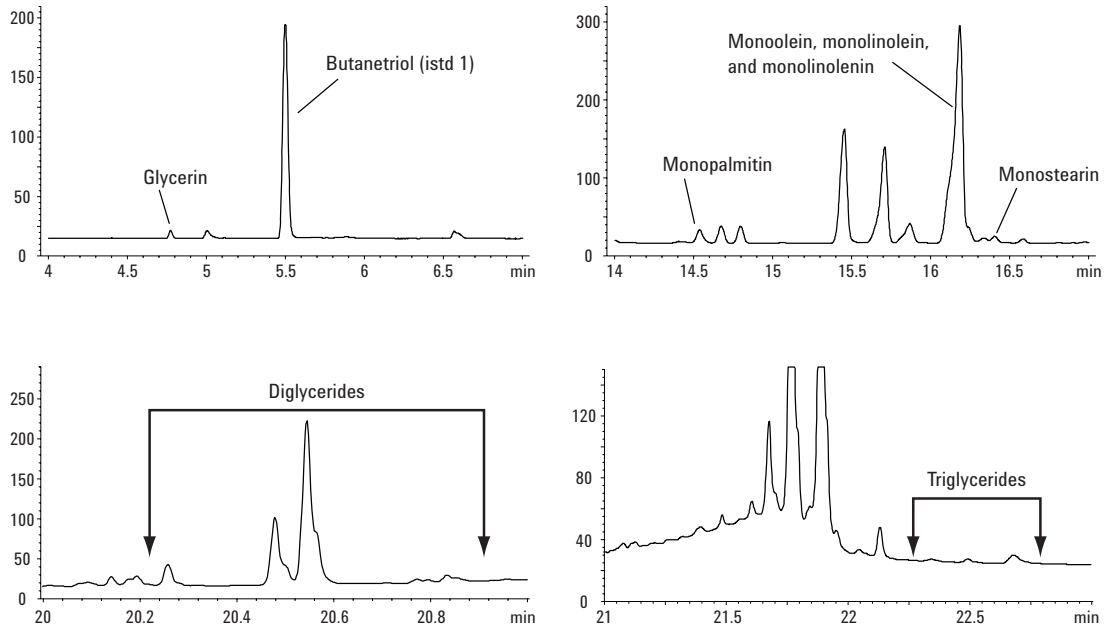


Figure 3. Details of glycerin, monoglycerides, diglycerides, and triglycerides found in a sample of rapeseed B100 biodiesel.

onto a 0.32-mm id column is not easily automated; and calibration can be difficult. However, there are a number of guidelines and procedures that can be followed to obtain good, precise results.

Sample and Standard Preparation

1. Prepare fresh calibration standards every day. Once the standards are prepared they should not be stored for more than several hours.
2. Use commercially prepared stock or final calibration standards packaged in sealed, glass ampoules. If all of the standard solutions are not used in a single day, do not save for later use. Water can accumulate in the solutions and this will inhibit derivatization.
3. Only use derivatization-grade MSTFA. Lesser grades contain solvents that can reduce the effectiveness of the reagent. It is best to purchase MSTFA in small quantities packaged in sealed, glass ampoules. As with the standards, discard any unused MSTFA.
4. Use only clean, dry glassware and pipettes.
5. Only analyze finished product B100. This method should not be used for process samples since high methanol content or water content will inhibit derivatization.
6. Run all samples immediately after preparation. Do not store prepared sample for more than several hours, especially in humid environments.

Table 5. Relative Retention Times Used for Peak Identification

	RRT (int std 1)	RRT (int std 2)
Glycerin	0.85	
1,2,3-Butanetriol (int std 1)	1.00	
Monopalmitin		0.76
Monoolein, monolinolein, monolinolenin, monostearin		0.83 – 0.86
Tricaprin (int std 2)		1.00
Diglycerides		1.05 – 1.09
Triglycerides		1.16 – 1.31

GC Analysis

It is recommended that a retention gap be used between the GC inlet and the column. The retention gap will improve peak shape and sample vaporization, as well as maintain column efficiency. Figure 4 shows the improvement in peak shape for glycerin and 1,2,3-butanetriol when using a 0.53-mm id retention gap. A retention gap will also prolong the column life since it traps any nonvolatile compound contained in the sample. A 0.53-mm id retention gap will also make sample injection easier since it can easily accommodate the standard single tapered syringe needle.

Table 6. Weight Percent of Free and Total Glycerin

	%(m/m) in Soybean B100 Biodiesel			
	Day 1 (avg)*	Day 2 (avg)*	Day 3 (avg)*	Day 4 (avg)*
Free glycerin	0.004	0.004	0.004	0.004
Monoglycerides	0.287	0.280	0.285	0.290
Diglycerides	0.533	0.527	0.533	0.546
Triglycerides	0.387	0.371	0.340	0.304
	%(m/m) in Rapeseed B100 Biodiesel			
	Day 1 (avg)*	Day 2 (avg)*	Day 3 (avg)*	Day 4 (avg)*
Free glycerin	0.002	0.002	0.002	0.002
Monoglycerides	0.365	0.375	0.370	0.371
Diglycerides	0.256	0.262	0.256	0.256
Triglycerides	0.021	0.019	0.018	0.016

*Average of 2 runs per day for each sample.

Table 7. Repeatability Results for Two B100 Biodiesel Samples Over Four Days

	Soybean B100 Biodiesel				
	ASTM D6584 Specification (% m/m)	Observed repeatability (%m/m) Day 1	Day 2	Day 3	Day 4
Glycerin	0.001	0.000	0.000	0.000	0.000
Monoglycerides	0.021	0.005	0.007	0.007	0.000
Diglycerides	0.021	0.008	0.008	0.014	0.000
Triglycerides	0.032	0.008	0.004	0.005	0.000

	Rapeseed B100 Biodiesel				
	ASTM D6584 Specification (% m/m)	Observed repeatability (%m/m) Day 1	Day 2	Day 3	Day 4
Glycerin	0.001	0.000	0.000	0.000	0.000
Monoglycerides	0.021	0.007	0.000	0.006	0.000
Diglycerides	0.021	0.003	0.002	0.000	0.000
Triglycerides	0.032	0.002	0.000	0.001	0.000

One problem with using a retention gap is the high oven temperature (380 °C) required for triglyceride elution. Most fused-silica tubing cannot be used above 350 °C. Also, traditional column unions can leak above that temperature. The Agilent Capillary Flow Technology Ultimate Union combined with special high-temperature fused-silica tubing can solve this problem. The Ultimate Union is made with deactivated stainless steel that can be taken to 400 °C without losing inertness. The high-temperature polyimide coating on the retention gap has extended lifetime up to 380 °C.

Successfully using this Union first requires that the retention gap and column be correctly installed using the metal ferrules designed for the Union. Next, the Union must be completely supported so that no weight is placed on the column connections. A bracket is supplied with the Ultimate Union Kit to support the union fitting to the GC oven wall. Failure to do this will result in a large leak after only a few runs above 350 °C, resulting in column damage. Figure 5 shows a correct installation with the Union supported on its bracket in the GC oven. From this photo it can be seen there is no stress on the column or retention gap. Additionally, to extend the lifetime of this connection, the oven temperature should be kept at 50 °C between analyses. It is also recommended that the Union be checked for leaks before running samples. If a leak is detected, make a new connection to the Union with a new ferrule, and evaluate the column performance before running samples.

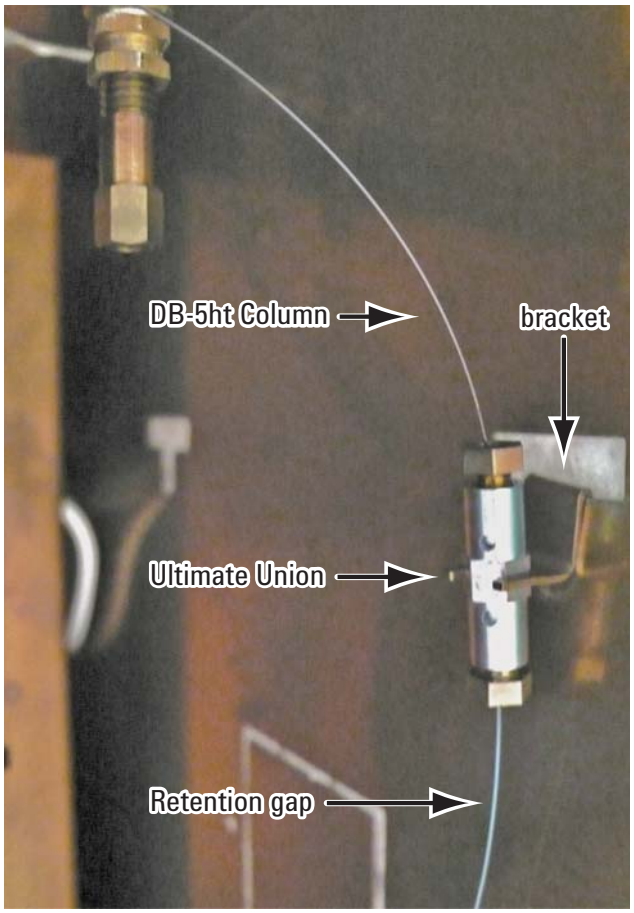


Figure 5. Details of the retention gap and analytical column joined with a Capillary Flow Technology Ultimate Union.

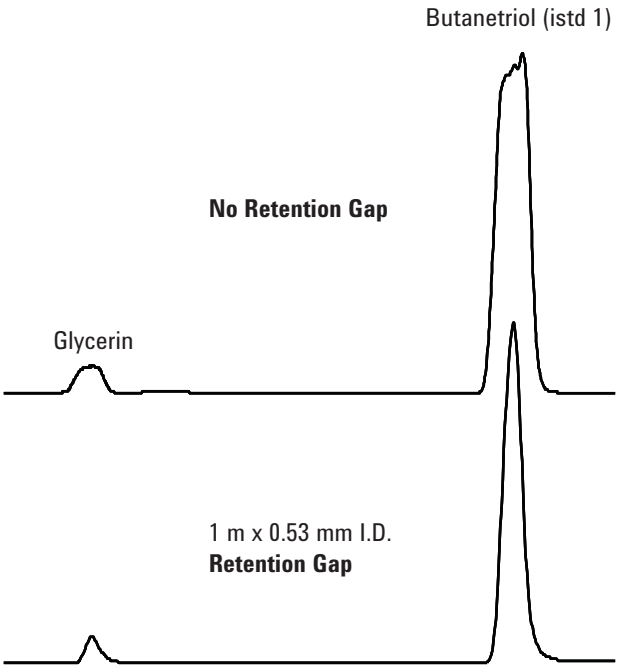


Figure 4. Improved peak shape for glycerin and 1,2,3-butanetriol when using a retention gap and the Capillary Flow Technology Ultimate Union.

Conclusions

The analysis of free and total glycerins can be done using ASTM D6584 or EN14105. Both methods are nearly identical in sample preparation and analysis. This application described the configuration of an Agilent 7890A gas chromatograph for these methods. By combining careful and deliberate sample preparation with a high-temperature retention gap and a Capillary Flow Technology Ultimate Union, this system can obtain results that meet or exceed the methods' calibration and precision specifications.

References

1. K. Shaine Tyson, “Biodiesel Handling and Use Guidelines,” National Renewable Energy Laboratory, NREL/TP-580-30004, September 2001
2. “D6751 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuel,” ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA
3. “EN14214 Fatty Acid Methyl Esters (FAME) for Diesel Engines, Requirements and Test Methods,” European Committee for Standardization: Management Centre, rue de Stassart 36, B-1050 Brussels, 2003

www.agilent.com/chem

4. “D6585 Test Method for Determination of Free and Total Glycerine in B-100 Biodiesel Methyl Esters by Gas Chromatography,” ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA, USA, 2003
5. “EN14105 Fat and Oil Derivatives–Fatty Acid Methyl Esters (FAME)–Determination of Free and Total Glycerol and Mono-, Di- and Triglyceride Content,” European Committee for Standardization: Management Centre, rue de Stassart 36, B-1050 Brussels, 2003

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
September 20, 2007
5989-7269EN

Agilent Technologies

Analysis of Denatured Fuel Ethanol using ASTM Method D5501-09

Application Note

HPI/Energy/Renewable Fuels

Author

James D. McCurry, Ph.D.
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Abstract

Denatured fuel ethanol is the feedstock used to make different types of high ethanol content motor fuels. Before it can be used, the amount of ethanol and methanol must be measured to assure product quality. ASTM method D5501-09 uses high resolution gas chromatography to perform this analysis. In this paper, the Agilent 7890A GC system was configured to run D5501-09. Excellent system performance and precision were demonstrated using the 7890A GC. Combined with the Agilent MultiTechnique ChemStation, this system offers a complete, automated solution for denatured fuel ethanol analysis.

Agilent Technologies

Introduction

Ethanol is a key additive in gasoline, serving both as a smog reducer as well as a fuel supplement to reduce the overall use of petroleum. It is relatively easy to produce by fermenting sugars obtained from food crops such as corn and sugar cane. However, the future of ethanol fuel cannot rely on food. To solve this problem, researchers are investigating ways to convert polymeric biomass carbohydrates, such as cellulose, to fermentable sugars. These sugars can then be used as an ethanol fermentation feedstock into the existing production infrastructure.

Whether ethanol comes from food sugars or converted biomass, it is first denatured before use as a motor fuel. Hydrocarbons are common denaturants and ASTM Standard D4806 specifies the types of hydrocarbons that can be used as denaturants [1]. Once the hydrocarbons are added, the product is called denatured fuel ethanol. Commercial fuels are then made by blending denatured fuel ethanol with gasoline. To assure product quality, ASTM has published method D5501-09, which uses gas chromatography to measure the ethanol and methanol content in ethanol fuels [2]. This paper describes the configuration and performance of the Agilent 7890A GC System when running ASTM D5501-09 for the analysis of denatured fuel ethanol.

Experimental

An Agilent 7890A GC System was configured according to D5501-09 and is shown in Table 1. The operating conditions for this method are shown in Table 2. Prior to sample analysis, the GC inlet splitter linearity was checked to assure there was no sample discrimination. A splitter linearity mix was prepared using the procedure described in ASTM Practice D4307 [3]. Ten hydrocarbons ranging from C_5 to C_{11} were gravimetrically blended and the final weight percent of each hydrocarbon in the mix was recorded. This mix was run using the GC conditions shown in Table 2. Calibrations for ethanol, methanol and hydrocarbons were performed using standards obtained from Spectrum Quality Standards, Sugarland, TX USA. After calibration, a commercial denatured fuel ethanol sample was analyzed to determine the ethanol and methanol content.

Table 1. The Agilent 7890A GC System Instrument Configuration for ASTM Method D5501

Standard Agilent 7890A GC System Hardware	
G3440A	Agilent 7890A Series GC System
Option 113	150 psi Split/Splitless Inlet with EPC control
Option 211	Capillary FID with EPC control
G4513A	Agilent 7693 Automatic Liquid Sampler
GC Capillary Column	
Analytical Column	PDMS, 150 m × 0.25 mm id × 1.0 µm film
Data System	
G2070BA	Agilent MultiTechnique ChemStation rev B.04.01
Consumables	
5181-1273	5 µL autoinjector syringe
5183-4647	Single taper split liner with glass wool
5183-4759	Advanced green inlet septa
Calibration Standards	
ETOH5501CAL	D5501 Calibration Set
Spectrum Quality Standards PO Box 2346 Sugarland, TX 77487-2346 USA	

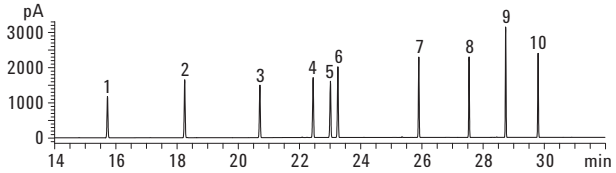
Table 2. GC Operating Conditions for ASTM Method D5501

Split/Splitless Inlet	
Temperature	300 °C
Pressure	Helium at 66 psi
Split ratio	200:1
Septum Purge	3 mL/min
Sample Size	0.5 µL injection
Initial column flow	2.34 mL/min, constant flow mode (24 cm/sec average linear velocity)
FID temperature	300 °C
Oven temperature program	60 °C for 15 min 30 °C/min to 250 °C, hold for 23 min

Results

The splitter linearity test was performed to assure quantitative transfer of all compounds from the inlet to the column without any boiling point discrimination. The test sample contained saturated hydrocarbons between C_5 and C_{11}, which covers the boiling range typically found in denatured fuel ethanol. Using a relative mass response factor of 1, each hydrocarbon in the splitter linearity mix was quantified using a normalized percent calculation. The D5501-09 method specifies that the measured mass percent of each hydrocarbon must match the known mass percent within ±3% relative difference. Figure 1 shows the chromatogram of the splitter linearity mix and the results that meet the ASTM D5501-09 specification. This shows that optimal split injection, with no discrimination, can be easily achieved using the Agilent 7693A ALS fast injection and the Agilent split optimized inlet liner.

System calibration for methanol, ethanol and hydrocarbons was done by running seven calibration standards using the GC conditions listed in Table 2. Methanol was calibrated between 0.05 and 0.6 wt% while ethanol was calibrated between 93 and 98 wt%. The calibration for the hydrocarbon



	Compound	Known wt%	Calc wt%	Relative difference (%)
1	n-pentane	6.9	7.0	**2**
2	2,4-dimethylbutane	9.5	9.6	**1**
3	2,4-dimethylpentane	8.5	8.6	**1**
4	3-methylhexane	10.1	10.1	**1**
5	2,2,4-trimethylpentane	9.5	9.7	**1**
6	n-heptane	11.4	11.4	**0**
7	n-octane	10.9	10.8	**1**
8	Nonane	9.6	9.6	**1**
9	Decane	13.3	13.3	**1**
10	Undecane	10.3	10.2	**1**

Figure 1. Analysis of the splitter linearity test mix containing saturated hydrocarbons from C_5 to C_{11}. These results meet the D5501-09 criteria for splitter linearity.

response was done using n-heptane between 1.95 and 7.4 wt%. After the calibration data was collected and the peak integration optimized, the individual response factors (R) for methanol, ethanol and n-heptane were calculated at each calibration level. Using the response factor of n-heptane, the relative response factors (RR) for methanol and ethanol were then determined at each level using the formulas described in ASTM Practice D4626 [4].

The D5501-09 method allows a single level calibration using a standard containing methanol and ethanol amounts expected in the users' samples in order to save time and resources. For this paper, the amount of alcohols in the sample was not known, therefore average RRs were calculated from all seven calibration standards and are shown in Table 3. These average RRs were then used to quantify the alcohols found in the sample of denatured fuel ethanol.

Table 3. Calibration Data for Denatured Fuel Ethanol Analysis

n-Heptane	Methanol	Ethanol
Average RR (1.95 – 7.4 wt%)	**Average RR (0.05 – 0.6 wt%)**	**Average RR (93 – 98 wt%)**
1.00	2.97	2.06

A sample of commercial denatured fuel ethanol was obtained from a producer and analyzed using the Agilent 7890A GC System running ASTM method D5501-09. Five aliquots of the sample were each measured two times for a total of ten runs. An example chromatogram is shown in Figure 2. It is important to optimize the peak integration in order to correctly measure the methanol peak area. Failure to do so could add peak response from nearby C_4 hydrocarbons to the methanol peak resulting in results that are too high. An example of optimized methanol peak integration is shown in Figure 3.

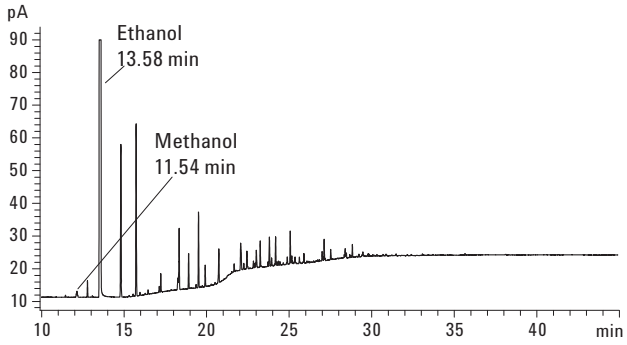


Figure 2. Analysis of a commercial denatured fuel ethanol sample using ASTM method D5501-09.

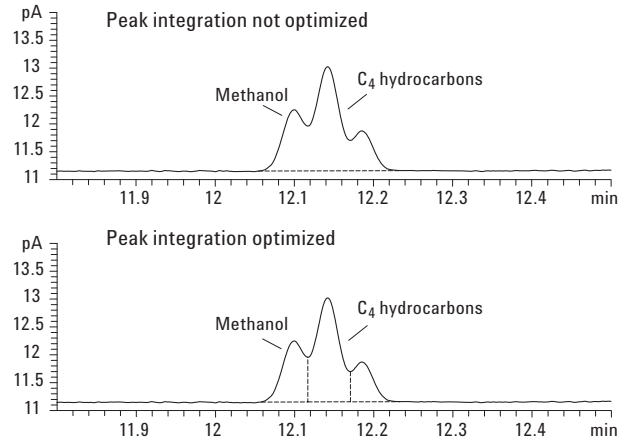


Figure 3. Optimizing the methanol peak integration is important for obtaining correct results.

Quantification of the alcohols in this sample was done using the average RRs calculated in Table 3. For all other peaks in the chromatogram, the n-heptane RR of 1 was used to measure the mass percent. Final reporting of all components was done using a normalized percent calculation as described in the D5501-09 method. The Agilent MultiTechnique ChemStation software can automatically perform both the average response factor calibration as well as the required normalized percent reporting. These results are shown in Table 4. Excellent system measurement precision was obtained for both the low level ethanol content as well as the very high level ethanol content.

Table 4. Results and Precision for the Analysis of Methanol and Ethanol in Denatured Fuel Ethanol.

Run	Methanol	Ethanol
1	0.02	97.81
2	0.02	97.83
3	0.02	97.81
4	0.02	97.82
5	0.02	97.79
6	0.02	97.81
7	0.02	97.78
8	0.02	97.76
9	0.02	97.77
10	0.02	97.74
Avg	**0.02**	**97.79**
Std Dev	**2.18e-4**	**0.03**
RSD	**1.16%**	**0.03%**

Conclusion

The measurement of methanol and ethanol in denatured fuel ethanol can be quite challenging due to the complexity of the hydrocarbon denaturant and the need to quantify near 100% ethanol as well as low level components in the sample. ASTM method D5501-09 uses high resolution gas chromatography to perform this measurement. In this paper, the Agilent 7890A GC Service was configured to run method D5501-09. The system showed no inlet discrimination so that quantitative sample transfer to the column could be made for the wide boiling range components found in denatured fuel ethanol. This was a key factor in the excellent precision shown in this paper. Calibration of a large ethanol concentration as well as a low-level methanol and hydrocarbon concentrations were done using the Agilent MultiTechnique ChemStation. The ChemStation was also able to automate the final calculations and reporting.

References

1. "D4806 - Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
2. "D5501-09 Standard Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
3. "D4307 - Standard Practice for Preparation of Liquid Blends for Use as Analytical Standards"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
4. "D4626 – Standard Practice for Calculation of Gas Chromatographic Response Factors"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
October 20, 2010
5990-6650EN

Agilent Technologies

Analysis of Sugars in Glycosylated Woody Biomass with the Agilent 1200 Series LC System

Application Note

Biofuels and Alternative Energy

Author

Atsuko Naito
Agilent Technologies Japan
Hachioji, Tokyo

Abstract

Although bioethanol is currently produced mainly from edible plants, research is underway into production methods based on non-edible plants, for example, wood. When wood is used as a raw material, glycosylation and fermentation are carried out by turning cellulose, hemicellulose, and lignin into small molecule compounds and subjecting the cellulose and hemicellulose to the action of enzymes. This is an example of analysis of sugars in wood sugar solutions obtained by low environmental impact hydrothermal treatment and mechanochemical treatment followed by enzyme-based glycosylation. The samples were kindly provided by Mr. Shigeki Sawayma, Head of the Research Team, and Mr. Katsuji Murakami, Chief Researcher, from the Biomass Research Center of the National Institute of Advanced Industrial Science and Technology.

Agilent Technologies

Configuration

Agilent 1200 Series LC System

- Agilent 1200 Series Quaternary Pump (G1354A)
- Agilent 1200 Series Standard Autosampler (G1329A)
- Agilent 1200 Series Thermostatted Column Compartment (G1316A)
- Agilent 1200 Series Evaporative Light Scattering Detector (G4218A)

Analytical Conditions

Column:	Shodex Asahipak NH2P-50 4E
Mobile phase:	Water/acetonitrile = 20/80
Flow rate:	1.0 mL/min
Column temperature:	30 °C
Injection volume:	20 µL
Sample concentration:	1000 ng/µL

A chromatogram of the reference solutions of sugars typically detected in wood sugar solutions is shown in Figure 1. Figures 2–6 show analytical results for wood sugar solutions obtained using different pre-treatment methods and raw materials. The samples were obtained by diluting wood sugar solutions with a mixture of water and acetonitrile (1:1) and passing the diluted solutions through a 0.22-µm filter.

The amount of the produced sugars and their ratios varied greatly depending on whether hydrothermal treatment or ball mill treatment was used. In addition, the amount of the produced sugars varied depending on the raw materials.

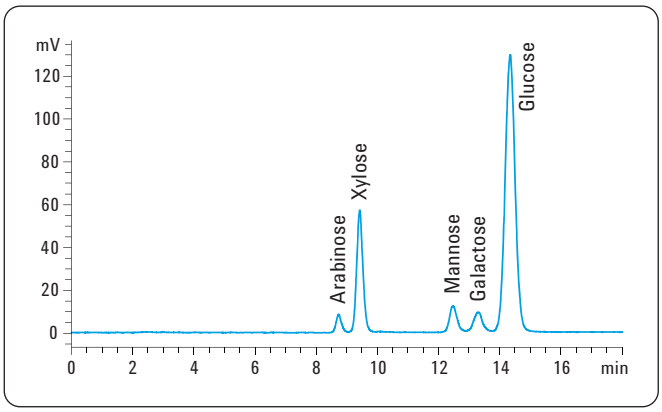


Figure 1
Chromatogram of reference solutions (1000 ng/µL each).

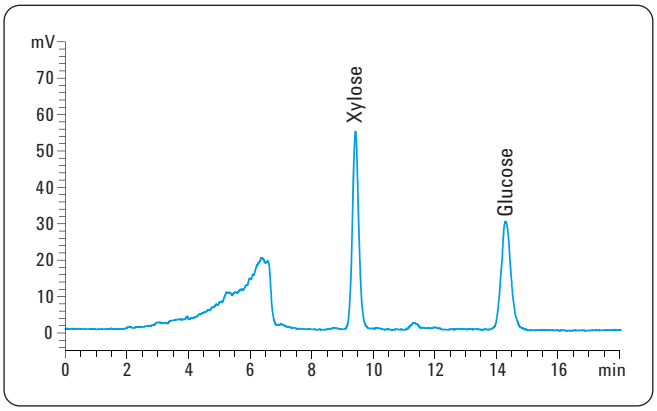


Figure 2
Bagasse, hydrothermal 180 °C 5 min.

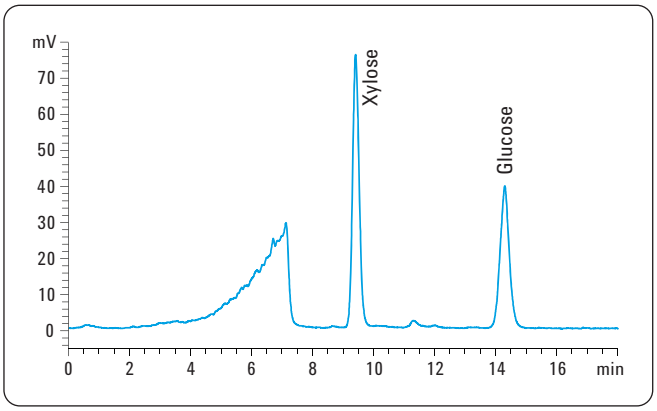


Figure 3
Bagasse, hydrothermal 160 °C 15 min.

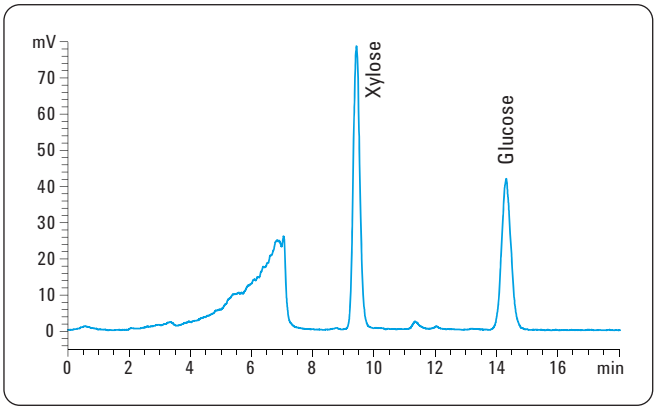


Figure 4
Bagasse, hydrothermal 160 °C 30 min, w/phosphoric acid.

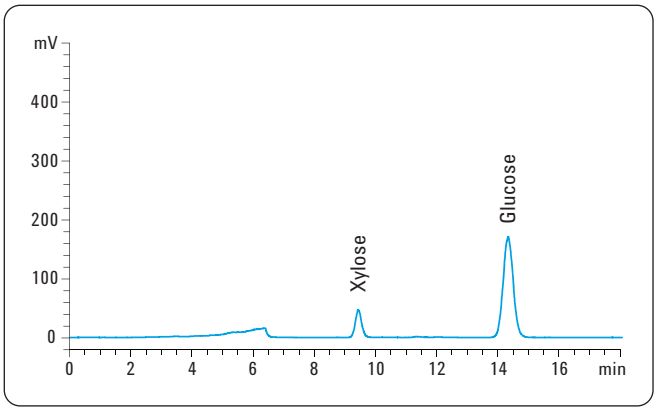


Figure 5
Bagasse, ball mill.

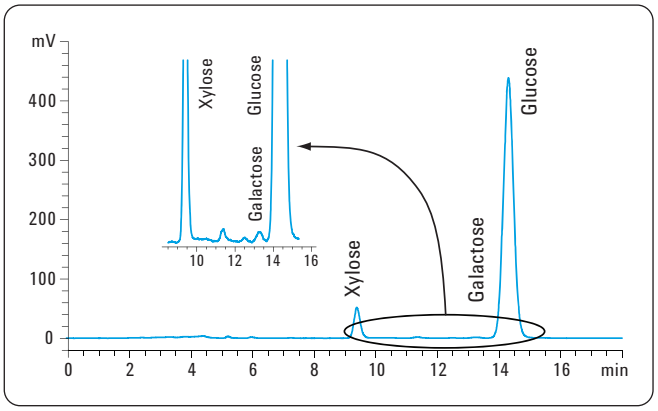


Figure 6
Eucalyptus, ball mill.

Figures 7–10 show analytical results for 2-fold dilution. A mannose peak was detected and several peaks believed to belong to oligosugars were observed subsequent to glucose elution. In addition, an unknown peak was detected prior to the mannose peak. It was found that there were few peaks believed to belong to oligosugars when the hydrothermal treatment was used and there were many peaks when the ball mill treatment was used.

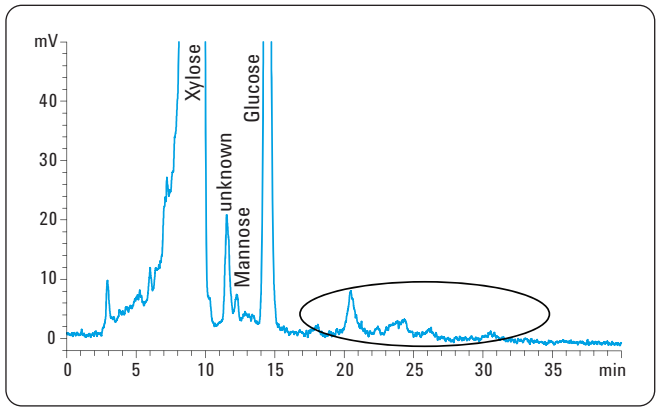


Figure 7
Bagasse, hydrothermal 180 °C 5 min (2-fold dilution).

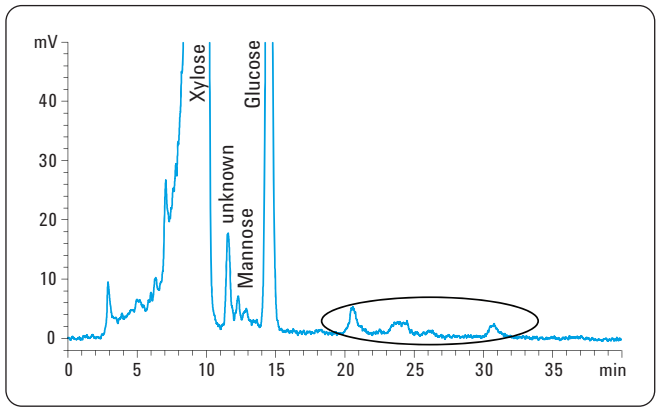


Figure 8
Bagasse, hydrothermal 160 °C 15 min (2-fold dilution).

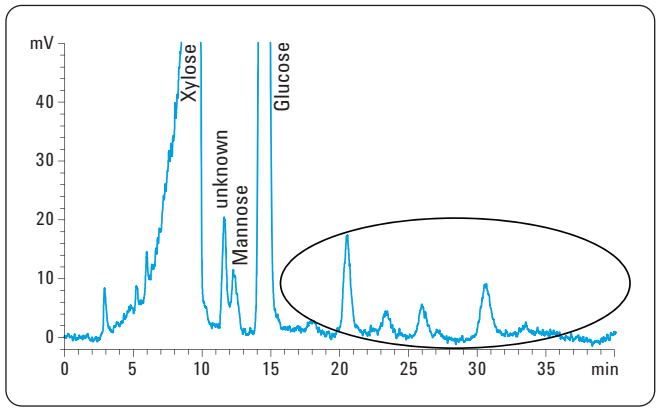


Figure 9
Bagasse, ball mill (2-fold dilution).

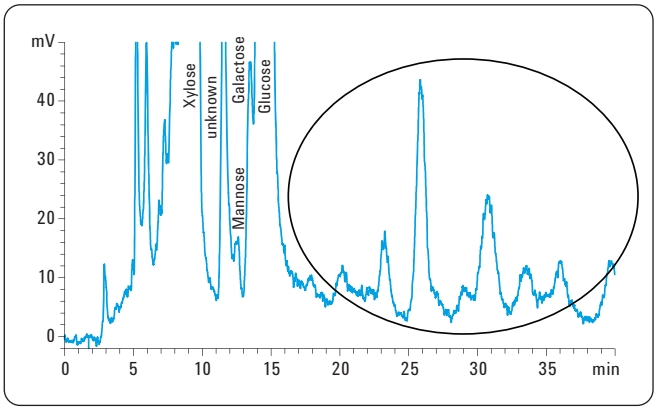


Figure 10
Eucalyptus, ball mill (2-fold dilution).

Conclusion

Sugars in glycosylated woody biomass are mainly xylose and glucose, but the concentration depends on the pre-treatment process. The Agilent 1200 Series LC system with the evaporative light scattering detector is suitable for sugar analysis in glycosylated woody biomass due to good sensitivity and good usability.

www.agilent.com/chem/lc

Published February 1, 2011
Publication Number 5990-7318EN

Agilent Technologies

Using the Agilent 490 Micro GC for the Monitoring of a Circulating Fluidized Bed Biomass Gasifier

Application Note

Micro Gas Chromatography, Reaction/Production Monitoring, Renewable Energy

Author

Marcin Siedlecki
Energy Technology Section
Process and Energy Department
Delft University of Technology
Delft, The Netherlands

Remko van Loon
Agilent Technologies, Inc.
Middelburg, The Netherlands

Abstract

Biomass has been recognized as a potential renewable and sustainable energy source. The Delft University of Technology researches the gasification of woody and agricultural biomass in a Circulating Fluidized Bed Reactor. The Agilent 490 Micro GC is used to characterize the product gas using a COX column for the permanent gases and a CP-Sil 5CB for the BTX compounds.

Introduction

There is a growing interest in sustainable heat and power generation using biomass. A possible way to use the biomass is through thermal conversion processes; combustion and gasification are the most well-known examples. The Process and Energy Department of the Delft University of Technology researched the gasification of woody and agricultural biomass in a Circulating Fluidized Bed. The product gas consists roughly of 5–15% Carbon monoxide, 10–15% Hydrogen, 3–5% Methane, 10–20% Carbon dioxide, 5–10% Nitrogen, and 40–70% Water, also (poly)aromatic compounds, minor inorganic species, and particles are present in the gas.

This product gas can be subsequently upgraded to Syngas (a mixture of Hydrogen, Carbon monoxide, Carbon dioxide and eventually water vapor). After applying the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$), Syngas could be used as a hydrogen-rich fuel gas for Fuel Cells. Other applications of Syngas are Fisher Tropsch processes (Gas to Liquid fuels), platform chemicals (like furfural), or the combustion in a gas turbine to generate heat and power. For the characterization of the product gas, the Agilent 490 Micro GC was used.

Experimental

Fluidization media and woody or agricultural biomass are fed into the Circulating Fluidized Bed Reactor, where the biomass is gasified at around 850 °C. The sample is taken from the product gas stream using a heated probe. Particles present in the sample are removed by the dust filter. Water vapor is stripped from the sample using two condensers. Figure 1 gives an overview of the sampling and sample conditioning setup. An external gas pump provides a continuous sample gas flow to the Agilent Micro GC. Every 3 min, the Micro GC starts an analytical run and analyses the gas sample on both column channels.

The Agilent 490 Micro GC used for the analysis of the product gas is equipped with a 1 m COX column channel for permanent gas analysis and a 4 m CP-Sil 5 CB column channel for the analysis of Benzene, Toluene and the Xylenes. The Micro GC conditions for both channels are displayed in Table 1.

Table 1. Agilent 490 Micro GC Instrument Conditions

	1 m COX	4 m CP-Sil 5 CB
Column temperature	100 °C	100 °C
Carrier gas	Argon, 200 kPa	Argon, 150 kPa
Injector temperature	110 °C	110 °C
Injection time	20 ms	40 ms
Detector sensitivity	Auto	High
Sample line temperature	110 °C	
Sampling mode	Continuous flow	
Sampling time	10 s	

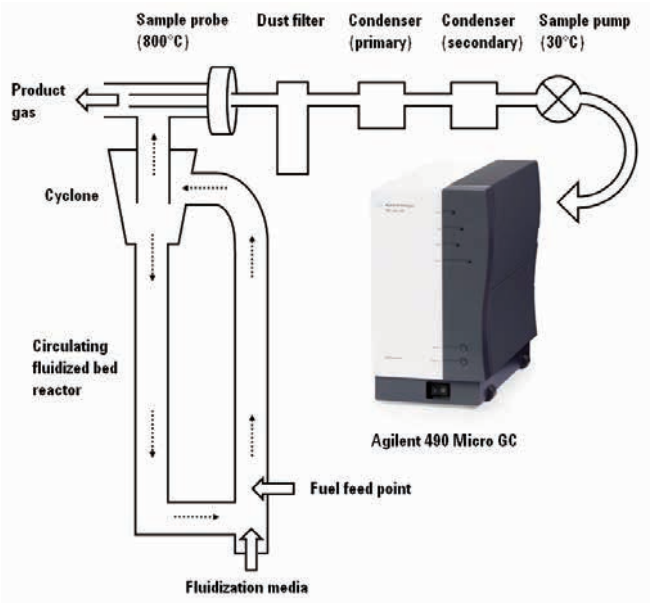


Figure 1. Reactor, sampling and sample conditioning setup.

Results and Discussion

The COX column shows an excellent separation for the permanent gases, as shown in Figure 2.

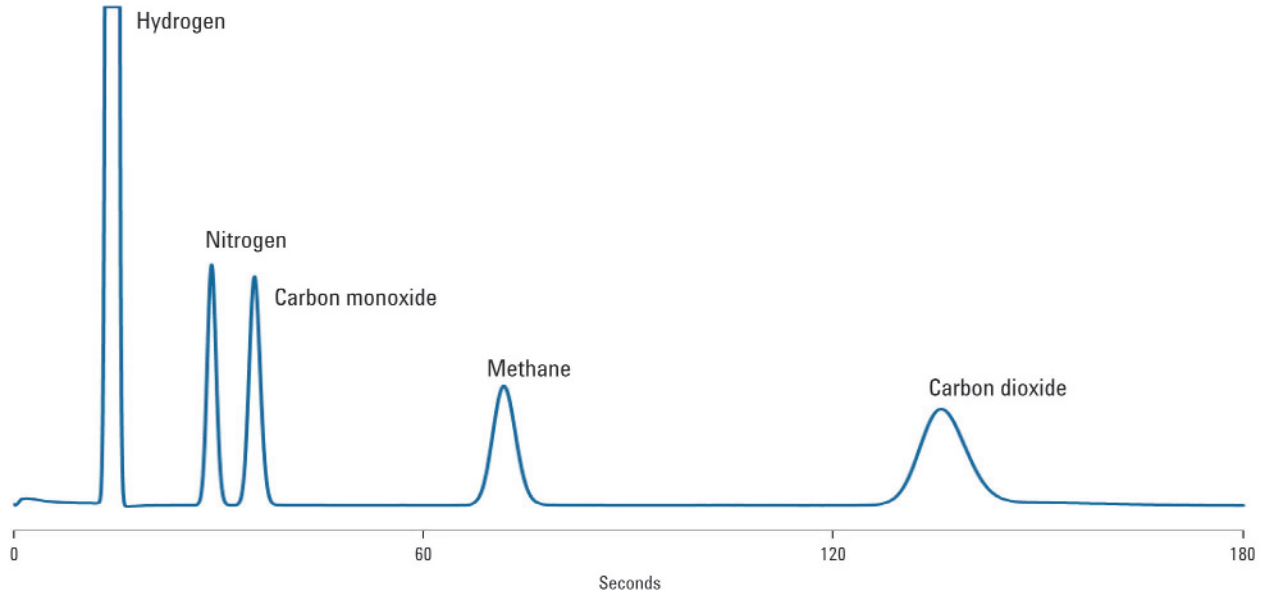


Figure 2. Permanent gases on the COX column.

Although the COX column does not separate oxygen and nitrogen, it is very suitable for the analysis of permanent gases including carbon dioxide. In the case of gasification, the product gas sample does not contain oxygen. When the sample contains both oxygen and nitrogen, and these gases need to be quantified separately, the use of a MolSieve5A column channel instead of the COX column channel is required. The COX column can be equipped with a back flush to vent. This option makes it possible to back flush later eluting compounds to reduce analysis time and to prolong column lifetime.

For each component a multi-level calibration (4 levels) is performed. Figures 3 and 4 show an excellent calibration curve for Methane and Carbon monoxide. For a linear regression, the R-Squared for these compounds is nearly perfect.

The BTX compounds are analyzed on a CP-Sil 5 CB column channel. The chromatogram in Figure 5 shows that all compounds are eluted in less than 90 sec. On the CP-Sil 5 CB column type it is not possible to separate meta- and para-Xylene. These compounds are reported in a single result. For all BTX compounds, a 4-level calibration is performed. Figure 6 shows an example of Benzene. R-squared (linear regression) for Benzene is 0.9969.

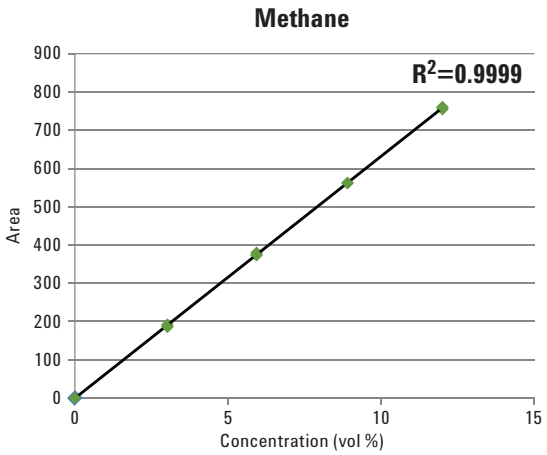


Figure 3. Calibration curve for methane.

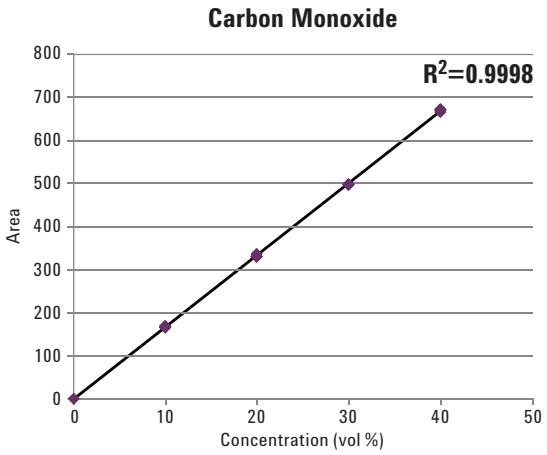


Figure 4. Calibration curve for Carbon monoxide.

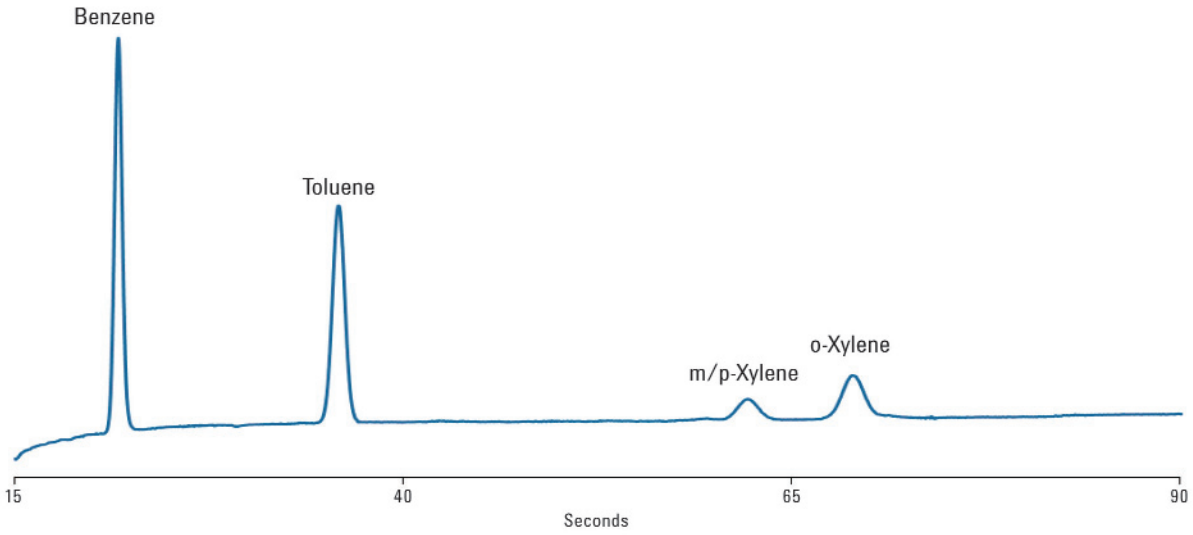


Figure 5. BTX analysis on the CP-Sil 5 CB column.

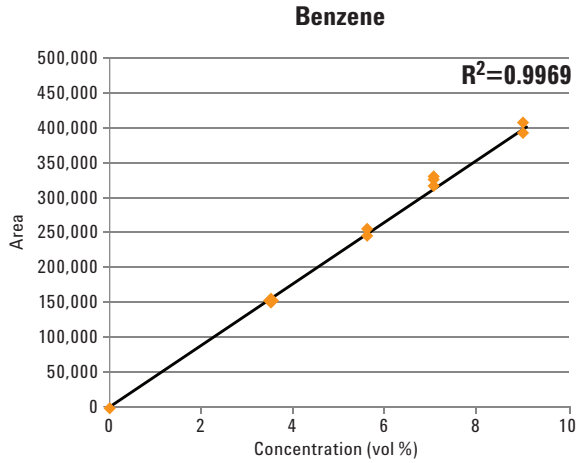


Figure 6. Calibration curve for Benzene.

Conclusion

The data presented in this application note clearly shows that the Agilent 490 Micro GC equipped with two column channels was capable of monitoring the product gas from the Circulating Fluidized Bed biomass gasifier. Within 180 sec the permanent gases were analyzed using a COX column channel. The BTX analysis was performed on a CP-Sil 5CB column channel with an analysis time of less than 90 sec.

The Agilent 490 Micro GC is considered a key apparatus for the quantification of the main product gas components in the gasification test rig at the Process & Energy Laboratory at Delft University of Technology. The main advantages of the 490 Micro GC analyzer are its reliability, short analysis times, ease of use (both hardware and software), and a certain degree of flexibility. The modular setup of the 490 Micro GC makes it possible to exchange the column modules if other gas components need to be analyzed.

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

References

1. M.Siedlecki, R. Nieuwstraten, E. Simone, W. de Jong and A.H.M. Verkooijen; Delft University of Technology; 'Effect of Magnesite as Bed Material in a 100 kWth Steam-Oxygen Blown Circulating Fluidized-Bed Biomass Gasifier on Gas Composition and Tar Formation'; 2009.

2. Application note 5990-7054EN; Simone Darphorn-Hooijschuur and Marijn van Harmelen, Avantium Technologies; Remko van Loon and Coen Duvekot, Agilent Technologies; 'Permanent Gases on a COX Module Using an Agilent 490 Micro GC'; 2010.

For More Information

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

www.agilent.com/chem

Printed in the USA
June 2, 2011
5990-8069EN

Agilent Technologies

EN 15779 - Gas Chromatographic Analysis of Polyunsaturated FAME in Biodiesel Made From Algae and Marine Oils

Application Note

Fuels

Author

James D. McCurry, Ph.D.
Agilent Technologies, Inc.
2850 Centerville Rd
Wilmington, DE
19808

Abstract

The GC analysis of four common polyunsaturated fatty acid methyl esters (PUFA FAMEs) in algal biodiesel is described using method EN 15779. An Agilent 7890A GC system was configured and calibrated according to the procedure outlined in the method. Two samples of B100 biodiesel made from algae oil were each prepared in duplicate and analyzed according to the conditions set forth in the method. In each sample, the four PUFA FAMEs were chromatographically separated and quantified. The analysis precision was calculated and shown to exceed the specifications of the EN 15779 methods.

Introduction

Currently, most worldwide stocks of biodiesel are made from vegetable oils or animal fats. While these sources are cheap and convenient, they compete with food production resources. Current research involves finding nonfood sources of triglycerides harvested from plants that do not compete with food production. A promising source is algae cultivated in contained bioreactors, where both growth rates and oil yields are greater when compared to land-based crops. One potential problem with algae and marine oils is the high concentrations of polyunsaturated fatty acids (PUFA). After conversion to biodiesel fuel, PUFA FAMEs exhibit lower oxidation stability and higher rates of self-polymerization. These properties can cause engine fouling and fuel line or filter plugging if the PUFA FAME content is too high.

Agilent Technologies

To assure good algal biodiesel quality, the European Committee for Standardization (CEN) has developed a GC method to measure the amount of four predominant PUFA FAMEs found in these biodiesels (Table 1). The method is designated as EN 15779 [1]. This application note describes the configuration and performance of the Agilent 7890A GC system when using this method for the analysis of B100 biodiesel derived from algae oil.

Table 1. Polyunsaturated FAMEs Measured Using Method EN 15779

CAS number	Chemical name	Abbreviation
2566-89-4	Methyl eicosatetraenoate	C20:4 (n-6)
2734-47-6	Methyl eicosapentaenoate	C20:5 (n-3)
108698-02-8	Methyl docosapentaenoate	C22:5 (n-3)
28061-46-3	Methyl docosahexaenoate	C22:6 (n-3)

Experimental

An Agilent 7890A GC was configured and the instrument conditions were set according to the EN 15779 method. These details are shown in Tables 2 and 3. A 1.0 mg/mL solution of methyl tricosanoate (C23:0) in n-heptane was prepared for use as an internal standard. A 0.1 mg/mL solution of the four PUFA FAMEs (Table 1) was prepared in n-heptane containing 1.0 mg/mL of the internal standard (C23:0). This standard was used to determine the retention times for each PUFA FAME and the C23:0 internal standard. Two samples of algal B100 biodiesel were obtained for testing. Each sample was prepared by weighing 100 mg into a 2-mL autosampler vial and adding 1.0 mL of the C23:0 internal standard solution followed by mixing. The samples were prepared and run in duplicate to determine the repeatability of the analysis.

Table 2. 7890A GC Configuration for EN 15779

Standard Agilent 7890A GC system hardware	
Agilent 7890A Series GC (G3440A)	
Option 112	100 psi split/splitless Inlet with EPC control
Option 211	Capillary FID with EPC control
Agilent 7693 Autoinjector (G4513A)	
123-7032	DB-Wax Column, 0.32 mm × 30 m id × 0.25 µm

Table 3. Instrument Conditions for EN 15779 Method

Column oven conditions	
Initial oven temperature	150 °C for 1 min
Oven ramp 1	15 °C/min to 200 °C
Oven ramp 2	2 °C/min to 250 °C
Inlet and sampling conditions	
Column flow	Hydrogen at 1 mL/min constant flow
Inlet temperature	220 °C
Inlet mode	Split at 50:1 split ratio
Injection size	1 µL
Flame ionization detector conditions	
Detector temperature	250 °C

Results and Discussion

Figure 1 shows a chromatogram of the PUFA FAME reference standard run under the EN 15779 GC conditions. The retention times of each peak were noted on the chromatogram. These retention times were used to identify each of the four PUFA FAMEs found in the biodiesel samples.

The GC analysis of the two algal biodiesel samples is shown in Figure 2. The FAME profiles of the two samples are very similar, but the PUFA FAME content appears higher in sample 1. Quantification of the PUFA FAMEs was done using the theoretical response factors for each PUFA FAME published in the EN 15779 method. These response factors were corrected using the detector response of the C23:0 FAME internal standard added to each sample. This procedure helps to improve the accuracy of the final results. The weight percent of each PUFA FAME was calculated, and the total PUFA FAME content in the samples was reported by summing the individual FAMEs. Table 4 shows the results for the duplicate analyses of both algal biodiesel samples.

The analysis precision for each sample was determined by calculating the repeatability (r) for the duplicate runs. Repeatability is defined as the difference between duplicate sample results analyzed by a single operator on the same equipment in a short period of time, usually the same day. For the EN 15779 method, a repeatability specification was only determined for the total PUFA FAME result. Table 4 shows that this specification was exceeded for both samples when using the Agilent 7890A GC system.

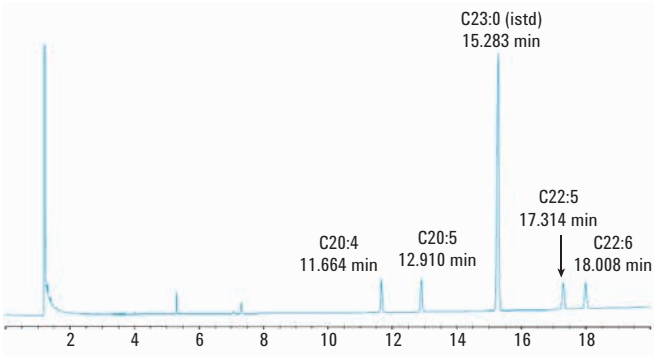


Figure 1. Chromatogram of the retention time standard containing the four PUFA FAMEs and the internal standard, methyl tricosonate (C23:0).

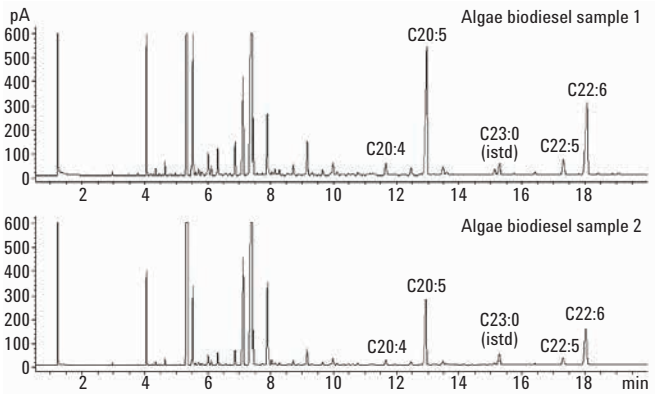


Figure 2. These chromatograms show the analysis of PUFA FAMEs in biodiesel samples made from two different algae oils.

Table 4. Reproducibility of Biodiesel Sample Runs

Run	C20:4 wt%	C20:5 wt%	C22:4 wt%	C22:6 wt%	Total PUFA
Algae biodiesel sample 1					
1	0.39	5.96	0.72	4.01	11.08
2	0.39	5.98	0.72	4.02	11.11
			Measured repeatability (r)		0.03
			EN 15779 Specification (r)		0.07
Algae biodiesel sample 2					
1	0.17	2.65	0.32	1.79	4.93
2	0.18	2.67	0.32	1.81	4.98
			Measured repeatability (r)		0.05
			EN 15779 Specification (r)		0.07

Excellent precision was observed for duplicate runs of each algal biodiesel sample. The reproducibility (r) measured for each sample exceeded the specification published in the EN 15779 method.

Conclusion

The analysis of PUFA FAMEs in biodiesel made from algal or marine oils can be easily done using EN method 15779 on an Agilent 7890A GC system. Calibration and reporting of the PUFA FAME content can be done according to the method's protocol using the standard tools within the Agilent Chemstation. After analyzing two algal oil biodiesel samples, the 7890A GC system provided results whose precision met the requirement of the EN 15779 method.

References

1. "EN15779 Petroleum products and fat and oil derivatives – Fatty acid methyl esters (FAME) for diesel engines – Determination of polyunsaturated fatty acid methyl esters (PUFA) by gas chromatography"; European Committee for Standardization: Management Centre, Avenue Matrix 17, B-1000 Brussels, 2009.

For More Information

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

www.agilent.com/chem

Printed in the USA
August 24, 2011
5990-8875EN

Agilent Technologies

Automated Standard and Sample Preparation Using the Agilent 7696A WorkBench for GC/MS Analysis of FAME Contamination in Jet Fuel

Application Note

Fuels

Author

James D. McCurry, Ph.D.
Agilent Technologies, Inc.
2850 Centerville Rd
Wilmington, DE
19808

Abstract

The Agilent 7696A Sample Prep WorkBench was used to prepare calibration standards and samples for the GC/MS analysis of total FAME in jet fuel using the IP585 method. The WorkBench needed 10 times less reagents and standards to achieve better analysis results when compared to manual sample preparation techniques. The GC/MS calibration using WorkBench prepared standards meet all performance criteria without any re-work, saving considerable time in the laboratory. WorkBench prepared jet fuel samples exceeded the method's precision requirements for several different levels of FAME contamination. The analysis results obtained from the WorkBench samples provided better recovery of the known FAME concentrations compared to the manually prepared samples.

Agilent Technologies

Introduction

The Energy Institute method, IP585, uses GC/MS to measure trace fatty acid methyl esters (FAME) in commercial jet fuel.[1] FAME contamination occurs when multiproduct pipelines (MPP) are used to transport both biodiesel and jet fuel. A limit of 5 mg/kg of total FAME content has been established by the Joint Inspection Group (JIG), a consortium of jet fuel producers and users. A recent Agilent paper describes the operation and performance of the Agilent 5975C Series GC/MSD system when running method IP585.[2]

As with most instrumental measurements, successful preparation of calibration standards and samples plays a significant part to achieving quality results. For the IP585 method, 1-mL volumes of calibration standards are made using graduated microliter pipettes. Using a microliter syringe, an expensive internal standard solution containing 1000 mg/mL of methyl heptadecanoate-d33 (C17:0-d33) is added to every calibration standard and sample. Due to the small volumes being measured, these procedures require considerable skill to correctly prepare standards and samples. A better approach would be to automate the sample preparation using an instrument specifically designed to dispense and mix liquids in microliter volumes with high accuracy and precision.

The Agilent 7696A Sample Prep WorkBench is a standalone instrument specifically designed to perform automated sample preparation. It uses two Agilent 7693A injection towers to volumetrically transfer liquids between 2-mL vials. Vials containing various chemical resources, standards, and samples are housed in three 50-positions trays. The sample tray compartment contains a robotic arm, a vortex mixing station, and a sample heating station. Calibration standard preparation using the Agilent WorkBench have been shown to provide better calibrations compared to manually prepared standards. Additionally, samples prepared in 2-mL vials using the WorkBench were shown to give the same quantitative results as manually prepared samples.[3] In this application note, the Agilent 7696A Workbench was used to prepare 11 calibration standards along with three jet fuel samples each containing different levels of FAME contamination. Standards and sample volumes were reduced 10-fold from 1 mL to 100 µL to save resources such as solvents, stock standard solutions and the internal standard solution. The analysis results from the WorkBench prep were compared to results from a manual prep using the precision specifications in the IP585 method.

Designing the Automated Workbench Procedure

Calibration Standards Prepared by Linear Dilution

The IP585 method uses 10 working calibration standards (WCS) to calibrate the GC/MS system. Each WCS contains different concentrations of the six FAMEs shown in Table 1. The linear dilution scheme outlined in Table 2 is described in the method to manually prepare 1 mL quantities of each WCS. For the automated WorkBench preparation, this manual scheme was translated from 1 mL to 100 µL final volumes for each standard as shown in Table 3. To prepare the standards, four resources were defined in the WorkBench software (Table 4). The first resource was 10 empty vials used to contain the final WCS. The next resource was a vial containing 1,000 µL of 99% n-dodecane used as the dilution solvent. The third resource was a vial containing 1,000 µL of the working standard solution (WSS). The last resource was a vial containing 500 µL of the internal standard solution. Figure 1 shows the resource layout used by the WorkBench software for automated preparation of the calibration standards.

Table 1. Compounds used to Quantify Total FAME in Jet Fuel

Chemical name	Common name	Symbol	Molecular formula	Molecular weight
Methyl hexadecanoate	Methyl palmitate	C16:0	$C_{17}H_{34}O_2$	270.45
Methyl heptadecanoate	Methyl margarate	C17:0	$C_{18}H_{36}O_2$	284.45
Methyl octadecanoate	Methyl stearate	C18:0	$C_{19}H_{38}O_2$	298.50
Methyl octadecenoate	Methyl oleate	C18:1	$C_{19}H_{36}O_2$	296.49
Methyl octadecadienaote	Methyl linoleate	C18:2	$C_{19}H_{34}O_2$	294.47
Methyl octadecatrienoate	Methyl linolenate	C18:3	$C_{19}H_{32}O_2$	292.45

These six FAMEs are found in 95% of the common feed stocks used to produce biodiesel.

Table 2. Manual Scheme to Prepare 1-mL of each Working Calibration Standard (WCS) using Linear Volumetric Dilution

Volume (µL) of working standard solution (WSS)	Volume (µL) of n-C12 solvent	Volume (µL) of internal standard (ISTD)	Final concentration (mg/kg) of each FAME
1000	0	10	100
800	200	10	80
600	400	10	60
400	600	10	40
200	800	10	20
100	900	10	10
80	920	10	8
60	940	10	6
40	960	10	4
20	980	10	2
0	1000	10	0

Table 3. Agilent WorkBench Linear Volumetric Dilution Preparation to Make 100 µL of each Working Calibration Standard (WCS)

Volume (µL) of working standard solution (WSS)	Volume (µL) of n-C12 solvent	Volume (µL) of internal standard (ISTD)	Final concentration (mg/kg) of each FAME	Working calibration standards (WCS)
100	0	1	100	High Std 5
80	20	1	80	High Std 4
60	40	1	60	High Std 3
40	60	1	40	High Std 2
20	80	1	20	High Std 1
10	90	1	10	Low Std 5
8	92	1	8	Low Std 4
6	94	1	6	Low Std 3
4	96	1	4	Low Std 2
2	98	1	2	Low Std 1
0	100	1	0	Blank

Table 4. WorkBench Resource Layout for Automated Preparation of IP585 Calibration Standards

Resource	Resource type	Vial range	Usage
Working calibration standards (WCS)	Empty container	51-60	1
n-Dodecane solvent	Chemical resource	61	1000 µL
Working standard solution (WSS)	Chemical resource	71	1000 µL
Internal standard solution (ISTD)	Chemical resource	81	500 µL

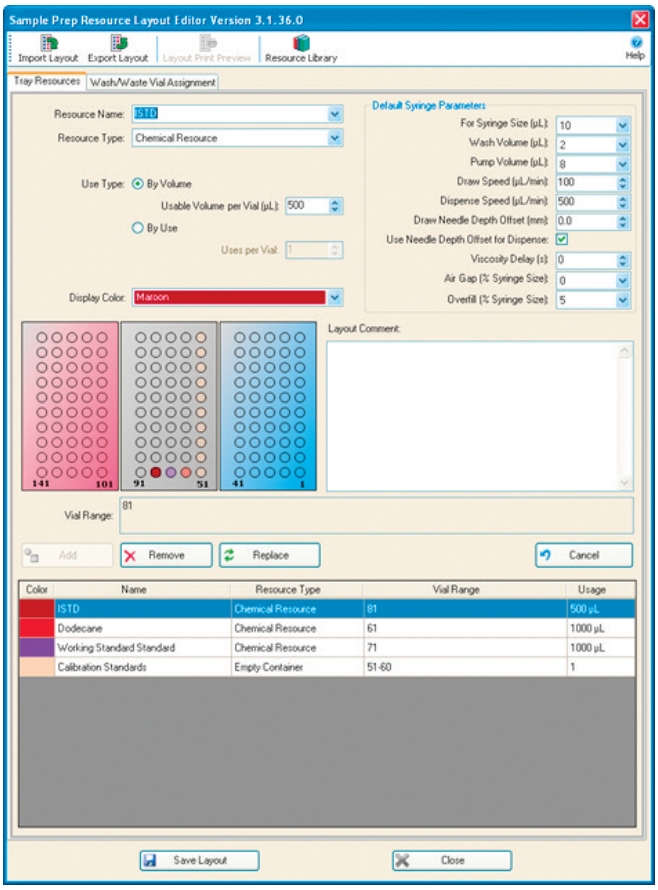


Figure 1. Agilent WorkBench resource layout for the automated preparation of IP585 calibration standards. The empty vials in positions 51 to 60 will contain each of the 10 calibration standards after the automated preparation is complete.

With the resource layout complete, two Agilent WorkBench methods were designed to prepare the standards listed in Table 3. The first method, "IP585_Low.M", was used for the 2 to 10 mg/kg low level standards and the second method, "IP585_High.M", was used for the 20 to 100 mg/kg high level standards. Details of the sample prep steps for each of these methods are listed in Tables 5 and 6. The WorkBench software allows the user to quickly and easily build methods using a graphical "drag-and-drop" interface. The IP585_Low.M method shown in Figure 2 is an example of a typical method.

Table 5. Agilent WorkBench Method to Prepare 100 µL of each Low Level Working Calibration Standard (WCS)

Step	Agilent WorkBench action	Description	Syringe
1	Wash	Solvent wash 250 µL syringe	250 µL
2	Add	100 µL n-C_{12} to Low Blank (Vial 1)	250 µL
3	Add	98 µL n-C_{12} to Low Std 1 (Vial 51)	250 µL
4	Add	96 µL n-C_{12} to Low Std 2 (Vial 52)	250 µL
5	Add	94 µL n-C_{12} to Low Std 3 (Vial 53)	250 µL
6	Add	92 µL n-C_{12} to Low Std 4 (Vial 54)	250 µL
7	Add	90 µL n-C_{12} to Low Std 5 (Vial 55)	250 µL
8	Wash	Solvent wash 25 µL syringe	25 µL
9	Add	2 µL WSS to Low Std 1 (Vial 51)	25 µL
10	Add	4 µL WSS to Low Std 2 (Vial 52)	25 µL
11	Add	6 µL WSS to Low Std 3 (Vial 53)	25 µL
12	Add	8 µL WSS to Low Std 4 (Vial 54)	25 µL
13	Add	10 µL WSS to Low Std 5 (Vial 55)	25 µL
14	Wash	Solvent wash 25 µL syringe	25 µL
15	Add	1 µL ISTD to Low Blank (Vial 1)	25 µL
16	Add	1 µL ISTD to Low Std 1 (Vial 51)	25 µL
17	Add	1 µL ISTD to Low Std 2 (Vial 52)	25 µL
18	Add	1 µL ISTD to Low Std 3 (Vial 53)	25 µL
19	Add	1 µL ISTD to Low Std 4 (Vial 54)	25 µL
20	Add	1 µL ISTD to Low Std 5 (Vial 55)	25 µL
21	Wash	Solvent wash 25 µL syringe	25 µL
22	Mix	Low Blank (Vial 1) for 30 s @ 1500 rpm	
23	Mix	Low Std 1 (Vial 51) for 30 s @ 1500 rpm	
24	Mix	Low Std 2 (Vial 52) for 30 s @ 1500 rpm	
25	Mix	Low Std 3 (Vial 53) for 30 s @ 1500 rpm	
26	Mix	Low Std 4 (Vial 54) for 30 s @ 1500 rpm	
27	Mix	Low Std 5 (Vial 55) for 30 s @ 1500 rpm	

Table 6. Agilent WorkBench Method to Prepare 100 µL of each High Level Working Calibration Standard (WCS)

Step	Agilent WorkBench action	Description	Syringe
1	Wash	Solvent wash 250 µL syringe	250 µL
2	Add	100 µL n-C_{12} to High Blank (Vial 2)	250 µL
3	Add	80 µL n-C_{12} to High Std 1 (Vial 56)	250 µL
4	Add	60 µL n-C_{12} to High Std 2 (Vial 57)	250 µL
5	Add	40 µL n-C_{12} to High Std 3 (Vial 58)	250 µL
6	Add	20 µL n-C_{12} to High Std 4 (Vial 59)	250 µL
7	Wash	Solvent wash 250 µL syringe	250 µL
8	Add	20 µL WSS to High Std 1 (Vial 56)	250 µL
9	Add	40 µL WSS to High Std 2 (Vial 57)	250 µL
10	Add	60 µL WSS to High Std 3 (Vial 58)	250 µL
11	Add	80 µL WSS to High Std 4 (Vial 59)	250 µL
12	Add	100 µL WSS to High Std 5 (Vial 60)	250 µL
13	Wash	Solvent wash 25 µL syringe	25 µL
14	Add	1 µL ISTD to High Blank (Vial 2)	25 µL
15	Add	1 µL ISTD to High Std 1 (Vial 56)	25 µL
16	Add	1 µL ISTD to High Std 2 (Vial 57)	25 µL
17	Add	1 µL ISTD to High Std 3 (Vial 58)	25 µL
18	Add	1 µL ISTD to High Std 4 (Vial 59)	25 µL
19	Add	1 µL ISTD to High Std 5 (Vial 60)	25 µL
20	Wash	Solvent wash 25 µL syringe	25 µL
21	Mix	High Blank (Vial 2) for 30 s @ 1500 rpm	
22	Mix	High Std 1 (Vial 56) for 30 s @ 1500 rpm	
23	Mix	High Std 2 (Vial 57) for 30 s @ 1500 rpm	
24	Mix	High Std 3 (Vial 58) for 30 s @ 1500 rpm	
25	Mix	High Std 4 (Vial 59) for 30 s @ 1500 rpm	
26	Mix	High Std 5 (Vial 60) for 30 s @ 1500 rpm	

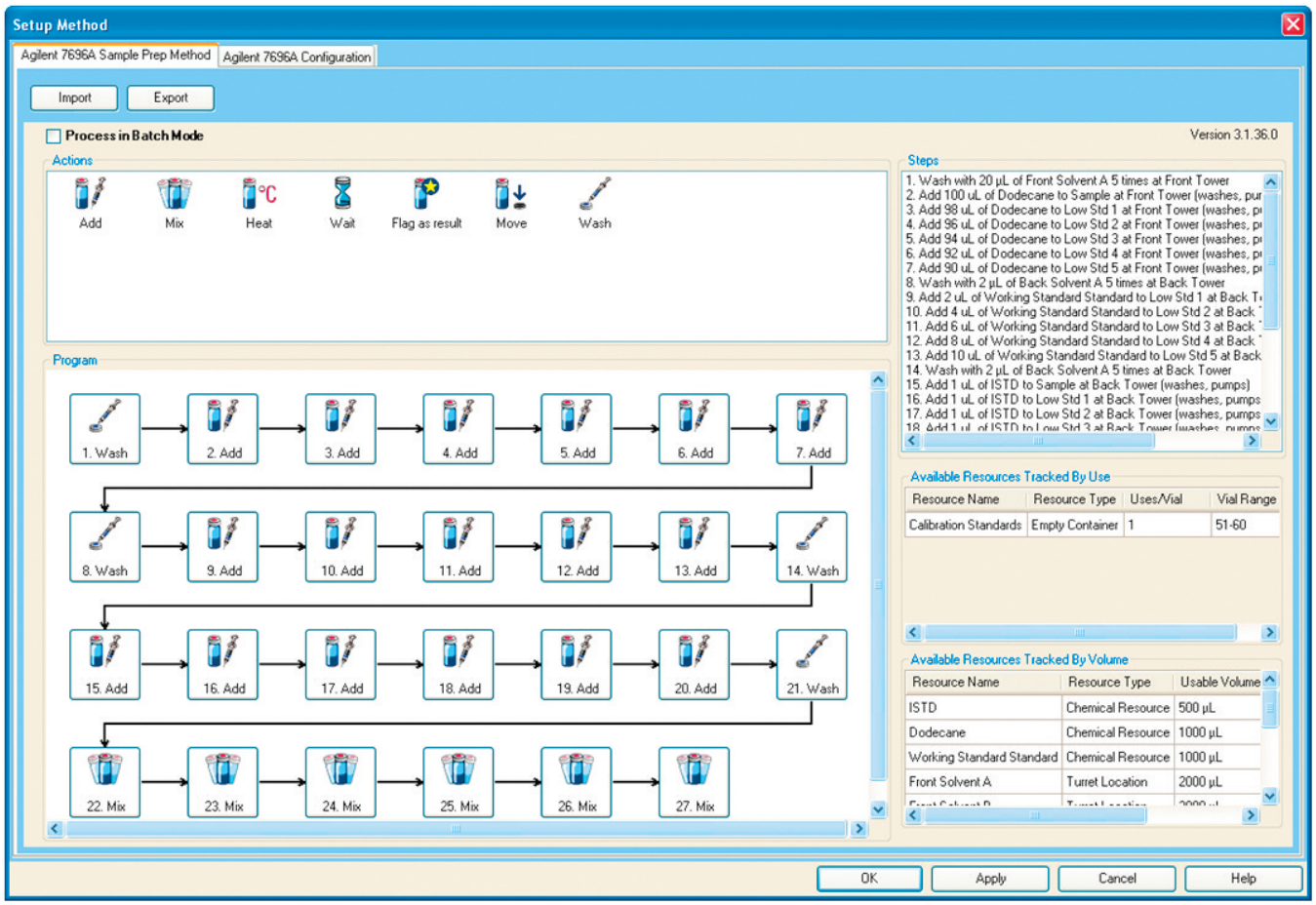


Figure 2. Agilent WorkBench method IP585_Low.M for preparing five low level calibration standards. Each of the method's steps were built using a "drop-and-drag" graphic ser interface.

Jet Fuel Sample Preparation Using Agilent Workbench Batch Mode

For the IP585 method, samples were prepared by pipetting 1 mL of jet fuel into a 2-mL vial followed by the addition of 10 µL of the internal standard solution. A laboratory chemist manually preparing multiple samples performs a workflow by adding each jet fuel sample into individual vials followed by adding the internal standard to each sample. This efficient workflow can be performed by using the Batch Mode feature of the Agilent WorkBench software. In Batch Mode, each sample preparation step was completed for every sample before moving on to the next step so that sample preparation time was minimized. Solvent wash and waste resources are also conserved since syringe solvent washing is only needed between resource changes.

For jet fuel sample preparation, the WorkBench needs only two resources; vials containing each jet fuel sample and a single vial containing the internal standard solution. In this application note, ten separate jet fuel samples were defined as resources for the WorkBench. These vials were placed in tray positions 51 to 60 and usage was set to one use per vial to eliminate any possibility of cross contamination during preparation. The internal standard vial was placed in tray position 81. During the sample preparation runs, 10 empty and capped 2-mL vials were placed in tray positions 1 to 10 (Figure 3). The batch mode WorkBench method, IP585_Samples.M, dispensed 100 uL of each jet fuel sample into separate, empty vials, followed by the addition of 1 µL of internal standard solution and mixing. Figure 4 shows this batch mode method for the jet fuel sample preparation.

Experimental

Manual Preparation of Working Calibration Standards (WCS) and Samples

Following the procedure described in the method (Table 2), the 10 calibration standards and a solvent blank were manually prepared in 2-mL vials using 1,000 µL graduated pipettes and a 25 µL pipetting syringe. Manual sample preparation was done by pipetting 1 mL each of three different jet fuel samples into individual 2-mL vials followed by addition of 10 µL of the internal standard. These samples contained known amounts of total FAME and were prepared in duplicate to determine overall repeatability. Each standard and sample was manually shaken to assure mixing.

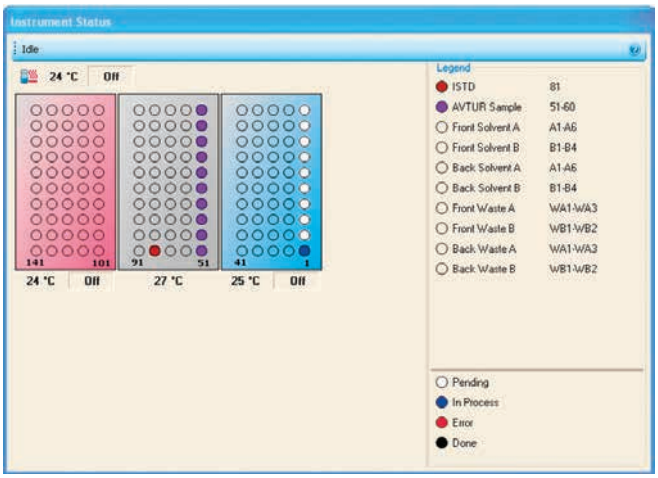


Figure 3. Agilent WorkBench resource layout for the automated preparation of 10 jet fuel samples. The empty vials in positions 1 to 10 will contain the final 100 mL of each jet fuel sample and internal standard after the automated preparation is complete.

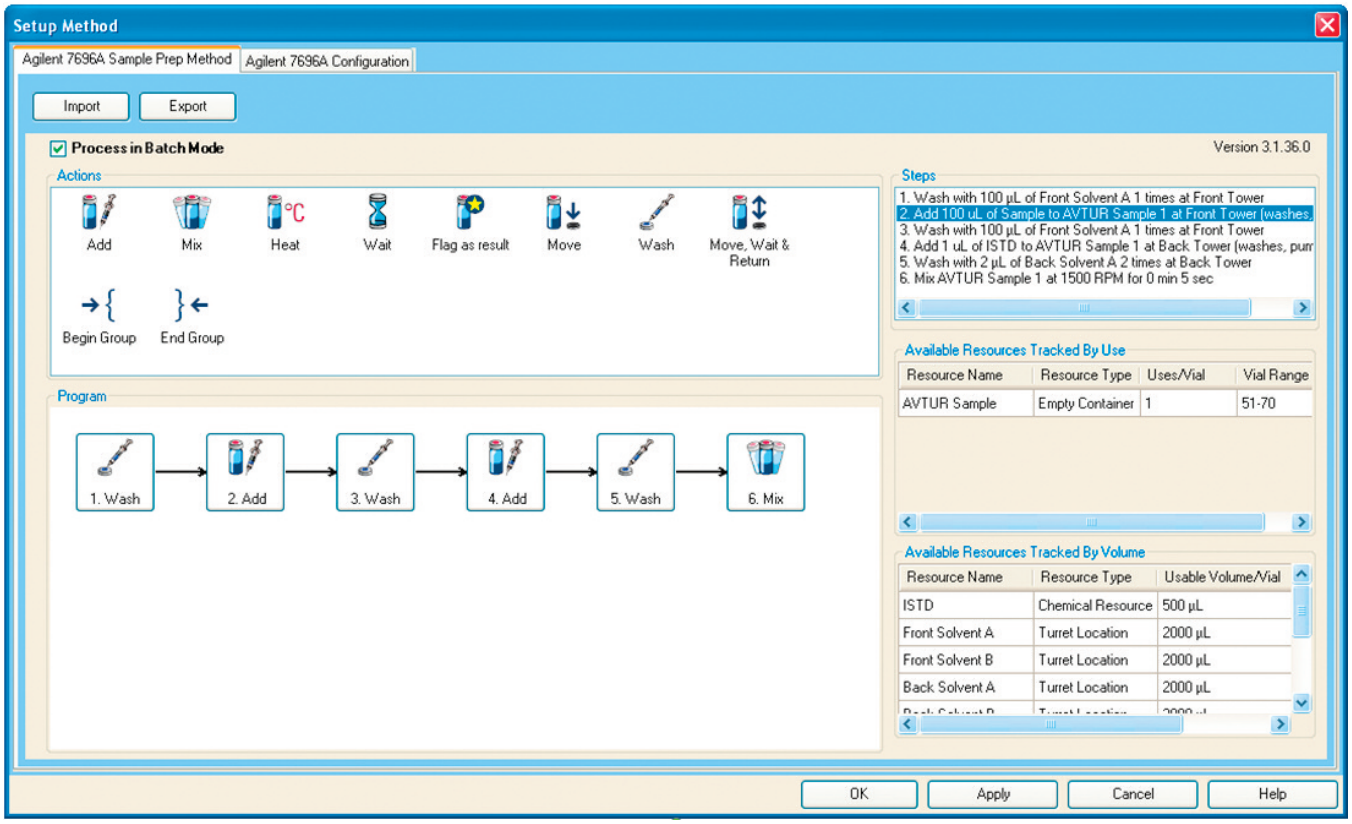


Figure 4. Batch mode Agilent WorkBench method for preparing 10 jet fuel samples. Each step was performed for all 10 samples before moving onto the next step. This efficient workflow minimized time and resource usage.

Automated Preparation of Calibration Standards and Jet Fuel Samples

The Agilent WorkBench was configured with a 250 µL syringe in the front tower and a 25 µL syringe in the rear tower. The 250 µL syringe used a draw speed of 500 µL/min and a dispense speed of 1000 µL/min. A draw speed of 100 µL/min and dispense speed of 500 µL/min was used for the 25 µL syringe. For each syringe, the dispense depth was set to 0 mm so the needle was close to the bottom of the vial when dispensing liquids. This ensured complete transfer of the liquid into the vial resulting in the best possible precision. High recovery vials were used because the internal v-shape allows the GC/MS autosampler to have access to the small 100 µL volumes of standards and samples.

The WorkBench sequence queue was used to prepare 5 low level standards and 5 high level standards using the IP585_Low.M and the IP585_High.M methods. After GC/MS calibration verification, the WorkBench batch mode method, IP585_Samples.M, was used to prepare duplicates of the three jet fuels samples spiked with different amounts of FAME.

GC/MS Analysis of FAME in Jet Fuel

An Agilent 5975C GC/MS system with an Agilent 7693A Automated Liquid Sampler was configured according to the IP585 method. This configuration is described in Table 7 and the instrument operating conditions are shown in Table 8. The mass spectrometer was tuned using the Agilent 5975C Autotune program before running any standards or samples. The calibration standards and the n-dodecane solvent blank were run first and the linear performance of the low level calibration and the high level calibration were evaluated before running the jet fuel samples. Upon successful calibration, a single GC/MS analysis of each jet fuel sample duplicate was made. The individual FAME peaks were quantified and the total FAME content in each sample was calculated by summing the individual FAME results.

Table 7. Instrument Configuration for GC/MS Analysis of FAMEs in Jet Fuel

Component	Description
Agilent 5975C Series MSD	Mass spectrometer with inert electron ionization source
Agilent 7890A GC system	Gas Chromatograph with 100 psi split/splitless inlet and mass spectrometer interface
Agilent 7693A ALS	Automatic liquid injector for Agilent 7890A GC with 150-vial tray
G1701EA	MSD Chemstation Software for data acquisition and analysis

Table 8. GC/MS Instrument Conditions

GC conditions	
Inlet temperature	260 °C
Inlet mode	Splitless
Inlet liner	Splitless liner, single taper glass wool (p/n 5062-3587)
Sample volume	1 uL
Column	HP-INNOWAX, 50 m x 0.2 mm, 0.4 µm film (p/n 19091N-205)
Column flow	Helium at 0.6 mL/min constant flow
Oven program	
Initial temperature	150 °C for 5 min
Oven ramp no 1	12 °C /min to 200 °C for 17 min
Oven ramp no 2	3 °C/min to 252 °C for 6.5 min
Mass spec interface	260 °C
Mass Spec Conditions	
Ionization source	70 eV electron ionization
Source temperature	230 °C
Quadrupole temperature	150 °C
Data acquisition delay	20 min

Results

Comparison of Manual and Agilent WorkBench Calibration Performance

The calibration standards from both the manual and the Agilent WorkBench preparations were run on the Agilent 5975C GC/MS system. The individual FAME calibration curves resulting from the low and high level WorkBench standards are shown in Figures 5 and 6. All of these curves appear to be linear after regression analyses with the origins forced through 0. Comparisons of the manual and WorkBench calibrations are shown in Table 9. For the low level calibrations, the slopes of the manual and WorkBench calibrations are very similar and the correlation coefficients (R^2) all meet the method requirement of greater than 0.985. The high level calibrations show the same performance with the exception of the methyl linoleate (C18:2) and methyl linolenate (C18:3) calibrations. In this case, the WorkBench prepared standards easily met the method requirements, while the manually prepared standards failed the linearity test. Therefore the manually prepared jet fuel samples could not be run until the high level standards were remade and the calibrations correctly verified. This added considerable time in obtaining results for the manually prepared samples. However, since the WorkBench calibrations were initially correct, the WorkBench prepared jet fuel samples could be run immediately.

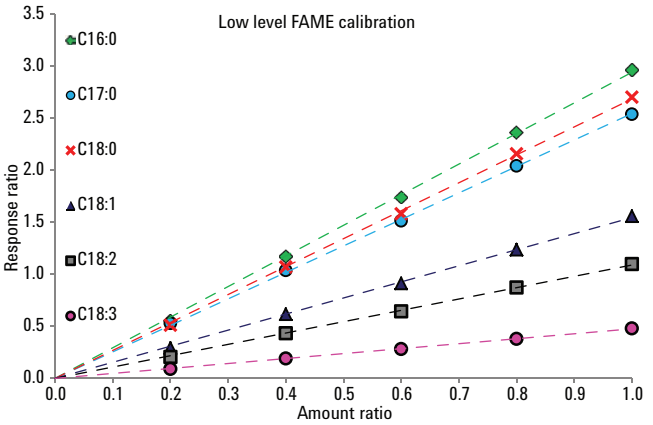


Figure 5. Low level calibration curves for 2, 4, 6, 8, and 10 mg/kg FAME standards prepared using the Agilent WorkBench. The calibration curves were forced through zero according to the method's protocol. Each curves exceeded the method's linearity requirement of $R^2 > 0.985$.

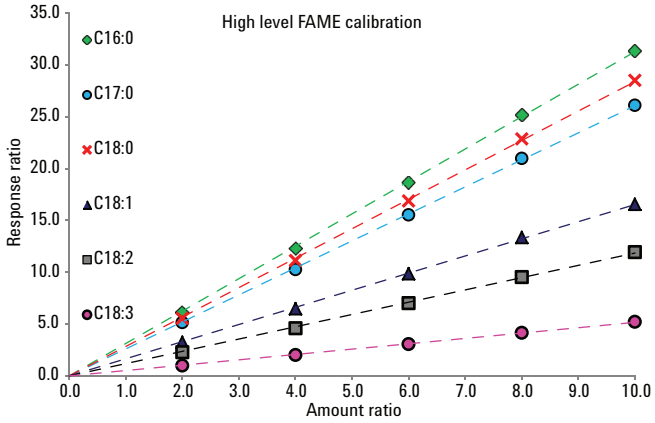


Figure 6. High level calibration curves for 20, 40, 60, 80, and 100 mg/kg FAME standards prepared using the Agilent WorkBench. The calibration curves were forced through zero according to the method's protocol. Each curve exceeded the method's linearity requirement of $R^2 > 0.985$.

Table 9. Comparison of the Slopes and Correlation Coefficients (R^2) Determined for Calibration Curves made using Manual and Agilent WorkBench Prepared Standards

Low Level Calibration (2–10 mg/kg)

	Slope		R^2	
FAME	**Manual**	**WorkBench**	**Manual**	**WorkBench**
C16:0	2.941	2.941	1.000	0.999
C17:0	2.441	2.544	1.000	1.000
C18:0	2.664	2.684	1.000	0.999
C18:1	1.539	1.545	1.000	0.999
C18:2	1.105	1.090	1.000	0.999
C18:3	0.478	0.475	1.000	0.999

High Level Calibration (20–100 mg/kg)

	Slope		R^2	
FAME	**Manual**	**WorkBench**	**Manual**	**WorkBench**
C16:0	4.962	3.127	0.985	1.000
C17:0	4.777	2.606	0.985	1.000
C18:0	4.815	2.840	0.985	1.000
C18:1	2.510	1.653	0.985	1.000
C18:2	1.713	1.184	0.984	0.999
C18:3	0.705	0.516	0.983	0.999

The manual high level calibrations curves for the C18:2 and C18:3 FAMEs failed the minimum R^2 requirement of 0.985.

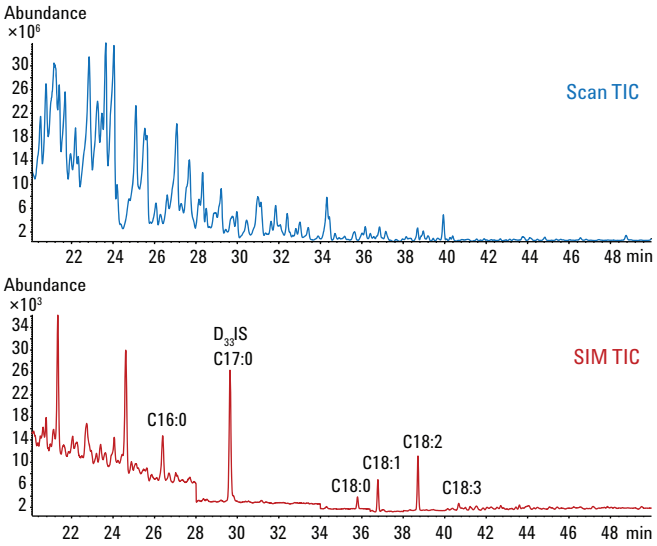


Figure 7. SIM/SCAN GC/MS data obtained from an Agilent WorkBench prepared jet fuel sample containing 5 mg/kg total FAME.

Comparison of Manual and Agilent WorkBench Sample Preparation

A typical GC/MS SIM/SCAN chromatogram for a jet fuel FAME analysis is shown in Figure 7. Comparisons of the analysis results for the manually prepared and the Agilent WorkBench prepared jet fuels are shown in Tables 10, 11, and 12. For each sample duplicate, repeatability (r) was calculated for the total FAME content and compared to the specification published in the IP585 method. Repeatability is a measurement of precision calculated by taking the difference between two duplicate results obtained on the same sample, by the same operator, using the same instrument, on the same day. For the 5 mg/kg FAME spike (Table 11), the repeatability of the manually prepared samples does not meet the IP585 method specification. Therefore, this result is invalid. However, for all WorkBench samples, the repeatabilities were much better than the method's specifications. Additionally, the results obtained with the Workbench samples more closely matched the total FAME content spiked into the jet fuel samples.

Table 10. Comparison of Analysis Results from a Manual and Agilent WorkBench Samples Preps for a 1 mg/kg FAME Jet Fuel Spike

1 mg/kg Jet fuel spike - Manual prep

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total
Run 1	0.8	0.0	0.1	0.3	0.1	0.0	1.3
Run 2	0.8	0.0	0.1	0.3	0.1	0.0	1.3
						Avg	1.3
						r (calc)	0.0
						r (IP585)	0.7

1 mg/kg Jet fuel spike - Agilent WorkBench prep

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total
Run 1	0.8	0.0	0.1	0.3	0.1	0.0	1.3
Run 2	0.7	0.0	0.1	0.3	0.1	0.0	1.2
						Avg	1.3
						r (calc)	0.1
						r (IP585)	0.7

Table 11. Comparison of Analysis Results from a Manual and Agilent WorkBench Samples Preps for a 5 mg/kg FAME Jet Fuel Spike

5 mg/kg Jet fuel spike - Manual prep

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total
Run 1	1.1	0.0	0.3	0.4	3.8	1.2	6.8
Run 2	0.5	0.0	0.2	0.9	2.6	0.7	4.9
						Avg	5.9
						r (calc)	1.9
						r (IP585)	1.4

5 mg/kg Jet fuel spike - Agilent WorkBench prep

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total
Run 1	0.5	0.0	0.1	0.9	2.7	0.5	4.7
Run 2	0.6	0.0	0.2	0.9	2.7	0.6	5.0
						Avg	4.9
						r (calc)	0.3
						r (IP585)	1.3

Table 12. Comparison of Analysis Results from a Manual and Agilent WorkBench Samples Preps for a 40 mg/kg FAME Jet Fuel Spike

40 mg/kg Jet fuel spike - Manual prep

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total
Run 1	4.4	0.0	1.7	7.9	24.0	4.1	42.1
Run 2	4.7	0.0	1.8	8.3	25.1	4.3	44.2
						Avg	43.1
						r (calc)	2.1
						r (IP585)	7.5

40 mg/kg Jet fuel spike - Agilent WorkBench prep

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total
Run 1	4.8	0.0	1.8	8.3	25.4	4.2	41.4
Run 2	4.3	0.0	1.7	7.9	24.0	4.1	39.1
						Avg	40.2
						r (calc)	2.3
						r (IP585)	7.1

Conclusion

The Agilent WorkBench was shown to successfully automate the preparation of the calibration standards and samples when measuring FAME in jet fuel using the IP585 GC/MS method. By comparison, it was also shown that good analysis results can be difficult to obtain when using manual preparation techniques that require precise handling very small amounts of samples and reagents. This application note has demonstrated that the WorkBench can achieve better overall method performance compared to manual preparation. Considerable time was saved in avoiding rework and 10 times less reagents used with the WorkBench.

References

1. "IP 585/10 "Determination of fatty acid methyl esters (FAME), derived from bio-diesel fuel, in aviation turbine fuel – GC-MS with selective ion monitoring/scan detection method", The Energy Institute, London, UK.
2. "GC/MS Analysis of Trace Fatty Acid Methyl Esters (FAME) in Jet Fuel Using Energy Institute Method IP585", James D. McCurry, Agilent Technologies, Agilent Publication Number 5990-6974EN, November 10, 2011.
3. "Improved Data Quality Through Automated Sample Preparation", Rebecca Veeneman and Dale Synder, Agilent Publication Number 5990-6874EN, December 2, 2010.

For More Information

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

www.agilent.com/chem

Printed in the USA
January 12, 2012
5990-9717EN

Agilent Technologies

Agilent 7696A Sample Prep WorkBench Automated Sample Preparation for the GC Analysis of Biodiesel Using Method EN14105:2011

Application Note

Fuels

Author

James D. McCurry, Ph.D.
Agilent Technologies, Inc.
2850 Centerville Rd
Wilmington, DE
19808

Abstract

The recently revised European Union method EN14105 describes complex, multistep procedures to manually prepare standards and samples for the GC analysis of glycerol contaminants in B100 biodiesel. The Agilent 7696A Sample Prep WorkBench was successfully used to automate the standard and sample prep of this method while reducing the reagent use and chemical wastes by a factor of 10. Calibration performance of the WorkBench prepared standards exceeded the method requirements. Using a commercial biodiesel sample, the WorkBench was shown to prepare the samples with an extremely high degree of precision that surpassed the method's specifications.

Agilent Technologies

Introduction

In countries adhering to European Union norms, B100 biodiesel quality is assured by measuring the amount of free and total glycerol and the mono-, di-, and triglycerides contained in the fuel. A gas chromatography (GC) method, EN14105, was developed to separate and quantify these compounds. Since glycerol, mono-, and diglycerides are not volatile, the method outlines a complex procedure to derivatize these compounds and create volatile silanized species prior to GC analysis. In 2011, the European Committee for Standardization (CEN) updated this method to improve GC performance, glyceride quantification, and overall precision [1]. This application note describes using the Agilent 7696A Sample Prep WorkBench to automate the preparation of calibration standards and samples for analysis with the Agilent 7890A Series GC.

The WorkBench is a standalone instrument specifically designed to perform automated sample preparation. It uses two Agilent 7693A injection towers to volumetrically transfer liquids between 2-mL vials. Vials containing various chemical resources, standards, and samples are housed in three 50-positions trays. The sample tray compartment contains a robotic arm, a vortex mixing station, and a sample heating station. For biodiesel analysis, the WorkBench was used to successfully prepare samples for ASTM method D6584, which is similar to the EN14105 method [2]. In that application note, the analysis results from WorkBench prepared samples were identical to results obtained with manually prepared samples.

The Agilent WorkBench Easy SamplePrep (ESP) software was recently updated to provide more efficient use of chemical resources and time. At its core, ESP provides a simple software platform allowing users to quickly build sample preparation methods using drag-and-drop icons representing each WorkBench action. A new mode of ESP operation called **Batch Mode** allows the WorkBench to repeat common actions for all samples before moving on to the next action. For methods where Batch Mode can be used, significant increases in solvent wash and waste capacity can be realized along with faster sample preparation times [3,4].

Experimental

WorkBench Preparation of EN14105 Calibration Standards

The WorkBench was configured with a Blue Line 25 µL gas tight syringe (p/n G4513-80241) in the rear tower and a Blue Line 500 µL gas tight syringe (p/n G4513-60561) in the front tower. The chemical resources used to prepare standards and samples are listed in Table 1. The three reference glycerides used to prepare the Standard Glycerides Solution were purchased as pure compounds from Nu-Chek Prep (www.nu-chekprep.com). Each chemical resource was placed into separate 2-mL high recovery vials (p/n 5183-2030) and sealed using screw caps with PTFE lined septa (p/n 5040-4682).

Table 1. Chemical Resources and Standards used for Method EN14105:2011

Resource	Description	Supplier
Heptane	Capillary GC grade	Sigma Aldrich p/n H9629
Glycerol stock	0.5 mg/mL in pyridine	Sigma Aldrich p/n 44892-U
Butanetriol solution	1 mg/mL in pyridine	p/n 5982-0024
MSTFA	Silanizing reagent	p/n 5190-1407
Std glycerides solution	2.5 mg/mL in THF	Nu-Chek Prep
Monoglycerides RT std	10 mg/mL in pryridine	p/n 5190-1410
Pyridine	Anhydrous grade	Sigma Aldrich p/n 270970

Using the Agilent ESP software, the chemical resources were arranged in the WorkBench and assigned initial properties. This resource layout is described in Table 2 and graphically shown in Figure 1.

Table 2. Agilent WorkBench Chemical Resources used to Prepare Standards and Samples as Shown in Figure 1

Resource name	Resource type	Use type	Capacity (µL)	Vial range
Heptane	Chemical resource	By volume	1,000	81–95
Glycerol stock	Chemical resource	By volume	1,000	61
Butanetriol solution	Chemical resource	By volume	1,000	62
MSTFA	Chemical resource	By volume	1,000	63
Std glycerides solution	Chemical resource	By volume	1,000	64
Monoglycerides RT std	Chemical resource	By volume	1,000	65
Pyridine	Chemical resource	By volume	500	71
Empty vials				51–55

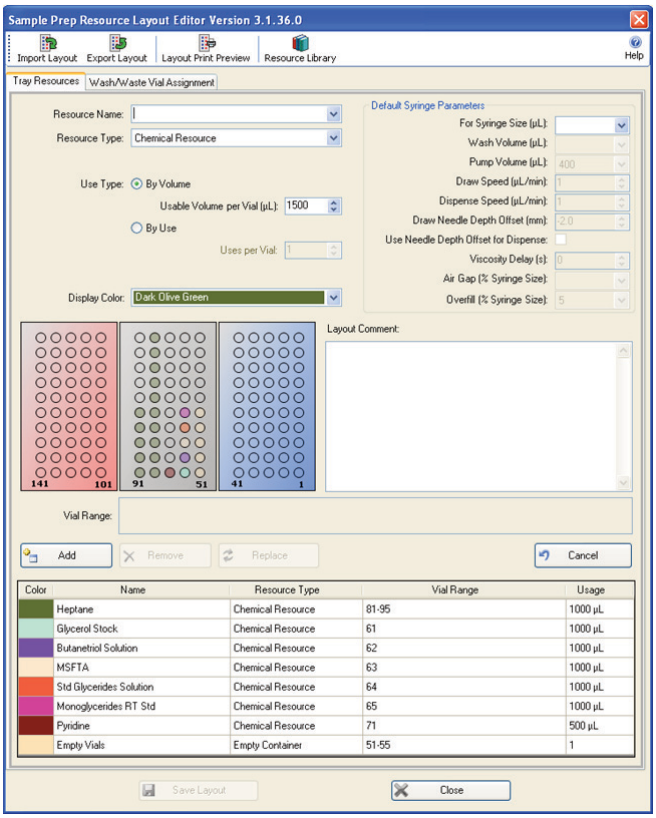


Figure 1. Easy Sample Prep (ESP) software layout for preparing standards and samples using method EN14105.

The EN14105 method requires the preparation of five calibration standards using a linear dilution technique. Four standards contain different amounts of glycerol and the same amount of the internal standard 1,2,3-butanetriol. The fifth calibration standard contains three monoglycerides used to identify these compounds in biodiesel by retention time comparison. The EN14105 method outlines the steps used to prepare approximately 10 mL of each calibration standard. Since the WorkBench uses 2-mL vials, automating the method required a volume reduction by a factor of 10 [2]. Table 3 describes the 37 individual steps used to prepare these five calibration standards. Since this is a linear dilution technique, the ESP Batch Mode was not used for standard preparation (Figure 2). It is important to note that a Needle Depth Offset of 0 was used in combination with the high recovery vials to assure complete mixing of the small volumes needed to prepare these standards. Additionally a 5% Overfill was used when dispensing each resource to eliminate any potential errors causes by bubble formation in the syringe.

WorkBench Preparation of B100 Biodiesel Samples for EN14105

The EN14105 method calls for weighing 100 mg of biodiesel sample into a reaction vial for silation. Since the WorkBench sample prep scale was reduced by a factor of 10, only 10 mg of sample was weighed into 2-mL high recovery vials. Automatic sample weighing cannot be performed using the WorkBench because there is no analytical balance. Since weighing 10 mg of biodiesel can be very challenging, an Eppendorf Reference Adjustable-Volume Pipettor (10–100 µL) was used to transfer the sample. Weighing 10 mg of biodiesel was done by manually pipetting 11.5 µL of biodiesel into tared 2-mL high recovery vials and recording the weight to the nearest 0.01 mg.

Table 3. WorkBench Method used to Prepare Calibration Standards for Method EN14105

Step	WorkBench action	Description	Syringe	Draw speed (µL/min)	Dispense speed (µL/min)	Needle depth offset (mm)	Viscosity delay (sec)	Overfill %
1	Wash	Syringe three times with 5 µL of butanetriol	25 µL	250	1,000		0	
2–6	Add	8 µL butanetriol to empty vials 1, 2, 3, 4, 5	25 µL	250	1,000	0	2	5
7	Wash	Syringe with wash solvent A	25 µL	250	1,000		0	
8	Wash	Syringe with 5 µL of glycerol stock	25 µL	250	1,000		0	
9	Add	1 µL glycerol stock to empty vial 1	25 µL	250	1,000	0	2	5
10	Add	4 µL glycerol stock to empty vial 2	25 µL	250	1,000	0	2	5
11	Add	7 µL glycerol stock to empty vial 3	25 µL	250	1,000	0	2	5
12	Add	10 µL glycerol stock to empty vial 4	25 µL	250	1,000	0	2	5
13	Add	5 µL monoglyceride RT std to empty vial 5	25 µL	250	1,000	0	2	5
14	Add	20 µL std glycerides to empty vial 5	25 µL	250	1,000	0	2	5
15	Add	20 µL of pyridine to empty vial 5	25 µL	250	1,000	0	2	5
16	Wash	Syringe three times with wash solvent A	25 µL	250	1,000		0	
17–21	Add	15 µL of MSTFA to empty vials 1, 2, 3, 4, 5	25 µL	250	1,000	0	2	5
22–26	Mix	Empty vials 1, 2, 3, 4, 5 at 2,500 RPM for 15 sec						
27	Wait	15 minutes						
28–32	Add	800 µL heptane to empty vials 1, 2, 3, 4, 5	500 µL	1,250	5,000	0	2	5
33–37	Mix	Empty vials 1, 2, 3, 4, 5 at 2,500 RPM for 15 sec						

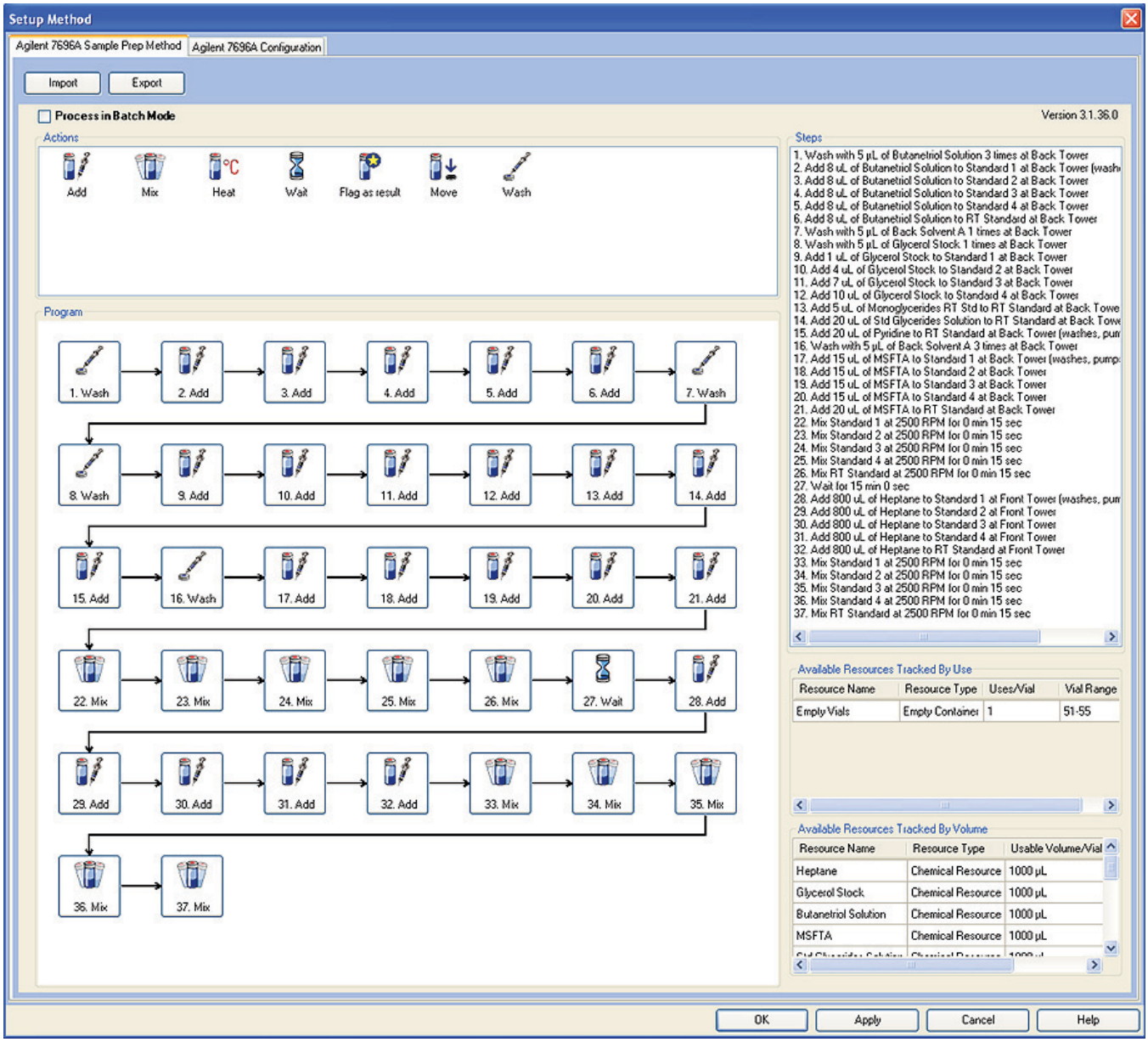


Figure 2. Easy Sample Prep (ESP) software method used to prepare calibration standards for method EN14105.

Sample preparation for the EN14105 method is performed by adding fixed volumes of the butanetriol stock, the standard glycerides stock, pyridine, and MSTFA to the sample to derivatize the non-volatile components. After the 15 minutes, heptane is added to the mix to quench the reaction. Since 2-mL vials were used for the WorkBench, the volumes of each added reagent was reduced by a factor of 10. The individual steps for this sample preparation are listed in Table 4. The ESP software was used to create a Batch Mode method for the sample prep while saving time and resources. This Batch Mode method is shown in Figure 3.

Since both the standards preparation and sample preparation use the same resource layout, the WorkBench can run both methods together using an ESP software Sequence Queue. For this application note, 10 duplicates of a soybean oil derived B100 biodiesel were prepared to evaluate the precision of the WorkBench sample prep.

Table 4. Ten Individual Steps used by the WorkBench to Prepare Biodiesel Samples for Method EN14105

Step	WorkBench action	Description	Syringe	Draw speed (µL/min)	Dispense speed (µL/min)	Needle depth offset (mm)	Viscosity delay (sec)	Overfill %
1	Wash	Syringe three times with 5 µL of butanetriol	25 µL	250	1,000		0	
2	Add	20 µL of pyridine to each sample	25 µL	250	1,000	0	2	5
3	Add	8 µL butanetriol to each sample	25 µL	250	1,000	0	2	5
4	Add	20 µL std glycerides to each sample	25 µL	250	1,000	0	2	5
5	Add	20 µL of MSTFA to each sample	25 µL	250	1,000	0	2	5
6	Mix	Each sample at 2,500 PRPM for 15 sec						
7	Wait	15 minutes						
8	Wash	Syringe one time with 200 µL of wash solvent A	25 µL	250	1,000		0	
9	Add	800 µL heptane to each sample	500 µL	1,250	5,000	0	2	5
10	Mix	Each sample at 2,500 RPM for 15 sec						

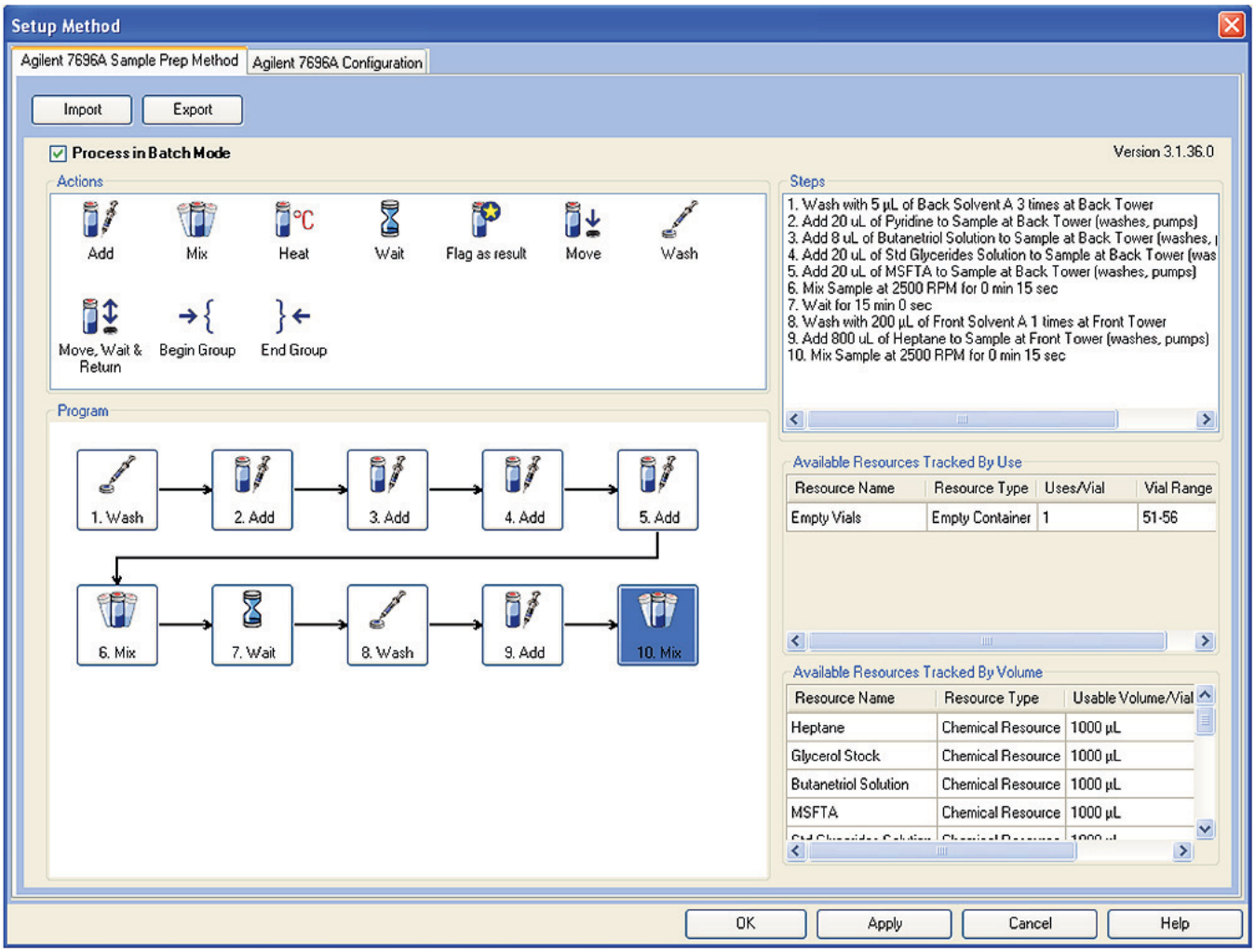


*Figure 3. Easy Sample Prep (ESP) software **Batch Mode** method used to prepare biodiesel samples for EN14105.*

GC Analysis of WorkBench Prepared Standards and Samples

An Agilent 7890A Gas Chromatograph (GC) was configured to comply with the EN14105:2011 requirements. Table 5 lists the instrument configuration and the instrument operating conditions. A single, 1-µL injection of each standard and each sample was made on this system. The Agilent OpenLab CDS Chemstation was used to control the 7890A GC, collect the data, and perform data analysis.

Table 5. Agilent 7890A GC Configuration and Operating Conditions for the Analysis of WorkBench Prepared Standards and Samples using Method EN14105:2011

Instrument configuration	
G3440A	Agilent 7890A Series GC
Option 122	Cool-on-column Inlet with EPC control
Option 211	Capillary FID with EPC control
G4513A	Agilent 7693A ALS
Column	Select Biodiesel for Glycerides
	15 m × 0.32 mm, 0.1 µm film (p/n cp9078)
Data system	Agilent OpenLab CDS Chemstation C.01.03

GC operating conditions	
Cool-on-column inlet	
Initial pressure	Helium at 11.353 psi
Initial temperature	50 °C
Temperature program	Oven track mode
Column flow	Helium at 5 mL/min constant flow
Column temperature	
Initial	50 °C for 1 min
Rate 1	15 °C/min to 180 °C, hold 0 min
Rate 2	7 °C/min to 230 °C, hold 0 min
Rate 3	10 °C/min to 370 °C, hold 10 min
Flame ionization detector	380 °C

Results and Discussion

WorkBench Prepared EN14105 Standards

The retention times of the three monoglycerides and the standard glycerides were determined using the data obtained from the retention time standard. This chromatogram is shown in Figure 4. A glycerol calibration curve was prepared using the data obtained from the four glycerol calibration standards. This curve is shown in Figure 5. The correlation coefficient for this curve was 1.000 which meets the EN14105 method requirement of 0.9.

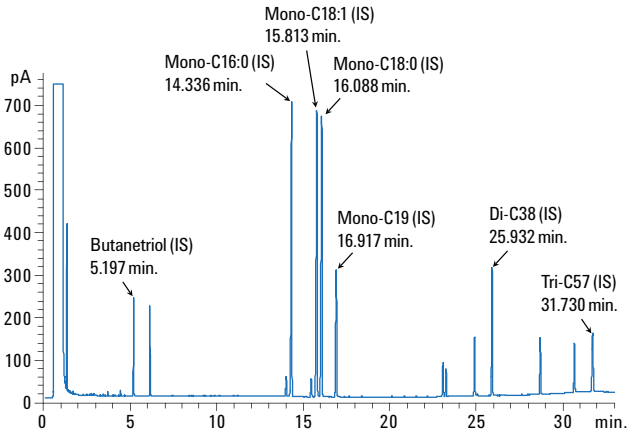


Figure 4. Retention time identification standard prepared using the WorkBench. In addition to the three monoglycerides, the four internal standards (Butanetriol, Mono-C19, Di-C38 and Tri-C57) were also added to this mix.

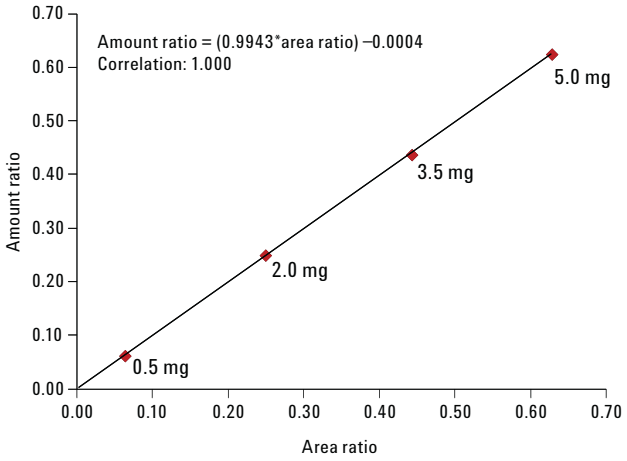


Figure 5. Glycerol calibration curve made using the data from four WorkBench prepared calibration standards. The correlation coefficient exceeds a value of 0.9 as required by the EN14105 method.

WorkBench Prepared B100 Biodiesel Samples

Figure 6 shows a chromatogram of a single sample compared to an overlay of the 10 WorkBench prepared samples. The 10 overlaid chromatograms are nearly identical to the single chromatogram in both retention time and peak response. This result graphically illustrates the WorkBench ability to prepare each sample with precision. Figure 7 shows the four quantification zones in greater detail. Again, these chromatograms are overlays of the 10 WorkBench prepared biodiesel samples and show nearly identical results. In the glycerol and the monoglyceride zones, only the identified peaks are quantified and reported. In the di- and triglyceride zones, any peaks eluting in the respective zone is quantified and reported as a diglyceride or triglyceride.

Before one can determine the final results, a column performance control must be calculated for the analysis. This control is measured by calculating the relative response factors (RRF) of the Di-C38 internal standard versus the Tri-C57 internal standard. The RRF must be lower than 1.8 to be certain of good triglyceride detection. This column performance control was passed for each WorkBench prepared sample as shown in Table 6.

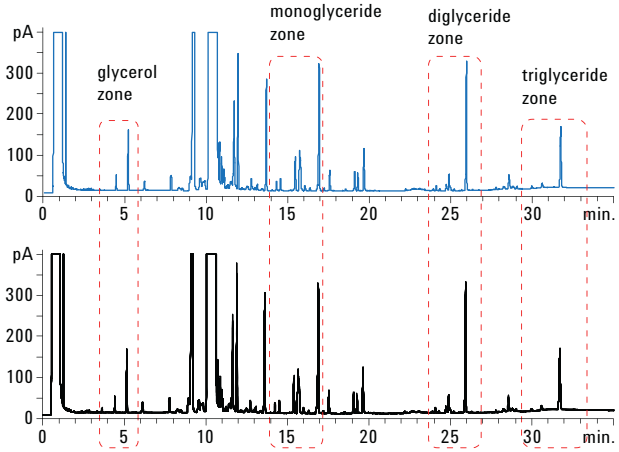


Figure 6. The upper chromatogram is a single run of a B100 sample prepared using the Agilent WorkBench. Each zone for quantification of glycerol and glycerides is outlined in red. The lower chromatogram is an overlay of 10 separate samples prepared using the WorkBench.

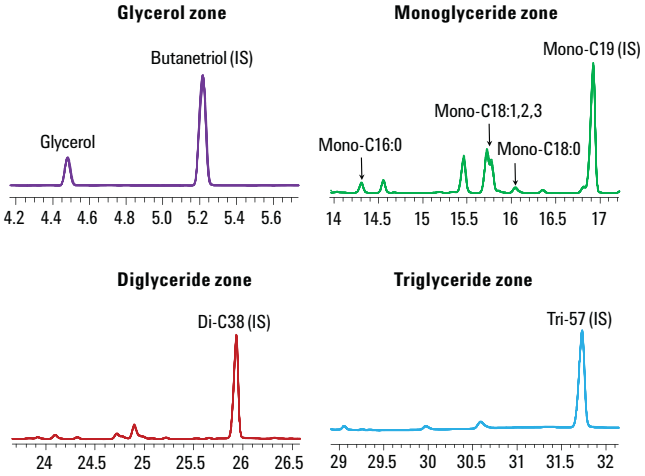


Figure 7. Expanded views of the four quantification zones identified in Figure 5. Note that these chromatograms are overlays of 10 separate samples prepared using the Agilent WorkBench.

Table 6. Column Performance Control Parameters

Sample	A_{DiC38}/M_{DiC38}	A_{TriC57}/M_{TriC57}	RRF
SRM01	24.4	16.5	1.5
SRM02	24.4	16.4	1.5
SRM03	24.4	16.4	1.5
SRM04	24.4	16.4	1.5
SRM05	24.5	16.5	1.5
SRM06	24.6	16.5	1.5
SRM07	24.5	16.0	1.5
SRM08	24.9	16.0	1.6
SRM09	24.9	16.0	1.6
SRM10	25.0	16.2	1.5

As a column performance control, the relative response factor (RRF) for the Di-C38 versus Tri-C57 internal standards must be less than 1.8. All 10 WorkBench prepared biodiesel samples meet this requirement. (A = peak area, M = compound mass)

With the glycerol calibration and column performance control criteria met, the contents of free glycerol, mono-, di-, triglycerides and total glycerol were determined for the 10 WorkBench prepared biodiesel samples. These results are shown in Table 7. The precision for these 10 results was excellent as measured by the low RSDs calculated for each component. However, the EN14105:2011 method does provide a complete statement for both single user and multiple lab precision. For this application note, single user precision can be determined from the results and compared to the method's criteria.

Single user precision is also known as repeatability (r). Repeatability is the difference between two test results obtained by the same operator using the same equipment on identical test material. The EN14105 method provides repeatability statements for each component measured in the sample. To use this statement, the two results with the largest difference, SRM01 and SRM10, were used. The absolute value of the difference for each sample's results was taken and compared to the minimum difference required by the method. As shown in Table 8, samples prepared using the WorkBech comfortably meet the method's repeatability specifications for all quantified components in biodiesel.

Table 7. Results for the Analysis of Ten B100 Biodiesel Prepared using the Agilent WorkBench

		Weight %				
Sample	**Sample weight (mg)**	**Free glycerol**	**Monoglycerides**	**Diglycerides**	**Triglycerides**	**Total glycerol**
SRM01	10.90	0.016	0.39	0.14	0.19	0.156
SRM02	10.40	0.017	0.39	0.14	0.19	0.157
SRM03	10.63	0.017	0.39	0.14	0.19	0.157
SRM04	9.59	0.017	0.39	0.14	0.19	0.157
SRM05	11.12	0.017	0.39	0.14	0.19	0.157
SRM06	9.93	0.017	0.39	0.14	0.19	0.157
SRM07	10.46	0.017	0.39	0.14	0.19	0.157
SRM08	9.66	0.017	0.39	0.14	0.19	0.157
SRM09	9.74	0.017	0.39	0.14	0.19	0.157
SRM10	10.01	0.017	0.39	0.14	0.19	0.157
	Avg	**0.017**	**0.39**	**0.14**	**0.19**	**0.157**
	Std Dev	**0.000**	**0.00**	**0.00**	**0.00**	**0.000**
	RSD	**1.871%**	**0.00%**	**0.00%**	**0.00%**	**0.202%**

Table 8. Analysis Precision as Expressed by Repeatability (r) for two B100 Biodiesel Samples Prepared using the Agilent WorkBench. The Repeatability for Each Component (r calc) Meets the Specification of the EN14105:2011 Method (r spec)

	Weight %				
Sample	**Free glycerol**	**Monoglycerides**	**Diglycerides**	**Triglycerides**	**Total glycerol**
SRM01	0.016	0.39	0.14	0.19	0.156
SRM10	0.017	0.39	0.14	0.19	0.157
r calc	**0.001**	**0.00**	**0.00**	**0.00**	**0.001**
r spec	**0.003**	**0.04**	**0.02**	**0.02**	**0.020**

Conclusion

The Agilent 7696A WorkBench is shown to have successfully performed an automated preparation of standards and samples for the GC analysis of glycerol contaminants in biodiesel according to the revised European Union method EN14105:2011. Since the WorkBench uses 2-mL vials, the scale of the EN14105 preparation was reduced by a factor of 10. This served to lower reagent costs and reduced the generation of waste chemicals when performing this analysis. Calibration standards prepared with the WorkBench met all performance criteria set forth by the method. Ten duplicates of a biodiesel sample were prepared using the WorkBench and the resulting GC analysis showed extremely high precision that exceeded the requirement of the EN14105 method.

References

1. DIN EN14105:2011-07 "Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of free and total glycerol and mono-, di-, and triglyceride contents", European Committee for Standardization, Management Centre: Avenue Marnix 17: B-1000 Brussels.
2. "Automation of a Complex, Multi-Step Sample Preparation Using the Standalone Agilent 7696A WorkBench", James D. McCurry, Agilent Technologies, Publication Number 5990-7525EN, March 1, 2011.
3. "Increase Capabilities Using Batch Enabled Sample Preparation", Rebecca Veeneman, Agilent Technologies Publication Number 5990-9271EN, December 21, 2011.
4. "Automated Standard and Sample Preparation Using the Agilent 7696A WorkBench for GC/MS Analysis of FAME Contamination in Jet Fuel", James D. McCurry, Agilent Technologies Publication Number 5990-9717EN, January 12, 2012.

For More Information

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

www.agilent.com/chem

Printed in the USA
April 27, 2012
5990-9893EN

Agilent Technologies

Analysis of Biogas Using the Agilent 490 Micro GC Biogas Analyzer

Application Note

Micro Gas Chromatography, Hydrocarbon Processing, Renewable Energy, Biogas Analysis

Author

Remko van Loon
Agilent Technologies, Inc.
Middelburg, the Netherlands

Abstract

Biogas is considered a renewable and sustainable energy source and therefore is of great interest worldwide. This application note shows the analysis of biogas, and related samples, using the Agilent 490 Micro GC Biogas Analyzer. Depending on the biogas composition two configurations are available; the Agilent 490 Micro GC Biogas Analyzer for pure biogas analysis and the Agilent 490 Micro GC Biogas Analyzer Extended when biogas is mixed with other hydrocarbon streams, such as natural gas or liquefied petroleum gas (LPG).

Introduction

Biogas is a gas mixture produced through biological processes; from anaerobic fermentation or digestion of organic material such as biomass, manure or sewage, municipal waste and energy crops. The composition of biogas is related to the origin of the organic material; the main components of biogas are methane and carbon dioxide, with some other permanent gases, hydrogen and hydrogen sulfide.

Biogas has a role in modern waste management and can fuel any type of heat engine to generate either mechanical or electrical power. To increase its caloric values it is sometimes necessary to remove some of the carbon dioxide or blend it with other hydrocarbon streams. Biogas can be compressed, much like liquefied natural gas, and used to power motor vehicles. For this purpose, it is essential to remove hydrogen sulfide if present. Biogas is a renewable fuel, and so it qualifies for renewable energy subsidies in some parts of the world.

The increased interest in biogas has resulted in a growing demand for fast and efficient analysis technology to determine its composition. The Agilent Micro GC Biogas Analyzers can play a significant role in achieving this goal.

Agilent Technologies

The Agilent 490 Micro GC Biogas Analyzers are shipped as a total solution; the analyzers are factory tuned, for optimal separation, and come with final test data, analytical method parameters, a user manual and a check-out sample.

Biogas Analyzer setup and conditions

Based on the Agilent 490 Micro GC, two Biogas Analyzers are available; the configuration required for biogas analysis depends on the sample composition.

For pure biogas analysis, including permanent gases and hydrogen sulfide, the Agilent 490 Micro GC Biogas Analyzer (p/n G3582A#110) is recommended, even ethane and propane can be analyzed with this setup. This Biogas Analyzer consists of a dual channel cabinet including a 10-meter CP-Molsieve 5A with argon as a carrier gas, providing excellent sensitivity and linearity for hydrogen, and a 10-meter CP-PoraPLOT U column channel with helium as carrier gas.

When biogas is mixed with other hydrocarbon streams such as natural gas or liquefied petroleum gas (LPG), the sample contains higher boiling hydrocarbons. To analyze these hydrocarbons the Agilent 490 Micro GC Biogas Analyzer Extended is the analyzer of choice. This Biogas Analyzer Extended (p/n G3582A#111) is a quad channel cabinet Micro GC including three column channels; a 10-meter CP-Molsieve column on argon as carrier gas, a 10-meter CP-PoraPLOT U column and an additional 6-meter CP-Sil 5 CB column on helium as carrier gas for the analysis of higher boiling hydrocarbons. Figure 1 shows the quad and dual cabinet housing for the Agilent 490 Micro GC Biogas Analyzers.

Figure 1. Agilent 490 Micro GC Biogas Analyzers.

Both Biogas Analyzers are equipped with heated sample line and injectors to eliminate any cold spot and prevent possible condensation of moisture, to ensure the integrity of the sample is maintained throughout the sample flow path. Both CP-Molsieve 5A and CP-PoraPLOT U columns have a backflush to vent option, moreover the CP-Molsieve 5A is equipped with the retention time stability (RTS) option. This RTS option consists of additional in-line filters between the electronic gas control and the column module to ensure moisture and carbon dioxide free carrier gas. Moreover the use of the RTS option enables a more efficient backflush of carbon dioxide. This enhances column lifetime and, most importantly, leads to more stable retention times.

Table 1 gives an overview of typical conditions used for the Biogas Analyzers.

Table 1. 490 Micro GC Biogas Analyzer Instrument Conditions

	CP-Molsieve 5A, 10 m	CP-PoraPLOT U, 10 m	CP-Sil 5 CB, 6 m
Column temperature	80 °C	80 °C	60 °C
Carrier gas	argon, 200 kPa	helium, 150 kPa	helium, 150 kPa
Injector temperature	110 °C	110 °C	110 °C
Injection time	40 ms	40 ms	40 ms
Backflush time [1]	11	14	no backflush
Detector sensitivity	auto	auto	auto
Invert signal	yes	no	no
Sample line temperature	110 °C		
Sampling time	30 seconds		

Note [1] Backflush time is column channel dependent and should be fine tuned for each new column.

The sample can be introduced to the Agilent 490 Micro GC Biogas Analyzer either pressurized (maximum limit 1 bar), through a Tedlar sampling bag using the internal sampling pump, or by using a continuous flow sampling mode. When the sample pressure exceeds the 1 bar limit, for example with a liquefied natural gas or liquefied petroleum gas, the pressure should be reduced. The use of the Agilent Micro-Gasifier, a heated pressure reducer, is recommended here.

Results and Discussion

The first column channel, a CP-Molsieve 5A, is used to analyze the permanent gases, including hydrogen, oxygen, nitrogen, methane, and carbon monoxide. Figure 2 shows a chromatogram for this column channel.

As biogas and related samples may contain larger amounts of carbon dioxide, moisture, and higher hydrocarbons it is necessary to backflush these components to maintain the separation effiency of the Molsieve 5A column. Moisture and carbon dioxide tend to adsorb quickly to the Molsieve 5A stationary phase and change its chromatographic properties. This would result, over time, in retention shifts and loss of separation. Higher hydrocarbons will eventually elute, but will cause higher detector noise levels and lead to reduced sensitivity. The backflush to vent functionality on the Molsieve 5A column channel prevents this from happening.

Table 2 shows excellent repeatability figures for both retention time, below RSD 0.05 %, and peak area below RSD 0.1 %, for the compounds analyzed on the Molsieve column channel.

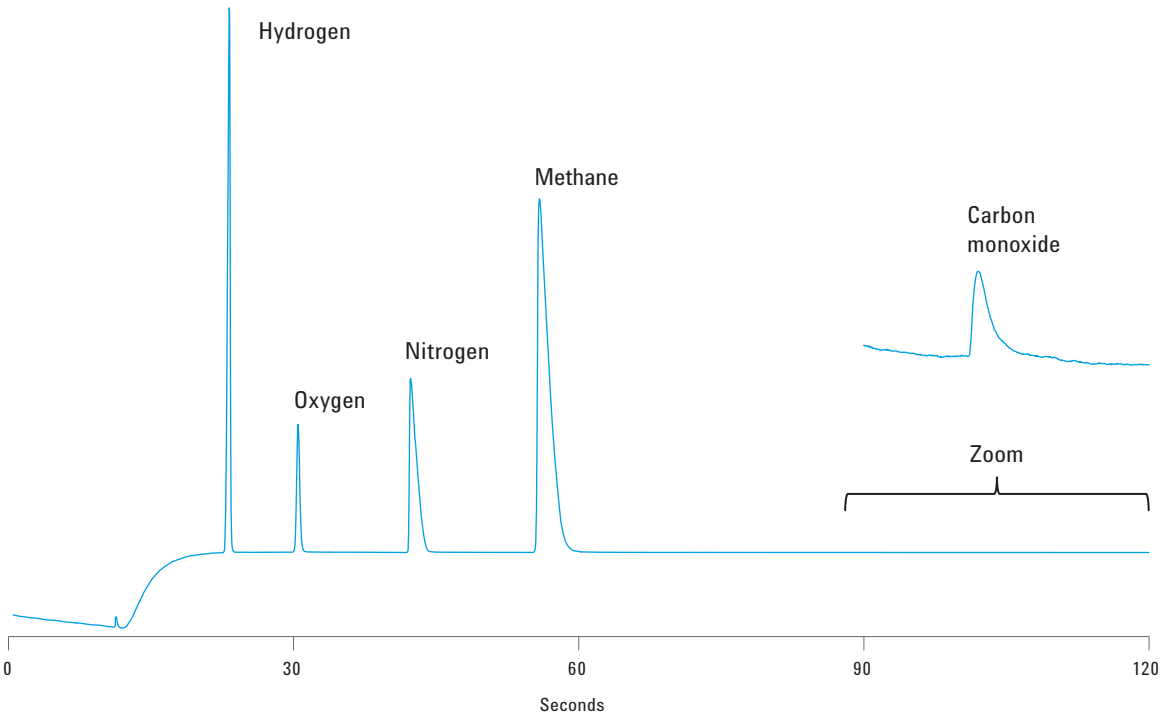


Figure 2. Chromatogram for permanent gases on the CP-Molsieve 5A column channel.

Table 2. Repeatability Figures for Retention Time and Peak Area on the CP-Molsieve Column

Run no.	Hydrogen Rt (sec)	Oxygen Rt (sec)	Nitrogen Rt (sec)	Methane area	Hydrogen area	Oxygen area	Nitrogen area	Methane area
1	23.23	30.46	42.31	55.85	5852426	1594746	4855956	15750694
2	23.22	30.46	42.31	55.85	5852402	1594913	4856189	15752646
3	23.22	30.45	42.30	55.85	5849806	1594074	4853402	15749892
4	23.22	30.45	42.30	55.85	5857044	1596055	4859671	15769519
5	23.22	30.46	42.31	55.86	5853222	1595289	4856426	15762840
6	23.23	30.46	42.30	55.85	5847437	1593546	4853332	15742096
7	23.22	30.45	42.30	55.85	5855831	1596512	4860136	15768153
8	23.23	30.46	42.31	55.86	5846434	1594241	4854710	15745279
9	23.22	30.46	42.30	55.85	5860122	1597659	4864955	15785858
10	23.22	30.45	42.30	55.85	5852819	1595989	4860359	15768762
Average	23.22	30.46	42.30	55.85	5852754	1595302	4857514	15759574
Std. dev.	0.0048	0.005	0.005	0.004	4210	1258	3691	13699
RSD (%)	0.021	0.017	0.012	0.008	0.072	0.079	0.076	0.087

For pure biogas, carbon dioxide and hydrogen sulfide are analyzed on a CP-PoraPLOT U column channel. When biogas is mixed with other hydrocarbon streams, ethane and propane can also be analyzed on this channel. Baseline separation of carbon dioxide, ethane, hydrogen sulfide, and propane is obtained, shown in Figure 2. Higher hydrocarbons present in the sample are backflushed to vent; which prevents late eluting components from interfering in the next analysis.

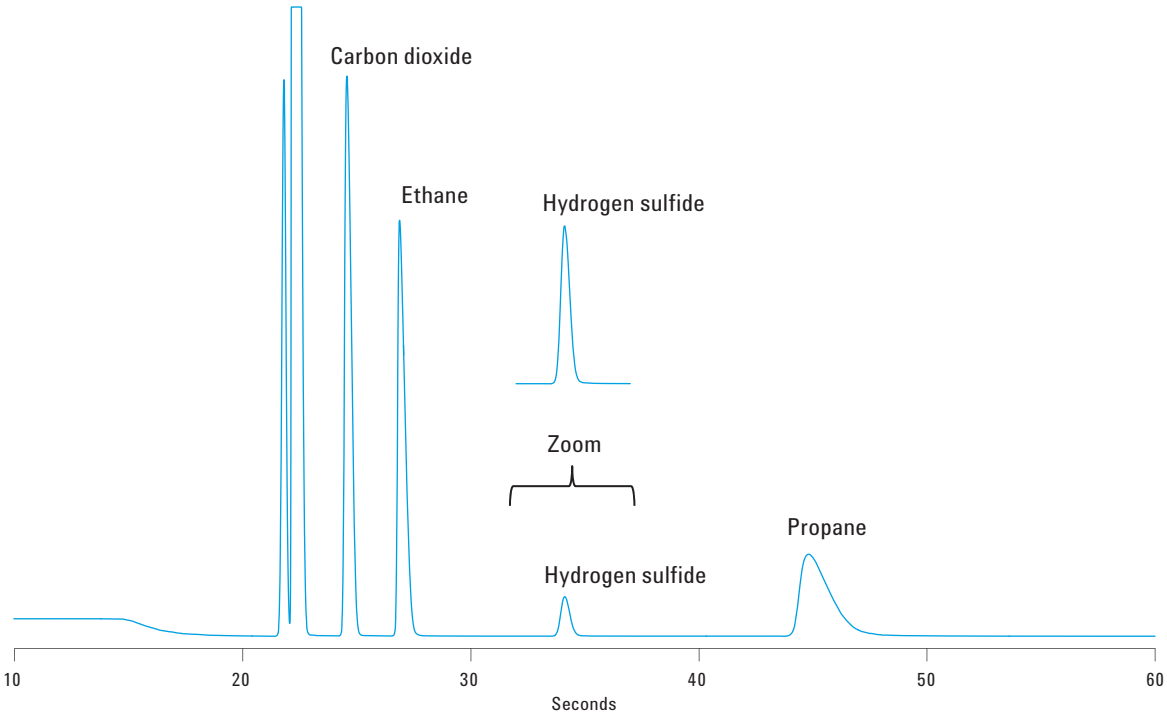


Figure 3. Chromatogram for carbon dioxide, hydrogen sulfide, ethane, and propane on the CP-PoraPLOT U channel.

The stainless steel tubing in the CP-PoraPLOT U channel and the sample inlet of the Micro GC have an UltiMetal deactivation layer, which results in an inert sample flow path and better performance for hydrogen sulfide analysis. Results presented in Table 3 shows very good repeatability figures for hydrogen sulfide and the other compounds (carbon dioxide, ethane, and n-propane) analyzed on the CP-PoraPLOT U channel. Relative standard deviation (RSD %) below 0.02 % for retention time and below 0.15 % based on area illustrates the system's suitability for this type of analysis. Moreover the UltiMetal deactivated sample inlet tubing provides an excellent peak shape for hydrogen sulfide, see Figure 3.

The CP-Molsieve and CP-PoraPLOT U channel, chromatograms as shown in Figure 3, are part of both the Biogas and Extended Biogas Analyzer.

Table 3. Retention Time and Peak Area Repeatability Results for the CP-PoraPLOT U Column

Run no.	Carbon dioxide Rt (sec)	Ethane Rt (sec)	Hydrogen sulfide Rt (sec)	n-Propane Rt (sec)	Carbon dioxide area	Ethane area	Hydrogen sulfide area	n-Propane area
1	24.56	26.87	34.11	44.80	3240882	2662227	320047	2175181
2	24.56	26.88	34.12	44.80	3239148	2660569	319969	2178315
3	24.56	26.87	34.12	44.80	3240617	2662025	320273	2181300
4	24.56	26.87	34.11	44.79	3239973	2661327	320031	2180366
5	24.56	26.87	34.11	44.79	3239006	2661163	319909	2178141
6	24.56	26.87	34.11	44.80	3240134	2661385	319833	2174648
7	24.55	26.87	34.11	44.79	3239972	2661379	320000	2173550
8	24.55	26.87	34.11	44.79	3238407	2660348	319721	2177678
9	24.56	26.87	34.11	44.79	3238332	2660512	320024	2179891
10	24.55	26.87	34.11	44.79	3237012	2659615	319789	2176390
Average	24.56	26.87	34.11	44.79	3239348	2661055	319960	2177546
Std. dev.	0.0048	0.0032	0.0042	0.0052	1197	797	157	2578
RSD (%)	0.020	0.012	0.012	0.012	0.037	0.030	0.049	0.12

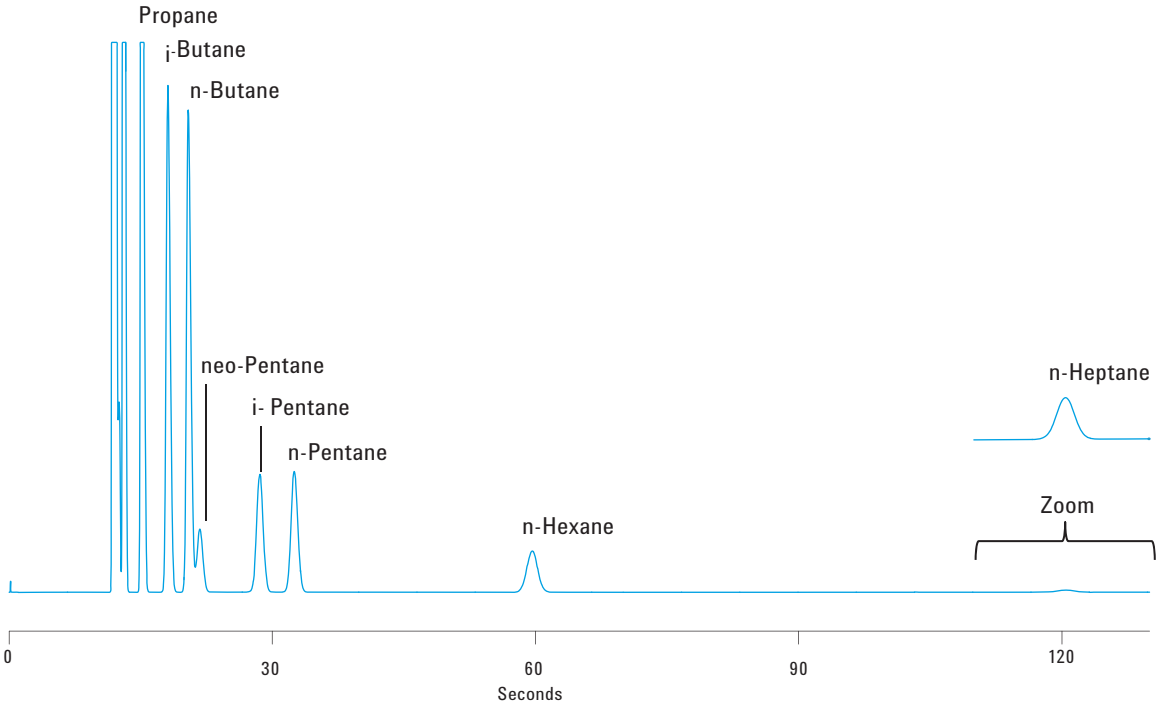


Figure 4. Chromatogram on the CP-Sil 5 CB, separating the hydrocarbons from butanes to n-heptane.

In Figure 4, the chromatogram illustrates the separation and quantification of the higher boiling hydrocarbons as part of the Extended Biogas Analyzer setup; the column used is a CP-Sil 5 CB. This additional channel expands the application range of biogas analysis to blends with natural gas or liquefied petroleum gas (LPG). In this particular case, the biogas was mixed with natural gas.

Tables 4a and 4b show repeatability on the CP-Sil 5 CB channel for the hydrocarbons. The repeatability data of approximately 0.05% for retention times and below the 0.2% mark for peak area can be considered as excellent. Even the partially separated neo-pentane shows a good peak area repeatability performance.

Table 4a. Retention Time Reproducibility Data for the CP-Sil 5 CB Channel

Run no.	i-Butane Rt (sec)	n-Butane Rt (sec)	neo-Pentane Rt (sec)	n-Pentane Rt (sec)	i-Pentane Rt (sec)	n-Hexane t (sec)	n-Heptane Rt (sec)
1	18.10	20.43	21.75	28.58	32.52	59.67	120.66
2	18.10	20.43	21.75	28.58	32.52	59.67	120.69
3	18.10	20.42	21.74	28.58	32.51	59.66	120.70
4	18.10	20.42	21.74	28.57	32.51	59.66	120.71
5	18.09	20.42	21.74	28.57	32.50	59.64	120.72
6	18.09	20.42	21.74	28.57	32.50	59.64	120.72
7	18.09	20.41	21.73	28.56	32.49	59.63	120.72
8	18.08	20.41	21.72	28.55	32.48	59.61	120.73
9	18.08	20.40	21.72	28.55	32.48	59.60	120.72
10	18.08	20.40	21.72	28.54	32.47	59.59	120.74
Average	18.09	20.42	21.74	28.57	32.50	59.64	120.71
Std. dev.	0.0088	0.0107	0.0118	0.014	0.018	0.029	0.023
RSD (%)	0.048	0.053	0.054	0.050	0.054	0.049	0.019

Table 4b. Reproducibility Data, Based on Peak Area, for the CP-Sil 5 CB Column

Run no.	i-Butane area	n-Butane area	neo-Pentane area	n-Pentane area	i-Pentane area	n-Hexane area	n-Heptane area
1	7014680	7186850	1265110	2702141	2781533	1552255	133755
2	7018181	7190966	1264813	2703703	2783345	1553847	133682
3	7018469	7187273	1269047	2704327	2783935	1554441	133642
4	7017302	7188209	1269045	2705176	2784640	1554809	133920
5	7017858	7190794	1264914	2705022	2784520	1554963	133951
6	7024447	7196790	1265962	2707439	2787091	1556518	133959
7	7025658	7196118	1269229	2708459	2787981	1557169	133959
8	7019982	7188645	1270146	2706467	2785715	1555951	133880
9	7018355	7189383	1267352	2706536	2785636	1556096	134091
10	7018173	7190297	1266144	2706696	2785947	1555806	134130
Average	7019311	7190533	1267176	2705597	2785034	1555186	133897
Std. dev.	3315	3418	2043	1888	1865	1439	162
RSD (%)	0.047	0.048	0.16	0.070	0.067	0.093	0.12

Conclusion

The Agilent 490 Micro GC Biogas Analyzer type required depends on biogas sample type. Regular biogas contains methane, carbon dioxide, nitrogen, and sometimes some hydrogen, hydrogen sulfide, and carbon monoxide. For this type of sample, the 490 Micro GC Biogas Analyzer is perfectly suited.

The first column channel, configured with a CP-Molsieve 5A column with argon as carrier gas, will separate and analyze hydrogen, oxygen, nitrogen, methane, and carbon monoxide. Moisture and carbon dioxide, as well as higher hydrocarbons present in the sample, are backflushed to vent, ensuring trouble free operation, perfect repeatability, and a long column lifetime without the need for extensive conditioning procedures. Moreover, this column channel is equipped with a Retention Time Stability option (RTS) to ensure stable retention time on the CP-Molsieve 5A column over time.

The second channel, equipped with a CP-PoraPLOT U column, analyzes carbon dioxide and hydrogen sulfide as part of the biogas sample. This column can even be used when ethane and propane are present in the sample. The sample inlet of the Micro GC and the CP-PoraPLOT U channel are treated with an UltiMetal deactivation process to guaranty good performance for hydrogen sulfide analysis.

When butanes and higher hydrocarbons need to be analyzed, the Agilent 490 Micro GC Biogas Analyzer Extended is recommended. This analyzer, suited for analysis of biogas mixed with other hydrocarbon streams such as natural gas or LPG, is equipped with an additional CP-Sil 5 CB column channel.

All results clearly illustrate that both analyzer configurations are perfectly capable of analyzing biogas and related sample streams. Typical repeatability figures show RSD's around 0.05 % for retention time and RSD's less than 0.2 % for peak area, while the factory specification for peak area repeatability is specified on 0.5% RSD (based on 1 % concentration level propane).

The Agilent 490 Micro GC Biogas Analyzers are factory tuned, including the appropriate settings for the backflush times for the CP-MolSieve 5A and CP-PoraPLOT U columns. The Agilent Biogas Analyzers are shipped with final test data, optimized analytical method, Biogas Analyzer User Manual, and a check out sample kit to have all information available at installation.

For More Information

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

www.agilent.com/chem/microgc

Printed in the USA
November 22, 2011
5990-9508EN

Agilent Technologies

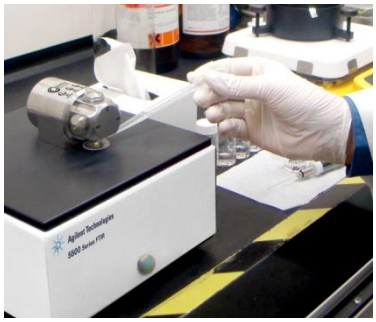
Portable measurement of biodiesel in diesel fuels by ASTM D7371-07 (FTIR-ATR-PLS method) with the Agilent 5500t FTIR spectrometer

Application Note

Author

Frank Higgins

Agilent Technologies
Connecticut, USA



Background

Biodiesel blending with current ultra low sulfur diesel (ULSD) fuels is increasing in popularity for both large scale fleet use and individual small scale consumers. The test method detailed in this application brief can be used for quality control purposes in the production and distribution of diesel fuel and biodiesel blends. The ASTM D7371 method is applicable to 1-100 volume % biodiesel (FAME) concentrations in diesel fuel oils; it applies to all common 5 % (B5), 10 % (B10), and 20 % (B20) biodiesel blends. The ASTM D7371 method coupled with the Agilent 5500t FTIR spectrometer provides an easy, accurate, and portable means for measuring the biodiesel content of a blended fuel with petroleum diesel fuel.

Agilent Technologies

Experiment

Following the ASTM D7371 procedures, three different diesel fuels are used to create the calibration standards. The cetane index in diesel fuels is varied by changing the relative percentage of aromatic to aliphatic hydrocarbons; higher cetane index fuels have less aromatic compounds. Cetane index is typically lower during cold months. The ASTM D7371 is designed to account for these seasonal differences in the diesel fuels. The ASTM certified B100 Biodiesel was mixed with diesel fuel blended at three different cetane indexes, referred to in the D7371 as diesel cetane check fuel low, high and ultra high. As specified in the method, a total of 70 standards were produced with biodiesel concentrations ranging from 0-100%. In addition to the calibration standards, 21 qualification standards were created with different concentrations than the calibration standards. The qualification standards were used to determine the method's accuracy and robustness.

All standards were measured using the Agilent 5500 Series FTIR spectrometers with an integrated 9 reflection diamond attenuated total reflectance (ATR) sample interface. The spectra were collected using 64 scans at 4cm-1 resolution yielding a 30 second sample measurement time. A partial least squares (PLS) model was developed using Thermo Galactic PLS/IQ software. The model concentrates on the ester carbonyl and other absorbance bands specific to fatty acid methyl esters (FAME). The PLS models were incorporated into Microlab software for an easy end-user biodiesel in diesel fuel application.

Results

A series of spectra from the calibration set are shown in Figure 1. Bands due to biodiesel can be seen both at 1741cm^{-1} and between 1170-1245cm^{-1}; these areas are correlated to the concentration of biodiesel in the D7371 method. The absorbance increases linearly with the concentration throughout the whole range from 0-100 %.

This provides a very accurate and precise measurement using the 5500 Series FTIR spectrometers.

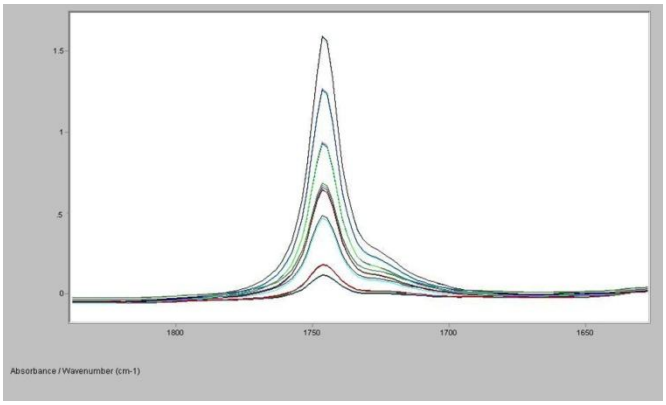


Figure 1. FTIR spectra overlaid of ASTM D7371 standards with biodiesel in diesel at 0, 2.5, 5, 10, 15, 20, 30, 50, 70, and 100 % biodiesel (v/v)

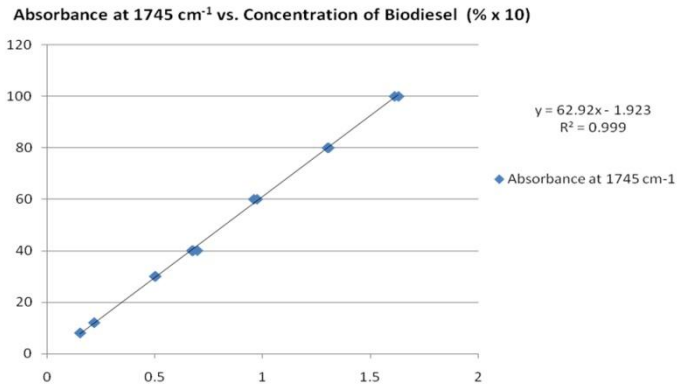


Figure 2. The PLS model's actual vs. predicted plot of biodiesel in diesel, low calibration set (0-10 % biodiesel)

ASTM D7371 specifies individual calibration models for the concentration ranges 0 -10 %, 10 - 30 % and 30 -100 %; each calibration model contains standards from each of the three cetane index diesel fuel stocks (ultra high, high and low). The 0-10 % calibration model results are plotted in Figure 2 as the actual (x-axis) vs. predicted (y-axis) biodiesel concentrations. The correlation coefficient for this model is R_2= 0.999. Results for the 10 - 30 % and 30 - 100 % models were similar. Each model uses 3 - 4 factors on mean centered data.

The three models based on the ASTM D7371 method were incorporated into a single method within the Microlab software. A screen shot showing one of the calibration definitions definition is shown in Figure 3.

The Microlab software also contains logic to report only the result from the correct model.

Using the "Component Reporting" feature, shown in Figure 4, which result will be shown to the user based on the predicted result. Using this feature, a single, correct result is present to the user even though results from three methods are calculated. This reduces confusion and allows samples to be measured by untrained users.

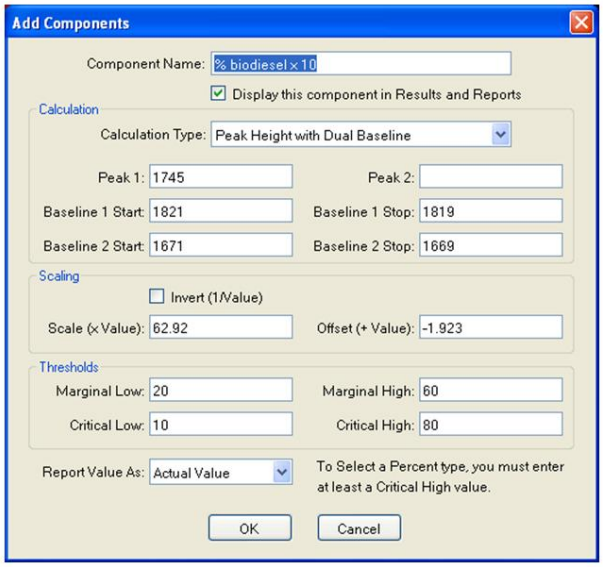


Figure 3. The Microlab methods editing feature where the 1-10 % biodiesel model is assigned

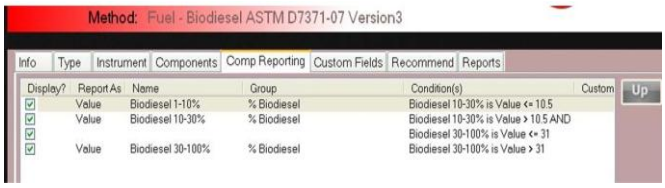


Figure 4. The conditional reporting setup window from the Microlab PC software, which determines the model results to be displayed when running a sample

The Microlab ASTM D7371 method was used to predict the concentrations of a separate qualification set. The qualification set covers the entire 0-100 % range of biodiesel in diesel, and the different cetane index diesel fuels were also used to make the qualification samples. The average relative error (1-100 % range) is 0.47 % and the maximum relative error is 1.56 %. The results of the separate validation are shown in Table 1. It should be noted that the standard error of qualification calculated for these tests is less than half the acceptable standard error of qualification listed in the ASTM method. A screen shot showing the software display for a 2.5 % biodiesel validation sample is shown in Figure 5.

Figure 5. Microlab results screen for a 2.50 vol % sample of biodiesel in diesel

Table 1. The results from the qualification set samples measured with the ASTM 7371 method in the Microlab software

Qualification Sample	Predicted Biodiesel (Vol %)	Actual Biodiesel (Vol %)	Error (%)
Q1	0.77	0.71	8.61
Q2	5.98	5.95	0.55
Q3	13.14	13.14	0.01
Q4	26.50	26.44	0.24
Q5	59.05	58.73	0.54
Q6	92.12	92.07	0.05
Q7	97.73	97.77	0.04
Q8	0.36	0.36	0.77
Q9	1.64	1.66	1.56
Q10	5.91	5.94	0.49
Q11	38.51	38.69	0.47
Q12	84.16	84.39	0.27
Q13	95.74	95.88	0.14
Q14	99.11	99.30	0.20
Q15	0.35	0.36	1.09
Q16	3.60	3.55	1.28
Q17	8.35	8.31	0.43
Q18	13.15	13.10	0.39
Q19	21.17	21.49	1.50
Q20	73.70	73.65	0.06
Q21	95.66	95.49	0.18
		Average Error Total (%)*:	0.47
		Maximum error (%*):	1.56
		Standard Error of Qualification (SEQ):**	0.08
		ASTM D7371 SEQ Limit (PSEQ):	0.21

Conclusions

This set of experiments show the ability of Agilent 5500 Series FTIR spectrometers with 9 reflection diamond ATR sample interface to meet the ASTM D7371 method. The method file which calculates the concentration in all ranges from 1 % to 100 % biodiesel and selectively reports the correct concentration is standard with all 5500 FTIR and 4500 FTIR systems. The results from a separate validation show that the instrument and method are very accurate while being very simple to use.

www.agilent.com/chem

Published May 1, 2011
Publication Number 5990-7807EN

Agilent Technologies

SIMULATED DISTILLATION

Streamline sample prep for Simulated Distillation characterizations

Sample preparation for simulated distillation can be difficult and time-consuming.

Agilent's Easy SamplePrep software automates tedious sample prep procedures, and makes it simple to replicate simulated distillation methods for use with additional systems.

The software works with the Agilent 7693A Automatic Liquid Sampler to deliver dual simultaneous injection, easy identification of resources, and the industry's fastest injections for 150 vials. So you can save time, improve lab safety, and reduce waste.

Back to table of contents ►

Learn more about solutions for the energy and chemical industry at **agilent.com/chem/energy**

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

Application Note

Hydrocarbon Processing

Author

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

Abstract

A dual tower Agilent 7693A and tray system installed on the Agilent 7890A GC system is used for the preparation of hydrocarbon calibration standards, solvent blanks, and petroleum samples for analysis by simulated distillation (SimDis). The front tower is equipped with a 5-µL syringe while the back tower is equipped with a 250-µL syringe. A 150 sample tray with heater and mixer/barcode reader is also used. Procedures are described for sample preparation for ASTM D2887, D7213, D7398 and D6352. The Multimode Inlet (MMI), G3510, operated in a temperature programmed split mode is used for all samples. On-line sample preparation programs are constructed using Easy SamplePrep software, an add-on software module for the multitechnique ChemStation.

Introduction

Sample and calibration standard preparation for various simulated distillation methods is normally a manual process requiring dilution, mixing, and heating. Many procedures use volatile toxic solvents such as carbon disulfide. ASTM method D2887 commonly uses CS_2 for sample dilution while D6352 may use CS_2 or toluene for polywax calibration standard preparation. Sample heating, mixing and solvent addition is available with the automation capabilities of the Agilent 7693A tower and tray system. Lab safety is improved by using small quantities of solvents with controlled heating, and mixing in sealed 2-mL vials.

Agilent Technologies

Experimental

The Agilent 7890A GC system was equipped with two Agilent 7693A towers and 150 sample tray. The front tower used a standard 5-µL or 10-µL syringe and the rear tower was equipped with the optional large syringe carriage with a 250-µL syringe. Sample prep procedures were done by manipulating vials in the sample tray and in the tower turrets. Sample injection occurred on the front tower. The Agilent 7890A was configured with the multimode inlet (MMI) operating in temperature programmed split mode. Detection was with FID. Instrumental parameters for various configurations are listed in Table 1.

Discussion

A number of options or paths to construct sample prep programs using the drag and drop icon implementation of Easy SamplePrep software is possible. This discussion will in general illustrate just one possible solution for each procedure. Screen captures are used to detail the steps and advanced syringe settings.

Table 1. Agilent 7890A GC System SimDis Parameters

System for D2887	
Column	10 m × 0.53 mm, 3.0 µm DB-2887
Oven	40 °C (0 min) to 350 °C (5 min) @ 15 °C/min
Inlet	Multimode (MMI), G3510, 100 °C (0 min) to 340 °C (to end of run) @ 250 °C/min
Liner	Single taper with glass wool, No. 5183-4711
Split	4 to 1
Flow	12 mL/min, constant flow mode
System for D7213 and D7398 (Polywax 500 calibration)	
Column	5 m × 0.53 mm, 0.15 µm DB-HT SimDis
Oven Program	35 °C (0 min) to 400 °C (5 min) @ 10 °C/min
Inlet	Multimode (MMI), 100 °C (0 min) to 400 °C (20 min) @ 250 °C/min
Split ratio	5 to 1
Flow	14 mL/min, constant flow mode
Agilent 7890A GC system for D6352 (Polywax 655 calibration)	
Column	5 m × 0.53 mm, 0.15 µm DB-HT SimDis
Oven Program	35 °C (0 min) to 435 °C (2 min) @ 10 °C/min
Inlet	Multimode (MMI), 100 °C (0 min) to 430 °C (hold to end of run) @ 250 °C/min
Split ratio	5 to 1
Flow	15 mL/min, constant flow mode
Agilent 7693A system	
Front tower	5 µL syringe, G4513A
Back tower	250 µL syringe, G4521A syringe carriage
Tray	150 sample capacity with Heater/Mixer/Bar Code Reader, G4520A
ChemStation	B.04.02 SP1
Sample Prep	G7300AA, Easy SamplePrep
Agilent 7890A GC system firmware	A.01.10.3 or greater
Standards and vials	
Calibration mix, C5-C40, No. 5080-8716	
Calibration mix, C5-C18, No. 5080-8768	
RGO, No. 5060-9086	
PW500, No. 5188-5316	
PW655, No. 5188-5317	
Empty vials with 100 µL inserts, No. 5188-6592	
Simulated Distillation Software	
G2887BA	

Two-milliliter vial resources are assigned in user defined tray locations as shown in Figure 1. These are the resources needed for methods D2887, D7213, D6352, and D7398. The polywax standards are handled differently, usually as "Sample (front)" vials when the front tower is used for injection. Resource vials are specified for use by maximum volume extracted or by number of allowed uses. Ensure that appropriate syringe details such as draw and dispense speeds for the handling of a given chemical resource are set. An example of advanced settings for use of CS_2 is shown in Figure 2.

A typical sample preparation program for D2887 setup (blank, calibration, reference gas oil) may consist of a sequence of three methods, each for a specific sample prep and injection. An example sequence is shown in Figure 3. This illustrates preparation of the blank, calibration standard, and reference gas oil (RGO) samples necessary to set up and verify a system for routine analyses.

The Easy SamplePrep programs used for methods CS2 BLANK, C5C40 CAL 2887, and RGO 2887 are shown in Figures 4, 5, and 6, respectively. Using three methods in a sequence is convenient since each method has different integration parameters.

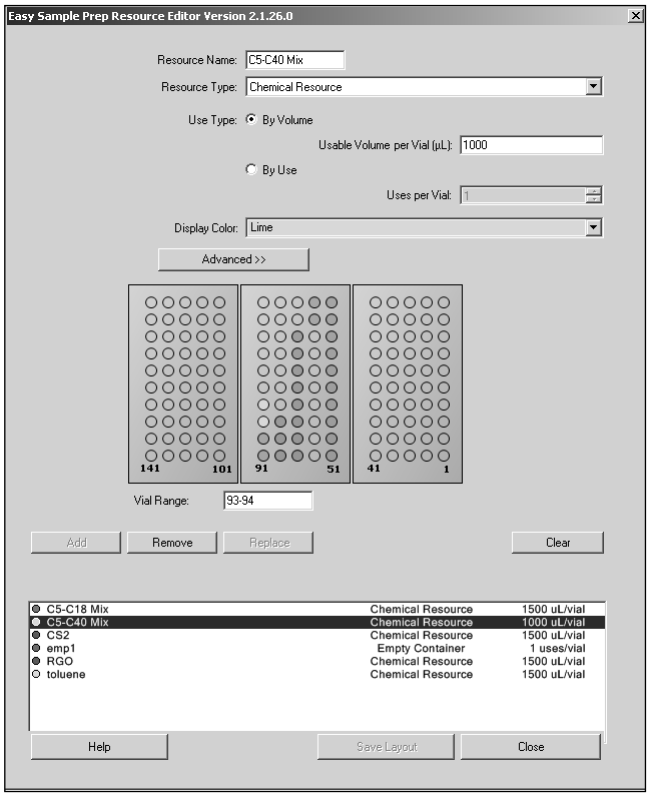


Figure 1. Example resource layout for various simulated distillation procedures. Each resource is assigned a unique color.

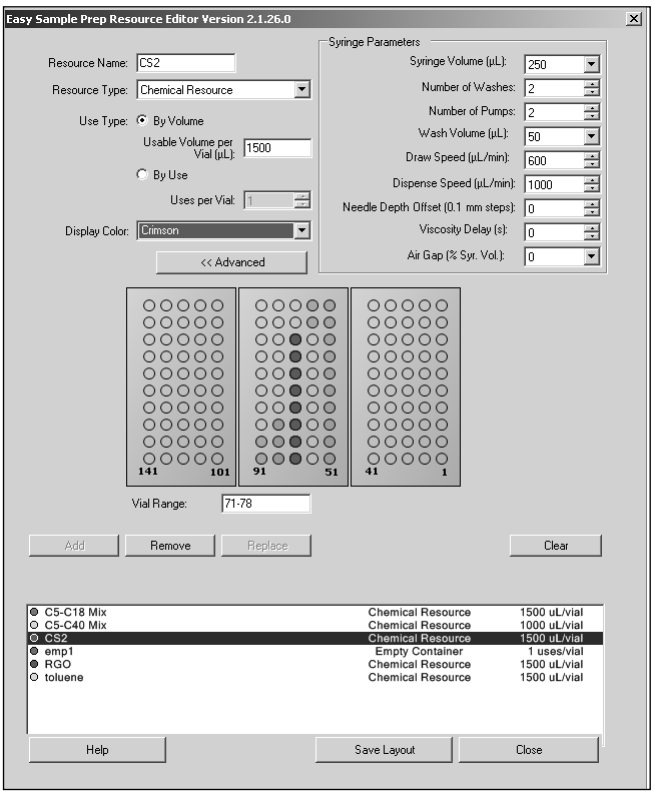


Figure 2. Advanced parameters shown (upper right box) for chemical resource CS2.

Line	Vial	Sample Name	Method Name	Inj/Vial	Sample Type
1	1	blank	CS2 BLANK	2	Sample
2	1	C5-C40	C5C40 CAL 2887	1	Sample
3	1	RGO	RGO 2887	1	Sample

Figure 3. Sequence for setup of D2887. Each method contains the appropriate EasySample Prep procedure.

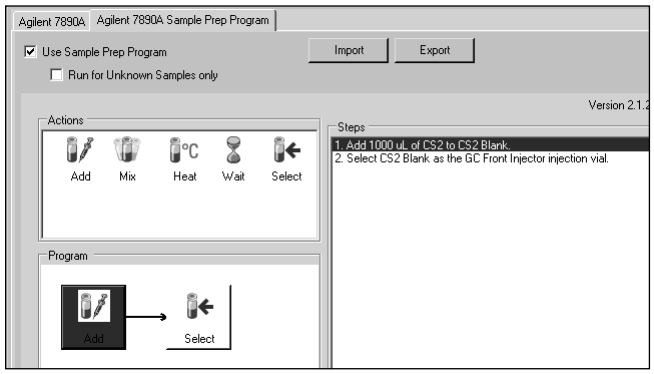


Figure 4. Easy Sample Prep program for the preparation of a CS_2 blank. An empty tray vial has been assigned the name "CS2 Blank". The select icon indicates that the prepared vial is to be injected.

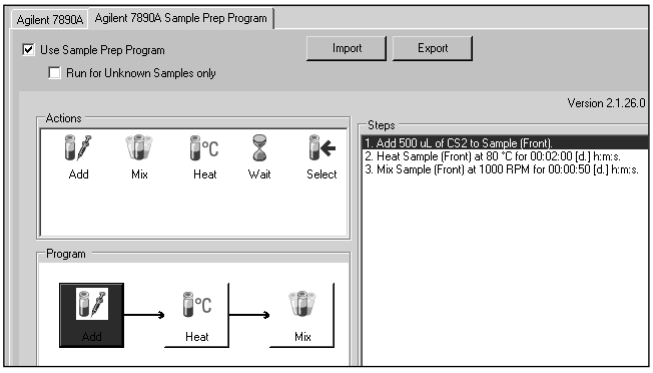


Figure 5. Easy Sample Prep program for preparation and injection of the C5 to C40 calibration mix. The "sample [front]" label defines sequence vials for the front tower.

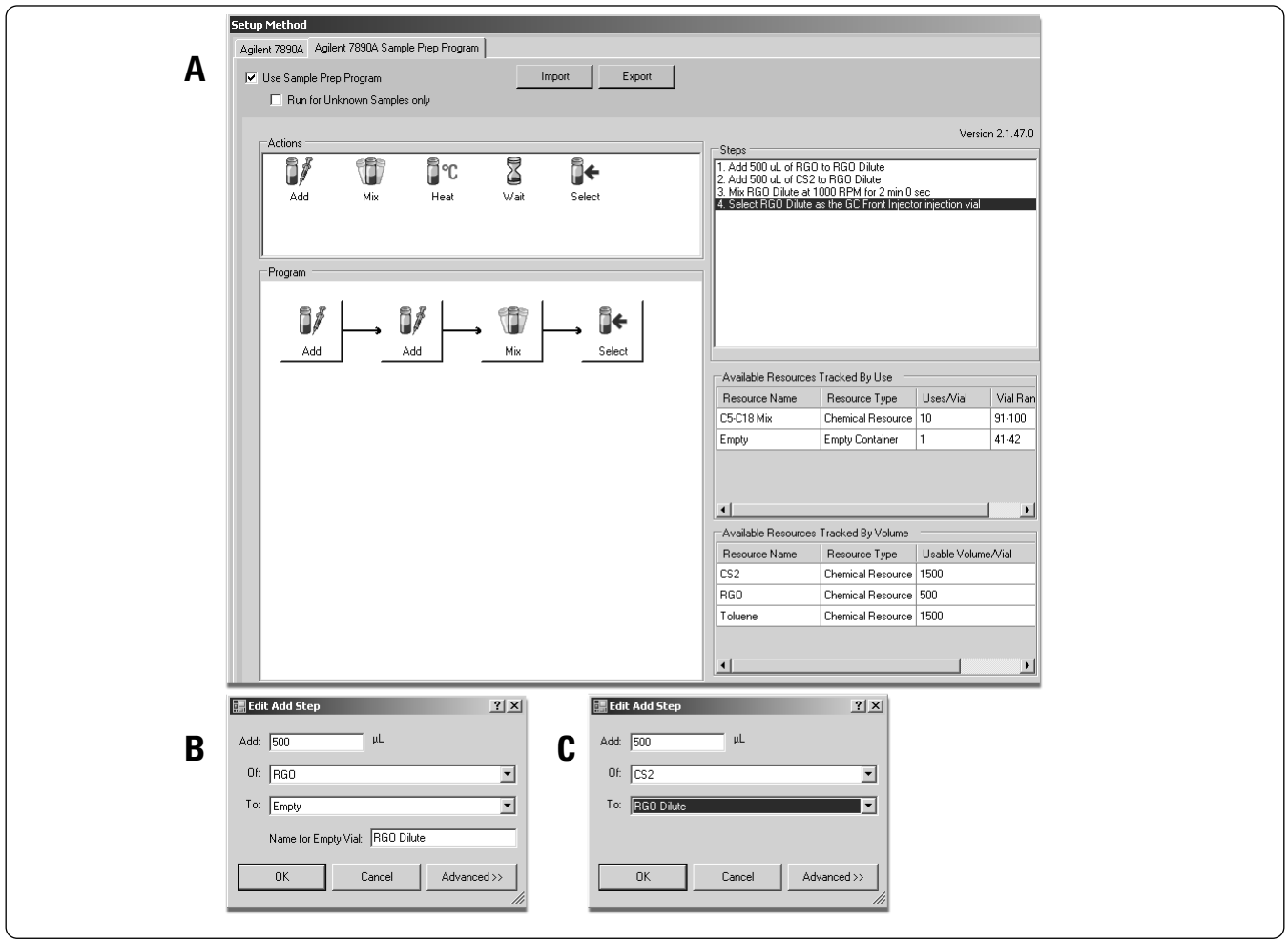


Figure 6a. Easy Sample Prep program for preparation and injection of RGO. An empty tray vial(empty) has been assigned the name "RGO Dilute" during the "Add" step and is selected for injection after prep. "Selected" vials override the vial number given in the sequence table.

Figure 6b. Add steps for RGO and vial naming.

Figure6c. Adding carbon disulfide to the RGO vial.

Upon completion of the sequence, all three prepared vials will have been injected producing data files ready for analysis by simulated distillation software. Note that two blanks are run to ensure both are the same; otherwise, additional blanks should be run. As an alternate setup, the calibration, prepared RGO, and blank vials can be fitted with 100-µL inserts to minimize solvent and resource amounts used for the procedure. Please note that when these inserts are used, limit mixing to speeds of approximately 500 rpm to avoid "spilling" liquid over the top of the insert into the bottom of the 2-mL vial.

Syringe washing is important to incorporate into these programs to avoid contamination or carryover for each vial addition. An example of settings is shown in Figure 7.

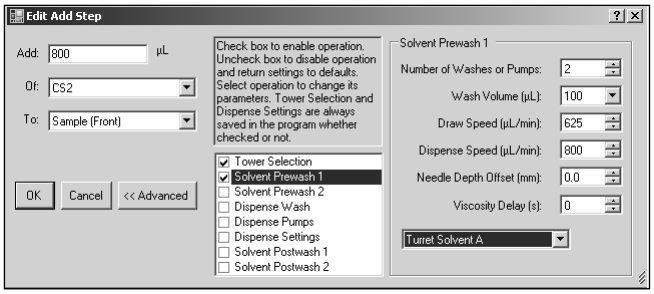


Figure 7. An example using solvent wash vial 1 (5 mL) in the turrent of tower A.

Preparation of polywax standards for the higher temperature SimDis methods can be challenging due to their low solubility. Solvents such as CS_2 and toluene are commonly used. Heating of the solvent/polywax vial is required just prior to injection. This entire procedure can be automated with the Agilent 7693A tower and tray system. The basic procedure for Polywax 655 is as follows:

- Manually place approximately 80 – 100 mg of polywax 500 in a 2 mL vial and seal
- Add 1.5 mL of toluene to the polywax vial
- Add 10 µL of C5-C18 to the polywax-toluene vial
- Mix the vial
- Heat the vial at 80 °C for 4 min.
- Return to tray
- Heat one final time just prior to injection by setting injection/tray parameters in the core ChemStation method

Figure 8 shows the basic prep procedure using a dual tower/tray system automating the steps shown above. The only manual step is adding the solid polywax 500 to Vial 1 (Sample front). This procedure is applicable to D7213 SimDis and D7398 (Boiling Range Distribution of Fatty Acid Methyl Esters).

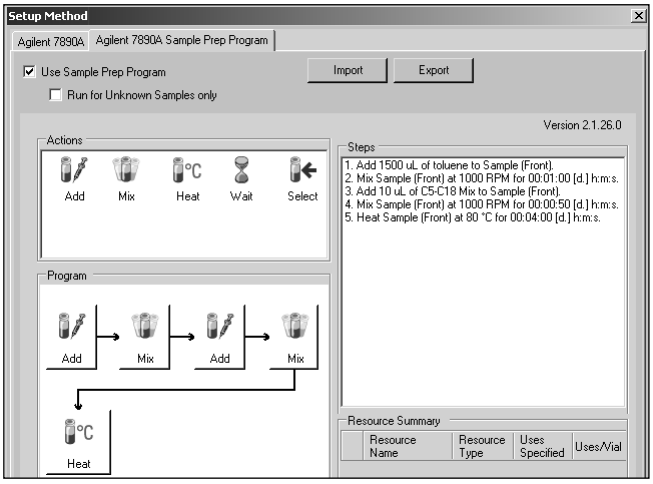


Figure 8. Polywax 500 prep procedure.

A resulting chromatogram for the injection of the prepared PW500 vial (vial 1) is shown in Figure 9. A symmetric distribution of the polyethylene fragments with good resolution to C80 is shown.

The preparation program for Polywax 655 is essentially the same as shown above for PW500 except that heating is extended for 6 minutes typically for dissolution. Prior to injection, the prepared vial is heated for another 3 minutes. Parameters for this second heating step are set under the core ChemStation injection parameter menu item. In the chromatogram shown in Figure 10, a small amount (5 µL) of C_5-C_{18} mix was added to the PW655/toluene solution as part of the automated procedure. This allows calibration starting at C12.

The chromatogram was produced with the multimode inlet set in temperature programmed split mode. Good definition of polyethylene fragments to over C110 are seen in Figure 11. The last 5 minutes of the chromatogram are zoomed to show detail. Producing this detail out to C110 is extremely difficult for any chromatographic system.

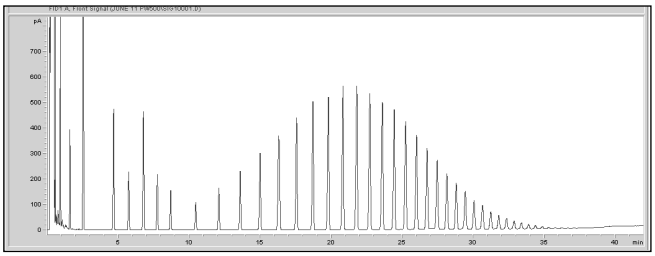


Figure 9. Polywax 500 with C5-C18 added. Multimode inlet, 2.5-µL injection.

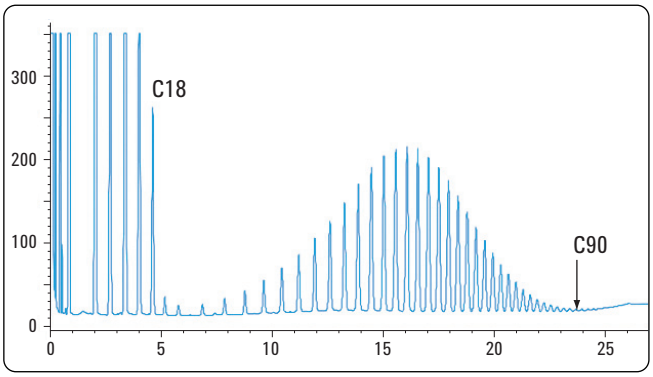


Figure 10. Chromatogram of PW 655.

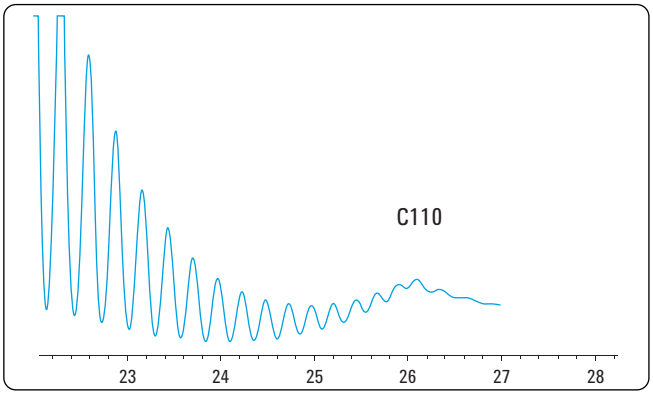


Figure 11. Polywax 655 to C110. Multimode inlet program: 150 °C (0 min) to 430 °C (hold to end of run) @ 200 °C/min. 7890A oven: 40 °C (0 min) to 430 °C (5 min) @ 15 °C/min. 3-µL injection. Solvent is toluene.

Reproducibility of sample preparation steps for the dilution of a heavy vacuum gas oil sample (HVGO) is illustrated in Figure 12. Carbon disulfide was used for sample dilution. Tray vial 1 is the stock HVGO sample, prepared by manually adding 0.5 g of the oil to a 2-mL vial. This material is extremely viscous and cannot be drawn into a syringe without dilution. The program performs a fully automated dilution prior to injection. (Figure 13)

Summary

Difficult sample preparation procedures that are commonly used for petroleum and fuel samples can be easily automated on-line with the Agilent 7693A tower and tray system for the Agilent 7890A GC system and Agilent 6890N Network GC system, including A, and Plus models using the Easy SamplePrep add-on software for the multitechnique ChemStation. The system is particularly well suited for preparation of polywax calibration samples used for higher temperature methods. Tasks such as mixing, solid dissolution, dilution, heating, viscosity reduction, and internal standard addition are easily accomplished by assembling icon based instructions. User contact with toxic solvents such as CS_2 is greatly reduced. The software monitors used resources and moves to the next available resource vial as assigned in the resource table when needed.

Chromatographic performance is enhanced through use of the multimode inlet. Using standard split injection liners, good sample capacity without carryover and with minimal discrimination of wide boiling samples is achieved. The inlet was used in the temperature programmed split mode for this work. Cryo cooling was not used, however, carbon dioxide cryo can be used optionally to shorten inlet cool down if desired.

The sample prep procedures listed here represent just one way of accomplishing a given task. Using the icon based commands available with the system, there are many variants that lead to the same end result.

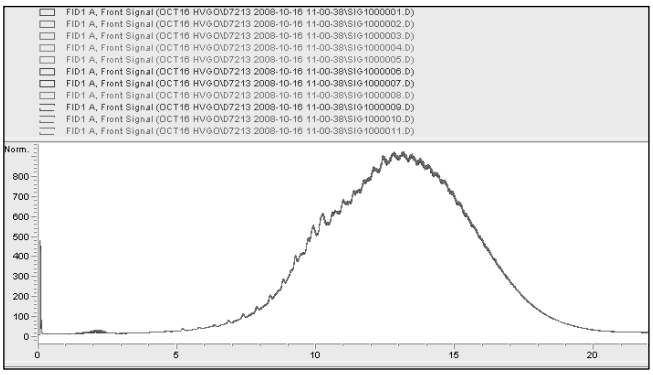


Figure 12. Overlay of 11 runs of HVGO, each prepared by using a Easy Sample Prep program.

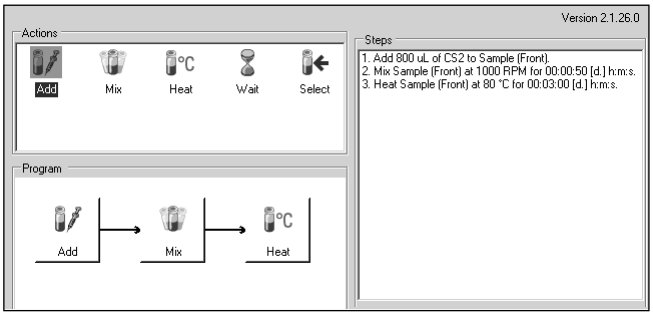


Figure 13. Preparation of HVGO for injection. CS_2 is used as the solvent.

Reference

1. Roger L. Firor, “Automated Preparation of Simulated Distillation Samples for ASTM Methods D2887, D7213, D7398, and D6352 using a Dual Tower 7693A and Tray System”, April 2009, Agilent Technologies publication 5990-3778EN.

www.agilent.com/chem

Printed in the USA
July 29, 2010
5990-6132EN

Agilent Technologies

Boiling Point Range of Fatty Acid Methyl Esters Using the 7890A Gas Chromatograph, Low Thermal Mass (LTM) System, and 7693A Tower and Tray

Application Note

Hydrocarbon Processing

Author

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

Abstract

Two Agilent 7890A Series GC systems were used to determine the boiling point distribution of Biodiesel (B100 and B20). First, the standard oven was used to produce runs of about 16 minutes. This was followed by a 7890A equipped with an LTM system and 1 five-inch module which does an 8 minute run. Both systems used the Multimode inlet in temperature programmed split mode for sample introduction and a dual tower Agilent 7693A Automatic Liquid Sampler configuration with a 150-vial sample tray for sample prep and injection.

Agilent Technologies

Introduction

ASTM method D7398 describes procedures for determining the boiling point range distribution of pure biodiesel (B100) and biodiesel blends of B1 and higher. To ensure that unreacted triglycerides are detected, the gas chromatograph is temperature programmed to 400 °C. Only the procedures involving calibration and running of pure biodiesel and biodiesel blends will be demonstrated in this work. Some sample preparation is normally involved which includes dissolution of a Polywax 500 standard that involves heating, mixing, and sample dilution of the biodiesel. These sample preps can be largely automated using the Agilent 7693A Series injector and tray system. Simulated distillation software is then used to compute the boiling range distribution. A standard 7890A GC and a 7890A/Low Thermal Mass (LTM) was used to analyze the prepared samples.

Experimental

Standard 7890A System

Inlet:	Multimode, G3510, 325 °C (0 min) to 400 °C at 200 °C/min
Liner:	Single taper liner with glass wool, 5183-4647
7890A oven:	40 °C (0 min) to 400 °C at 15 °C/min
Column:	5M × 0.53 mm × 0.15 µm DB-HT SimDis, 145-1001
Flow:	Constant flow mode at 14 mL/min He
Injection:	0.1 µL split 4:1, PW500 standard, 1 µL

7890A/LTM System

Inlet:	Multimode, G3510, 220 °C (0 min) to 400 °C (2 min) at 300 °C/min
LTM column module:	5 m × 0.53 mm × 0.15 µm DB-HT SimDis
Module connections:	0.7 m deactivated ProSteel on inlet and outlet
7890A oven:	325 °C isothermal
LTM module program:	40 °C (0 min) to 400 °C at 50 °C/min
FID:	400 °C
Inlet pressure ramp:	2.5 psi (0 min) to 9.5 psi (1 min) at 1 psi/min
Injection:	0.1 µL, split 10 to 1, PW500 standard, 1 µL

Deactivated Ultimate Unions, part no. 3182-60580, are used with the LTM module for connection of the ProSteel retention gaps to the column ends.

The 7693A injectors are installed with the 150-vial sample tray which includes a mixer/barcode reader and heater compartment for the purpose of sample prep and injection. The front tower uses a 5-µL syringe and the rear tower uses a 250-µL syringe which requires the large syringe carriage G4521A.

Data is processed using ChemStation 4.01 and the Agilent SimDis software, part number G2887BA. Example sample preparation programs from the ChemStation are shown below for system calibration and biodiesel samples.

Sample Prep Programs Using the 7693A

Table 1. Sample Program for the Preparation of PW500 with C5-C18 Mix Added

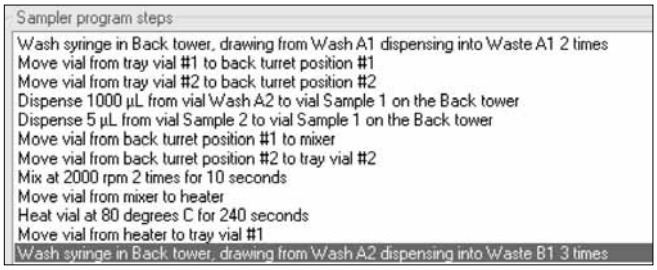
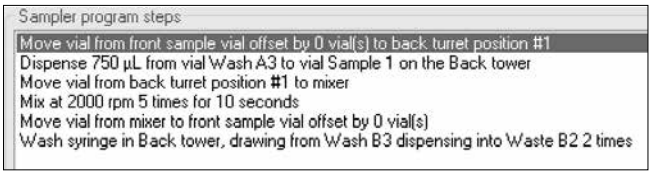


Table 2. Sample Program for the Dilution of a Biodiesel Sample Starting with 0.5 mL Biodiesel in a 2 mL Vial



Discussion

The calibration setup pane from the SimDis software is shown in Figure 1 for the LTM system. The mix of C5-C18 plus Polywax 500 gives a calibration from C_8 to C_{78}, covering the boiling point range of B100 (including unreacted components) and biodiesel blends. In Figures 1 and 2, calibration plot panes from the SimDis software with assigned carbon numbers are shown for the LTM and standard 7890A systems, respectively. Typical elution times for C_{70} are 7.5 minutes and 22 minutes for LTM and standard systems, respectively. Both show symmetric distributions indicating good inlet sample transfer with minimal discrimination. Figure 3 shows the chromatogram of a B20 soy-based biodiesel run on the LTM system. C_{16} and C_{18} fatty acid methyl esters can be seen above the diesel background.

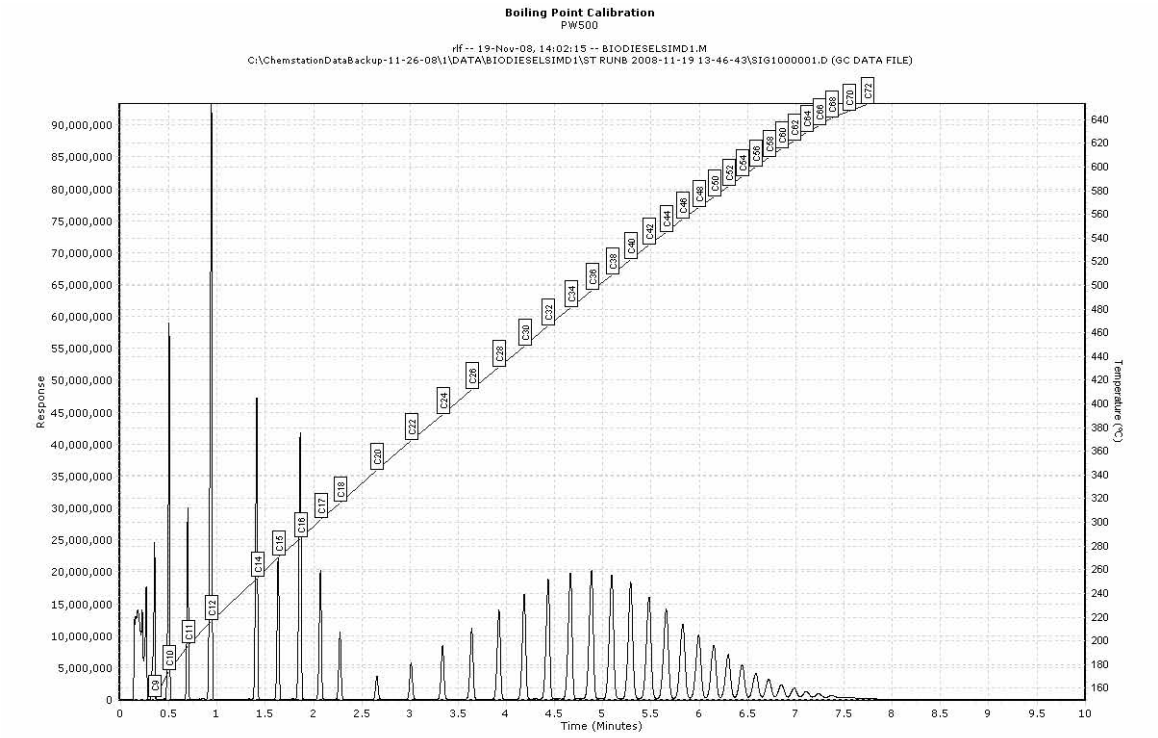


Figure 1. Calibration curve on LTM system from C9 to C72 prepared from PW500 and C5-C18 mix.

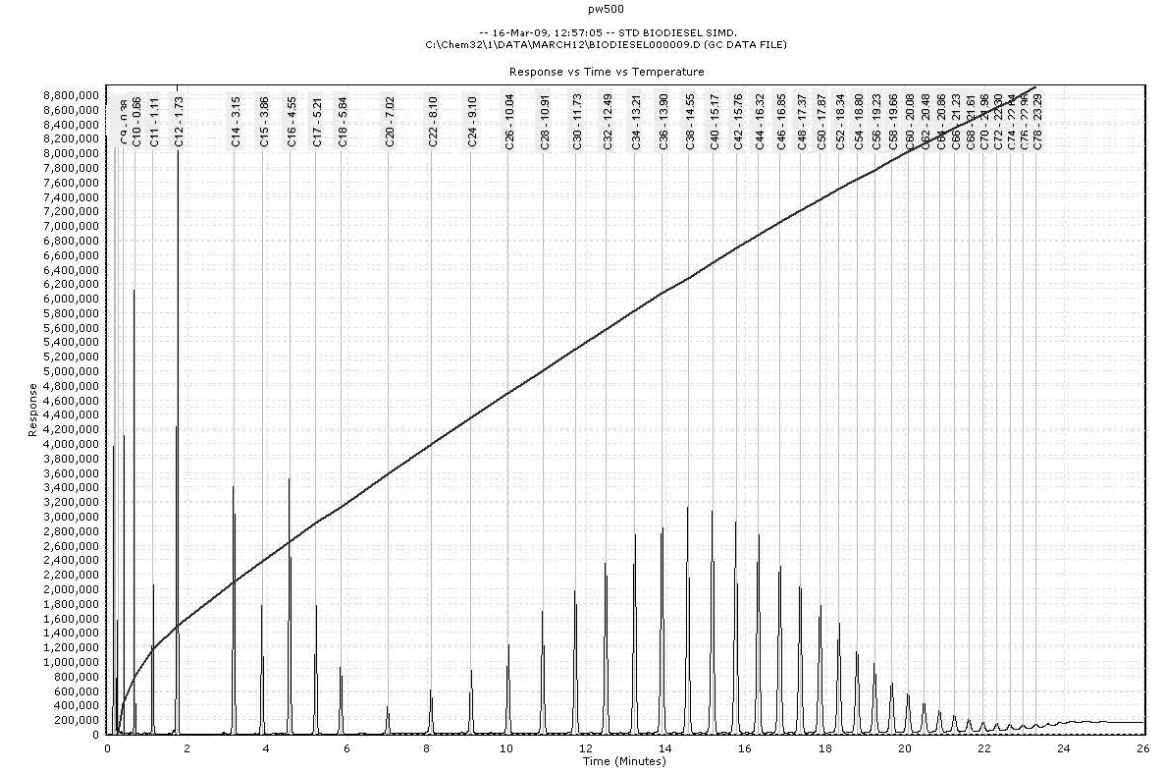


Figure 2. Calibration curve on standard 7890A GC.

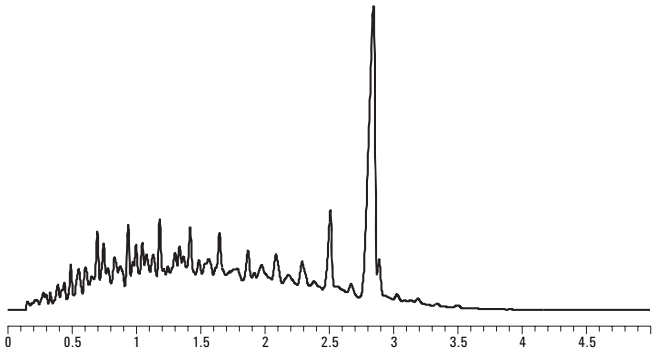


Figure 3. Chromatogram of B20 Soy based biodiesel using the LTM system.

A boiling point distribution of B100 sourced from rapeseed is shown in Figure 4. In Figure 5, two chromatograms are shown in an overlay. These are both B100 production biodiesel from two different plants. Note the different ratios of the C_{16} group (6.6 min.) to the C_{18} group (7.5 min.) in these samples. Lastly, calculated boiling point distributions for both samples are shown in Figures 6 and 7.

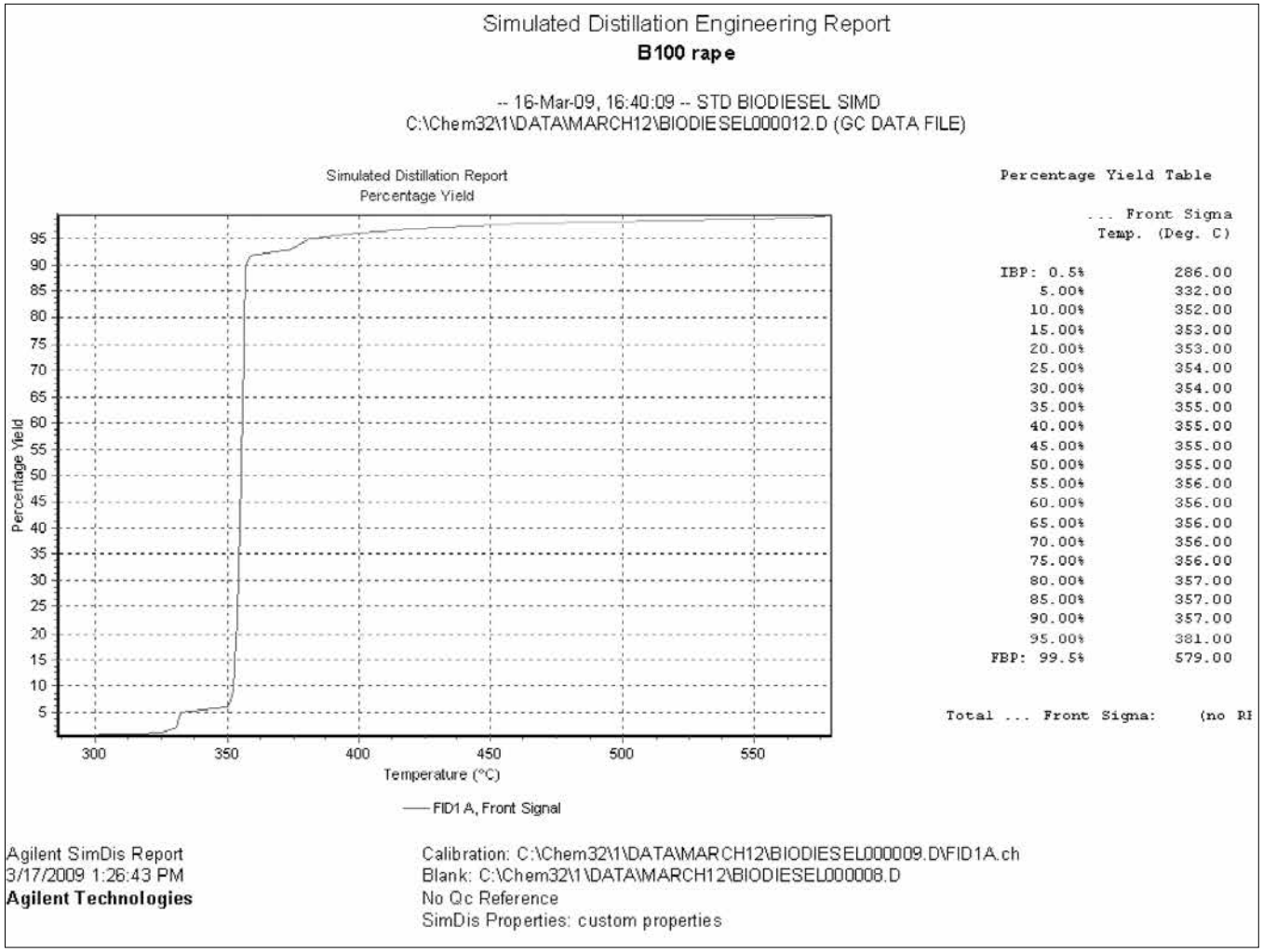


Figure 4. Boiling point distribution for rapeseed B100.

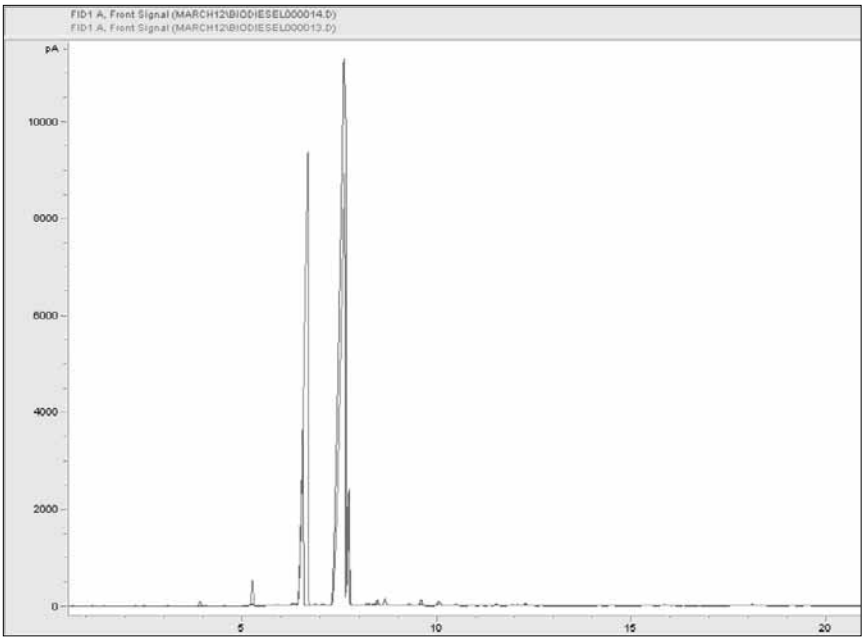


Figure 5. Overlay of two B100 samples from different producers. Both are soy based biodiesel. Producer A: signal 14, Producer B: signal 13.

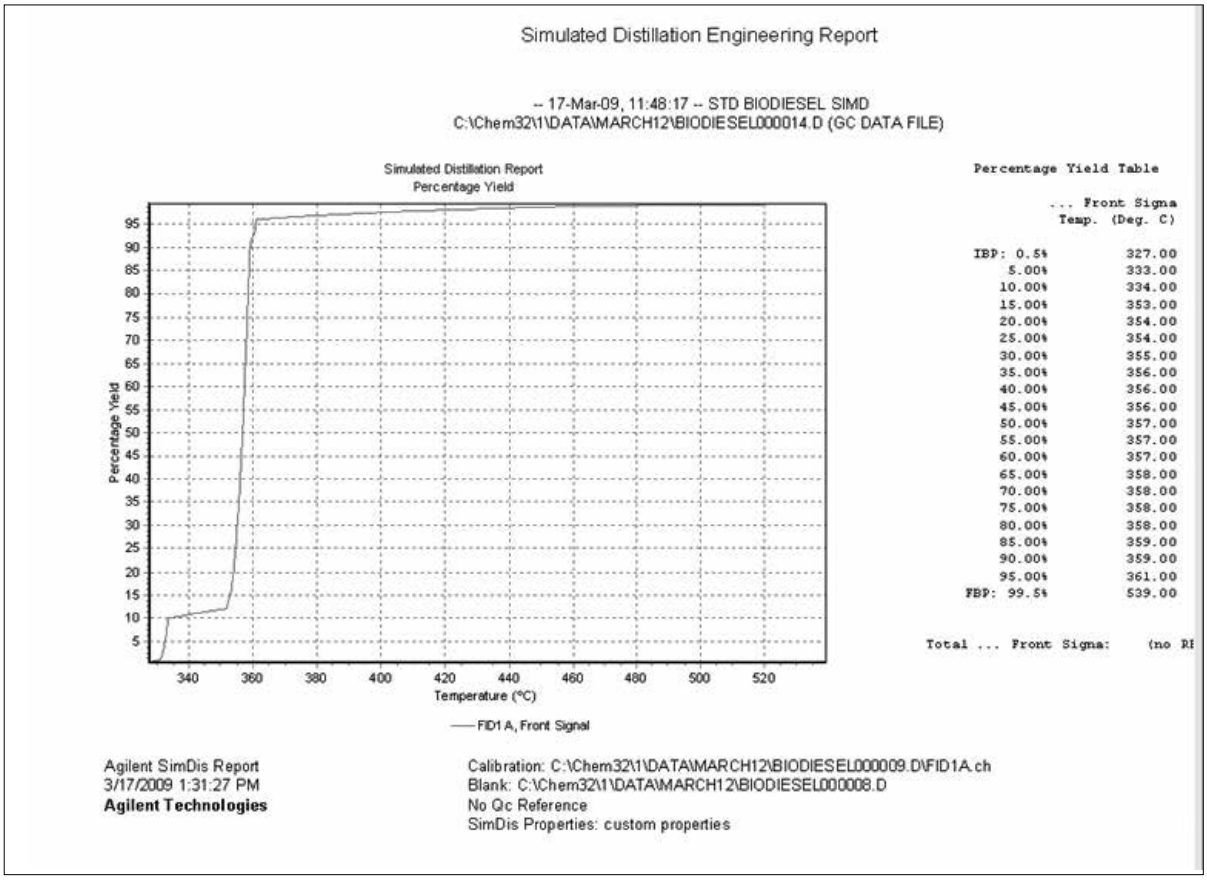


Figure 6. Boiling point distribution of B100, producer A.

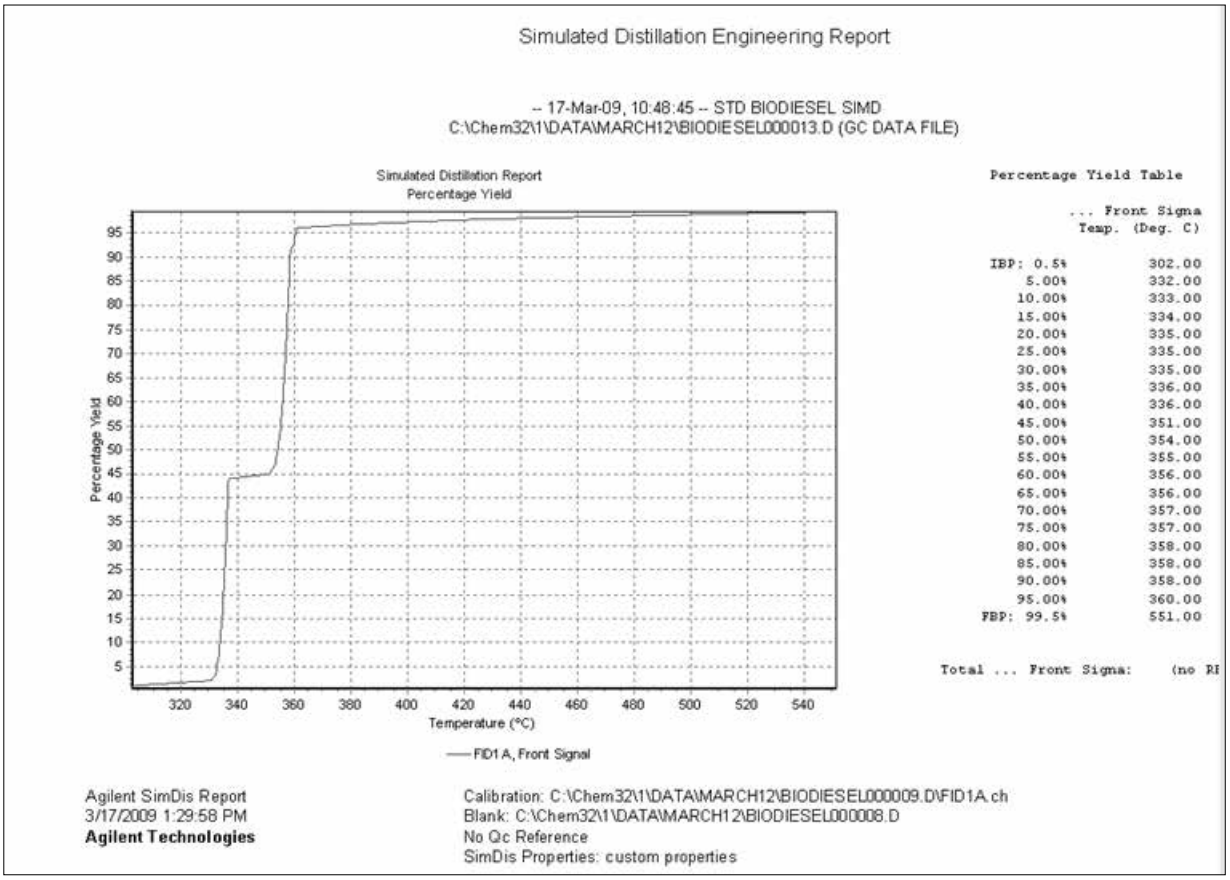


Figure 7. Boiling point distribution of B100 from producer B.

Summary

Simulated distillation is a powerful tool for characterization of biodiesel and biodiesel blends for a variety of starting oils. Besides determining the fatty acid methyl ester boiling point distribution, some information on the amount of un-reacted oil can be ascertained. The technique is also useful to determine authenticity and product consistency for quality control. The Agilent 7890A Series GC with the Agilent 7693A Automatic Liquid Sampler tower/tray system forms a complete analysis system from sample prep to boiling point distribution reporting using SimDis software integrated in the GC ChemStation.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
April 20, 2009
5990-3868EN

Agilent Technologies

Automated Preparation of Simulated Distillation Samples for ASTM Methods D2887, D7213, D7398 and D6352 using a Dual Tower 7693A and Tray System

Application Note

Hydrocarbon Processing

Authors

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

Abstract

A dual tower 7693A and tray system installed on the 7890A Gas Chromatograph was used for preparation of hydrocarbon calibration standards, solvent blanks, and actual petroleum samples for the purpose of analysis by simulated distillation (SimDis). The front tower is equipped with a 5 or 10 µL syringe while the back tower is equipped with a 250 or 500 µL syringe. A 150 sample tray with heater and mixer/barcode reader is also used. Procedures are described for sample preparation for ASTM D2887, D7213, D7398 and D6352. The Multimode Inlet, G3510, operated in a temperature programmed split mode was used for all samples.

Agilent Technologies

Introduction

Sample and calibration standard preparation for various simulated distillation methods is normally a manual process requiring dilution, mixing, and heating. Many procedures use volatile toxic solvents such as carbon disulfide. ASTM method D2887 commonly uses CS_2 for sample dilution while D6352 may use CS_2 or toluene for polywax calibration standard prepration. Sample heating is required for many of these procedures. Using the automation capabilities of the 7693A tower and tray system improves lab safety as well when working with CS_2 and other solvents by avoiding manual handling and uncontrolled heating of mixtures.

Experimental

For all experiments, the 7890A GC was equipped with dual 7693A towers and tray. The front tower used a standard 5 or 10 µl syringe and the rear tower was equipped with the optional large syringe carriage with either a 250 or 500 µL syringe. Sample prep procedures were done on the rear tower and sample injection occurred on the front tower. The 7890A was configured with the multimode inlet operated in temperature programmed split mode. Detection was with FID. In addition, two 7890A oven systems were used. The first configuration used the conventional air bath oven and the second used the Low Thermal Mass (LTM) system. Instrumental parameters for various configurations are listed in Table 1.

Table 1. 7890A SimDis parameters

LTM System for D2887	
LTM module	5M × 0.32 mm × 0.50 µm DB1, 5 inch format
7890A oven	300 °C isothermal
Inlet	Multimode, 270 °C (0 min) to 355 °C at 200 °C/min
Liner	Single taper with glass wool, 5183-4647
Split ratio	20:1
Pressure program (Inlet)	8 psi (0 min) – 42 psi (0.9 min) at 14 psi/min
LTM program	40 °C (0 sec) to 350 °C (30 sec) at 100 °C/min
Standard System for D2887	
Column	10M × 0.53 mm × 3.0 µm D2887
Oven	40 °C (0 min) to 350 °C (5 min) at 15 °C/min
Inlet	Multimode, G3510, 50 °C (0 min) to 330 °C (4 min) at 200 °C/min
Liner	Single taper with glass wool, 5183-4647
Split	4 to 1
Flow	3.2 psig at 40 °C, constant flow mode
7890A system for D7213 and D7398 (Polywax 500 calibration)	
LTM	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis 5-inch LTM format
Oven	LTM configuration, 7890A oven 325 °C isothermal, module 40 °C (0 min) to 400 °C (30 sec) at 50 °C/min
Inlet	Multimode, 270 °C (0 min) to 400 °C (3 min) at 300 °C/min
Split ratio	4 to 1 and 10 to 1
Pressure program	2.5 psi (0 min) to 9.5 psi (1.0 min) at 1 psi/min
Standard Air Bath Oven	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis
Oven program	40 °C (0 min) to 400 °C (5 min) at 15 °C/min
Inlet	Multimode, 210 °C (0 min) to 400 °C (10 min) at 200 °C/min
Split ratio	4 to 1
Flow	15 mL/min, constant flow mode
7890A system for D6352 (Polywax 655 calibration)	
Column	5M × 0.53 mm × 0.15 µm DB-HT SimDis
Oven program	40 °C (0 min) to 430 °C (5 min) at 15 °C/min
Inlet	Multimode, 250 °C (0 min) to 430 °C (hold until end of run) at 200 °C/min
Split ratio	4 to 1
Flow	16 mL/min, constant flow mode
7693A System	
Front tower	5 or 10 µL syringe, G4513A
Back tower	250 or 500 µL syringe, G4521A syringe carriage
Tray	150 sample capacity with heater and mixer/barcode reader, G4520A
Inlet	G3510 Multimode, CO_2 cooled
ChemStation	B.04.01
7890A firmware	A.01.10 or greater

Discussion

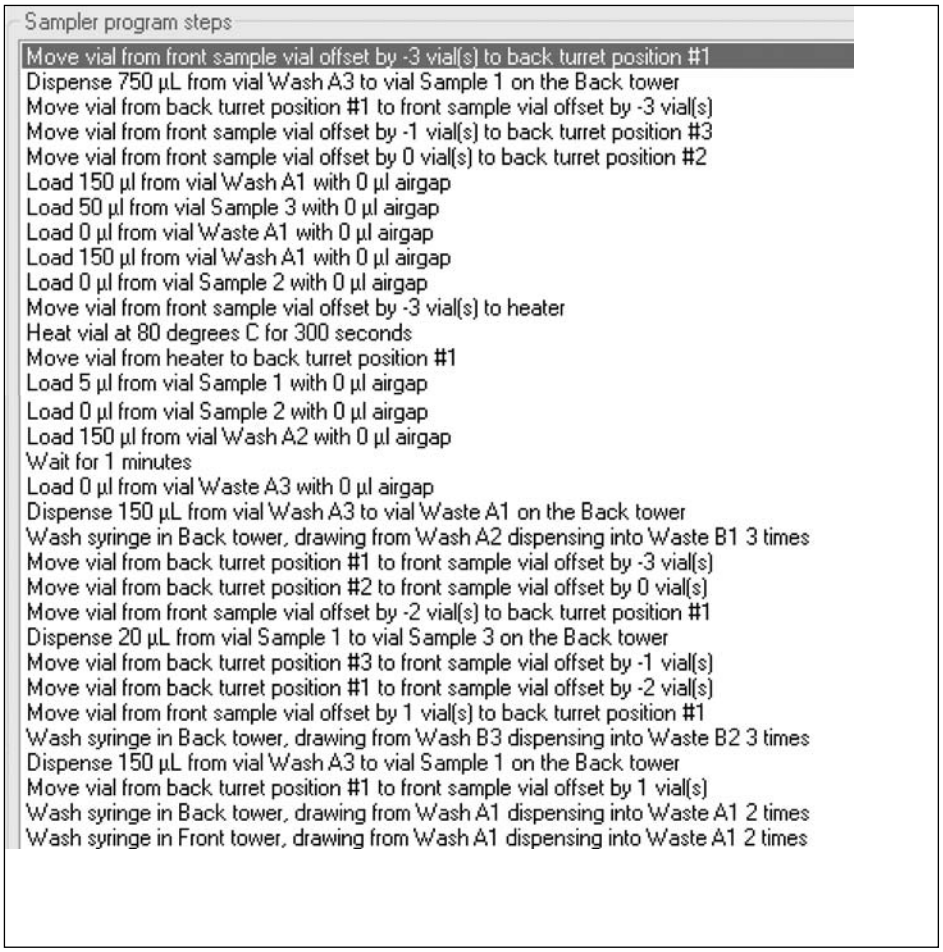
A typical sample preparation program for D2887 setup is shown in Table 2. This illustrates just one way to program preparation of the calibration standard, reference gas oil (RGO), and blank that are necessary to set up a system for routine analyses. The commands can be assembled in other ways to produce the same end result. The following vials and tray locations are used with this program.

Tray position 1	Calibration mix, 0.5 µL of C5 to C40, Agilent part number 5080-8716
Tray position 2	1 mL RGO, Agilent part number 5060-9086
Tray position 3 to 5	Empty vials with 100 µL inserts, Agilent part number 5188-6592

When the procedure is complete, vial 3 will be the prepared RGO for injection, vial 4 will be the prepared calibration mix for injection, and vial 5 will be a CS_2 blank. Next, a three-line sequence is set up that starts with vial 4 (calibration mix). Vial 4 is run with the ChemStation method set with this procedure active, then vial 3 (RGO) and vial 5 (CS2 blank) are run using the same method but with the prep procedure inactive (unchecked in ChemStation's 7890A Injector Program pane under edit 7890A Parameters parameters menu because these samples are already prepared from the method in the first line of the sequence table). For all three samples, the core ChemStation method performs a sample preheat at 80 °C and a sample mix at 500 rpm for 20 seconds before injection. Lastly, the calibration, prepared RGO, and blank vials are fitted with 100 µL inserts so that the solvent amounts used for the procedure are minimized. Please note that when these inserts are used, mixing should be limited to speeds of approximately 500 rpm to avoid "spilling" liquid over the top of the insert into the bottom of the 2-mL vial.

Preparation of polywax standards for the higher temperature SimDis method is always challenging due to their low solubility. Solvents such as CS_2 and toluene are commonly used, and

Table 2. Sample prep procedure for D2887



heating of the solvent/polywax vial is required just prior to injection. This entire procedure can be automated with the 7693A tower and tray system. The basic procedure for Polywax 500 is as follows:

- Place approximately 80–100 mg of Polywax 500 in a 2-mL vial and seal
- Add 125 µL of a C20/toluene solution to the polywax vial
- Add 1.25 mL of toluene to the polywax-C20 vial
- Mix the vial
- Heat the vial at 80 °C for 4 min
- Return to tray
- Heat one final time (3 min. typical) just prior to injection

Table 3 shows the basic prep procedure using a dual tower/tray system automating the steps shown above. The only manual step is adding the solid polywax to Vial 1. Vial 2 contains a C20/toluene mixture. Preparation of this sample could be automated as well. This procedure is applicable to D7213 SimDis and D7398 (Boiling Range Distribution of Fatty Acid Methyl Esters).

A resulting chromatogram from injection of the prepared Polywax 500 vial (vial 1) is shown in Figure 1. A symmetric distribution of the polywax fragments with good resolution to C80 can be seen.

Table 3. Preparation of Polywax 500

Sampler program steps
Wash syringe in Back tower, drawing from Wash A1 dispensing into Waste A1 2 times
Move vial from tray vial #1 to back turret position #1
Move vial from tray vial #2 to back turret position #2
Dispense 1000 µL from vial Wash A2 to vial Sample 1 on the Back tower
Dispense 5 µL from vial Sample 2 to vial Sample 1 on the Back tower
Move vial from back turret position #1 to mixer
Move vial from back turret position #2 to tray vial #2
Mix at 2000 rpm 2 times for 10 seconds
Move vial from mixer to heater
Heat vial at 80 degrees C for 240 seconds
Move vial from heater to tray vial #1
Wash syringe in Back tower, drawing from Wash A2 dispensing into Waste B1 3 times

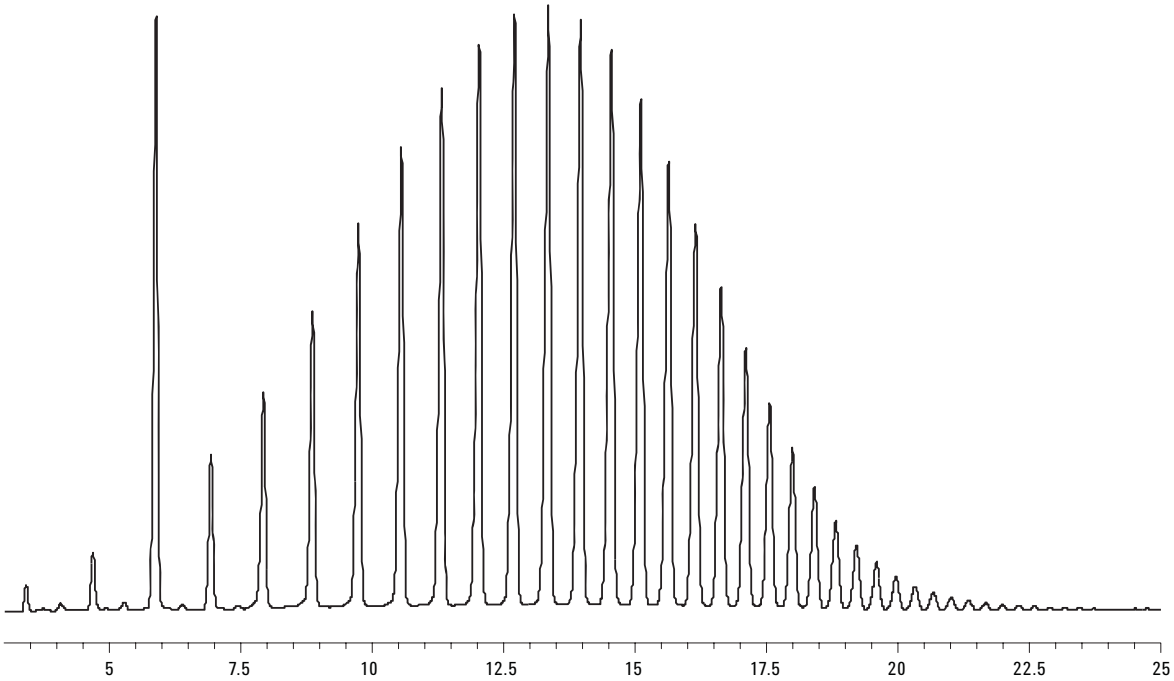


Figure 1. Polywax 500 with C20 marker. Multimode inlet with 7890A oven.

The preparation program for Polywax 655 is essentially the same as shown above for Polywax 500 except that heating is extended to 6 minutes, for better dissolution. Then just prior to injection, the prepared vial is heated for another 3 minutes. In the chromatogram shown below in Figure 2, a small amount (5 µL) of C5-C18 mix was added to the Polywax 655/ toluene solution as part of the automated procedure.

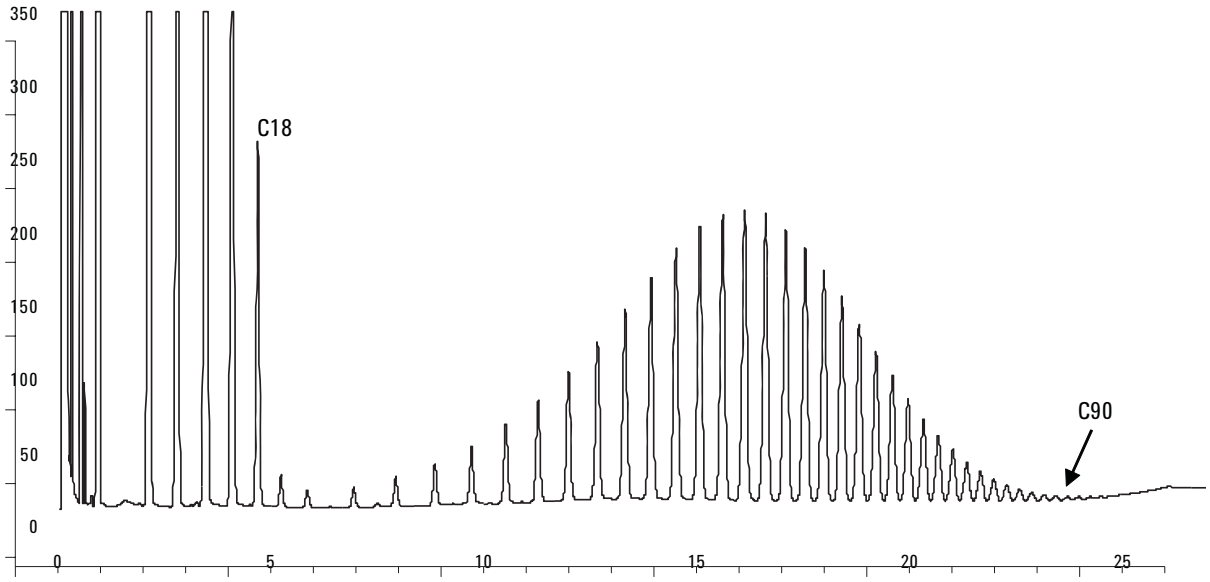


Figure 2. Chromatogram of Polywax 655.

The chromatogram was produced with the multimode inlet used in temperature-programmed split mode. Good definition of polyethylene fragmented to C110 is shown in Figure 3 where the last 5 minutes of the chromatogram are enlarged to show detail. Producing this detail out to C110 is extremely difficult for most chromatographic systems. The 7890A/7693A system produces excellent results with this sample.

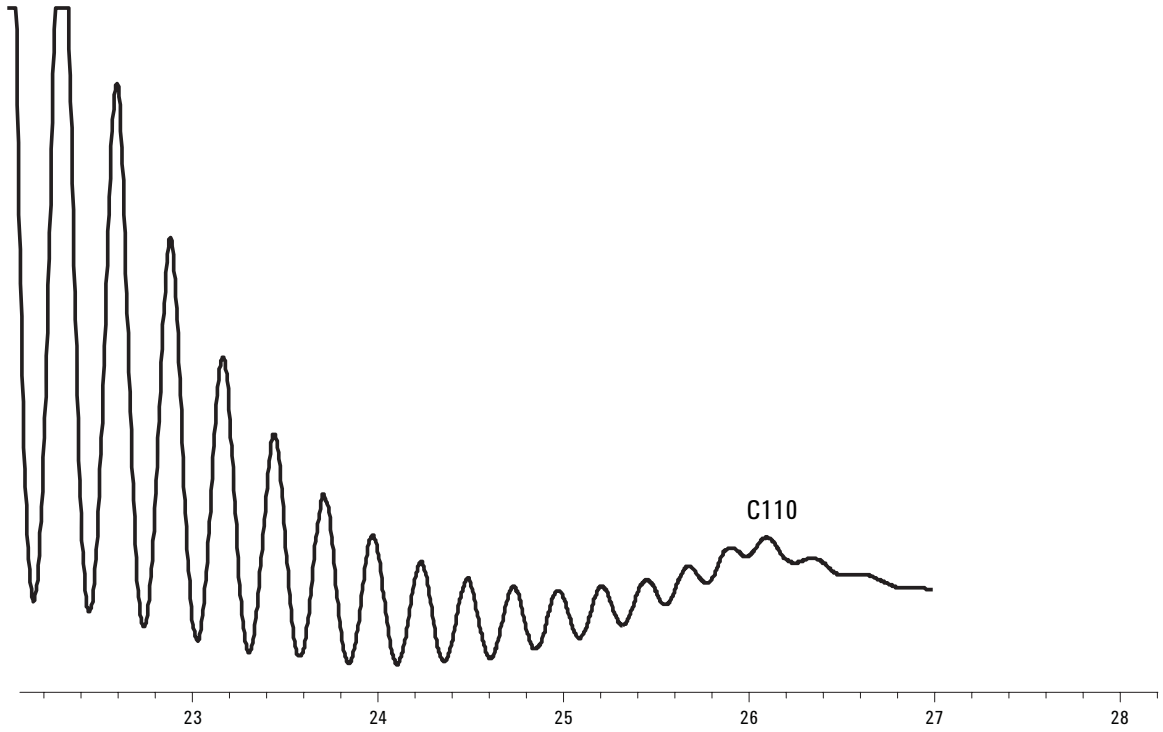


Figure 3. Polywax 655 to C110. Multimode inlet program: 150 °C (0 min) to 430 °C (hold until end of run) at 200 °C/min. 7890A oven: 40 °C (0 min) to 430 °C (5 min) at 15 °C/min. 3 µL injection. Solvent is toluene.

Reproducibility of the sample preparation steps is excellent as seen in Figure 4, for the dilution of a heavy vacuum gas oil sample (HVGO). The program steps that were followed to produce these chromatograms are given in Table 4. The back tower equipped with a 500-µL syringe, was used for sample preparation and the front tower with a 5-µL syringe was used for sample injection. Carbon disulfide was used for sample dilution. This program assumes a sequence is run using vial 2. Vial 1 is the stock HVGO sample that is first prepared by adding 0.5 g of the oil to a 2-mL vial. This material is extremely viscous and cannot be drawn into a syringe. Therefore the program performs a fully automated two-stage dilution prior to injection.

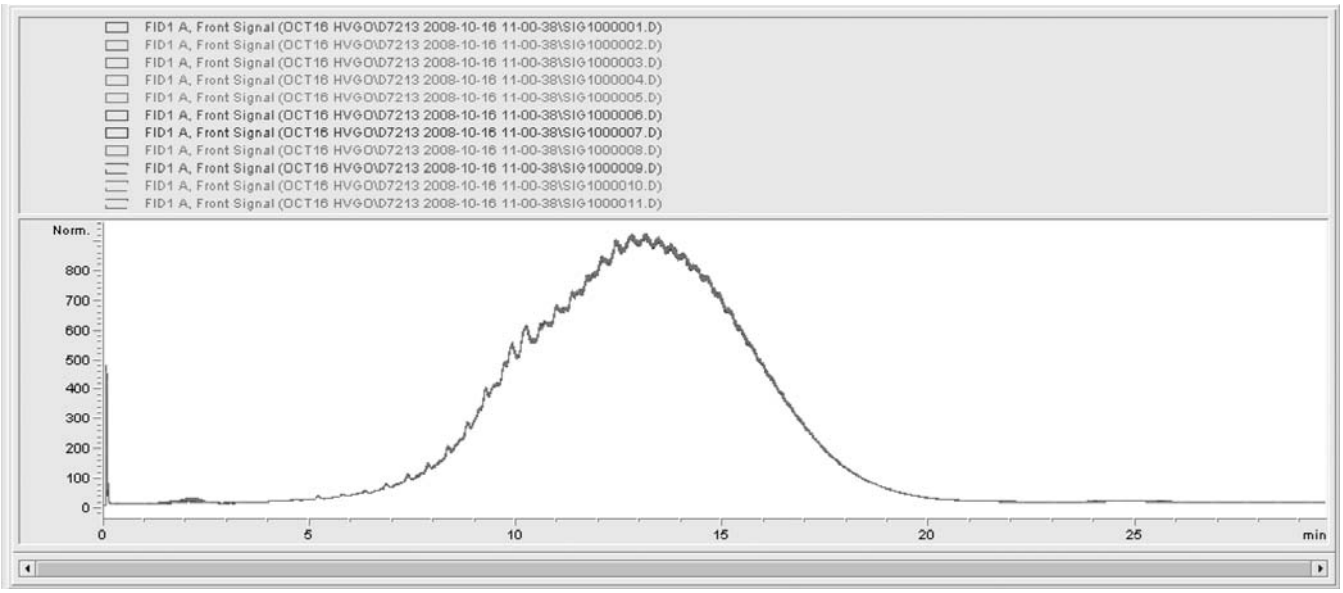


Figure 4. Overlay of 11 runs of HVGO, each prepared using 7693A towers and tray.

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

Sampler program steps
Move vial from front sample vial offset by -1 vial(s) to back turret position #1
Dispense 600 µL from vial Wash A3 to vial Sample 1 on the Back tower
Move vial from back turret position #1 to heater
Move vial from front sample vial offset by 0 vial(s) to back turret position #1
Heat vial at 60 degrees C for 180 seconds
Mix at 3000 rpm 3 times for 20 seconds
Move vial from heater to back turret position #2
Dispense 250 µL from vial Sample 2 to vial Sample 1 on the Back tower
Wash syringe in Back tower, drawing from Wash A3 dispensing into Waste A1 3 times
Dispense 1000 µL from vial Wash A1 to vial Sample 1 on the Back tower
Move vial from back turret position #2 to front sample vial offset by -1 vial(s)
Move vial from back turret position #1 to mixer
Mix at 3000 rpm 4 times for 20 seconds
Move vial from mixer to front sample vial offset by 0 vial(s)

Conclusions

Difficult sample preparation procedures that are commonly used for petroleum and fuel samples can be easily automated with the 7693A tower and tray system for the 7890A and the 6890A. The system is particularly well suited for preparation of polywax calibration samples that are used for higher temperature methods. Tasks such as mixing, solid dissolution, dilution, heating, and internal standard addition are easily accomplished.

Chromatographic performance is enhanced through use of the multimode inlet. Using standard split injection liners, good sample capacity without carryover and with minimal discrimination of wide boiling samples is seen. The inlet was used in the temperature-programmed split mode for this work. Cryo cooling was not used, however, cryo can be used optionally to shorten inlet cool down between runs if desired.

For samples that fall within the boiling point range of D2887, D7213, and D7398, the Low Thermal Mass (LTM) system can be used to shorten typical analysis cycle times by 30 to 50% [1]. The high temperature method D6352 requires the standard 7890A oven.

The sample prep procedures listed here represent just one way of accomplishing a given task. Given the commands available with the system, there are many variants that will lead to the same end result.

Reference

1. C. Wang, R. Firor, and P. Tripp, "Fast Hydrocarbon and Sulfur Simulated Distillation Using the Agilent Low Thermal Mass (LTM) System on the 7890A GC and 355 Sulfur Chemiluminescence Detector," November 2008, Agilent Technologies publication 5990-3174EN.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
March 26, 2009
5990-3778EN

Agilent Technologies

POLYMERS

Simplify QA/QC and prevent large-scale losses using FTIR spectroscopy

The right quality assurance (QA) and process control tools are critical when you are manufacturing commodity polymers such as polyethylene, polypropylene, and polyvinyl chloride in large volumes. That's because even "minor" problems can cost thousands of dollars per hour in lost revenue due to price concessions for off-specification (or inferior) product.

Infrared spectroscopy is an ideal QA and process-control tool because it is fast, requires minimal sample preparation, and can be automated for greater efficiency. It also generates the qualitative and quantitative data you need to solve problems quickly and minimize losses.

Agilent's full line of infrared spectrometers – including the award-winning **Cary 630 FTIR** – are designed to meet the unique demands of polymer industry applications. Two specialized accessories are also available for labs that switch between ASTM 7371 and EN 14078 methods for measuring biodiesel in diesel fuel:

- **The Agilent 5 Bounce ZnSe ATR** provides the longer effective path length and improved detection limits needed for ASTM 7371
- **Agilent's proprietary TumbIIR** replaces cumbersome IR cells and, when set to 200 µm, complies with EN 14078

Both easily attach to the Cary 630 FTIR and run on MicroLab software that automatically confirms that the accessory and method match before allowing the sample run to begin.

Gel Permeation Chromatography (GPC) and Size Exclusion Chromatography (SEC) can also be used to optimize the properties of polyolefin resins, and to investigate production-related catalyst issues.

Back to table of contents ▶

Determination of percent polyethylene in polyethylene/polypropylene blends using cast film FTIR techniques

Application note

Energy and chemicals; Materials testing

Author

Frank Higgins

Agilent Technologies
Danbury, CT, USA

Introduction

Polyethylene (PE) is the most common group of thermoplastic polymers due to its low cost and versatile physical properties. PE is blended with polypropylene (PP) to improve physical properties, such as low temperature impact performance. The composition of these blends is important with regard to performance, and the correct mixing of the pure homopolymers (PE and PP) can eliminate the need for costly synthesis of new block copolymers. Knowing the composition of these blends is also critical to the recycling and regeneration of polyolefins in waste and scraps.

In this application note, we demonstrate a method for rapidly determining the PE:PP ratio in blends using the Agilent Cary 630 FTIR spectrometer.

Experimental

Calibration standards of PE/PP blends in the 35–85% PE range were prepared by dissolving different ratios of the polymers in hot (110–120 °C) tetrachloroethylene (perchloroethylene), making a roughly 3% polymer to solvent solution.

The dissolved polymer mixture was then used to cast films on either PTFE coupons or KBr plates for analysis by FTIR. In the case of KBr plates, approximately 0.3 mL of the polymer solution was evenly placed on the plate. The plate was then placed on a ~70 °C hotplate until all the solvent evaporated. The coated KBr plate was allowed to cool and analysis was carried out using the Cary 630 FTIR spectrometer, equipped with a transmission sampling accessory. The ratios of the methyl IR bands (mainly PP) and the methylene CH_2 bands (both PE and PP) were used to accurately measure the weight % PE in the blend. The thickness of the film was controlled to ensure that the strongest absorbance in the 1500–1200 cm^{-1} region did not exceed 1.2 absorbance units (AU) and remained in the preferable 0.3–1.0 AU range (Figure 1, Y-axis). Infrared spectra recorded on these salt plate cast films consisted of 74 co-added interferograms measured at 4 cm^{-1} resolution. Total measurement time was 30 seconds.

We developed a second, novel procedure for measuring the PE:PP blend ratio. This procedure used the same calibration solutions, but rather than salt plates, the solutions were applied to a smooth piece of PTFE. After drying in an oven at 70–80 °C, the resulting 20–50 µm thick films were easily peeled off the still warm PTFE. These self-supporting polymer cast films were then analyzed by the Cary 630 FTIR equipped with the DialPath (or TumblIR) accessory using the 100 micron pathlength cell. The polymer films easily slide between the cell windows, allowing for convenient repositioning and analysis of multiple areas of the film. This makes finding the optimal thickness (0.3–1 AU) faster, since larger pieces of polymer film can be sampled in many locations. Infrared spectra recorded of these self-supporting films consisted of 74 co-added interferograms measured at 4 cm^{-1} resolution. Total measurement time was 30 seconds.

The new DialPath method can be used on the Agilent 4500 and 5500 FTIR spectrometers as well as the Agilent Cary 630 FTIR. The 4500 is a portable, battery operated FTIR spectrometer available with the DialPath technology. The 5500 is a dedicated, benchtop FTIR spectrometer also available with the DialPath sample interface. These instruments have the same reliable performance and patented interferometer technology as the Cary 630 FTIR, but allow for onsite and near line analysis.

A calibrated method was developed and added to the Cary 630 FTIR methods library so that future unknown samples can be analyzed. The method enables an automatic calculation of the PE:PP ratio, and the numerical value and spectra of the unknown is automatically displayed and/or printed.

Results and discussion: PE/PP blend cast film FTIR calibration

The salt plate cast film FTIR procedure is consistent with ASTM D3900-05a (Rubber-Determination of Ethylene Units in Ethylene-Propylene Copolymers (EPM) and in Ethylene-Propylene-Diene Terpolymers (EPDM) by Infrared Spectrometry). To correct for film thickness, the absorbance of a variable component peak (in this case, PP) is measured as a ratio to another matrix peak (in this case, PE). Both the novel PTFE and the original salt plate cast film method use the same peak height ratio of the 1376 cm^{-1} to the 1462 cm^{-1} bands (Figure 1) to determine composition. The new cast film method, based on the DialPath accessory linear regression calibration plot yields R^2=1.000 (Figure 2) and the salt plate cast film method yields the identical calibration and R^2 value.

Fringing patterns are sometimes observed when smooth polymer films are measured in the mid infrared region. Fringing appears as a baseline sine wave pattern in the spectra and arises from internal reflection of the IR light inside smooth polymer films. The techniques described in this application note do not produce fringing in the areas of interest by either the salt plate or the DialPath transmission methods. In the latter case, the concave/convex matching cell window design of the DialPath and TumblIR minimizes fringing, while providing an easy to open and clean optical cell with precise pathlength reproducibility.

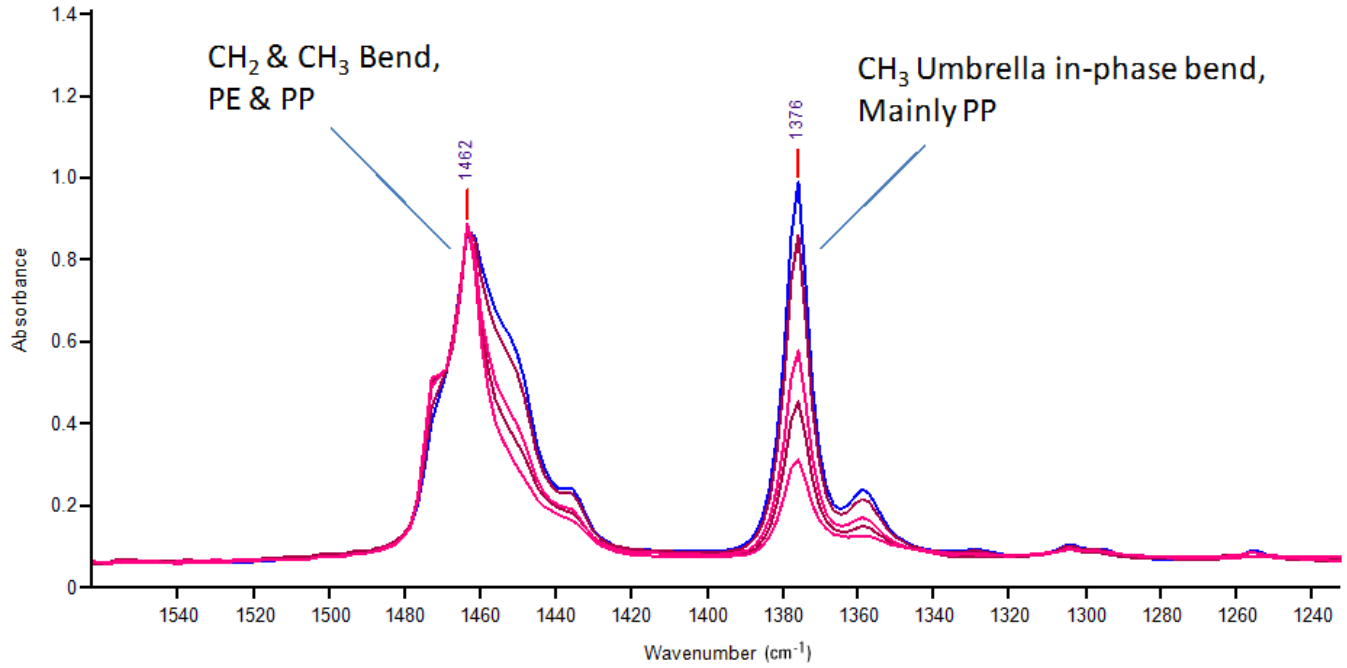


Figure 1. The overlaid aliphatic bend region of the FTIR PE/PP blend calibration spectra. The quantitative method for %PE uses a ratio of the methyl 1376 cm^{-1} (mainly PP) to the 1462 cm^{-1} (methyl and methylene bend) band.

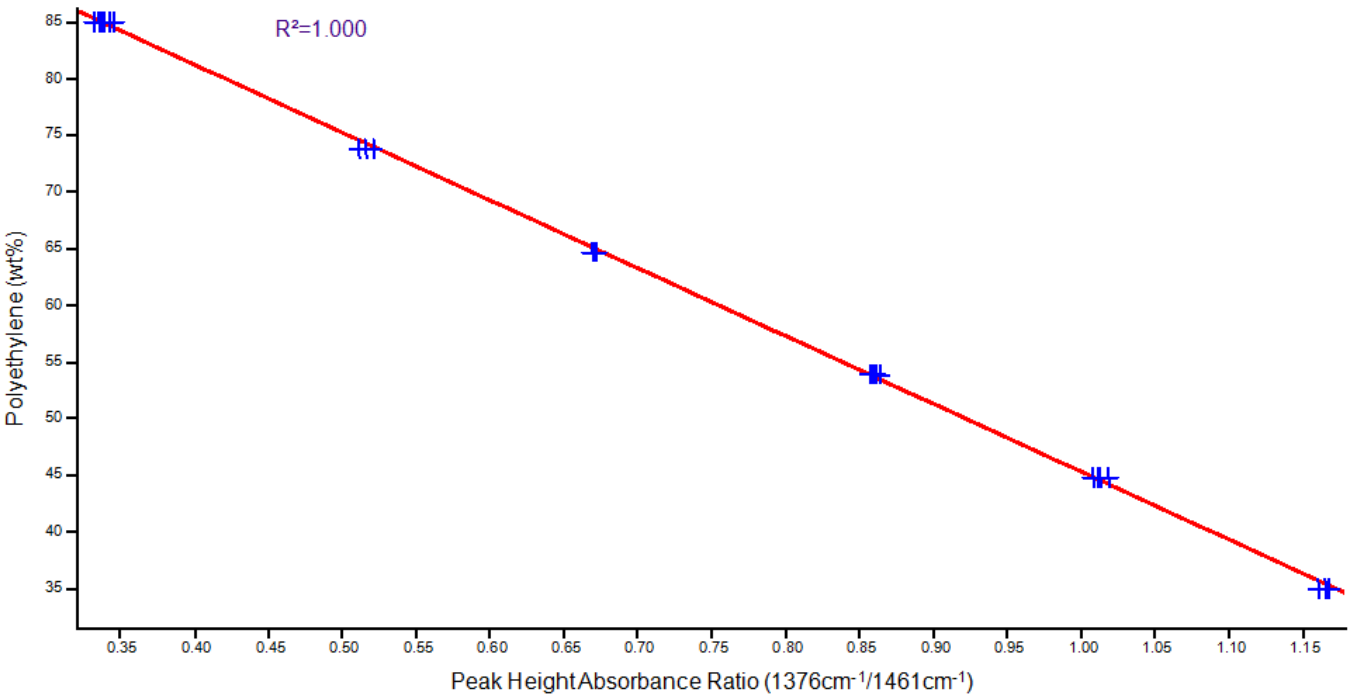


Figure 2. The calibration plot of PE/PP blends prepared as cast films, and analyzed using the TumbIIR or DialPath on the Agilent Cary 630 FTIR. The same calibration with traditional transmission compartment (film cast in salt plate) yields similar calibration results. The calibration uses the ratio of the PP band at 1376 cm^{-1} to that of the 1462 cm^{-1} band in both PE and PP.

Conclusions

The FTIR analysis of 35–85% PE concentrations in PE/PP blends is now easier than ever using the versatile Agilent Cary 630 FTIR spectrometer. An excellent calibration was developed using the same cast film technique and IR peaks as the ASTM D3900 PE/PP copolymer method. The Cary 630 FTIR standard transmission compartment is used for the measurement of these cast polymer films on salt plates.

A second, novel method has been developed using the Cary 630 FTIR DialPath transmission accessory, which is easier and more versatile, because larger pieces of self-supporting films can be analyzed in a short amount of time. The polymer films can be repositioned and measured in multiple regions without opening the cell, thus allowing the analyst to find the ideal film thickness for the measurement.

Both methods yielded the same excellent calibration and identical R^2 value. The PE:PP calibration is now part of a method that has been added to the Cary 630 FTIR software, allowing the polymer ratio in unknown samples to be instantly calculated and displayed.

www.agilent.com/chem

Published January 19, 2012
Publication number: 5990-9785EN

Agilent Technologies

A new approach to sample preparation free micro ATR FTIR chemical imaging of polymer laminates

Application Note

Materials Testing & Research

Author

Dr. Mustafa Kansiz

Agilent Technologies,
10 Mead Rd, Yarnton,
Oxfordshire, OX5 1QU, UK

Abstract

Micro ATR chemical imaging of polymers and in particular polymer laminates typically requires significant application of pressure to ensure good contact between the ATR crystal and the sample. To ensure that such thin samples can withstand the pressure without buckling, elaborate sample preparation procedures are often required to support cross-sectioned materials: embedding of sample in resin, cutting the resin and polishing the contact surface. Such procedures are tedious, require overnight resin curing and carry the added risk of cross-contamination. Presented here is a novel method of ultralow pressure micro ATR FTIR chemical imaging that removes the need for any structural support. This allows samples to be measured "as-is" using direct contact with the ATR crystal. This unique capability is made possible through the use of Agilent's "Live ATR imaging" technique which provides enhanced chemical contrast, and enables the exact moment of contact between the sample and ATR crystal to be determined and provides a visual measure of the quality of contact. Adhesive layers as thin as a few microns can be clearly observed in 50-micron thick polymer laminates without sample preparation.

Introduction

What are polymer laminates and what are they used for?

Polymer laminates are film structures consisting of two or more layers adhered together to make a structure. The polymeric materials forming these laminates have varying thickness—from a few microns to tens of microns. This can influence a variety of properties, such as chemical, mechanical and barrier (e.g., impervious to oxygen and/or moisture) properties.

Agilent Technologies

To construct these materials, adhesive (tie) layers are often required between two adjacent but chemical incompatible layers. Typically these incompatibilities are between materials with differing polarities, such as nylon and polyethylene.

The adhesives typically have intermediate polarity or contain functional groups with an affinity to both polar and non-polar layers and hence act as good binding material. Such adhesive layers in laminates can be very thin, e.g., between 2 to 10 microns.

Polymer laminates can range in complexity and thickness from those containing only two layers to more than 10 layers (not including adhesive layers). With total cross-sectional thicknesses ranging from <50 microns to >200 microns, polymer laminates are used in a variety of packaging applications, which are employed in industries such as food and pharmaceuticals.

What are the analytical challenges/requirements for polymer laminates?

With ever increasing manufacturing sophistication enabling more complex and thinner laminate structures to be produced, the analytical challenges to ensure good product quality control, troubleshooting or the reverse engineering of competitive products are also increasing in complexity.

The analytical tools available to analyze such laminates are wide and varied and include a range of optical microscopy techniques, thermal techniques (such as differential scanning calorimetry) and various spectroscopic techniques.

In particular, Fourier Transform Infrared (FTIR) microscopy has proven most useful for the analysis of polymer laminates. This has resulted from the core application of FTIR spectroscopy in the identification and characterization of polymers, combined with the ability to obtain this information from small areas.

When applied to polymer laminate analysis, FTIR microscopy is typically performed in transmission mode and requires that the total sampled thickness be within a certain limit. For polymeric materials, this is typically 10–20 microns. Preparing thinly sliced polymer and polymer laminate materials at a thickness of 10–20 microns presents some challenges. Typically, dedicated (and often expensive) specialized cutting devices such as microtomes are required. Even then, the cut samples are often difficult to handle due to curling or difficulties with static stick. To minimize these effects, samples can be embedded in resin before cutting and microtomed together within the resin support (Figure1). This unfortunately adds another material with a complex IR spectrum to the sample. Once cut, if the sample is flat, it can be placed in a sandwich between infrared transparent windows and sampled in transmission mode. However, because of internal reflections between the front and back surfaces of the sample, “fringing effects” can commonly be observed. This results in a sinusoidal baseline during such measurements.

With these issues and sampling preparation steps aside, transmission FTIR microscopy is a relatively simple technique to obtain spectra from small areas. It does however suffer from one major limitation: spatial resolution is relatively poor, especially when compared to optical microscopy techniques. Typical spatial resolution limits for transmission mode FTIR microscopy are about 10–15 microns.

In comparison to transmission mode, the use of micro attenuated total reflectance (ATR) as the mode of analysis removes the requirement for samples to be a certain thickness, so samples no longer need to be thinly cut. However, as ATR requires intimate contact with the samples, there are still some important sample preparation requirements. Primarily, the sample must be flat and smooth to ensure that there is full and complete contact across the ATR measurement’s field of view. Additionally, and of paramount importance to the detection of ultrathin layers, micro ATR FTIR

microscopy provides for a factor of four spatial resolution enhancement over transmission mode.

To ensure complete and intimate contact, a significant amount of pressure must be applied between the sample and ATR crystal. Many micro ATR imaging systems rely on indirect methods of ensuring good contact, by using coarse pressure sensors, often with preset pressure levels.

The inability to directly monitor the exact moment and quality of contact in most micro ATR imaging systems is also another factor that requires the use of higher pressures to ensure good contact. For naturally hard materials, the pressures needed to ensure a good contact between the ATR and surface is typically not an issue. However, given samples may have cross-sectional thicknesses of only 50–200 microns, even very slight pressures will cause an unsupported polymer laminate to buckle or deform in a way that prevents good contact.

Therefore, to avoid buckling or other structural distortions of delicate and thin samples under applied ATR pressure, it is mandatory to provide some degree of support. This is most commonly achieved by resin embedding of the sample, followed by cutting and polishing of the surface (Figure 1).

The process of resin embedding is tedious and time consuming (>12 hours), typically consisting of the following steps:

1. Cut a small piece of sample and place it vertically in a holding clamp.
2. Place sample and clamp into a mold and pour in resin to fully cover sample.
3. Allow resin to cure, typically overnight, and then remove the resin-embedded sample from mold.
4. Cut the top surface of resin, so as to expose a cross section of the sample.
5. Polish the cut surface with successively finer and finer lapping paper (from 30 microns to 1 micron).

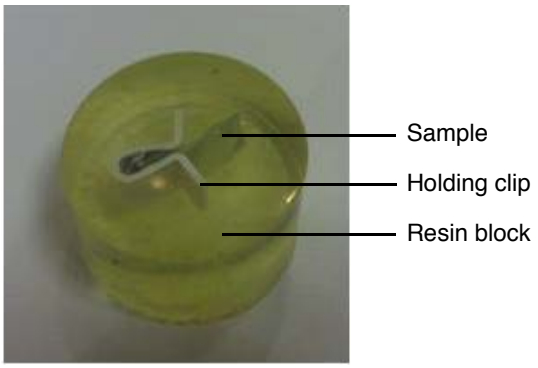


Figure 1. An example of a polymer film, held by a clip and embedded in a resin block

Cutting and polishing also introduces the risk that resin and polishing material may contaminate the sample or complicate the image and spectral interpretation.

Once prepared, resin-embedded samples are brought into contact with the micro ATR and pressure is applied. Often, the levels of pressure applied—even at lower settings—are enough to produce indentations at the surface of the samples, potentially preventing the subsequent analysis of the sample with other analytical techniques. This technique is then potentially destructive.

A new approach to *"pressure free"* micro ATR imaging

Agilent Technologies has developed a radically new approach that removes the need for resin embedding or any other sample preparation. This enables delicate and thin samples to be measured "as-is". The new approach hinges upon the fact that the infrared detector in an Agilent FTIR imaging system is a focal plane array (FPA*) and so affords simultaneous two-dimensional (2-D) data collection. And, most importantly and uniquely, it utilizes the "Live ATR imaging" feature with enhanced chemical contrast to ensure that the minimum pressure necessary for good contact is applied. This results in a non-destructive measurement—a remarkable capability.

Unlike linear array IR detectors, which must be scanned across an area to generate a 2-D image, FPAs provide instantaneous "real-time" imaging of the sample's surface, as it is in contact with the ATR. Such real-time imaging permits a visual assessment of the quality of sample contact before any data collection.

However, having a 2-D FPA alone does not provide for enough contrast to determine the moment of sample contact with the ATR. To overcome these issues Agilent Technologies has recently developed a unique "Live ATR imaging" mode, which significantly enhances the chemical contrast of the real-time FPA image, so the exact moment of sample contact can be visualized and contact monitored as the pressure is increased.

This mode provides for direct and real-time monitoring of the quality of contact (i.e., has the sample made complete contact across the entire field of view), which allows for extremely low levels of pressure to be applied. And it is this extremely low level of pressure that now allows for delicate and thin samples to be mounted, cross-sectioned end on, without any need for sample support using resin.

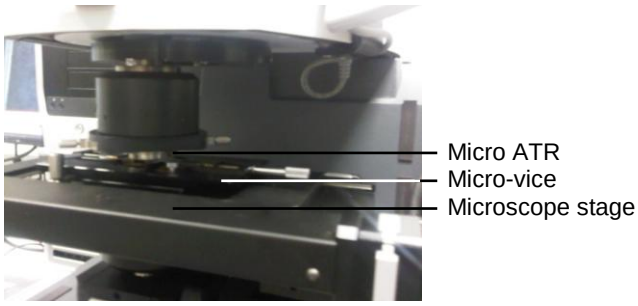
Sample measurement with "Live ATR imaging"

In five simple steps which only take only a few minutes (Figure 2), a sample of polymer laminate (i.e., a sausage wrapper) can be prepared for measurement using "Live ATR imaging"—removing the need to spend hours embedding, cutting, and polishing!

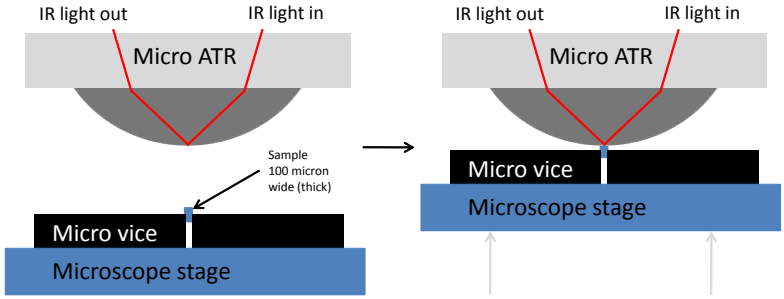
Step 1. Cut a small piece of sample.

Step 2. Place sample into micro-vice.

Step 3. Cross-section sample with razor.



Step 4. Place micro-vice onto microscope stage.



Step 5. Raise stage to make contact and then collect data.

Figure 2. Easy five-step process—from raw sample to data collection—allows sample measurement of polymer laminates to be achieved in minutes using "Live ATR imaging" with enhanced chemical contrast. Note: Micro ATR and sample are drawn to scale

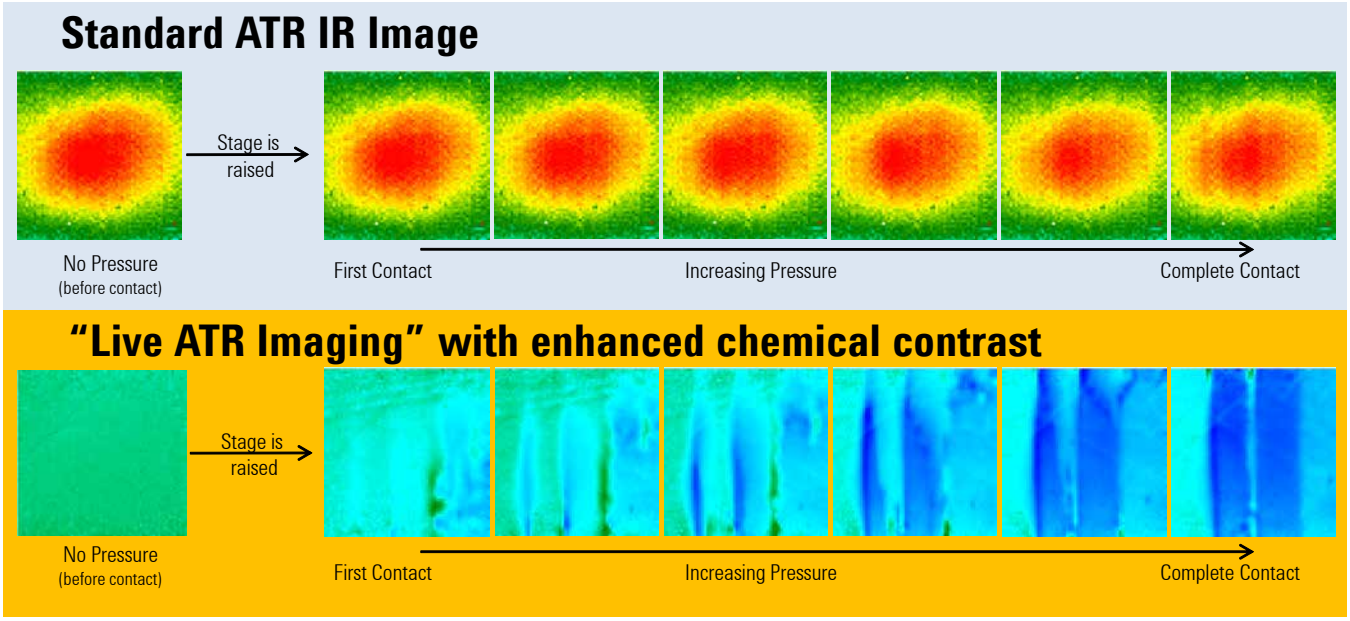


Figure 3. Comparison of a standard ATR IR image and Agilent's "Live ATR imaging" with enhanced chemical contrast—clearly showing the latter can detect first contact of the ATR crystal with the sample and that contact quality can be monitored real-time as the pressure is increased and before any data collection

Figure 3 shows a side-by-side comparison of Agilent's unique "Live ATR imaging" with enhanced chemical contrast and a standard ATR IR image.

Reviewing the upper series of images, the similarity of all the standard ATR IR images makes it impossible to determine when the ATR crystal makes contact with the sample's surface or make any reasonable assessment of the quality of the contact as the pressure being applied increases.

Whereas, as seen in the lower series of images, Agilent's unique "Live ATR imaging" with enhanced chemical contrast enables real-time monitoring of the sample contact as the sample is being raised and pushed up against the germanium crystal of the Micro ATR. The real-time monitoring allows for a near "pressure free" contact to be made between the sample's surface and the Micro ATR, this means unsupported cross-sections of ultrathin polymer laminates can be measured directly—even very thin samples of less than 50 microns—without the need for being embedded in resin!

Results

To further demonstrate the capabilities of "Live ATR imaging", a polymer laminate sample was obtained from the plastic wrapper of a sausage (~55 microns total thickness).

The results below were collected using the following conditions:

FTIR Spectrometer	Agilent Cary 670 FTIR
FTIR Microscope	Agilent Cary 620 FTIR
Focal Plane Array*	64 × 64 MCT
Spectral Resolution	4 cm^{-1}
Number of Scans	64 (2 mins)
Spatial Resolution	1.1 microns (pixel size)
Collection mode	Micro ATR (Ge)
Sample Type:	Sausage wrapper

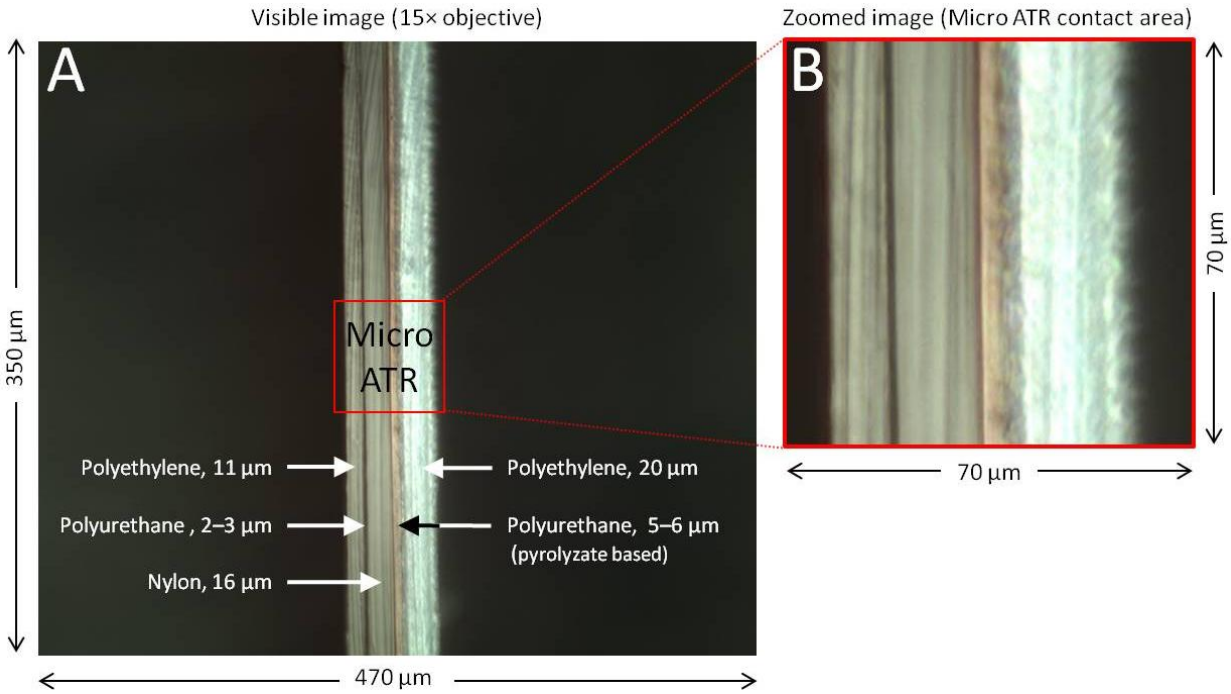


Figure 4. Optical images: A—the full field of view visible through microscope, annotated with the chemical composition and approximate thickness of the various layers in the sample; and B—zoomed image corresponding to the contact area of the Micro ATR

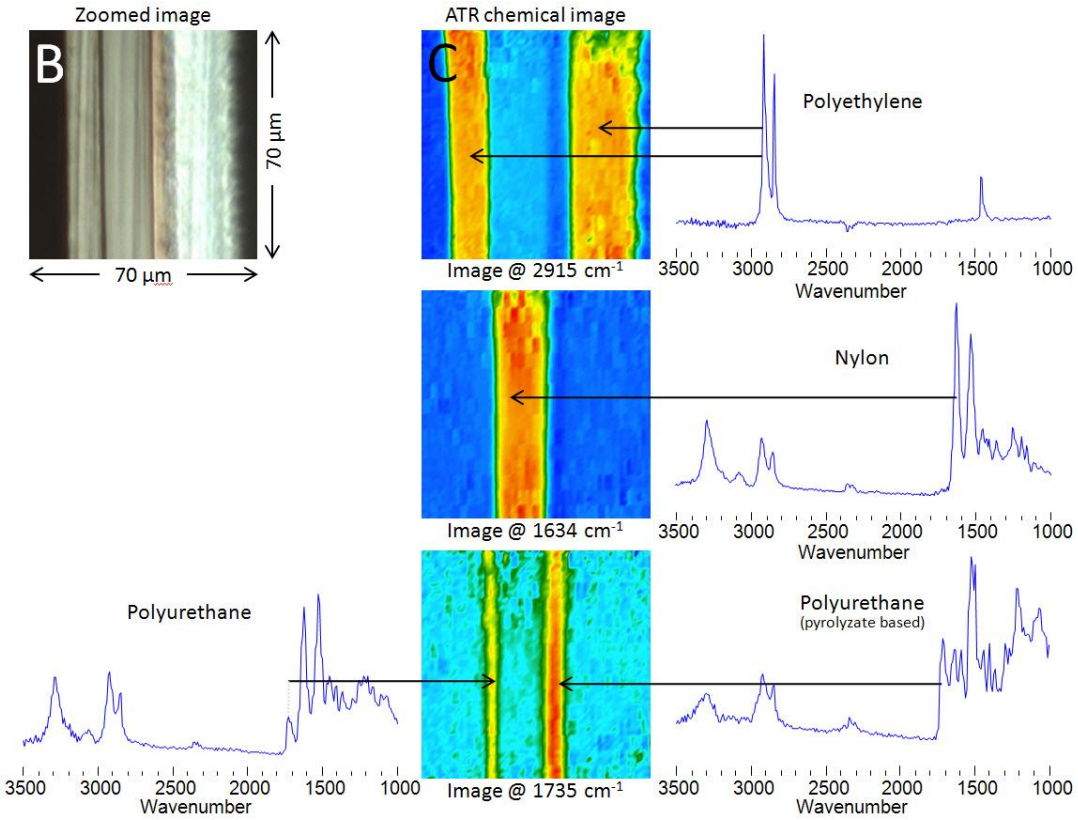


Figure 5. Identifying layers: B—as per Figure 4, above; and C–three chemical images created with different wavenumbers to highlight the main layers and tie layers with corresponding representative spectra as indicated by the arrows. Note: All spectra are shown in absorbance units, with axes omitted for clarity

A visual inspection of the sample using the standard binocular or internal visible camera revealed the sample to be a polymer film containing three main layers with two adhesive layers (Figure 4).

A summary of the results is presented in Figure 5. This shows how the three main layers are clearly identified: a 16-micron thick layer of nylon sandwiched between two layers of polyethylene, 11 and 20 microns in thickness.

However, as demonstrated, the power of Micro ATR chemical imaging with an Agilent FPA detector is in its ability to measure layers as thin as a few microns. Two tie layers were clearly identified and easily determined as being composed of subtly different polyurethane adhesives. The thinner of the two polyurethane layers was only 2–3 microns across and the pyrolyzate-based layer was thicker at 5–6 microns. The measurement of both these layers would be impossible with any other technique other than micro ATR chemical imaging on the Agilent Cary 620 FTIR chemical imaging system.

Summary

There are two clear benefits to analyzing polymeric laminates using Agilent's Cary 620 FTIR chemical imaging system:

1. Analyze ultra-thin samples without resin embedding

Through the use of Agilent's unique "Live ATR imaging", ultra-thin films of 50 microns or less can be measured as-is with Micro ATR chemical imaging.This avoids the need for any of the traditional and complicated resin embedding requirements. As such, instead of waiting hours for resin to cure and then spending time cutting and then polishing the surface, multiple samples or multiple locations on one sample can be measured in a few minutes.

2. Unrivalled spatial resolution

In combination with the use of a FPA detector*, Agilent's unique Micro ATR design provides for a pixel size of 1.1 microns that allows ultra-thin adhesive layers as narrow as two microns to be identified. This level of spatial resolution provides unrivalled levels of detail and chemical information to assist in the most complicated and difficult sample measurements.

*This product is regulated by the U.S. Department of State under the International Traffic in Arms Regulations, 22 CFR 120-130 ("ITAR"). An export license from the U.S. government is therefore required to export this product from the United States, and other ITAR restrictions apply to the shipment, use, service and other aspects of this product and the FTIR instrument in which it is used.

www.agilent.com/chem

Published April, 2011
Publication Number 5990-7999EN

Agilent Technologies

Quantitative analysis of copolymers using the Cary 630 FTIR spectrometer

Application note

Materials testing and research

Author

Frank Higgins and Alan Rein

Agilent Technologies
Danbury, CT, USA

Introduction

FTIR spectrometers employing attenuated total reflectance (ATR) sampling interfaces are a proven and powerful tool for the analysis of polymeric materials. Because of its unique combination of features and class-leading performance, the new Agilent Cary 630 FTIR spectrometer makes quantitative analysis of polymers especially fast and easy.

In this application note, the amount of key components in two important copolymeric materials are measured — the styrene content in styrene butadiene rubber (SBR) and the ratio of polyethylene to vinyl acetate in polyethylene vinyl acetate (PEVA) polymer. The Cary 630 FTIR equipped with its single reflection Diamond ATR sampling accessory (Figure 1) is used for these measurements.

Figure 1. Agilent Cary 630 FTIR spectrometer equipped with single reflection Diamond ATR sampling accessory

Styrene concentration in SBR polymer

Styrene butadiene rubber (SBR) is the most common synthetic rubber material and its main use is in the manufacture of tires, which accounts for nearly 70% of its production. The properties of SBR rubber can be altered by varying the ratio of styrene to butadiene monomers in the manufacturing process. The normal ratio is 3:1 butadiene to styrene (25% styrene). Higher styrene concentrations make the material harder, but less elastic. Most performance industries, such as racing tires and specialty military applications, are requiring more consistent SBR product, which drives the need for better quality assurance and control by both end users and manufacturers.

The measurement of a polymer sample by the Cary 630 FTIR equipped with an ATR accessory is extremely straightforward. The polymer material is placed on the diamond crystal and the sample pressure press is rotated downward until adequate pressure is placed on the sample to observe a spectrum in the Cary 630's real-time analysis MicroLab FTIR software (Figure 2). The real-time analysis mode provides instantaneous spectral update and makes it easy for even novice users to get highly repeatable results. The sample press on the Cary 630 is designed so that it cannot be over-tightened, thus protecting the diamond crystal against over-pressure.

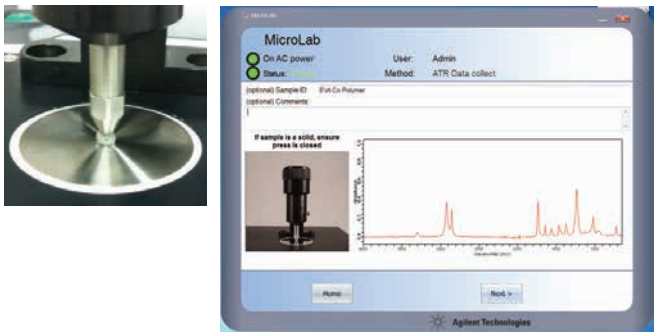


Figure 2. Polymer is placed directly on ATR sampling accessory. Uniform, constant pressure is provided by the sample press, ensuring that high quality spectra are obtained. Real-time analysis software provides an immediate indicator of spectral quality

To develop a quantitative FTIR method, four commercial SBR calibration standards, with polystyrene concentrations of 0%, 5%, 23%, and 45%, were measured in triplicate using the Cary 630 FTIR. The spectra reveal the expected polystyrene (PS) absorbance bands (Figure 3) at 699 cm^{-1}, 759 cm^{-1}, and a weaker band at 1031 cm^{-1}. Spectral bands at 911 cm^{-1}, 964 cm^{-1}, and 995 cm^{-1} arise from unsaturations (*vinyl* and *trans* CH wag) in polybutadiene, which decrease as the PS bands increase. The exception is the pure polybutadiene, which has far more *cis* unsaturations relative to the other polymers, since it is not cross-linked and in liquid form. The PS absorbance bands appear to follow Beer's Law by increasing proportionately with concentration, and therefore are excellent candidates for quantitative analysis.

The plot of the peak height absorbance for the strongest IR band of PS at 699 cm^{-1} as a function of concentration indicates great linearity and a strong correlation coefficient of R^2=0.999 in the calibration (Figure 4). Using the linear regression slope and offset from this calibration, a method is added to the MicroLab FTIR software that enables the polystyrene percentage in an unknown sample to be automatically displayed. The limit of detection for the quantitative analysis of PS in SBR is 0.09%, calculated as three times the standard deviation of the 0% replicate data (StDev= 0.03% PS).

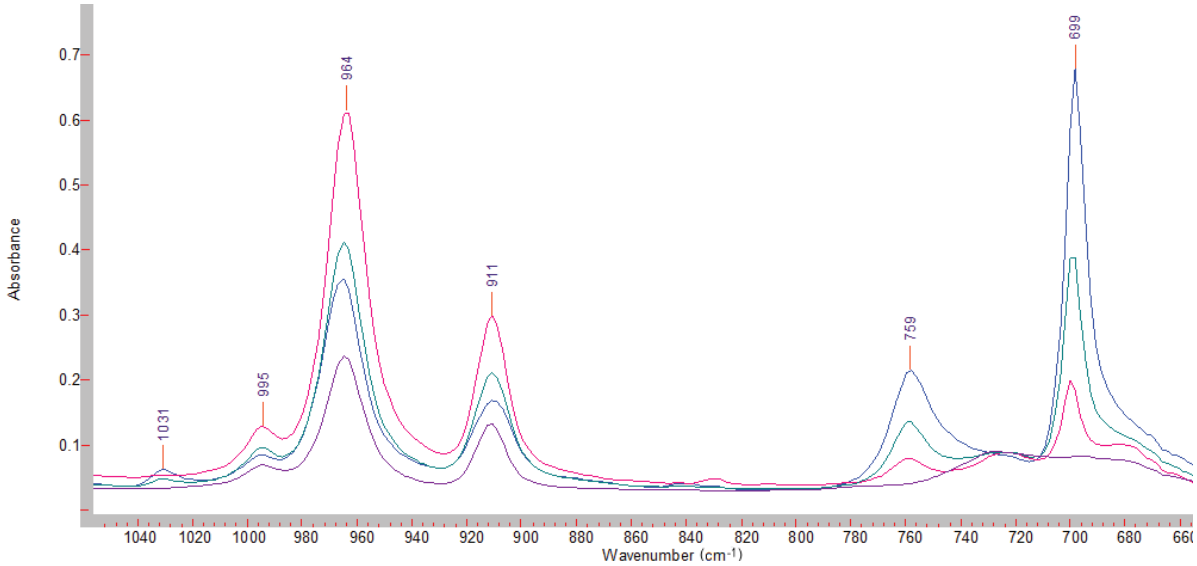


Figure 3. The FTIR spectra of four SBR rubber standards with increasing polystyrene concentrations: 0% (purple), 5% (red), 23% (green), and 45% (blue)

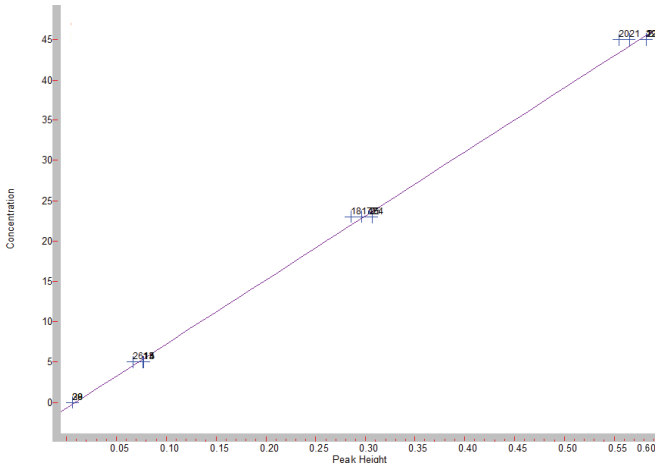


Figure 4. FTIR calibration curve for polystyrene in SBR rubber using the 699 cm^{-1} peak height absorbance; R^2=0.999.

Ratio of polyethylene to vinyl acetate in PEVA

Polyethylene vinyl acetate (PEVA) is very common in everyday products used in the home, sports equipment, industrial and medical applications. In the latter applications, medicines can be mixed in solution with PEVA and then the mixture dried to produce biologically-inert, slow-release plastic implants and transdermal patches.

Since the ratio of polyethylene (PE) to vinyl acetate (VA) in PEVA can affect the physical properties of the final product, it is important for manufacturers to have a fast, easy measurement procedure for these components. As in the previous example, the Cary 630 FTIR spectrometer with single reflection diamond ATR is ideal for this measurement.

In this example, seven commercially-available standards of PEVA were measured with the Cary 630 FTIR system. The calibration standards used were:

- Polyethylene, low density (0% vinyl acetate)
- Ethylene/vinyl acetate copolymer #506 (9 wt% vinyl acetate)
- Ethylene/vinyl acetate copolymer #243 (14 wt% vinyl acetate)
- Ethylene/vinyl acetate copolymer #244 (18 wt% vinyl acetate)
- Ethylene/vinyl acetate copolymer #245 (25 wt% vinyl acetate)
- Ethylene/vinyl acetate copolymer #316 (28 wt% vinyl acetate)
- Ethylene/vinyl acetate copolymer #326 (40 wt% vinyl acetate)

The calibration samples were measured with one minute collection times, at a resolution of 4 cm^{-1}. The FTIR spectra exhibit strong acetate ester carbonyl bands at 1737 cm^{-1} and an ester C-O stretch band at 1236 cm^{-1} (Figure 5) arising from polyvinyl acetate (VA). Both of these bands are ideal for quantitative analysis of the VA in the polyethylene (PE) matrix. The characteristic PE absorbance bands are located at 2921cm $^{-1}$, 2852 cm^{-1}, 1467 cm^{-1} and 720 cm^{-1}. The best calibration is obtained by a peak area ratio of the 1236 cm^{-1} VA absorbance band ratioed to the PE absorbance at 1467 cm^{-1}. This IR absorbance ratio technique corrects for random variables that may affect the measurement, such as contact pressure or contact area of the polymers on the ATR diamond crystal. This is important since reliable ATR measurements require the sample to make good optical contact with the diamond, and hard, round polymer beads may not contact the whole diamond surface.

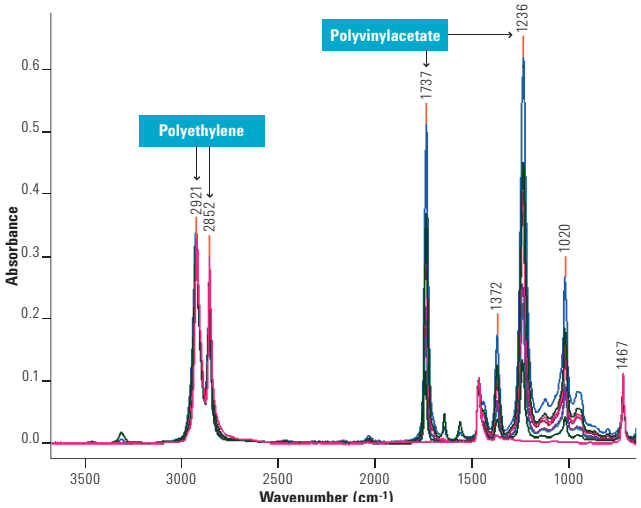


Figure 5. Spectral overlay of the calibration standards for polyethylene vinyl acetate). The spectra are all scaled to the polyethylene absorbance. The blue spectrum is 40 wt% VA, and the red spectrum is 0% VA

The resulting linear regression calibration curve from the above peak area ratio is excellent (Figure 6) with a correlation coefficient of $R^2 = 0.999$. The slope and offset for the linear regression is easily inserted into the MicroLab FTIR method editor (Figure 6), and the resultant method is now permanently calibrated. To test the robustness of the method, validation standards were made by diluting (by weight) the 9% VA with the pure PE (0% VA) standards to make 1% and 0.55% VA samples. The polymer validation samples were then dissolved in toluene and heated to 75 °C until all the polymer dissolved. The toluene mixtures were then cast as thin films onto aluminum foil over a 60 °C hotplate and allowed to dry. The resulting polymer validation samples were then measured with the stored method. These validation samples were measured with a much shorter scan time (5 seconds) than the calibration set of spectra (60 seconds). This allows for multiple measurements of incoming raw materials in a very short time; this fast sample analysis is important for quality assurance and quality control (QA/QC) analysis. The speed of this analysis is also a benefit for incoming raw materials analysis in which a batch of PEVA can have some uniformity differences, requiring sampling from multiple areas of the container or on a molded part. The results of this fast analysis (5 second) yield exceptional repeatability and accuracy (Table 1) on the validation samples. A standard deviation of nominally 0.01% VA was obtained with limits of detection (LOD) and limits of quantitation (LOQ) of 0.03 wt% VA and 0.10 wt% VA, respectively. When a sample is run using this calibrated FTIR method, the results can also be displayed in color-coded format (Figure 7), indicating that the sample is in-spec (green), marginal (yellow), or out of spec (red). This enables an operator to get a rapid, visual indicator of the quality of the material.

Table 1. VA prediction values from the calibrated VA FTIR method for validation standards at 0.55% VA and 1.00% vinyl acetate in polyethylene. These validation samples were run with only 5 second collection times

Validation sample	0.55% VA	1.00% VA
Rep 1	0.53	0.97
Rep 2	0.54	0.96
Rep 3	0.55	0.96
Rep 4	0.56	0.96
Rep 5	0.55	0.99
Standard deviation	0.0114	0.0130
Average	0.55	0.97

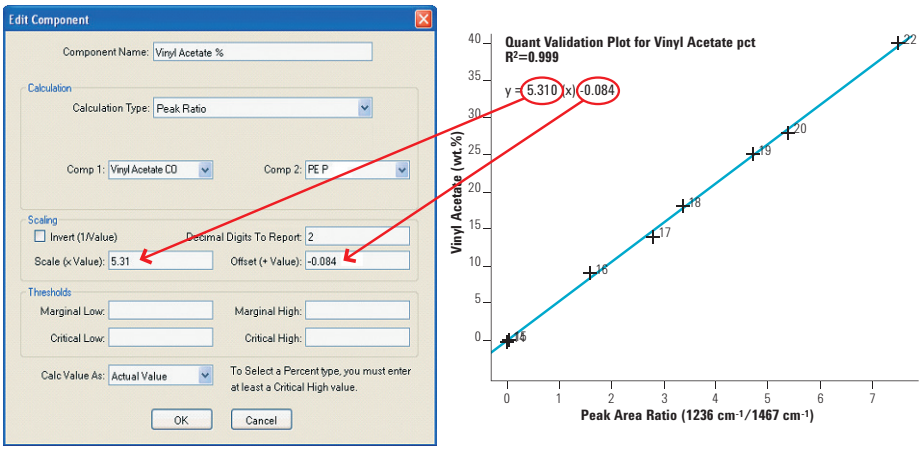


Figure 6. The method editor in the MicroLab FTIR software and the calibration plot for VA in PE

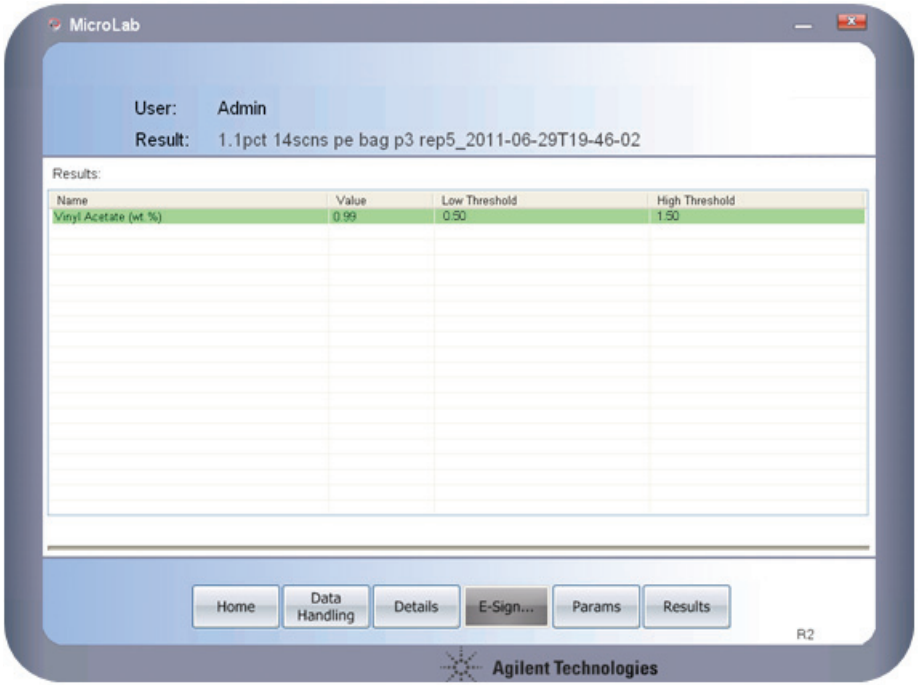


Figure 7. The result for the 1% VA validation standard — green color indicates an in-spec sample

Conclusion

The Agilent Cary 630 FTIR equipped with ATR sampling technology is an exceedingly effective spectrometer for analyzing copolymer blends. The combination of its compact size, sampling technology, performance, speed of analysis, and intuitive software enables quantitative methods for polymers to be rapidly developed and deployed in quality assurance and quality control applications. The measurement of both SBR and PEVA copolymers yields highly linear calibrations with excellent quantitative accuracy and reproducibility.

www.agilent.com/chem

Published September 1, 2011
Publication number: 5990-8676EN

Agilent Technologies

Solutions for Polymers and Materials

AGILENT CARY FTIR SPECTROSCOPY, MICROSCOPY AND IMAGING SOLUTIONS

The Measure of Confidence

Agilent Technologies

SEE MORE. SEE CLEARLY. SEE FASTER.

Agilent introduces a complete suite of FTIR solutions to meet all your polymers and materials application needs — from kinetics studies, to automating QA/QC SOPs, to the study of polymer interfaces, surface modification and functionalization, and the investigation of thermal effects.

World-class solutions for Polymers and Materials

Our spectrometers, microscopes, and chemical imaging systems deliver:

- Fastest kinetics speeds to study dynamic polymer reactions.
- Simplified monolayer analysis and depth-profiling photoacoustic experiments.
- Highest signal-to-noise (S/N) performance — up to four times better than any other available FTIR, providing the highest sensitivity and productivity.
- Intelligent electronics for accessory and component recognition, providing seamless changeovers and automatic method optimization.
- Micrometer to meter measurements using the large sample microscope objective, to analyze a wide range of samples.
- Multi-measurement modes including transmission, reflection, Attenuated Total Reflectance (ATR) and grazing angle.
- ATR micro- and macro-imaging, which extend traditional imaging measurements to new boundaries, reducing sample preparation and improving spatial resolution.
- Full upgrade path for spectrometers and microscopes for the ultimate in flexibility, to meet your changing application needs.
- Versatile, easy to use software, making FTIR spectroscopy, microscopy and imaging accessible to users of all levels.

The Agilent Cary 600 Series FTIR provides the highest level of sensitivity combined with detailed structural and compositional information for information-rich detection.

Molecular Spectroscopy Innovations

1947 First commercial recording UV-Vis, the Cary 11 UV-Vis	**1954** Release of the Cary 14 UV-Vis-NIR	**1969** First rapid-scanning fourier transform infrared spectrometer, the FTS-14	**1971** First use of a mercury cadmium telluride (MCT) detector in an FTIR	**1982** First FT-IR microscope, the UMA 100	**1989** Release of the acclaimed Cary 1 and 3 UV-Vis	**1991** First infinity corrected infrared microscope
1997 Cary 50 Series released to coincide with 50th anniversary of Cary 11	**1995** Launch of the 8453A, the first small-footprint, full-featured diode-array	**1999** Launch of the Cary Eclipse Fluorescence Series	**2000** First ATR chemical imaging system	**2002** Cary 4000/5000/ 6000i research grade UV-Vis-NIR series released	**2008** Launch of the 600 Series FTIR spectrometers, microscopes and imaging systems	**2011** Agilent offers out-of-lab FTIR solutions

FOR YOUR APPLICATION

Agilent is committed to providing solutions for your application. We have the technology, platforms, and expert guidance you need to be successful.

Power enough for all your Polymers and Materials applications

Tackle any analytical challenge from routine measurements and troubleshooting, through to cutting edge research in polymers and materials applications.

Investigate heterogeneity and identify contaminants

- Analyze multi-layer laminates, silicon wafers, LCD screens, and paper products.
- Characterize surface heterogeneity and component distribution.
- Investigate packaging laminates.
- Characterize deficiencies in electronics and polymer manufacturing processes.
- Identify sample heterogeneity non-destructively using photoacoustic spectroscopy (PAS).
- Analyze polymer and paper coating defects.
- Evaluate polymer dispersed liquid crystals.
- Identify manufacturing defects in semiconductors, electronics and electronic materials.
- Characterize microscopic contaminants and defects in large samples using Agilent's unique large sample objective.

Confirm consistency of raw materials and finished products

- Perform QA/QC of raw materials and finished goods.
- Verify materials using Agilent's Easy ID QC software.
- Simplify method development for infrared analyses.
- Characterize materials and synthesis products.
- Identify product contaminants and defects by searching spectral databases.

Study surface modification and reaction dynamics

- Monitor polymer curing kinetics or structural changes in materials during temperature fluctuations.
- Characterize monolayer films using polarization modulation — infrared reflection absorption spectroscopy (PM-IRRAS).
- Probe fundamental chemical and physical processes simultaneously using dedicated software.
- Analyze chemical changes with a high spatial resolution over a large area of analysis in real time.

INVESTIGATE HETEROGENEITY AND IDENTIFY CONTAMINANTS

Analyze material heterogeneity and sample contaminants within seconds

With Agilent Cary FTIR systems, see data that other systems do not. Using an Agilent Cary microscope, featuring a wide range of spatial resolution options, combined with quality data produced by an Agilent Cary spectrometer, characterize the spatial distribution of components within heterogeneous materials and identify the specific nature of a sample.

With infrared mapping and chemical imaging using a focal plane array detector, Agilent Cary systems give you superior quality information, even from the most challenging of samples, in the shortest possible time.

Perform both microscopic and macroscopic measurements using the multiple measurement modes of the Agilent Cary infrared microscopes, including transmission, reflection, attenuated total reflectance (ATR), grazing angle reflection analysis and 'large sample' mode.

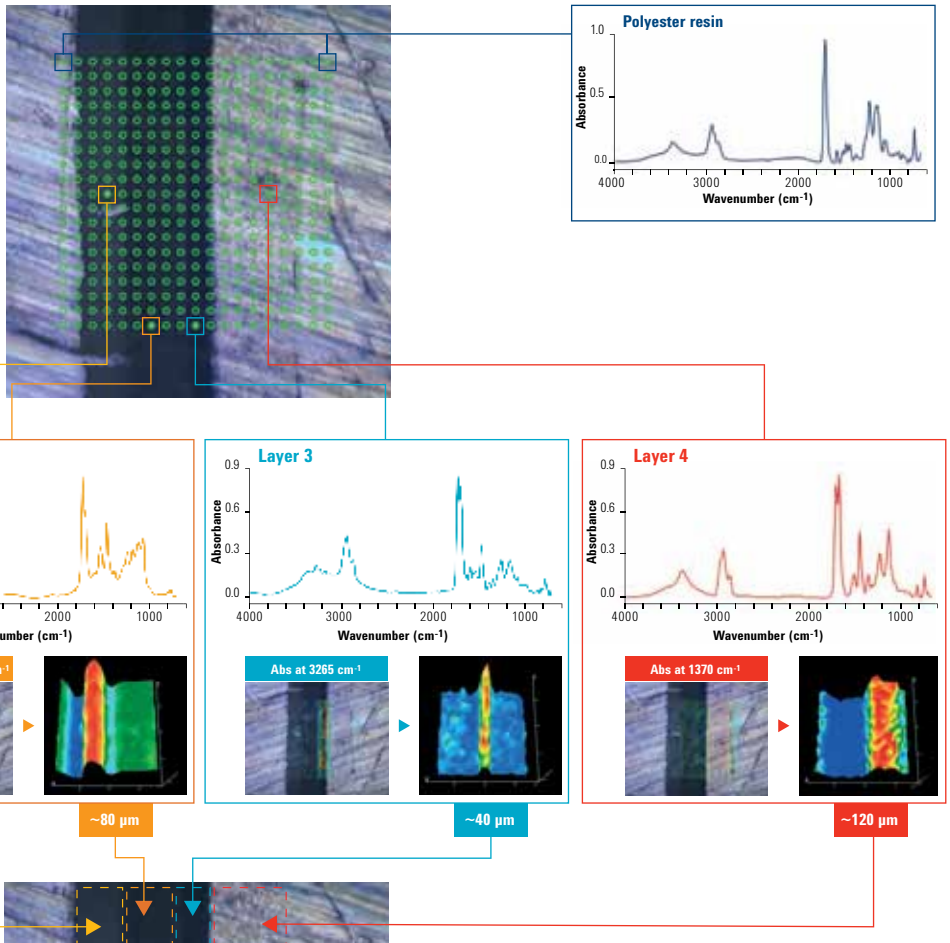
In the following examples, material heterogeneity and sample contaminants were characterized within seconds or minutes to provide a comprehensive understanding of sample chemistry on the micron scale.

The Agilent Cary 600 Series FTIR delivers:

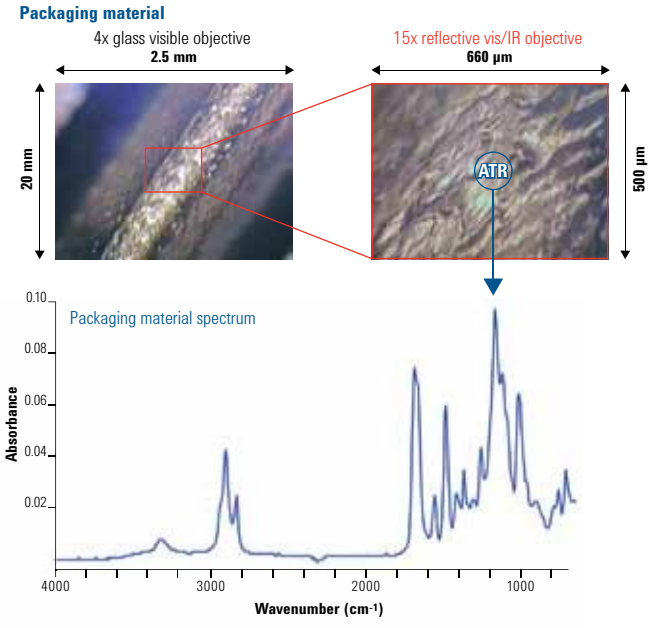
- Dedicated hardware that is ideal for both simple and advanced materials characterization.
- The best sensitivity to detect the smallest contaminants quickly and seamless database searching for easy sample identification.
- Simple to use, versatile microscopes that can be customized to suit any desired area of analysis.

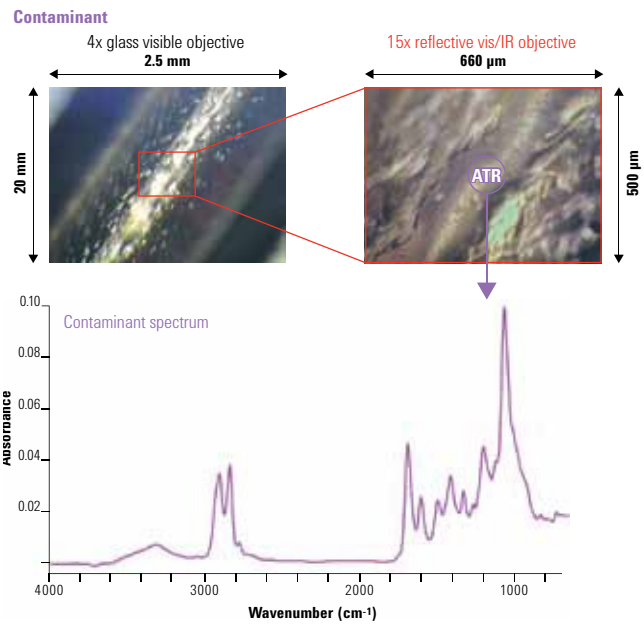
Infrared mapping analysis of a paint chip sample (below) found at an automobile crime scene revealed that the sample was composed of four chemically distinct layers.

Three of the spatially-resolved layers are in the black vertical bar, while one layer is transparent. Based on these spectra and the width of each layer, forensic scientists were able to search against spectral databases of paint and coating samples to identify the vehicle's make, model, year, and color.

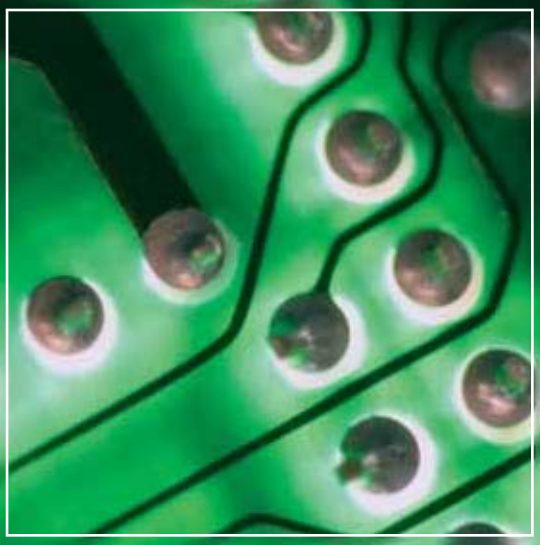


Identify contaminants with no sample preparation using the Agilent versatile slide-on ATR, making data collection easy and fast. High quality infrared spectra were collected in 5 s from packaging material (top) and a contaminant on the packaging material (bottom). The resulting IR spectra provided insight into the manufacturing issue. In this case, an adhesive glue had overflowed onto the packaging material.





identify



INVESTIGATE HETEROGENEITY AND IDENTIFY CONTAMINANTS

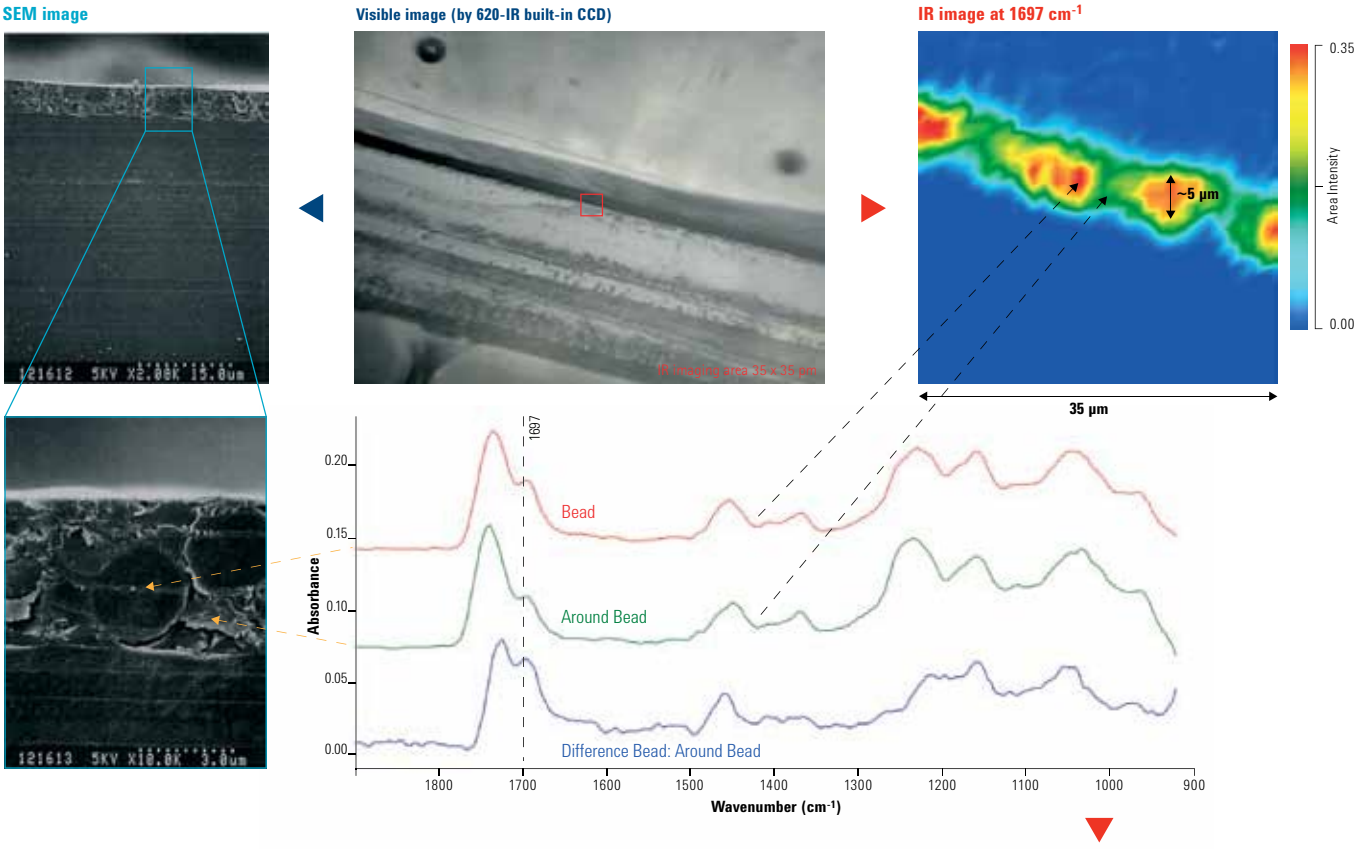
As manufacturing processes and associated materials become more advanced, multi-layer materials and polymers (especially the adhesive layers in polymer laminates) are becoming thinner and therefore more difficult to analyze using traditional FTIR microscopy.

Whether it is the identification of three micron adhesive layers in multilayer laminates, the orientation of surface-bound monolayer species on silicon, or the identification of contaminants on manufactured paper and cardboard products, the Agilent Cary FTIR spectroscopy range provides an arsenal of analytical techniques to solve your analytical challenge.

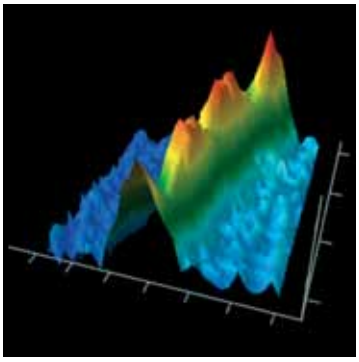
In these examples, the Agilent Cary micro ATR Focal Plane Array (FPA) imaging system was used to resolve sample layers of only a few microns, in seconds (well below the air diffraction limit). This unique technology reveals miniscule structural features that other systems overlook, and allows for unmatched control over critical manufacturing processes.

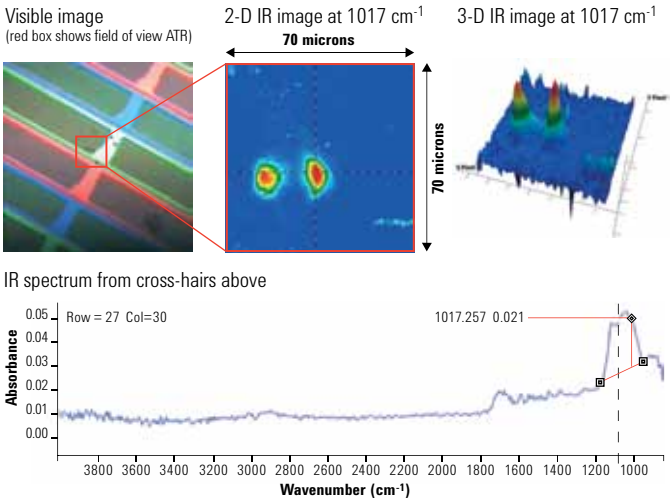
For these applications, the Agilent Cary 600 Series FTIR delivers:

- Unsurpassed spectral collection of hundreds to thousands of spectra within seconds to characterize any sample, providing you with more information from a single collection.
- Intelligent imaging with the most comprehensive spatial resolution modes of 1.1, 5.5, 11, and >22 µm for information rich detection of even the smallest sample features.
- Unique software capabilities to monitor the 'live' infrared image and ensure optimum contact at the moment of ATR measurement, ensuring the maintenance of sample integrity that is not possible with alternative systems.

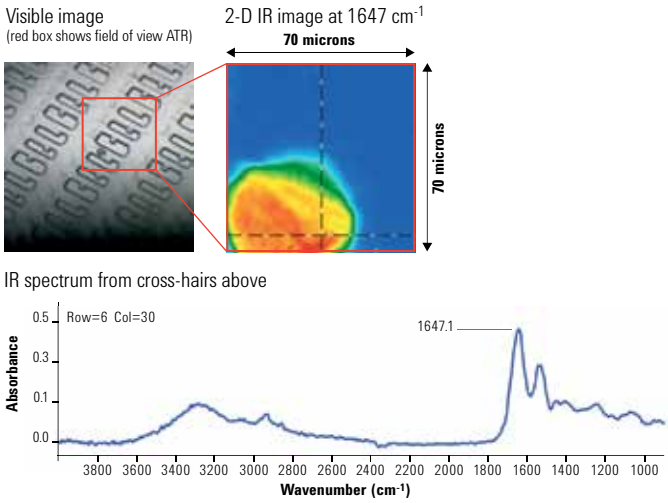


Infrared imaging analysis goes beyond visible sample characterization (SEM and Visible image) to provide chemical information about product failure of functional films in LCD screens. The ability to acquire data at such a high spatial resolution from several small beads and their surroundings, provided a comprehensive means of troubleshooting product defects in the manufacturing process. Easy sample visualization tools let you investigate the samples in 2-D and 3-D chemical view in order to improve process control.





Discovering the chemical reasons for component failure of LCD filters using micro-ATR imaging with a FPA detector. Visible images, chemical images, and one of thousands of IR spectra that were collected in seconds allowing the source of the inorganic contaminants to be identified.



Agilent's unique ability to see the chemical image in real-time during ATR-sample contact ensured that there was no sample deformation during routine quality control analysis of this LCD screen. The foreign material under investigation was quickly identified as a skin flake.

confirm

CONFIRM CONSISTENCY OF RAW MATERIALS AND FINISHED PRODUCTS

Quickly identify product defect, contamination and blemish issues to minimize downtime and prevent significant revenue loss.

Forget tedious, wasteful and subjective wet chemical techniques for assessing the consistency of your raw goods, intermediates and finished product. With an Agilent Cary FTIR spectrometer, you can simultaneously obtain qualitative and quantitative information about the chemical composition of your samples.

Automate your QA/QC manufacturing SOPs to provide rich chemical information by searching the largest FTIR libraries in the world, including dedicated polymer and material databases.

The example here illustrates the seamless process of detecting and identifying an unknown contaminant in a manufacturing environment.

The Agilent Cary 600 Series FTIR delivers:

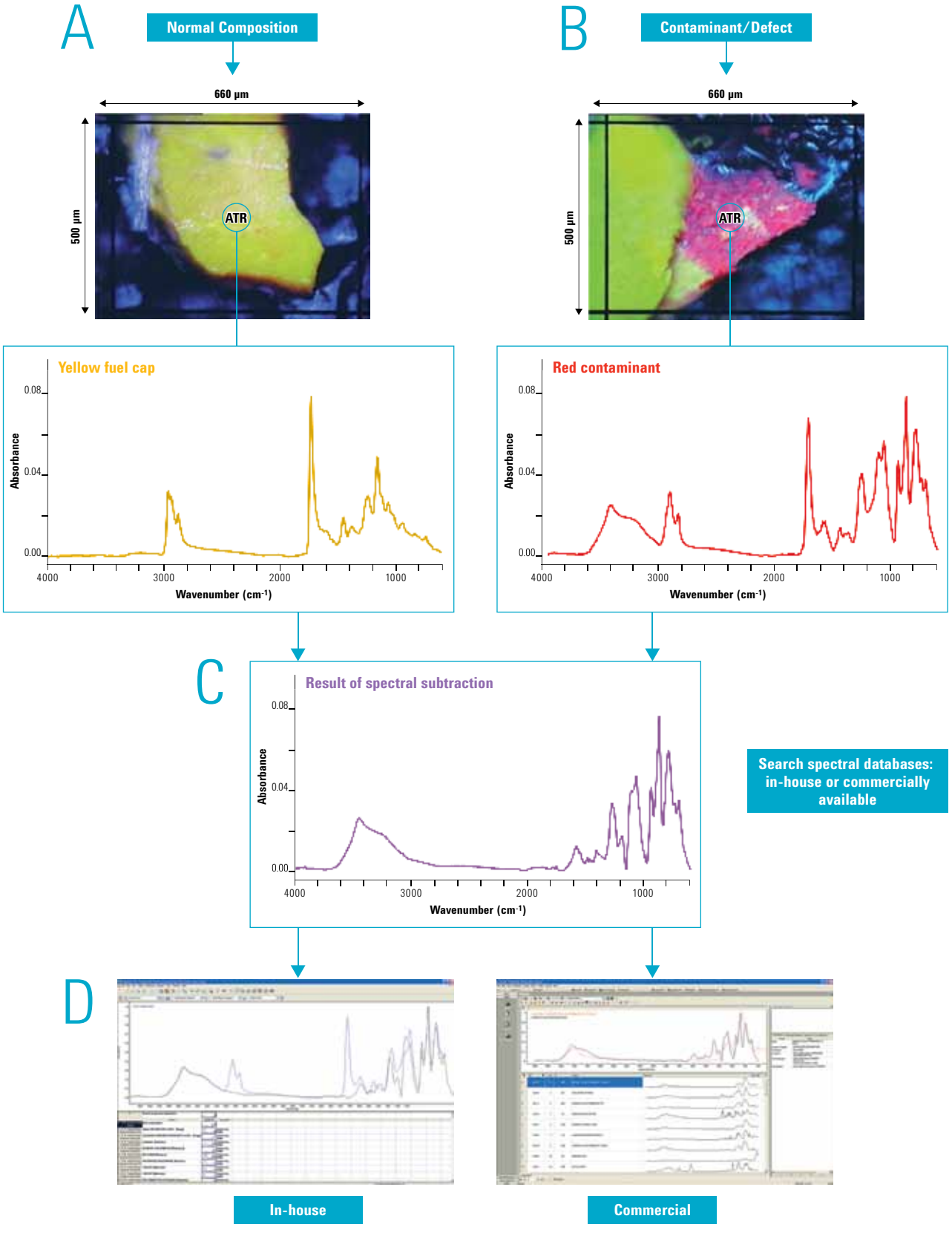
- Modern ATR accessories to analyze virtually all sample types (solids, powders, pastes, liquids, and more) with little or no sample preparation, in a non-destructive manner.
- Superior data quality, sensitivity and spatial resolution to identify even the smallest defects and contaminants faster.
- Easily searchable in-house spectral libraries of proprietary data and commercially-available libraries to identify and verify your sample with a single mouse click.

The problem

During production, yellow polymer fuel caps (shown in A), are being contaminated by an unknown compound. The contaminants (shown in B) range in size from ~20-300 µm and are visible to the naked eye.

The solution

Analysis by micro-ATR with an Agilent Cary 610 single element detector. Spectra were collected in 5 s, compared visually and then subtracted (shown in C) to gain a better understanding of the contaminant. The spectra were compared to in-house and commercially-available spectral libraries (shown in D) to identify the source of the contamination in the manufacturing process – in this case, the wearing of a plastic O-ring.



STUDY SURFACE MODIFICATION AND DYNAMIC REACTIONS

Perform dynamic studies and kinetics experiments that other systems cannot.

If you need to mimic real-world sample conditions such as the exposure to chemicals, extreme temperature, and harsh environments, you can with Agilent's unique products. Our unmatched ATR solutions along with custom software can simultaneously acquire external experimental parameters and spectral information to comprehensively understand your reaction in real time.

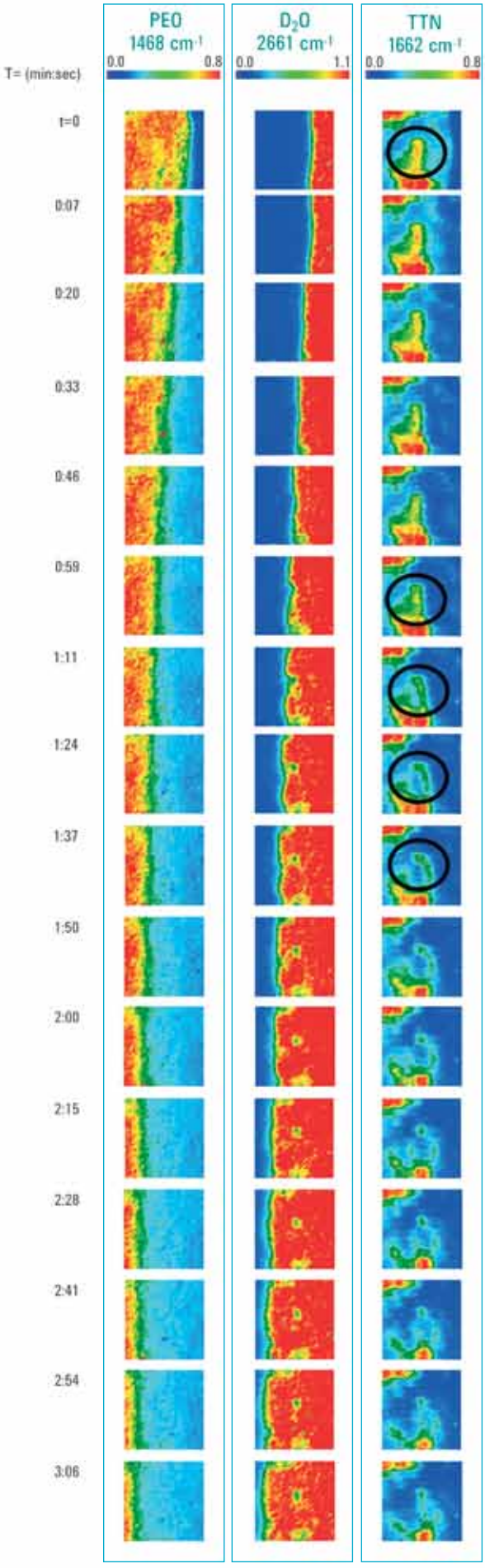
Are you performing dynamic studies and kinetics experiments such as investigating the curing of polymers? Agilent's intuitive software makes these simple.

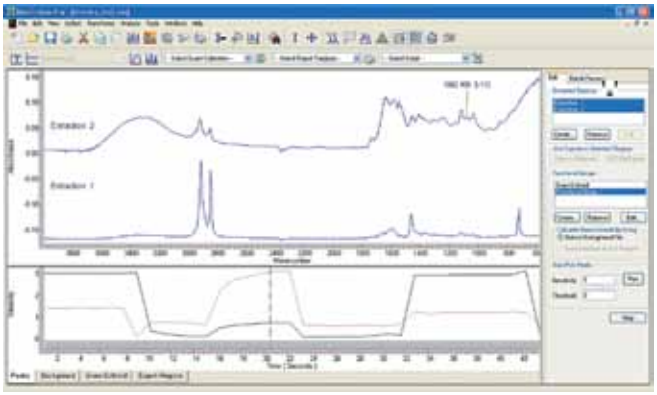
With superior energy throughput, grazing angle accessories, microscopes and ATRs, Agilent Cary FTIR systems provide the complete solution for your surface functionalization and study of reaction dynamics.

In these examples, our easy-to-use Resolutions Pro software and unique patented hardware give you the edge by allowing you to see what others are missing.

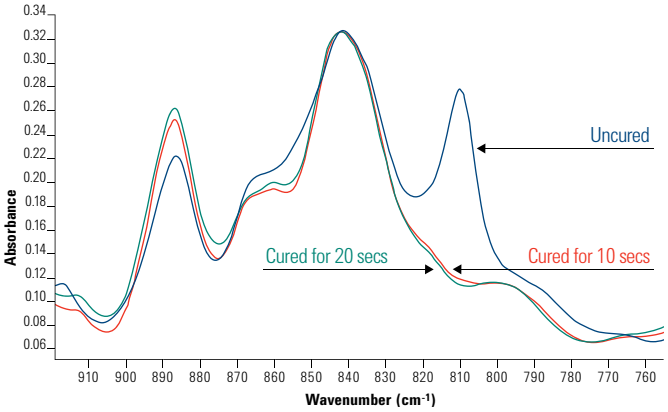
The Agilent Cary complete solution delivers:

- An unsurpassed ability to probe the chemical nature of coatings and thin films and monitor the smallest chemical changes during sample modification.
- The fastest kinetics speeds to investigate changes that occur within a fraction of a second during fast curing and dynamic experiments.
- The unique ability to investigate sample changes in real time via time-based imaging kinetics using a focal plane array detector.





Agilent provides dedicated software to monitor reaction dynamics and kinetics experiments such as polymer curing studies in real time. Create functional group plots with a single click to extract the data that you want.



Intuitive kinetics software makes dynamic reaction monitoring easy. In this example of polymer curing with UV light, samples were monitored in real-time to optimize curing conditions and to characterize the chemical state of transient components.

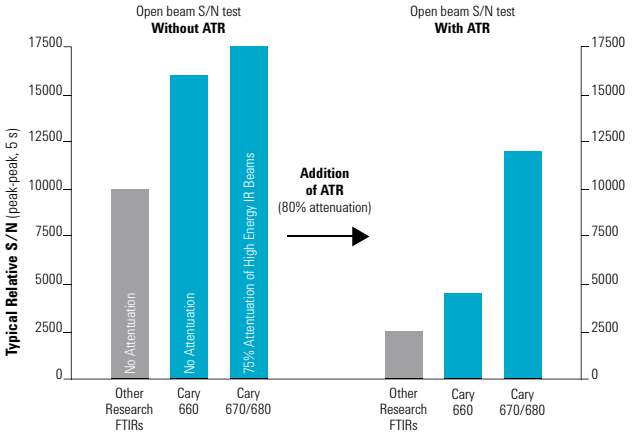
explore

THE WORLD'S BEST FTIR

Every component of the Agilent Cary 600 Series is engineered for performance and usability, ensuring you get the right answer every time.

Real results. Real conditions.

The Agilent Cary 600 Series FTIR provides enhanced source throughput, beamsplitter and detector efficiencies and reduced instrument noise effects. The result is superior performance and sensitivity, up to four times better than any other research FTIR.



NOTE: Measured at 4cm^{-1} resolution using a DLaTGS detector.
ATR measurements performed using a diamond single bounce ATR.

The S/N difference

Traditional S/N tests
Performed without a sample or sampling accessory in the instrument, so they are effectively measuring air.

Agilent S/N tests
Measured under real-world conditions, giving you a true indication of performance.

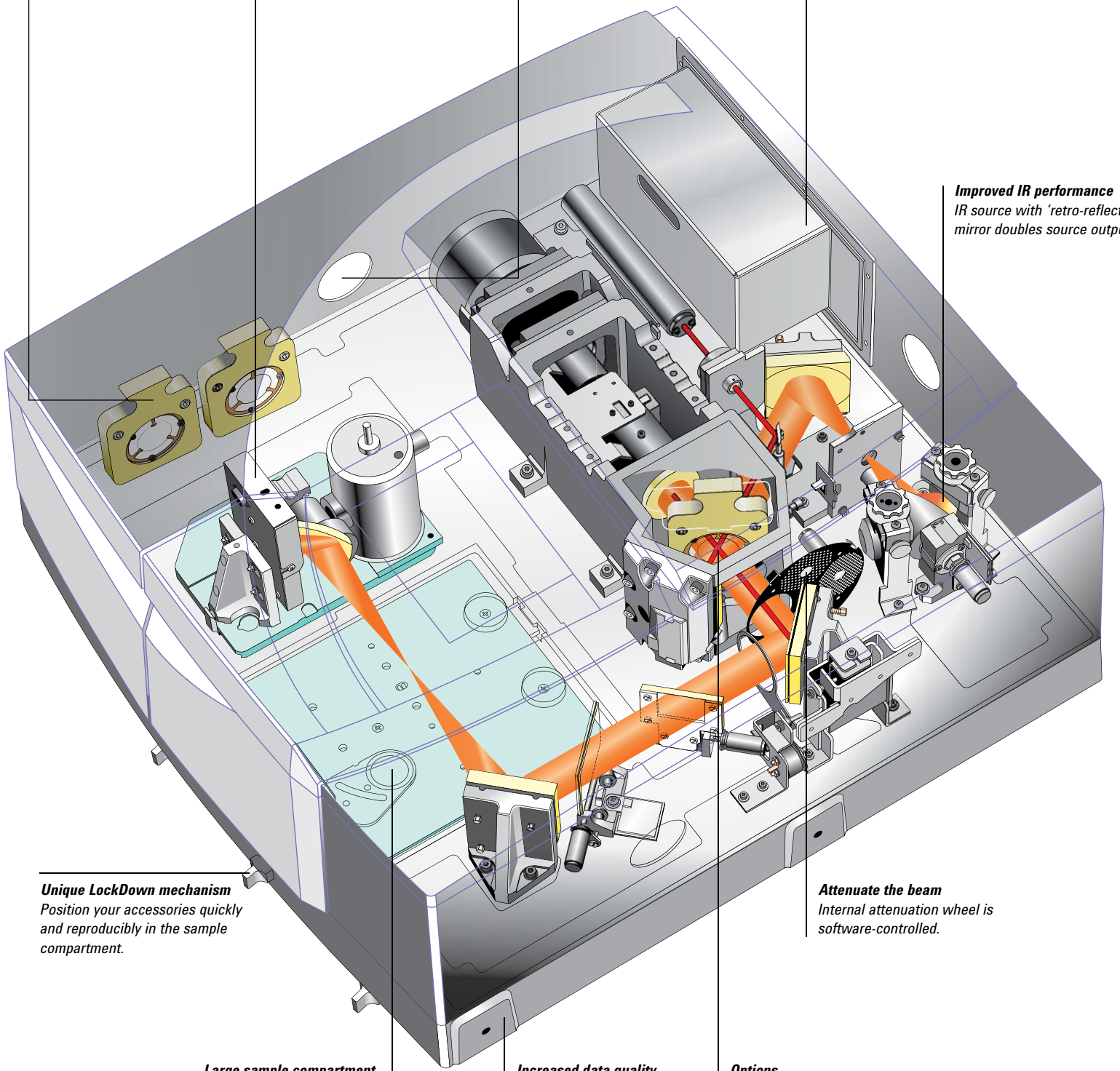
Internal beamsplitter storage
Provides a dry, protected storage location.

Increased productivity
Easy-to-change detectors and beamsplitters enable quick and reproducible spectral range change-overs.

True digital 24-bit dynamic range Delta-Sigma A/D converter delivers maximum S/N, sensitivity, spectral accuracy and precision.

Experimental flexibility
With multiple external/emission ports.

Improved IR performance
IR source with 'retro-reflection' mirror doubles source output.



Unique LockDown mechanism
Position your accessories quickly and reproducibly in the sample compartment.

Attenuate the beam
Internal attenuation wheel is software-controlled.

Large sample compartment
Includes removable floor plate for maximum flexibility when mounting samples.

Increased data quality and reproducibility
The sealed and desiccated enclosure, or full purge with purge shutter options, minimize environmental disturbances.

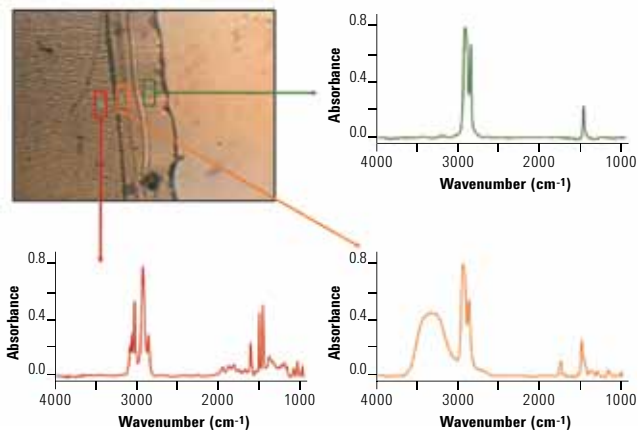
Options
57 mm dynamically aligned 60° air-bearing interferometer maximizes throughput and S/N performance (Cary 670/680 only).

Step-scan extends the capabilities for probing samples (advanced PAS, polymer stretching, and TRS), resulting in comprehensive sample characterization.

SPEED AND SENSITIVITY BY DESIGN

See more than ever – fast

The Cary 610/620 FTIR microscopes provides superior quality information in the shortest time, even with challenging samples. The microscopes offer the highest available optical throughput for the best S/N performance. The control panel enables all common software actions to be performed at the microscope, and aperture changes are quick and simple.



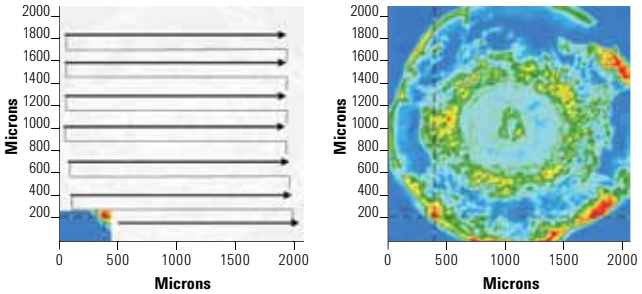
Set the Cary 610 microscope aperture to your sample size to obtain specific, exceptional quality spectra within seconds. Shown is a three-layer polymer laminate visible image (top left) and the resulting spectra, allowing for comprehensive characterization.

True chemical imaging

The Cary 620 provides the most sensitive and fastest available chemical imaging. The FPA[1] detectors enable simultaneous collection of up to 16,384 spectra within seconds. With a range of detector options (16x16, 32x32, 64x64, 128x128) and spatial resolution modes of 1.1, 5.5, 11 and >22 µm, you can characterize any sample.

Large sample analysis

Extend chemical imaging beyond the microscope with macro imaging, using Agilent's Large Sample (LS) accessory. With a field of view of up to 5x5 mm, you get more information from a single collection. Combine this with our range of macro ATR solutions for even simpler sampling.

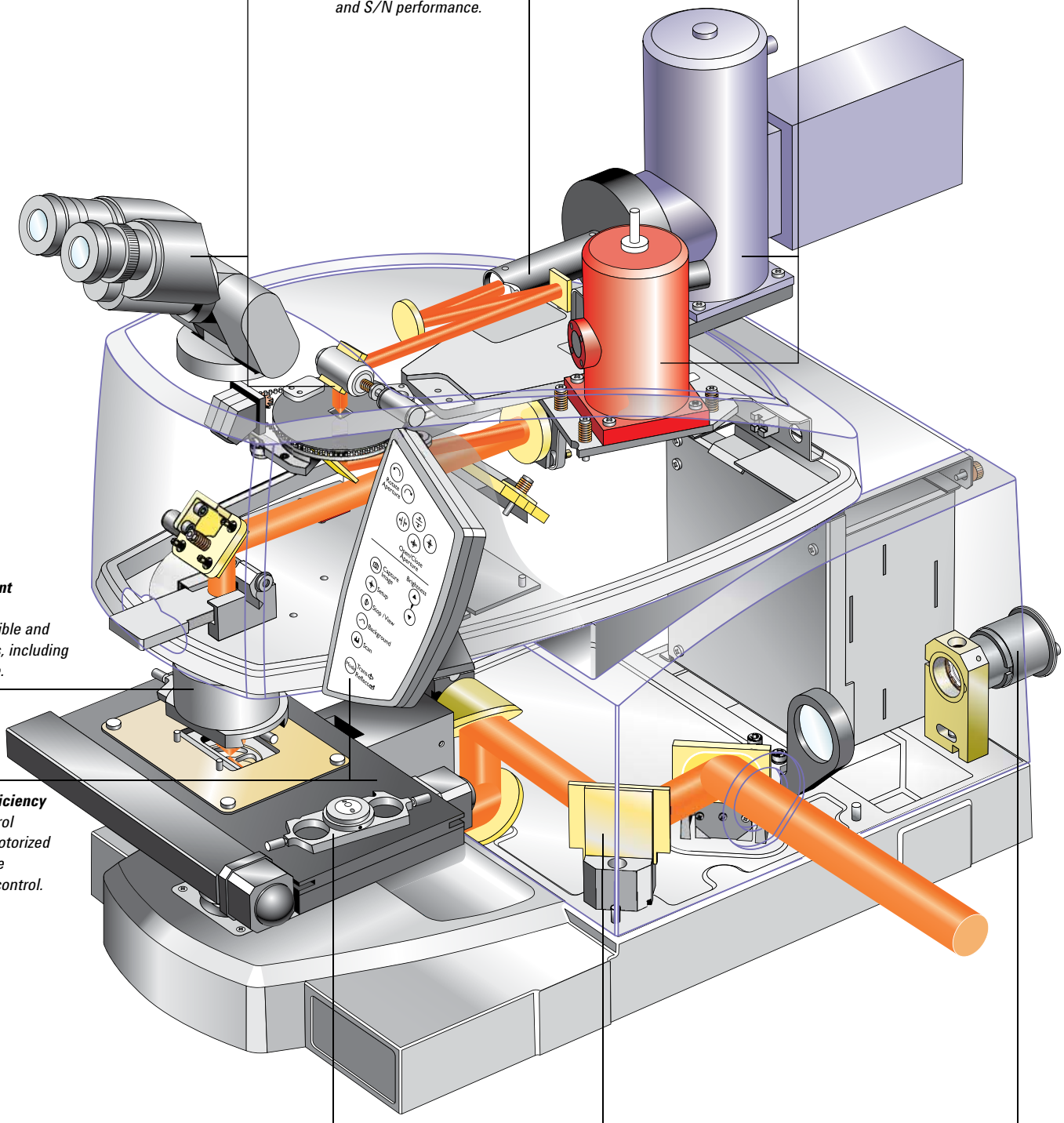


Get the full picture — fast. Left: Linear array mapping. In 20 minutes, only 5% of this large, high spatial resolution image is collected. Right: Agilent Cary 610 chemical imaging. In 20 minutes, 100% of the image is collected.

Simplify sample analysis
Binoculars and internal video CCD camera make sample analysis more flexible.

Quadruple the area of analysis
With field-expanding optics you can analyze larger samples in significantly less time, while maintaining excellent spatial resolution and S/N performance.

Sample flexibility
A range of detectors, from single element to FPA1 imaging (Cary 620).



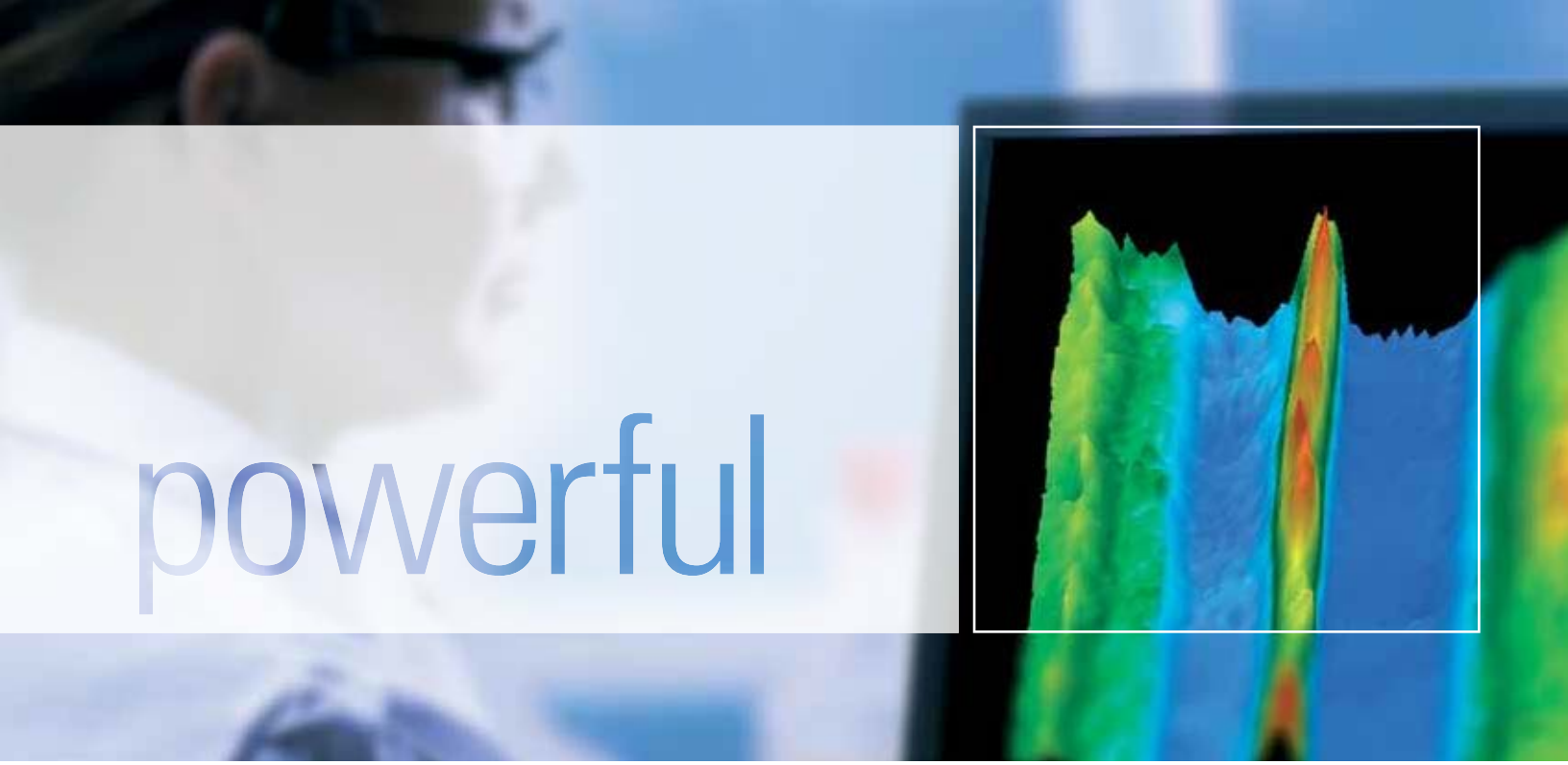
Measurement flexibility
Range of visible and IR objectives, including large sample.

Increase efficiency
Unique control panel and motorized sample stage provide full control.

Multiple modes
Transmission, reflection, ATR or grazing angle analysis mode.

Information-rich results
Advanced optical design provides maximum IR throughput and better S/N performance.

Fast setup
Ultra-bright white LED visual illumination ensures the highest quality sample visualization, even with difficult to see samples.



POWERFUL, INTUITIVE SOFTWARE

Whether you are performing routine measurements or cutting edge research, with Resolutions Pro software you will be able to acquire, process, analyze and manage your FTIR data quickly and easily.

Intuitive

- Use 'Method Editor' to easily set up a method and start a measurement from one window.
- Spend less time on setup — the accessory and component recognition detects instrument configurations and automatically optimizes the method.
- Customize — use the built-in scripting tool to simplify analytical tasks for the multi-user laboratory, or to develop advanced routines for challenging applications.

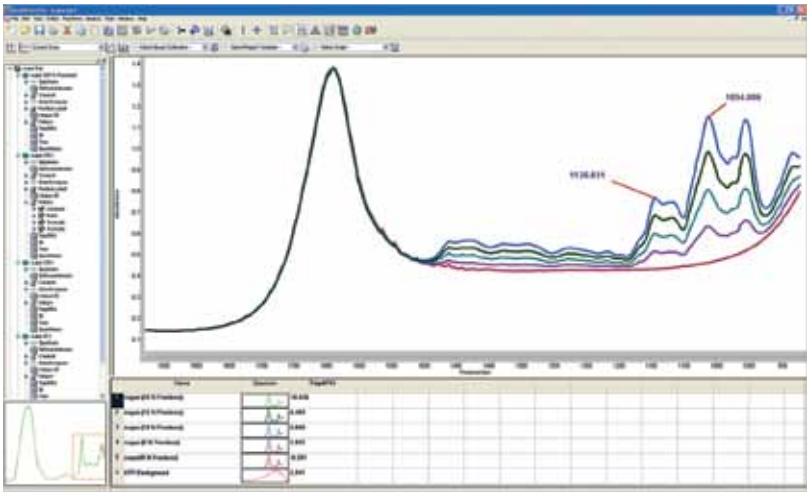
Data security and integrity

- 'User Manager' enables administrators to set user privileges, providing protection of data and methods from change or deletion.
- Access to ALL original data — including sample and background interferograms and post-collection — ensures data integrity, and allows for data reprocessing.
- Built-in instrument performance tests provide proof of performance and confidence in your results.

Intelligent imaging

For chemical imaging experiments, Resolutions Pro provides:

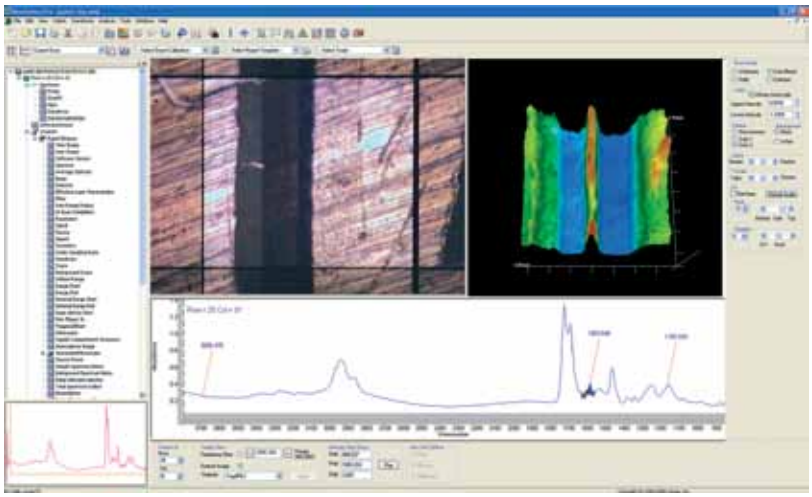
- Unsurpassed spectral collection of hundreds to thousands of spectra.
- Mosaic option to extend the field of view for unlimited image size.
- Individual spectra corresponding to a selected part of the image and conversely, image region corresponding to a selected wavenumber. This is useful as a quick check of a sample's heterogeneity.
- Control of chemical imaging detector integration time so you can maximize dynamic range and S/N performance to increase the quality of data for difficult to analyze samples.
- 2-D and 3-D views, which simplify the interpretation of spatially-resolved components.

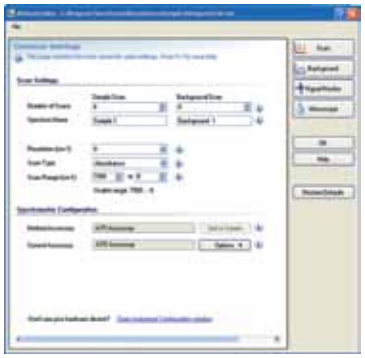


Left: Unique 'Spectral Spreadsheet' view allows multiple spectra to be overlaid, compared, and their parameters simultaneously tabulated with ease and speed.

Below left: Powerful Resolutions Pro software has multiple views including image, 3-D chemical image and spectrum, for comprehensive confirmation.

Below: 'Method Editor' enables users of all levels to easily set up a method.





Confirm what you see

For single point and mapping experiments, Resolutions Pro provides:

- Fully automated mapping for consecutive, unattended analysis of large sample areas or multiple samples.
- Grid mapping templates customized to your sample to create chemical contour maps for speedy analysis.
- Ability to create application-specific methods to simplify routine experiments.

Advanced data analysis

Resolutions Pro features sophisticated post-run analysis capabilities.

- Easily relate spectral information to a corresponding image.
- 'Play', 'Extract' and 'Image Peak' functions to easily explore imaging results.
- Full access to all collection and processing parameters for simple reprocessing of spectra and chemical images.

flexible

MEET ALL YOUR ANALYSIS CHALLENGES

Agilent has a range of complementary UV-Vis-NIR and Fluorescence solutions for Polymers and Materials applications.

The Agilent Cary research-grade UV-Vis-NIR and Fluorescence spectrophotometers combine leading edge technology with flexibility and ease of use. Offering performance and versatility, the Agilent Cary 4000, 5000, 6000i and Agilent Cary Eclipse spectrophotometers are equipped to handle the most demanding materials applications:

- Thin films
- Laser mirrors
- Nanocomposites
- Film thickness
- Bandpass properties
- Filters
- Refractive index
- AR coatings
- Bandgap
- Etalons
- Crystals, Powders, Liquids

Flexible and functional

Spend more time on analysis and less on set-up with Agilent's comprehensive suite of LockDown accessories. The unique LockDown mechanism guarantees fast, reproducible accessory changeover.

Use an integrating sphere to swap from absolute specular reflectance to diffuse reflectance measurements in seconds, or remove the sample compartment floor to measure large samples.

The Agilent Cary Eclipse fluorescence fiber optic system enables the properties of difficult-to-measure materials to be analyzed. The coupler and probe are easily installed and aligned, and no sample preparation is required. Fluorescence spectra are acquired simply by placing the solids tip on the surface of the sample. And because the Cary Eclipse is immune to room light, spectra can be acquired without the need for light shielding.

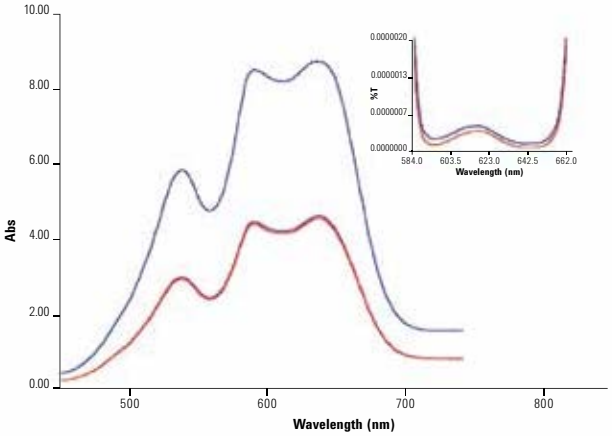
Application

Measurement of high optical density filters

Solution

Agilent Cary 4000
The ultimate in UV-Vis photometric performance

The addition of two filters demonstrates photometric range (> 8 Abs) and linearity in the UV-Vis. The insert compares the mathematical addition of the two filters with their combined measurement (a difference of less than 8x10-8 %T).



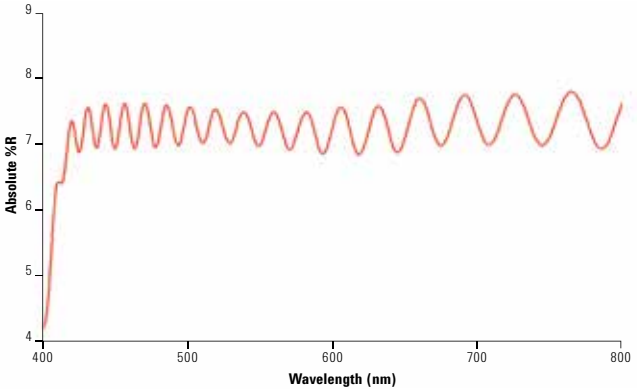
Application

Determination of thin film thickness of a polymeric coating

Solution

Agilent Cary 5000
The 'VW' Absolute Specular Reflectance Accessory

The film thickness of a thin film can be calculated from its interference pattern obtained from the absolute reflectance spectrum. Using Agilent's thin film application, the thickness of a coated polycarbonate sample was calculated to be 4.95 µm.



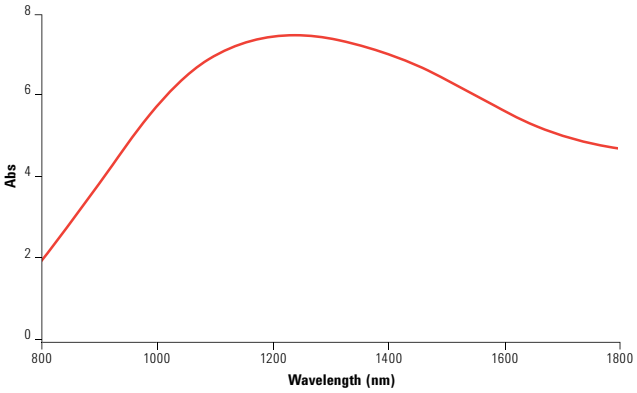
Application

QA/QC of highly absorbing laser safety goggles

Solution

Agilent Cary 6000i
Superior photometric linearity and accuracy enables measurements >7 Abs to be made in the NIR

The superior speed and sensitivity of InGaAs can dramatically increase productivity. In this instance, the blocking power of laser safety goggles is quickly and easily verified.



Trust Agilent to keep your lab running at peak productivity

Agilent's Advantage Service protects your investment in Agilent instruments and connects you with our global network of experienced professionals who can help you get the highest performance from every system in your lab. Count on us for the services you need at every stage of your instrument's lifecycle – from installation and upgrade to operation, maintenance and repair.

And if ever your Agilent instrument requires service while covered by an Agilent service agreement, we guarantee repair or we will replace your instrument for free. No other manufacturer or service provider offers this level of commitment.

Further information

For full details of the Agilent Cary range of molecular spectroscopy products, ask for a brochure or visit our web site at www.agilent.com/chem/

Cary 600 Series FTIR Spectrometers
Publication number 5990-7783EN

Cary 610/620 Series FTIR Microscopes
Publication number 5990-7784EN

FTIR Solutions for Biomedical and Biological Applications
Publication number 5990-7974EN

Molecular Spectroscopy Portfolio
Publication number 5990-7825EN

Our catalogue of new applications is ever growing.

To learn about the latest, contact your local Agilent Representative or visit us at:
www.agilent.com/chem/

Find out how Agilent's Molecular Spectroscopy Solutions can deliver the performance, accuracy and flexibility you need.

Learn more: **www.agilent.com/chem**

Buy online: **www.agilent.com/chem/store**

Find an Agilent customer center in your country:
www.agilent.com/chem/contactus

U.S. and Canada
1-800-227-9770
agilent_inquiries@agilent.com

Europe
info_agilent@agilent.com

Asia Pacific
adinquiry_aplsca@agilent.com

1 This product is regulated by the U.S. Department of State under the International Traffic in Arms Regulations, 22 CFR 120-130 ("ITAR"). An export license from the U.S. government is therefore required to export this product from the United States, and other ITAR restrictions apply to the shipment, use, service and other aspects of this product and the FTIR instrument in which it is used.

Published: May 1, 2011
5990-7975EN

The Measure of Confidence

Agilent Technologies

Analysis of polyolefins by GPC/SEC

Application Compendium

Authors

Greg Saunders, Ben MacCreath
Agilent Technologies, Inc.

The Measure of Confidence

Agilent Technologies

Contents

Page

Polyolefin analysis by GPC/SEC

Introduction

Polyolefin is a general term describing polymers created from simple olefins or alkenes. Many different types of olefin exist, from the most simple, ethylene, to alpha-olefins of increasing complexity. Polyolefins are of great interest as two of them, polyethylene (polythene) and polypropylene, are among the highest tonnage polymers produced in the world. Interest in the analysis of polyolefins comes from the desire to create new materials with custom properties, from the development of new catalysts and from the need to perform quality control on polymer production.

Agilent has a long history of involvement in the analysis of polyolefins by gel permeation chromatography (GPC, also known as size exclusion chromatography, SEC). This application booklet describes Agilent's product portfolio for polyolefin analysis. Instrumentation, software, columns and standards are described, providing a complete package for the analysis of these important products. In addition, a wide range of applications are included that illustrate the performance of the complete solutions for polyolefin analysis offered by Agilent.

Gel permeation chromatography is a well-known technique for assessing the molecular weight distribution of polymers such as polyolefins. Molecular weight influences many of their physical characteristics, as shown in Table 1. In general, increasing molecular weight leads to higher performance, while an increase in the width of the distribution (the polydispersity) leads to a loss of performance but an increase in the ease of processing.

Many polyolefins, typically those containing over 10% ethylene and polypropylene monomers, are of limited solubility in a number of solvents. This is because the characteristic high strength and toughness of these materials results from their high crystallinity. Increased crystallinity requires break up of any inter-chain bonds in order to dissolve the material. Several solvents can be used, but in general the most effective is trichlorobenzene, a viscous solvent with a distinct odor. Ortho-dichlorobenzene is also used in some laboratories, but solubility in this solvent is less effective.

Table 1. *Effects of molecular weight (Mw) and the impact of decreasing the width of distributon of Mw on polyolefins*

	Strength	Toughness	Brittleness	Melt viscosity	Chemical resistance	Solubility
Increasing Mw	+	+	+	+	+	-
Decreasing distribution	+	+	-	+	+	+

Polymer Laboratories was formed in 1976 to offer high quality columns, standards, instruments, and software for GPC/SEC. For over 30 years the company developed many market-leading products, including PLgel, PL aquagel-OH, PlusPore, PLgel Olexis, PolarGel columns, and EasiVial standards. Built on advanced in-house manufacturing technology, PL's products have the highest reputation for quality and performance, backed up by world-class technical and applications support.

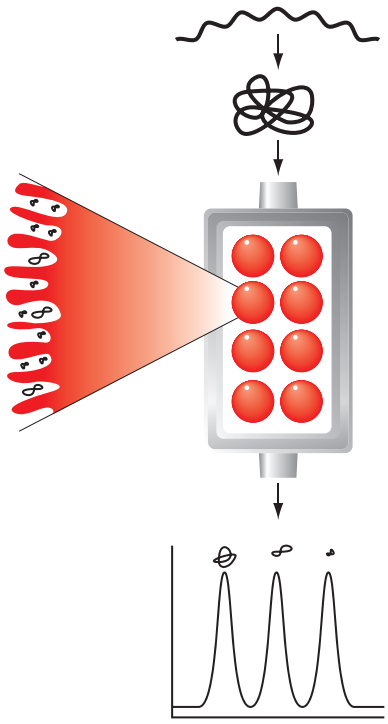
With the acquisition of PL, Agilent offers an even wider range of GPC and SEC solutions for all types of polymer characterization of synthetic and bio-molecular polymers, with options for conventional GPC all the way up to complex determinations using multi-column and multi-detection methods.

The GPC separation mechanism

- Polymer molecules dissolve in solution to form spherical coils with size dependent on molecular weight
- Polymer coils introduced to eluent flowing through a column
- Column packed with insoluble porous beads with well-defined pore structure
- Size of pores similar to that of polymer coils
- Polymer coils diffuse in and out of the pores
- Result is elution based upon size – large coils first, smaller coils last
- Size separation converted to molecular weight separation by use of a calibration curve constructed by the use of polymer standards

Highly crystalline polymers such as polyethylene are soluble only at high temperatures. This is because elevated temperatures are required to break down the ordered crystalline structure, and on cooling the material will re-crystallize and precipitate from solution. For these applications, high temperature is required throughout the entire analysis to ensure that the samples remain in solution. This places several requirements on the instrument for the successful analysis of polyolefins.

- Solvent choice is limited, mainly to 1,2,4-trichlorobenzene (TCB)
- Elevated temperature is required for dissolution, typically for 1 to 4 hours depending on molecular weight and crystallinity
- Column selection must be appropriate for the application in terms of molecular weight resolving range and efficiency of separation
- A high temperature GPC system is required to maintain all components at the analysis temperature, typically 135 to 170 °C, depending on molecular weight and crystallinity



Key

- Smaller coils can access many pores
- Larger coils can access few pores
- Very large coils access very few pores

GPC system requirements for polyolefin analysis

Autosampler, detectors, columns, injection valve and transfer tubing must all be capable of handling elevated temperatures during polyolefin analysis. A typical system schematic is shown in Figure 1.

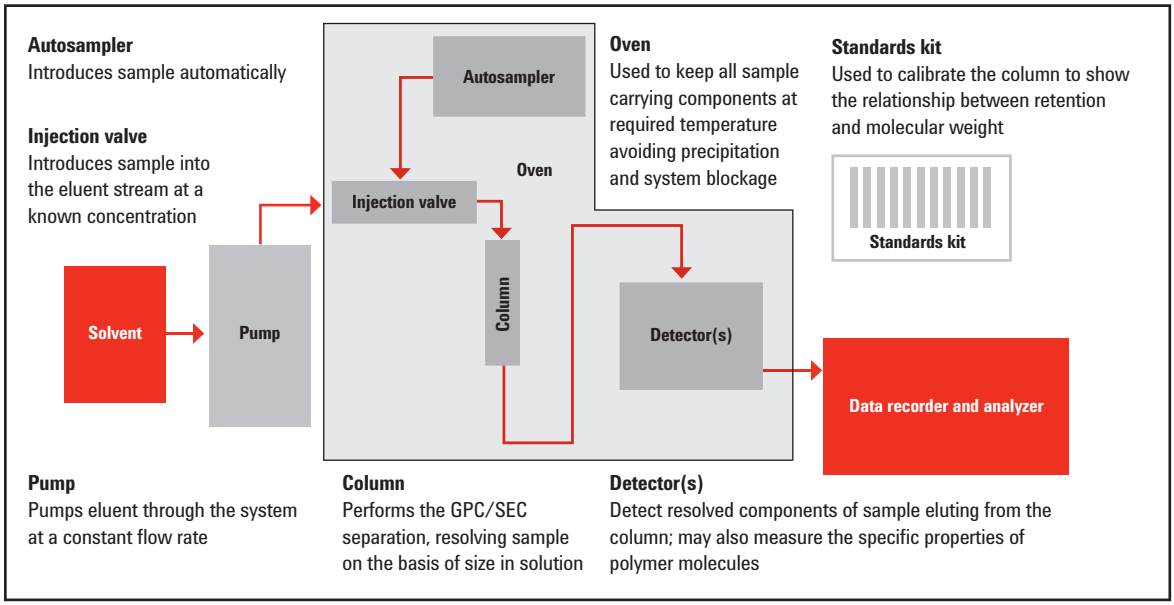


Figure 1. *Schematic of a GPC system for polyolefin analysis*

Sample preparation

Preparing polyolefin samples is time-consuming because high temperatures and long heating times are required to dissolve the sample (Table 2). Many polyolefins also display a lower density than common analytical solvents such as TCB, and so agitation of the sample is essential to ensure complete dissolution. Filtration may also be necessary to remove insoluble material such as fillers.

Table 2. *Preparing a polyolefin sample for analysis*

Material	Typical concentration (mg/mL)	Typical prep temp (°C)	Typical heating time (h)
Olefin wax	2 to 3	150	1
General PE or PP	2	150	4
Ultra-high-molecular-weight polyolefin	0.25 to 0.5	150	4 to 8

Agilent PL-SP 260VS Sample Preparation System

The PL-SP 260VS is designed for the manual dissolution and filtration of samples such as polyolefins prior to GPC analysis. The unit combines controlled heating across a temperature range of 30 to 260 °C (± 2 °C), with gentle agitation, user-selectable between 85 to 230 (± 10%) rpm. With its temperature range and speed capabilities, the PL-SP 260VS is ideal for a wide range of polymer types, including even the most difficult of samples such as ultra-high-molecular-weight polyethylene.

Choice of vial types

The removable aluminium blocks for the heated compartment are available in several formats to accommodate a variety of vial types. The Standard Accessory Kit is used with standard sample preparation 20 mL vials (supplied) and either PL-GPC 220 2 mL autosampler vials or 4 mL autosampler vials from other vendors. The Custom Accessory Kits let you choose alternative vials, if necessary.

Agilent PL-SP 260VS Sample Preparation System

Efficient dispensing

A unique pipettor device efficiently dispenses filtered sample solution from the sample preparation vial directly into destination (autosampler) vials with minimal handling.

Choice of filtration media

Filtration of polyolefin samples is often required to remove insoluble fillers or gel content (Figure 2). Two filter media are available:

- Glass-fiber (nominal porosity 1 µm) – the preferred system for general applications (Figure 2)
- Porous stainless steel (nominal porosity 0.5, 5, and 10 µm)

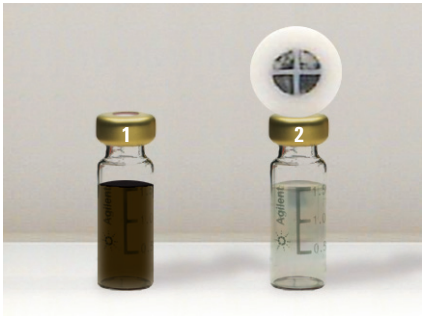


Figure 2. *Filtering a carbon black polyethylene solution – 1. without filtration, 2. after filtration using a 1 µm glass-fiber filter*

System, software and standards

The Agilent PL-GPC 220 Integrated GPC/SEC System for polyolefin analysis

The PL-GPC 220 is a leading system for the analysis of polyolefins at high temperature. Containing a number of features that have been specifically designed for polyolefin analysis, the PL-GPC 220 is the most versatile instrument for gel permeation chromatography.

Widest temperature range

The PL-GPC 220 features the widest operating range available: 30 to 220 °C, permitting analysis of virtually any polymer in any solvent. The multi-heater, forced-air oven is extremely stable, and accurately controls the temperature to within 0.05 °C. This minimizes detector baseline drift, ensuring the reproducible retention times so important in GPC.

High-precision isocratic pump – unrivalled reproducibility for precise results

The PL-GPC 220 incorporates a high-precision pump for the best pump performance available. Unbeatable flow reproducibility of 0.07% is achieved, not only in THF at near-ambient temperature, but also in TCB at temperatures above 140 °C.

Easy-access oven – changing columns and routine maintenance made simple

The column oven can comfortably hold six, 300 x 7.5 mm GPC columns. The oven operates at a convenient angle to allow for easy access for changing columns and the injector loop, providing comfortable and safe operation.

Agilent PL-GPC 220 Integrated GPC/SEC System

Enhanced RI sensitivity and stability

The improved refractive index (RI) detector includes a new photodiode and uses fiber optic technology to maximize sensitivity while minimizing baseline drift and noise, vital for good GPC/SEC. This RI detector delivers outstanding signal-to-noise ratios, even at 220 °C (Figure 3).

Conditions

Columns: 2 x Agilent PLgel 10 µm MIXED-B, 300 x 7.5 mm (Part No. PL1110-6100)
Flow Rate: 1 mL/min
Inj Vol: 200 µL
Detector: PL-GPC 220

Peak Identification

1. Mp = 1,460,000, conc. = 0.62 mg/mL
2. Mp = 9,860, conc. = 1.08 mg/mL

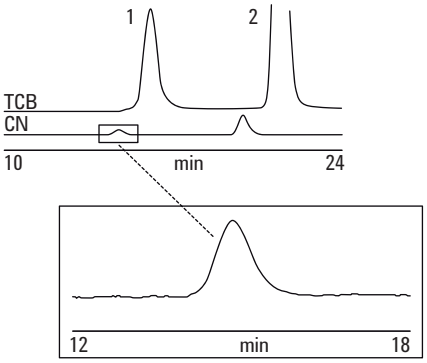


Figure 3. *Excellent signal-to-noise demonstrated in the separation of polystyrene standards*

Safety first – solvent leak detection and automated shutdown

Agilent's GPC/SEC systems incorporate integral sensors that constantly monitor the system. Vapor sensors are fitted in both the solvent module and column oven. The sensors can be programmed for sensitivity according to the solvent in use.

In the case of an unattended error, the system selects and activates the appropriate shutdown sequence depending on the nature of the error. Low solvent flow will be maintained, where possible, to avoid damage to valuable GPC columns.

An audit trail feature offers full status and error logging for system traceability.

Customized upgrade solutions

The oven easily handles multiple-detector upgrades such as light scattering and viscometry, and coupling to other techniques such as TREF (temperature rising elution fractionation), FTIR (fourier transform-infrared spectroscopy) and ELSD (evaporative light scattering detection). The oven holds up to four detectors in combination. For example, integrating RI, viscometry and light scattering would provide complete polymer characterization.

PC control – easy to program, easy to use

The PL-GPC 220 system for polymer characterization up to 220 °C features intuitive, comprehensive PC software control for full and flexible system management. With safety a pre-requisite, PC control uniquely permits remote use so that you do not need to be in the laboratory.

Interactive color-coded graphics provide ease-of-use. Simply click on the color-coded modules via the main screen to alter any run parameters. Flow rate, temperature and autosampler sequence are quickly and easily updated, and on-screen help is always available, if required (Figure 4).

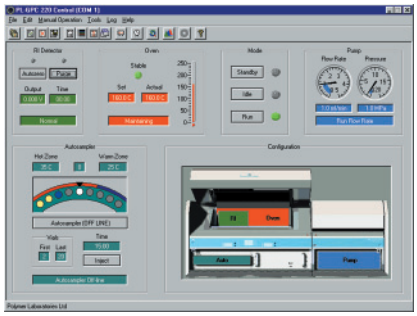


Figure 4. *Software control of the PL-GPC 220*

The time estimator calculates the amount of solvent you will need to run your samples. Input the day and time you want the system to start, then load your samples into the autosampler and let the PL-GPC 220 take care of the analysis for you.

The PL-GPC 220 is designed for true unattended operation. The system gradually heats to the analysis temperature, while the pump maintains a low flow of solvent through the column set. Once temperature is reached and stable, the pump ramps gradually to the flow rate required to run your sample. The PL-GPC 220 then automatically purges the RI detector and autozeros the baseline. Detector output is monitored and when stable, the autosampler loads and injects the first sample. Once the run sequence is complete, the flow rate automatically reduces to conserve solvent.

Integrated solvent delivery – safety by design

The solvent module in the PL-GPC 220 provides a safe, controlled environment in which solvent and waste are managed. Solvent handling is fully integrated and vented for operator safety, and the system does not need to be located in a fume hood.

The PL-GPC 220 includes an integral solvent degasser with a choice of solvent reservoir from 2 L bottles up to a 13 L stainless-steel tank. The solvent delivery module is thermostatically controlled to 30 °C, which ensures efficient, continuous and reproducible solvent delivery, even if the solvent is viscous or may be solid at near-ambient temperature (Figure 5).

Figure 5. *Agilent PL-GPC 220 integrated solvent delivery system*

Dual-zone-heated autosampler – no degradation of samples before injection

Agilent's innovative autosampler accommodates 39 samples in industry-standard 2 mL vials. Injection precision has been measured at better than 1% RSD with no cross contamination between samples, and without the need for rinse vials. The autosampler design features dual-zone heating to minimize thermal degradation. The warm and hot zones are independently programmable from ambient to 220 °C, and so the samples in the carousel waiting for injection are maintained at a lower holding temperature, then heated to analysis temperature prior to injection.

The vial is transferred to the column oven where the sample equilibrates before injection. This minimizes baseline disturbance and completely eliminates the risk of sample precipitation.

Agilent Cirrus GPC Software – the universal GPC solution

Cirrus is the powerful suite of GPC/multi-detector software from Agilent. Polymer Laboratories, now a part of Agilent, has been a supplier of industry-standard GPC software since the 1980s. Cirrus makes GPC calculations easy, whether in conventional GPC using a concentration detector or for multi-detector analysis with light scattering and viscosity.

Integration with existing LC software

Powerful, yet easy to use and learn, Cirrus is available for standalone GPC or for integrating GPC with LC. Cirrus utilizes the latest advances in software design to provide comprehensive calculation options, customized reporting, and high-resolution data capture with the Agilent PL DataStream.

Modular, flexible, and scalable

Cirrus is made to grow as your needs change. A suite of modules provides support for a variety of GPC techniques, such as multi-detector GPC, online FTIR detection and short-chain branching (SCB). Cirrus can be run on a standalone PC or provide a networked GPC solution.

Easy-to-use interface

Cirrus uses an intuitive graphical-user interface, so straightforward that new users can report results within an hour of installing the software. Cirrus is based on Agilent's Workbook concept to provide:

- A simple 'container' for data, parameters and results
- Automatic archiving of chromatograms, calibrations, and results
- Data traceability and data integrity
- Templates allowing predefinition of parameters and report content

Comprehensive calibration and calculation options

Cirrus offers a choice of calibration options.

- Conventional calibration using narrow standards
- Universal Calibration by viscometry or using Mark-Houwink coefficients
- Replicate entries of calibration points
- Three broad-standard calibration methods
- Averages and distributions can be calculated for any number of peaks in a chromatogram
- % of material can be reported for specific MW limits

A calibration overlay facility lets you view the effects of column performance over time.

Reviewing, collating, and condensing results

Cirrus meets the requirements of both QC/Routine and R&D environments, providing fully automated or interactive analysis. The software offers a number of powerful options to review, compare and extract information from archived data and results for inclusion into final reports.

Chromatograms and results can be reviewed both textually and graphically. This information can be exported in a variety of industry-standard formats. A powerful report designer provides total flexibility in report content and presentation. In Cirrus, all parameters relating to a chromatogram or results file are easily accessible via a comprehensive range of export options. Cirrus also ensures that data integrity and traceability are maintained throughout all operations.

Standards for column calibration in polyolefin analysis

Polymer standards from Agilent Technologies are the ideal reference materials for generating accurate, reliable GPC/SEC column calibrations, with the assurance of the ISO 9001:2000 quality standard. Additional applications for our highly characterized homopolymers exhibiting unique characteristics are as model polymers for research and analytical method development. These quality polymer standards are supplied with extensive characterization that utilize a variety of independent techniques (e.g. light scattering and viscometry) and high performance GPC to verify polydispersity and assign that all important peak molecular weight (Mp).

For polyolefin analysis, polyethylene and polystyrene standards are commonly employed. Agilent provides you with the widest choice of these materials to maximize your specific characterization needs. In addition, we supply other polymers as individual molecular weights, and broad distribution polymers for system validation or broad standard calibration procedures. A range of polymer standards available from Agilent are listed in Table 3.

Table 3. *Standards selection guide*

Polymer type	Individual Mw	Calibration kits	Agilent EasiCal	Agilent EasiVial	Type of GPC/SEC
Polystyrene	Yes	Yes	Yes	Yes	Organic
Polymethylmethacrylate	Yes	Yes		Yes	Organic
Polyethylene	Yes	Yes			Organic

Recommendations for setting up a GPC/SEC system for polyolefin analysis

The following questions will help you find the recommended columns and standards for any given application, as well as the system parameters such as injection volumes.

Choosing a column for GPC/SEC of polyolefins

Columns shown in bold are the best initial choice

Question	Answer	Recommendation	Comments
1. What is the expected molecular weight? *It may seem strange to ask this question, but in GPC/SEC the resolution of a column is related to the resolving range. Knowing something of the expected molecular weight of a sample helps to choose the best column that will give optimum results.*	High (up to several millions)	**PLgel Olexis**	PLgel Olexis is specifically designed for polyolefin analysis, offers optimal performance, also suitable for light scattering
		PLgel 10 µm MIXED-B or PLgel 20 µm MIXED-A	The PLgel MIXED-A column resolves higher than the PLgel MIXED-B but at lower efficiency due to larger particle size
		PLgel MIXED-B LS or PLgel MIXED-A LS	Suitable for light scattering
	Intermediate (up to hundreds of thousands)	PLgel 5 µm MIXED-C or PLgel 5 µm MIXED-D	These PLgel columns are the most widely applicable for the majority of applications
	Low (up to tens of thousands)	**PLgel 5 µm 500Å**	The PLgel column provides high resolution and is designed for low-molecular-weight applications
	Very low (a few thousand)	**PLgel 5 µm 100Å**	The PLgel column gives high resolution at low Mw
	Unknown	**PLgel Olexis**	This PLgel column is designed for polyolefin analysis
2. How many columns to use? *The greater the particle size of the media in the column (which is dependent on the expected molecular weight of the samples), the lower the resolution and the more columns are required to maintain the quality of the results. For higher molecular weight samples, larger particles are necessary to reduce the danger of shear degradation of samples during analysis.*	Depends on the particle size of the columns	Particle size 20 µm, use 4 columns	Increased number of columns required for large particle sizes to make up for low efficiences – PLgel Olexis is 13 µm
		Particle size 13 µm, use 3 columns	
		Particle size 10 µm, use 3 columns	
		Particle size 5 µm, use 2 columns	
3. What standard is best? *Depending on analysis there are two options.*		**Polystyrene (PS)** or polyethylene (PE)	Polystyrene is the most commonly used standard in convenient EasiVial format, polyethylene is useful for generating PE based molecular weights

Columns for GPC analysis of polyolefins

Agilent produces a broad array of columns for the analysis of synthetic polymers and many of them are suitable for the analysis of polyolefins. However, the PLgel Olexis column is specifically designed for polyolefins with a wide range of molecular weights.

Agilent PLgel Olexis

PLgel Olexis is the optimum column choice for the analysis of very high-molecular-weight polymers such as polyolefins. Designed and manufactured specifically for these compounds, the column resolves up to 100,000,000 g/mol (polystyrene in THF). Packed with 13 µm particles for maximum resolution with minimal polymer shear, the columns also operate up to 220 °C for the analysis of highly crystalline materials. The column packing exhibits the excellent mechanical stability and robustness expected from the PLgel product range.

No shear degradation

The columns have a particle size of 13 µm, selected to give good efficiency in excess of 30,000 plates/m. In addition, the excellent size consistency of the particles (Figure 6) results in a very narrow particle size distribution that ensures no shear degradation.

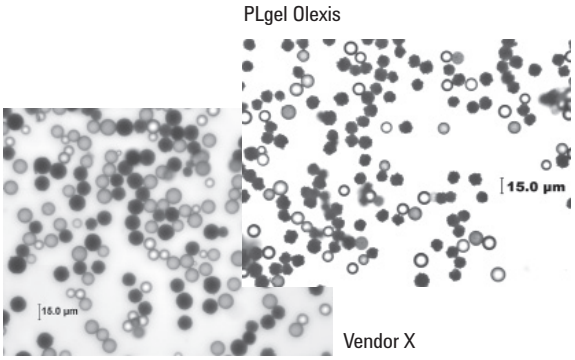


Figure 6. *The superior size consistency of PLgel Olexis particles is clearly evident*

High resolving range

Many new types of polyolefins have been developed recently with very high polydispersities. Determination of accurate polydispersities and modalities is critical in the research and development of these new polymers. PLgel Olexis completely satisfies this demand, for all polyolefin applications up to 100,000,000 g/mol.

Easy extrapolation

The large pore size of the particles makes them effective with many types of polyolefin. Linearity was introduced into the Agilent manufacturing process as a control criterion to ensure linear resolution across the operating range (Figure 7). The result is simplified extrapolation for calibrations.

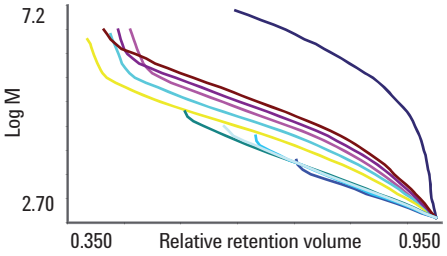


Figure 7. *Some of the components of PLgel Olexis that contribute to its lack of artifacts*

One column for all polyolefin applications

As the packing material in PLgel Olexis is an accurate blend of many components, smooth distributions are produced that truly reflect the sample composition (Figure 8). Dislocations are absent, so you can be sure that any unusual peak shapes represent the true nature of the sample and are not artifacts.

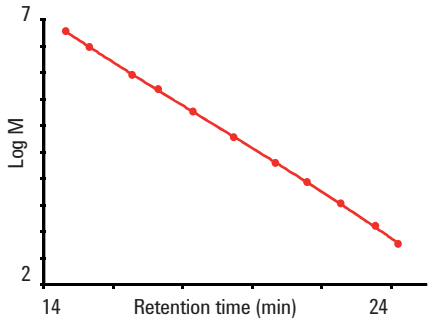


Figure 8. *Careful blending delivers highly linear polystyrene calibrations with PLgel Olexis in TCB*

The quality of the blending in PLgel Olexis columns means that polyolefins of very different polydispersity can be confidently analyzed on the same column set. Once again, PLgel Olexis provides trustworthy, clean and mono-modal peaks.

Polyolefin applications

The applications in this booklet illustrate the diversity of polyolefin samples, and reveal the flexibility of PLgel columns and the necessity for the PL-GPC 220 in addressing the analysis of such compounds.

Columns for high-molecular-weight polyolefins

Polyolefins range from low-molecular-weight hydrocarbon waxes to ultra-high-molecular-weight rigid plastics. The molecular weight distributions of polyolefins is directly related to physical properties such as toughness, melt viscosity and crystallinity. High-molecular-weight polyolefins tend to exhibit very broad molecular weight distribution (MWD). For such samples, small particles with small pore sizes are not desirable since shear degradation may occur, and so the high-pore-size particles of PLgel Olexis are recommended.

Conditions

Samples:	Polyethylenes
Columns:	3 x PLgel Olexis, 300 x 7.5 mm (Part No. PL1110-6400)
Eluent:	TCB + 0.015% BHT
Flow Rate:	1 mL/min
Inj Vol:	200 µL
Temp:	160 °C
Detector:	PL-GPC 220 (RI) + viscometer

Artifacts known as dislocations can arise in blended columns, resulting from a mismatch of the pore volume of components in the blend. Dislocations lead to false modalities and polydispersities. Avoiding dislocations was an integral part of the design brief for PLgel Olexis columns. Accurate blending of these components produces a column that gives a smooth molecular weight distribution, providing a true reflection of the shape of the MWD (Figure 9). PLgel Olexis is perfect for studies that require accurate polydispersity index and modality information.

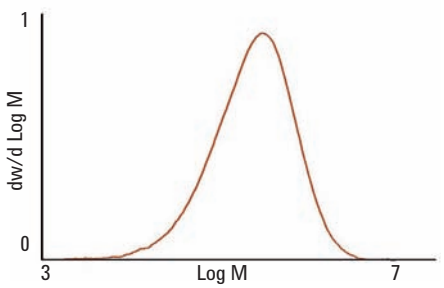


Figure 9. *True representation of polyolefin molecular weight distribution with PLgel Olexis*

Figure 10 shows a range of polyolefin samples analyzed on a PLgel Olexis column, covering the spread of molecular weights. There are no dislocations and the peak shape of the very broad samples shows true sample modality.

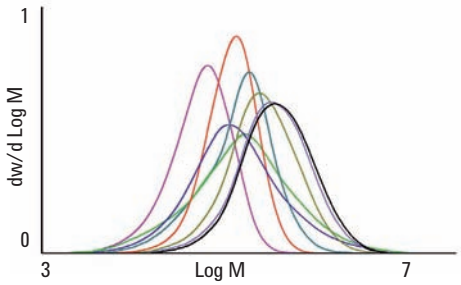


Figure 10. *PLgel Olexis reveals true modalities across the range of polyolefins*

Given the accurate resolving power of PLgel Olexis you can be sure that unusual peak shapes are real and not artifacts; unusual peak shapes of some samples will be true reflections of their modality. This is important for studies into reaction mechanisms and catalyst behavior (Figure 11).

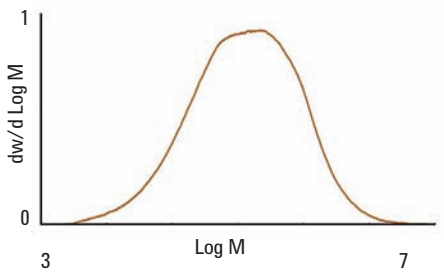


Figure 11. *A true change in peak shape revealed by PLgel Olexis of a multi-modal material manufactured from a multi-site catalyst*

Columns for lower-molecular-weight polyolefins

Crude oil, or petroleum, is the main source of organic chemicals for industry. The major chemicals are derived from two constituents of oil, xylene and naphtha. These raw materials are then broken down into more basic products, e.g. polyethylene, polypropylene, elastomers, asphalts and liquid hydrocarbons. Characterization of such products is commonly achieved using GPC. This involves a liquid chromatographic separation from which a molecular weight distribution calculation can be made following calibration of the system with suitable polymer standards. The diversity of petroleum products demands a variety of GPC column types for optimized analysis. Low-molecular-weight liquid hydrocarbons require high resolution of individual components. This is illustrated in Figure 12, where three linear hydrocarbons are resolved easily to base-line in a reasonably short analysis time.

Conditions

Samples:	Linear hydrocarbons
Columns:	2 x Agilent PLgel 5 µm 100Å, 300 x 7.5 mm (Part No. PL1110-6520)
Eluent:	TCB
Flow Rate:	1 mL/min
Temp:	145 °C
Detector:	PL-GPC 220

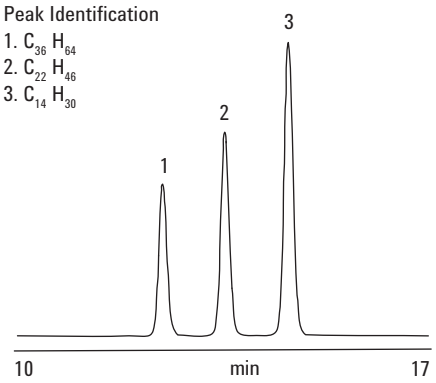


Figure 12. *Linear hydrocarbons separated to base-line on a PLgel column set*

Figure 13 shows the separation of a selection of low-molecular-weight linear hydrocarbons.

Conditions

Samples:	Linear hydrocarbons
Columns:	2 x Agilent PLgel 3 µm 100Å, 300 x 7.5 mm (Part No. PL1110-6320)
Eluent:	TCB
Flow Rate:	0.8 mL/min
Inj Vol:	20 µL
Temp:	145 °C
Detector:	PL-GPC 220

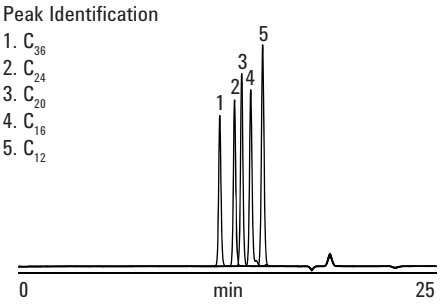


Figure 13. *Separation of low-molecular-weight hydrocarbons*

The PLgel 100Å columns have a GPC exclusion limit of 4,000 molecular weight (polystyrene equivalent). Intermediate products can be analyzed using the PLgel MIXED-D column that has a linear molecular weight resolving range up to an exclusion limit of around 400,000 molecular weight. The 5 µm particle size maintains high column efficiency and thus fewer columns are required and analysis time is relatively short.

Figure 14 shows a chromatogram of a relatively low-molecular-weight hydrocarbon wax obtained on PLgel 5 µm MIXED-D columns.

Conditions

Samples:	Linear hydrocarbons
Columns:	2 x Agilent PLgel 5 µm MIXED-D, 300 x 7.5 mm (Part No. PL1110-6504)
Eluent:	TCB
Flow Rate:	1 mL/min
Inj Vol:	200 µL
Temp:	160 °C
Detector:	PL-GPC 220

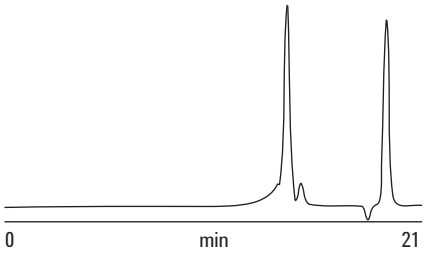


Figure 14. *A low-molecular-weight wax*

Figure 15 shows the analysis of an asphalt used in road surfacing. Subsequently derived information regarding the molecular weight distribution of such materials is invaluable in determining their processibility and final properties.

Conditions

Columns:	2 x PLgel 5 µm MIXED-D, 300 x 7.5 mm (Part No. PL1110-6504)
Eluent:	THF
Flow Rate:	1 mL/min
Temp:	40 °C
Detector:	RI

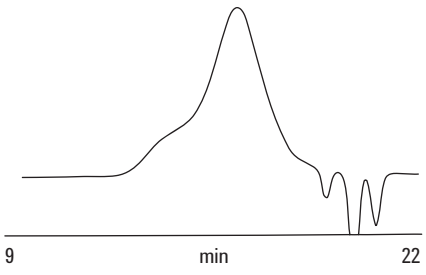


Figure 15. *Fast analysis of asphalt on PLgel 5 µm MIXED-D columns*

Repeatability study 1

A commercial sample of high-density polyethylene (HDPE) was prepared at 2 mg/mL using the PL-SP 260VS Sample Preparation System, with a dissolution temperature of 160 °C and a dissolution time of two hours. Eight aliquots of the master batch solution were dispensed into PL-GPC 220 autosampler vials and placed in the autosampler carousel of the PL-GPC 220 where the hot zone temperature was 160 °C and the warm zone 80 °C (Figure 16).

Conditions

Columns:	3 x PLgel 10 µm MIXED-B, 300 x 7.5 mm (Part No. PL1110-6100)
Eluent:	TCB + 0.0125% BHT
Flow Rate:	1 mL/min
Inj Vol:	200 µL
Temp:	160 °C
Detector:	PL-GPC 220

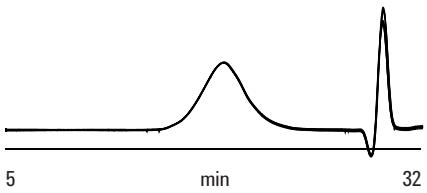


Figure 16. *Overlay of the raw data chromatograms obtained for eight consecutive injections of HDPE*

The data were analyzed against a polystyrene standards calibration using the following Mark-Houwink parameters to obtain the polypropylene equivalent molecular weight averages that are shown in Table 4.

Polystyrene in TCB[1] $K = 12.1 \times 10^{-5}$ $\alpha = 0.707$

Polyethylene in TCB[2] $K = 40.6 \times 10^{-5}$ $\alpha = 0.725$

Table 4. *Summary of results from eight injections of HDPE*

Injection number	Mn	Mp	Mw
1	17,289	76,818	333,851
2	16,988	77,434	335,496
3	17,428	77,514	332,616
4	17,521	77,052	335,635
5	17,348	76,520	334,212
6	17,487	77,728	333,511
7	16,898	77,578	335,642
8	17,457	77,288	334,923
Mean	17,302	77,241	334,485
Std Dev	220	387	1,048
% Variation	1.3	0.5	0.3

Figure 17 shows an overlay of the molecular weight distribution calculated for the eight consecutive injections of the HDPE sample, and illustrates the excellent repeatability obtained with the PL-GPC 220 using PLgel 10 µm MIXED-B columns.

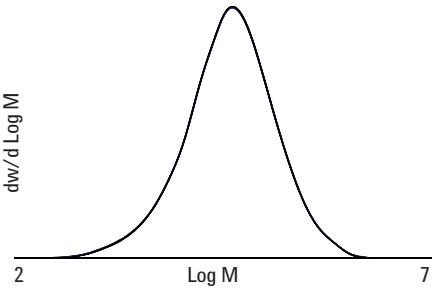


Figure 17. *Molecular weight overlay of eight consecutive injections of HDPE*

Repeatability study 2

A commercial sample of high-density polypropylene (HDPP) was prepared at 1.5 mg/mL using the PL-SP 260VS Sample Preparation System with a dissolution temperature of 160 °C and a dissolution time of two hours. Six aliquots of the master batch solution were dispensed into PL-GPC 220 autosampler vials and placed in the carousel where the hot zone temperature was 160 °C and the warm zone 80 °C.

Figure 18 shows an overlay of the raw data chromatograms obtained for six consecutive injections of the sample.

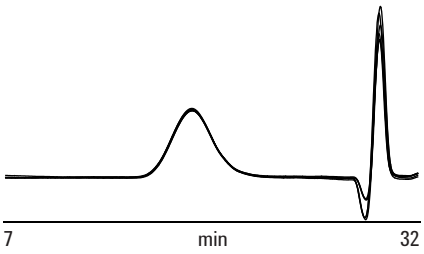


Figure 18. *Overlay of the raw data chromatograms obtained for six consecutive injections of HDPP*

The data were analyzed against a polystyrene standards calibration using the following Mark-Houwink parameters to obtain the polypropylene-equivalent molecular weight averages that are shown in Table 5.

Polystyrene in TCB[1] $K = 12.1 \times 10^{-5}$ $\alpha = 0.707$

Polypropylene in TCB[2] $K = 19.0 \times 10^{-5}$ $\alpha = 0.725$

Table 5. *Overlay of the raw data chromatograms obtained for six consecutive injections of HDPP*

Injection number	Mp	Mn	Mw
1	127,132	65,086	185,795
2	131,893	65,089	185,236
3	128,673	66,802	186,202
4	132,062	67,417	188,048
5	131,625	69,320	188,679
6	130,227	69,677	186,188
Mean	130,202	67,232	186,691
Std Dev	1,693	1,815	1,239
% Variation	0.13	2.70	0.66

Conditions

Columns:	3 x PLgel 10 µm MIXED-B, 300 x 7.5 mm (Part No. PL1110-6100)
Eluent:	TCB + 0.0125 BHT
Flow Rate:	1 mL/min
Inj Vol:	200 µL
Temp:	160 °C
Detector:	PL-GPC 220

Figure 19 shows an overlay of the molecular weight distribution calculated for the six consecutive injections of the HDPP sample that illustrates the excellent repeatability obtained with the PL-GPC 220 using PLgel 10 µm MIXED-B columns.

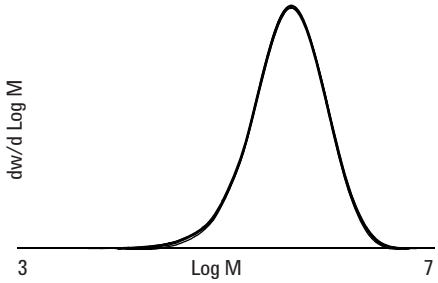


Figure 19. *Molecular weight overlay of six consecutive injections of HDPP*

References

[1] H. Coll and D. K. Gilding (1970) Universal calibration in GPC: a study of polystyrene, poly-α-methylstyrene, and polypropylene. *Journal of Polymer Science Part A-2: Polymer Physics*, 8, 89-103.

[2] T. G. Scholte , N. L. J. Meijerink, H. M. Schoffeleers and A.M.G. Brands (1984) Mark-Houwink equation and GPC calibration for linear short chain branched polyolefins, including polypropylene and ethylene-propylene copolymers. *Journal of Applied Polymer Science*, 29, 3763.

Specialist detectors

Multi-detector options for polyolefin analysis

Conventional GPC employs a refractive index or other concentration detector. However, polyolefins can be analyzed by multi-detector GPC that combines a concentration detector with a viscometer, a static light scattering detector, or both.

GPC viscometry – analysis using a concentration detector and viscometer

A viscometer may be housed inside the oven of the PL-GPC 220 to allow analysis of polyolefins by GPC viscometry. Using GPC viscometry, molecular weights are determined using the Universal Calibration method. A plot of molecular size as log (molecular weight x intrinsic viscosity) versus retention time is constructed for a series of narrow standards, based on the relationships in Equations 1 and 2.

Equation 1:

Hydrodynamic volume α molecular weight x intrinsic viscosity

Equation 2:

Log (MW x intrinsic viscosity) versus retention time ≃ log (hydrodynamic volume) versus retention time

PLgel Olexis columns are separated and calibrated in terms of size and so a Universal Calibration is obtained (Figure 20).

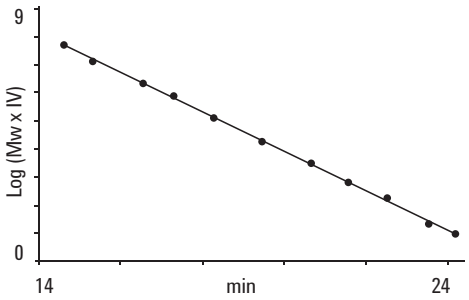


Figure 20. *Multi-detector GPC Universal Calibration of a PLgel Olexis column*

The Universal Calibration technique gives polyolefin molecular weights regardless of the calibrants used in the analysis. This allows cheaper calibrants such as polystyrene to be used while still providing accurate polyolefin results.

- Intrinsic viscosities are measured from the viscometer and concentration detector
- Accurate molecular weights are calculated assuming that the sample obeys the Universal Calibration (pure size exclusion is obtained)
- Radius of gyration is calculated using a model for the polymer behavior in solution

GPC light scattering – analysis employing a concentration detector and a light scattering detector

A dual-angle light scattering detector can be sited inside the oven of the PL-GPC 220 to allow analysis of polyolefins by GPC light scattering, employing the dissymmetry method. In GPC light scattering, accurate molecular weights are determined directly by using the response of the light scattering detector and the intensity of scattered light, as described in Equation 3.

Equation 3:

$R_\theta = CM\,(dn/dc)^2\,P_\theta K_\theta$

R_θ is the detector response, CM is concentration x mass, dn/dc is the specific refractive index increment, P_θ is the particle scattering function and K_θ is the light scattering constant.

- Molecular weights are calculated directly from the light scattering response, calculating the particle scattering function from the ratio of intensities at 15° and 90°
- Radius of gyrations are determined from the particle scattering function by comparison of the two angles, but only if the molecule is over about 10 nm in size and the scattering intensity shows angular dependence
- Intrinsic viscosity is calculated using a model for the polymer behavior in solution

GPC triple detection – analysis using concentration, viscometry and light scattering data

In this technique, both a viscometer and a dual-angle light scattering detector are housed inside the PL-GPC 220. With GPC triple detection, molecular weights are determined directly using the response of the light scattering detector as described above.

- Molecular weights are calculated directly from the light scattering response, calculating the particle scattering function from the ratio of intensities at 15 ° and 90 °
- Radius of gyrations are determined from the particle scattering function by comparison of the two angles but only if the molecule is over about 10 nm in size and the scattering intensity shows angular dependence
- Intrinsic viscosity is calculated from the viscometer trace

Comparisons between conventional GPC, GPC viscometry, GPC light scattering and GPC triple detection

Conventional GPC using only a concentration detector generates molecular weights on the basis of comparison to a series of calibration standards. However, unless the standards and samples are of the same chemistry and therefore same size in solution at any given molecular weight, the results are only relative as the GPC column separates on the basis of size not molecular weight. Conventional GPC only gives accurate results if standards of the same chemistry as the samples under investigation are used.

GPC viscometry and GPC light scattering, or GPC triple detection, can be used to determine 'absolute' molecular weights of samples, independent of the chemistry of standards used in the column calibration (GPC viscometry) or independent of column calibration entirely (GPC light scattering and GPC triple detection).

The values of molecular weight can vary between these techniques because the viscometer and light scattering detectors respond to different properties of the polymer, the viscometer to molecular density, and the light scattering detector to size in solution. Therefore, molecular weights calculated by these approaches will not necessarily have the same values.

Branching

Comparing long-chain branching in polyethylenes

Multi-detector GPC combined with branching calculations is an excellent way of comparing and identifying different kinds of polyethylene. These different materials, although of the same basic chemical structure, differ in their mode of manufacture and have very different physical properties.

LDPE – low-density polyethylene

Low-density polyethylene was the first grade of polyethylene manufactured in the 1930s. It exhibits relatively low crystallinity compared to other forms of polyethylene due to the presence of long branches on the polymer backbone (on about 2% of the carbon atoms). As a result, the tensile strength of the material is lower while resilience is higher. These long-chain branches are a result of 'backbiting' reactions in the synthetic processes used to manufacture the material. Multi-detector GPC can measure the level of branching in LDPE.

HDPE – high-density polyethylene

High-density polyethylene is manufactured using different catalysts than those used for LDPE, selected to give very low levels of branching from the backbone. HDPE therefore has higher density and crystallinity than LDPE, resulting in a tougher, more temperature-stable product. HDPE does not display long-chain branching.

LLDPE – linear low-density polyethylene

Linear low-density polyethylene is a newer material manufactured by incorporation of small quantities of alpha-olefins such as butane, hexane or octene into the polymer. LLDPE materials are more crystalline than LDPE, but are elastomeric and have a higher tensile strength and puncture resistance. Multi-detector GPC employing a viscometer and/or light scattering detector cannot be used to investigate the branching in LLDPE as changes in the density and size of the molecules compared to linear materials are very small and cannot be detected. GPC-FTIR is employed for short-chain branching analysis, as discussed on page 24.

Investigating branching in polyolefins

In multi-detector GPC, branching is assessed by investigating changes in molecular size or intrinsic viscosity as a function of increasing molecular weight. In all cases for polymers of the same chemistry, branched molecules always have lower Rg and IV values than linear analogs due to the presence of branch points.

In all methods, branching calculations can be performed on either the intrinsic viscosity (measured or calculated) or radius of gyration (measured or calculated) data. The quality of the branching results will depend on the quality of the source data (intrinsic viscosity or radius of gyration). Contraction factors are determined from the Mark-Houwink (log intrinsic viscosity versus log MW) or conformation (log radius of gyration versus log MW) plots using the relationships in Equation 4.

Equation 4:

Radius of gyration contraction factor

$$g = \left(\frac{\text{Rg branched}}{\text{Rg linear}} \right)_{MW}$$

Intrinsic viscosity contraction factor

$$g' = \left(\frac{\text{IV branched}}{\text{IV linear}} \right)_{MW}$$

where $g = g'^{(1/\epsilon)}$

ϵ (structure factor) = 0.5 to 1.5, typically 0.75

The value of g (directly or taken from the value of g' and an estimation of the structure factor, typically 0.75) is used along with the branching repeat unit (the molecular weight of the monomer multiplied by 1,000) to obtain branching numbers using a branching model. In the absence of structural data for the sample, a number-average ternary-branching model is used as shown in Equation 5.

Equation 5:

$$g = [(1 + B_n/7)^{1/2} + 4B_n/9\pi]^{-1/2}$$

where B_n = branches per 1,000 carbons

Branching numbers are expressed as number of branches per 1,000 carbons (from polyethylene investigations). If the polymer in question is not polyethylene then the actual branching number may not be directly meaningful. However, comparison between samples is still possible.

Analysis of branching in polyethylenes

Samples of LDPE, HDPE and LLDPE were analyzed with the PL-GPC 220 by triple detection.

Conditions

Columns:	3 x PLgel Olexis, 300 x 7.5 mm (Part No. PL1110-6400)
Eluent:	TCB + 0.015% BHT
Flow Rate:	1.0 mL/min
Inj Vol:	200 µL
Temp:	160 °C
Detector:	PL-GPC 220 (RI) + viscometer + dual-angle light scattering

Refractive index, dual-angle light scattering and viscometry detectors were employed and the data was analyzed with Cirrus GPC Multi Detector Software. A polystyrene standard was used to generate the detector constants for the triple detection analysis.

Figure 21 shows the molecular weight distributions for the three samples. Although there was some overlap, the samples clearly had significantly different molecular weights.

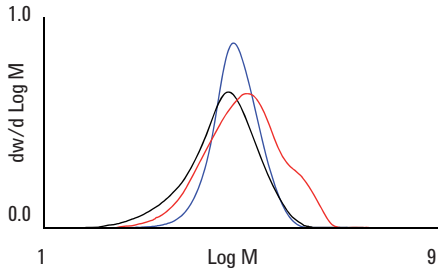


Figure 21. *Overlaid molecular weight distributions for three samples of polyethylene, HDPE – black, LLDPE – blue, LDPE – red*

Figure 22 shows the Mark-Houwink plots for the three samples using intrinsic viscosities generated from the viscometer and molecular weights from the light scattering detector.

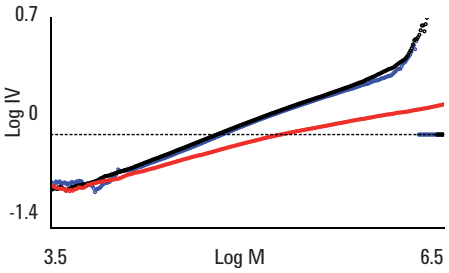


Figure 22. *Overlaid Mark-Houwink plots for three samples of polyethylene, HDPE – black, LLDPE – blue, LDPE – red*

The Mark-Houwink plot describes the change in the viscosity of the polymers as a function of increasing molecular weight. The HDPE and LLDPE samples overlay on the Mark-Houwink plot, indicating that the polymers have very similar structures. The Mark-Houwink parameters K (the intercept) and alpha (the slope) indicate that the materials contain no branching that can be detected by multi-detector GPC. However, the LDPE shows a clear deviation from the HDPE and LLDPE lines, with a decreasing slope as molecular weight increases. This is due to increased branching of the LDPE compared to the other materials as molecular weight increases lead to a reduction in viscosity.

Branching analysis of polyethylenes with Cirrus GPC Multi Detector Software

The presence of long-chain branching (over six carbons in length) in polyolefins strongly influences physical properties such as melt viscosity and mechanical strength. The distribution chain branches in polyolefins are determined by the polymerization mechanism and there is significant interest in the production of materials with well-defined and characterized molecular weight and branching distributions for specific applications.

Three samples of polyethylene, one HDPE and two LDPE, were analyzed using the PL-GPC 220 by GPC/viscometry. Two of the samples had been synthesized by a mechanism to promote branching, while the third was a standard linear reference material, NBS 1475.

Refractive index viscometry detectors were employed and the data was analyzed with Cirrus GPC Multi Detector Software using the Universal Calibration approach. Polystyrene standards were used to generate the Universal Calibration and the unbranched sample was used as a linear model in the determination of branching.

Figure 23 shows the molecular weight distributions for the three samples. The black plot is for the unbranched sample. Although there was some overlap, the samples clearly had significantly different molecular weights.

Figure 24 shows the Mark-Houwink plots for the three samples. The upper-most sample is the unbranched material. The other two samples have lower intrinsic viscosities at any given molecular weight, with the unbranched polymer indicating the presence of branching. This can be expressed in terms of g, the branching ratio, defined in Equation 6, where ϵ is a constant.

Equation 6:

$$g = \left(\frac{\text{IV branched}}{\text{IV linear}} \right)^{1/\epsilon}$$

Conditions

Samples:	Polyethylenes
Columns:	3 x PLgel Olexis, 300 x 7.5 mm (Part No. PL1110-6400)
Eluent:	TCB + 0.015% BHT
Flow Rate:	1.0 mL/min
Inj Vol:	200 µL
Temp:	160 °C
Detector:	PL-GPC 220 (RI) + viscometer

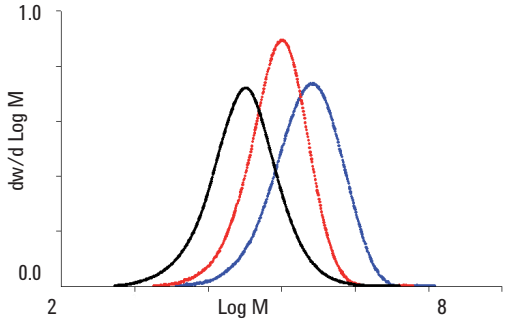


Figure 23. *Molecular weight distribution plots for three polyethylene samples – the black plot is the unbranched sample*

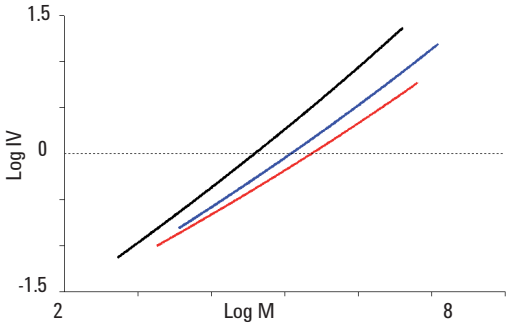


Figure 24. *Mark-Houwink plots for three samples of polyethylene*

The unbranched sample was used as the linear model and so gives a g value of unity (except at high molecular weight due to scatter in the data). The other two samples both exhibit a decrease in g as a function of molecular weight, indicating that as molecular weight increases the number of branches also increases. Based on these calculated g values, a branching number or number of branches per 1,000 carbon atoms can be generated. This is achieved by fitting the data into a model. The Cirrus GPC Multi Detector Software offers a selection of branching models that can be employed in this approach. In this case a model was used that calculates a number-average branching number assuming a random distribution of branches on the polymer. Figures 25 and 26 show the g plots and branching number plots obtained for the samples.

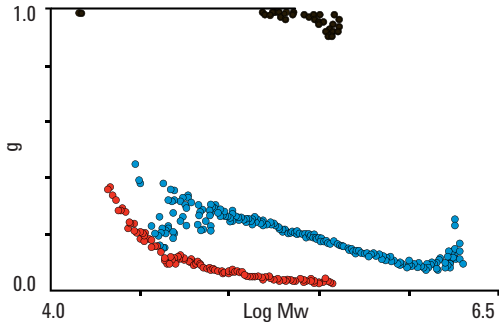


Figure 25. *Branching ratio g plots for three polyethylene samples – the black plot is the unbranched sample*

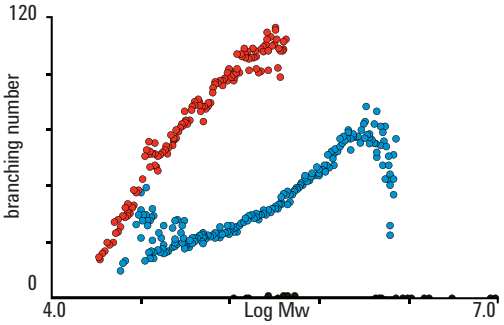


Figure 26. *Calculated branching numbers as a function of molecular weight for three samples of polyethylene – the black plot is the unbranched sample*

The results show that of the two, branched samples, the trend in molecular weight distribution does not follow the trend in branching distribution. The sample showing the most branching at any given molecular weight has a lower molecular weight than the second sample. Clearly, understanding both the molecular weight and branching distributions will give an insight into the processibility of the two materials.

Analysis of branching in linear low-density polyethylene (LLDPE)

Fourier transform-infrared (FTIR) spectroscopy is a well-established technique used in compositional analysis of materials through the measurement of vibrational absorption bands. Polymers typically exhibit relatively simple absorption spectra, allowing them to be readily identified by comparison to library data and are therefore well suited to analysis by FTIR. Coupling FTIR detection with gel permeation chromatography is particularly advantageous as FTIR detection can be utilized as both concentration detector for molecular weight calculations and as a spectroscopic tool for compositional analysis, significantly enhancing the information available from a single GPC experiment.

Coupling a PL-GPC 220 system to one of the range of Agilent's FTIR spectrometers can be achieved using the PL-HTGPC-FTIR interface, which consists of a heated flow cell, a heated transfer line, and a temperature control box. The flow cell and transfer line can be heated up to 175 °C with an accuracy of ± 0.5 °C for polyolefin applications. To obtain good quality spectra, the FTIR spectrometer is fitted with a fast MCT (mercury-cadmium-telluride) detector. Data acquisition is performed through the spectrometer's time-resolved data-acquisition software.

GPC/FTIR analysis of polyethylene

Highly crystalline polyethylene is difficult to analyze by GPC due to its limited solubility in most organic solvents, and the high temperatures required for dissolution (typically over 135 °C). Trichlorobenzene (TCB) is the most commonly used solvent for these materials. TCB is also a suitable solvent for GPC analysis with FTIR detection as the solvent has a good absorption window between about 3,500 and 2,700 cm^{-1}, which corresponds to the >C-H stretching region. CH vibrations dominate the solid-state spectra of polyethylene and so this absorption region is of key importance.

Focusing on the >C-H stretching region, differences in the proportions of $>CH_2$ and $-CH_3$ groups in a sample can be seen in the relative intensities of the absorption bands. This dependence of the infrared spectra on the presence of $-CH_3$ and $>CH_2$ groups can be used to measure the level of short-chain branching (SCB) in polyethylene[1]. These are branches less than six carbons long introduced by co-polymerization of ethylene with other alpha-olefins that cannot be detected by traditional multi-detector GPC experiments, as they do not affect the viscosity of the polymer. The level of SCB does, however, strongly influence crystallinity, density, and stress-crack resistance of polyethylene. By measuring the spectra of polyethylene containing SCB, the relative intensities of the stretching vibrations due to $-CH_3$ and $>CH_2$ groups can be measured and, providing that the monomers used to introduce SCB are known, the level of SCB can be estimated using chemometrics. Coupling the detector to a GPC system allows the SCB to be assessed (as a function of molecular weight).

Analysis of an ethylene-hexene copolymer by GPC/FTIR

A sample of ethylene co-polymerized with hexane was analyzed using the PL-GPC 220 coupled to an Agilent FTIR to assess the levels of short-chain branching.

Conditions

Column:	2 x PLgel Olexis, 300 x 7.5 mm (Part No. PL1110-6400)
Eluent:	Trichlorobenzene (with BHT)
Inj Vol:	200 µL
Flow Rate:	1.0 mL/min
Temp:	160 °C
Data Collection:	Time-resolved Agilent Resolutions Pro software collecting at 8.0 cm^{-1} resolution with 16 scan accumulations for 11 minutes, range 3,500 – 2,700 cm^{-1} with automatic solvent background subtraction
Detection:	Agilent PL-HTGPC-FTIR interfaced to an Agilent FTIR spectrometer fitted with an MCT detector

Cirrus GPC-FTIR SCB software was used to perform the experiments, calculating SCB based on a rigorous chemometrics approach. To determine molecular weight, the FTIR data was used as a concentration source for the generation of Figure 27, showing an overlay of the polymer weight and short-chain branching distribution obtained for a copolymer of ethylene and another alpha-olefin by FTIR. Clearly, in this case the level of co-monomer incorporation was uniform across the distribution.

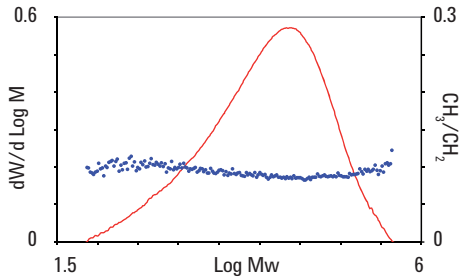


Figure 27. *Overlaid chromatogram of polymer weight and short-chain branching distribution for a sample of ethylene-hexene copolymer*

Reference

[1] P.J. DesLauriers, D.C. Rohlfing and E.T. Shieh (2002) Quantifying short chain branching microstructures in ethylene-1-olephin copolymers using size exclusion chromatography and Fourier transform infrared spectroscopy (SEC-FTIR). *Polymer*, 43, 159-170.

Ordering Information

Columns

Description	Part No.
Agilent PLgel 3 µm 100Å, 300 x 7.5 mm	PL1110-6320
Agilent PLgel 5 µm 100Å, 300 x 7.5 mm	PL1110-6520
Agilent PLgel 5 µm MIXED-D, 300 x 7.5 mm	PL1110-6504
Agilent PLgel 10 µm MIXED-B, 300 x 7.5 mm	PL1110-6100
PLgel 10 µm MIXED-B LS, 300 x 7.5 mm	PL1110-6100LS*
PLgel 20 µm MIXED-A, 300 x 7.5 mm	PL1110-6200
PLgel 20 µm MIXED-A LS, 300 x 7.5 mm	PL1110-6200LS*
Agilent PLgel Olexis, 300 x 7.5 mm	PL1110-6400

Standards

Description	Part No.
Agilent PS-H EasiVial 2 mL pre-weighed polystyrene calibration kit	PL2010-0201
Agilent PS-M EasiVial 2 mL pre-weighed polystyrene calibration kit	PL2010-0301
Agilent E-M-10 polyethylene calibration kit, 10 x 0.2 g	PL2650-0101
Agilent E-MW-10 polyethylene calibration kit, 10 x 0.1 g	PL2650-0102
Agilent E-SCB polyethylene short-chain branching calibration kit, 10 x 0.1 g	PL2650-0103

Instruments

Description	Part No.
Agilent PL-SP 260VS Sample Preparation System**	
Agilent PL-GPC 220 Integrated GPC/SEC System	PL0820-0000
Agilent PL-HTGPC-FTIR**	
Agilent PL-BV 400HT Online Integrated Viscometer	PL0810-3050
Agilent PL-HTLS 15/90 Light Scattering Detector	PL0640-1200
Agilent custom accessory kit**	

Software

Description	Part No.
Agilent Cirrus GPC Multi Detector Software	PL0570-2020
Agilent Cirrus GPC Software	PL0570-2000
Agilent GPC-FTIR SCB Software	PL0570-2300

** Low shedding for light scattering applications*
*** Contact your local sales office or distributor for different options*

More Agilent solutions for polyolefin analysis

As well as high-temperature GPC, Agilent offers other solutions for the analysis of polyolefins.

FTIR

Fourier transform-infrared spectroscopy is an essential tool in the analysis of polymer films and other materials. Applications range from quality testing of raw materials to failure analysis of large objects. Our solutions feature Agilent's high performing 600-IR Series spectrometers and microscopes, software and accessories.

The 600-IR Series accommodates a variety of polymer and material sample types, including spray-on liquids, pastes, resins, plastics, and coating materials. Attenuated Total Reflectance (ATR) is the easiest method as it typically requires little to no sample preparation. With Agilent ATR or grazing-angle accessories, you can investigate changes in polymer surfaces such as functionalization or weathering.

The Agilent 600-IR series provides the highest level of sensitivity combined with detailed structural and compositional information for information-rich detection

NMR

Agilent NMR has long been an effective tool for the characterization of polymers. 1D and 2D NMR methods have been routinely used for many years. A more advanced method developed at Agilent uses pulsed-field gradient-heteronuclear multiple-bond correlation with 2D NMR to detect weak signals in the presence of much larger resonances. This technique permits assignment of signals from minor structures such as chain ends and defects, essential information for a full understanding of these complex synthetic compounds.

The Agilent 400-MR provides unmatched productivity for diverse chemical applications by combining easy-to-use software with the outstanding performance of DirectDrive and DirectDigital spectrometer architecture. Push-button experiments, along with straightforward processing and data export capabilities, make the 400-MR the best choice for compound detection, quantification and structure confirmation.

Agilent GPC/SEC products:
www.agilent.com/chem/gpcsec

Buy online:
www.agilent.com/chem/store

Find an Agilent center in your country:
www.agilent.com/chem/contactus

U.S. and Canada:
1-800-227-9770
agilent_inquiries@agilent.com

Europe:
info_agilent@agilent.com

Asia Pacific:
adinquiry_aplsca@agilent.com

India:
india-lsca_marketing@agilent.com

Printed in the USA January 28, 2011
5990-6971EN

Agilent Technologies

Determination of Irganox 1010 in polyethylene by infrared spectroscopy

Analytical method

Polymers

Authors

Dr. Wayne Collins*, John Seelenbinder† and Frank Higgins†

Agilent Technologies
* Wilmington, DE, USA
† Danbury, CT, USA

Scope

This method is for the determination of Irganox 1010 and chemically identical antioxidants in polyethylene where the additive package is known. The method utilizes a characteristic ester carbonyl band associated with the additive that is common in many other additives. Therefore, the total additive package must be known to confirm that other additives present do not contain bands that would interfere with the measurement. The method is typically used for process control of additive addition and is not recommended for filled or pigmented resins. The sample must be pressed into a film or coupon prior to the analysis.

Agilent Technologies

Summary

An analytically representative sample of the polyethylene resin is molded into a 0.5 to 0.7 mm thickness film. Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the films have a smooth, consistent surface. The film is placed in the infrared spectrometer to obtain the spectrum at 4 wavenumber resolution or better. Using the Agilent DialPath or TumbIIR accessories, the film or coupon can be inserted into the infrared beam path between the top and bottom crystals (Figure 1). Both these accessories are unique to Agilent and provide a revolutionary new way to measure thin polymer films or liquids. The horizontal mounting provides a simple, fast and reproducible mechanism to mount the sample by simply laying it down flat and rotating the crystal into position, eliminating errors and providing accurate and reliable answers — fast! The absorbance of the additive band is measured at 1745 cm^{-1} and the absorbance is measured for the reference band at 2019 cm^{-1} to provide a path length or film thickness correction. To obtain the additive concentration in the sample, the ratio of the additive band to the reference band is substituted into a linear regression calibration equation constructed from measurements of prepared standards with known concentrations of additive. Triplicate films are averaged to obtain a result.

Figure 1. The Agilent DialPath transmission cell used for polymer analysis of coupons or films

Apparatus

- Data is obtained using an Agilent Cary 630 FTIR spectrometer equipped with a DialPath or TumbIIR sample interface with a 1000 µm path length. Equivalent FTIR spectrometers, such as the mobile or portable Agilent 5500/4500 Series FTIR, can also be used.
- Film micrometer — capable of measuring 0.5–0.7 mm thickness.
- Hydraulic press — with heated platens capable of maintaining 200 °C and a ram force of 40,000 pounds.
- Chase mold — to control thickness.
- Aluminum sheet — 0.051–0.178 mm thick.
- Scissors.

Calibration

Standards are prepared by blending known amounts of Irganox 1010 with polyethylene powder, and compounding under a nitrogen blanket until thoroughly mixed.

To perform the calibration, prepare and analyze at least three films for each standard resin in accordance with the requirements of this method. Perform a linear least squares regression of the concentration of the analyte versus normalized absorbance using all data points; do not include the origin as a data point.

$$\text{Wt\% Irganox 1010} = M \times (A_{1745}/A_{2019}) + N$$

Where:

Wt% Irganox 1010	= Weight % of Irganox 1010 in the polyethylene
A_{1745}	= Absorbance of Irganox 1010 at 1745 cm^{-1}
A_{2019}	= Absorbance of polyethylene reference band at 2019 cm^{-1}
M	= Calibration constant
N	= Intercept

The calibration curve for the determination of Irganox 1010 in polyethylene for the standards used in this study is shown in Figure 2.

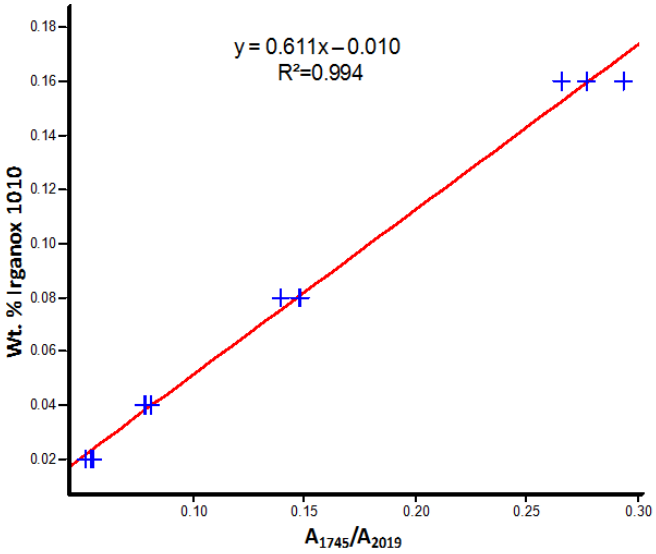


Figure 2. Calibration curve for wt% Irganox 1010 in polyethylene

Procedure

Sample preparation

Molding techniques and conditions used to prepare the sample do not significantly influence the results, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the prepared films have a smooth, consistent surface. A typical preparation procedure is as follows:

Obtain a representative sample of the resin to be analyzed; statistical sampling techniques are recommended (cone and quarter technique, chute splitter, rotary splitter, roto-riffler, and so forth). Place the chase mold on a sheet of aluminum and slightly overfill each cavity in the chase with the resin. Another sheet of aluminum is placed on top and the stack is carefully placed in the press with the platens heated to 200 °C. The press is closed to apply minimal force for 1 or 2 minutes while the sample melts. The force is increased to at least 25,000 pounds, held for approximately 30 seconds, and released. The stack is then removed from the press and allowed to cool on the benchtop. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash. Examine the sample for surface defects and check to ensure that the thickness is between 0.5 and 0.7 mm. Samples with defects or thickness outside of the range are discarded; at least three suitable films are required for the analysis.

Operating conditions

The infrared spectrometer should be turned on for at least 15 minutes prior to analysis. The resolution should be set to at least 4 wavenumbers.

Collect for a minimum of 30 seconds (70 scans) for each of the triplicate film samples.

Method configuration

To determine the additive concentration, measure the area under the absorbance band for Irganox 1010 at 1745 cm^{-1} relative to a baseline drawn between 1775 and 1706 cm^{-1}. The specified peak areas and baseline points can easily be set in an Agilent MicroLab PC FTIR software method. Each peak measurement is called a component and the baseline limits are easily set as shown in Figure 3. The peak type of 'Peak Area with Duel Baseline' is first set. Then parameters for measurement of the area under the reference polyethylene absorbance band at 2019 cm^{-1} relative to a baseline drawn between 2108 and 1981 cm^{-1} (Figure 4) are set. The component is further configured to report the absorbance value to five decimal places as shown in Figures 3 and 4.

A ratio of the analyte band absorbance to the reference band is used for this analysis.

$$\text{Wt\% Irganox 1010} = M \times (A_{1745}/A_{2019}) + N$$

with M and N as determined in the the Calibration section.

The MicroLab PC FTIR software makes the peak ratio calculation easy to set up. Simply edit the method by selecting the 'Peak Ratio' calculation type and the peak components that are to be ratioed (Figure 5).

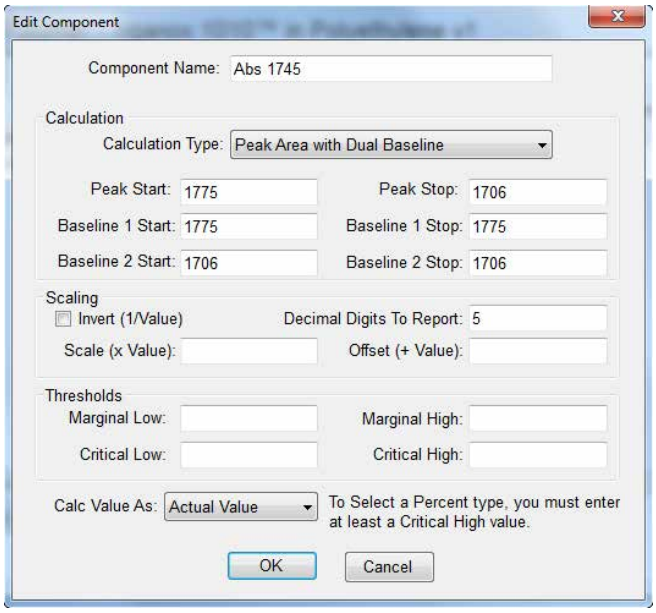


Figure 3. The Irganox 1010 peak area absorbance (component) measurement at 1745 cm^{-1} in the MicroLab PC FTIR software. The peak start and stop refers to the area under the peak to be integrated. Single point baselines should be set up with the same baseline start and stop points.

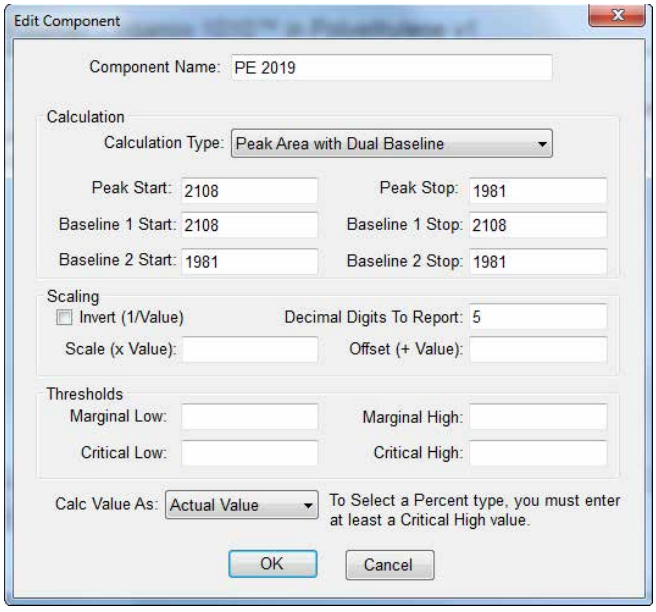


Figure 4. The polyethylene reference peak component addition in the MicroLab PC FTIR software

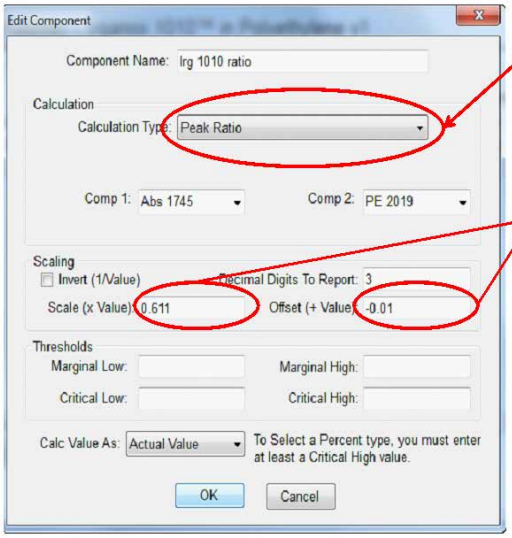


Figure 5. The peak ratio component addition in the MicroLab PC FTIR software. After plotting the calibration data, the resulting linear regression line's slope is entered in the 'Scale' field and the Y-axis offset in the 'Offset' field.

Analysis

With the ratio defined, the new method is ready to be used to obtain at least triplicate measurements of each calibration standard. Unknown polymer coupons should also be run with a minimum of three measurements around the coupon. This process is made simple and convenient with the DialPath or TumbIIR transmission cells. Users can see the exact point of measurement in real time, and quickly reposition the sample for the replicate measurements.

Plot the values measured for the ratio relative to the Irganox 1010 concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figure 5. Once the slope and offset values have been entered, the Microlab PC FTIR software method will report the Irganox 1010 concentration.

The MicroLab PC software method, Polymer — Irganox 1010 in Polyethylene v1, includes the calibration data from Figure 2. This calibrated method is available with the Agilent 5500 and 4500 Series DialPath or TumbIIR FTIR spectrometers, as well as the Cary 630 FTIR spectrometers. This method and software performs all the calculations automatically and reports the final value as wt% Irganox 1010 (Figure 6).

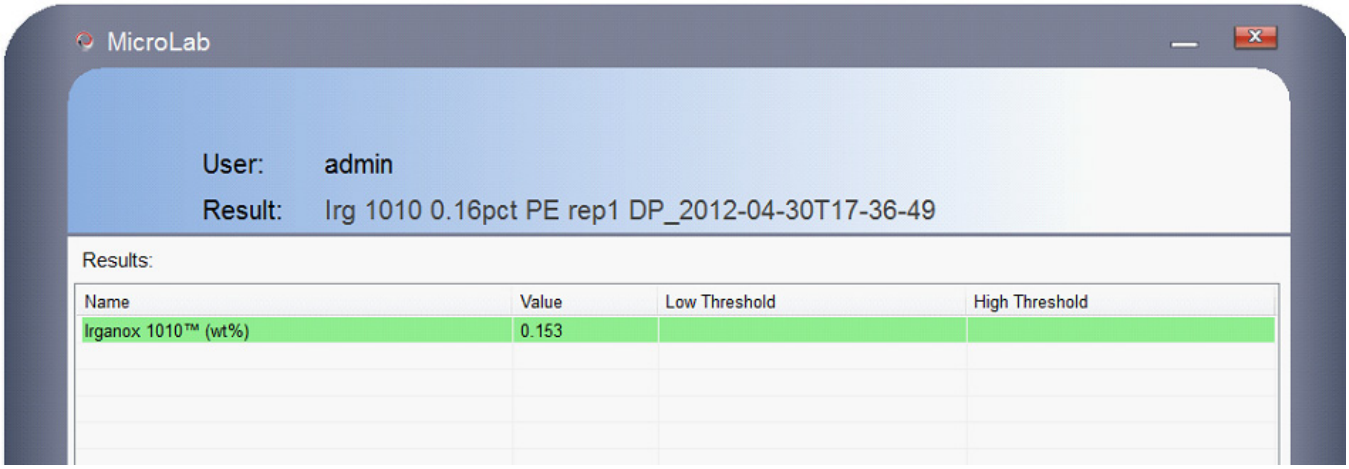


Figure 6. The MicroLab PC FTIR software prediction result for a 0.16 wt% Irganox 1010 in polyethylene sample

The values obtained from triplicate determinations should be averaged to give the final reported concentration.

Conclusion

This analytical method demonstrates how the Agilent Cary 630 FTIR can be used to easily and accurately measure polymer thin films. The unique sampling capabilities of the DialPath and TumbIIR provide a simple mechanism to mount your sample, while the step-by-step method-driven software with color-coded, actionable results guides you through your analysis to ensure that your samples are measured with minimum effort and highest accuracy.

www.agilent.com/chem

Published May 11, 2012
Publication number: 5991-0457EN

Agilent Technologies

Determination of the vinyl content of polyethylene resins

Analytical method

Polymers

Authors

Dr. Wayne Collins*, John Seelenbinder† and Frank Higgins†

Agilent Technologies
* Wilmington, DE, USA
† Danbury, CT, USA

Scope

This method is for the determination of the number of vinyl groups (C=C) in polyethylene resins by infrared spectroscopy. The test is used primarily for resins made with chromium catalyst technology, which gives a vinyl group at the end of each polymer chain, rather than resins made with titanium-based catalysts, which have few unsaturation sites. The method is applicable to powder, pellets or pieces cut from finished parts, but cannot be used for filled or pigmented samples.

Summary

This method determines the number of sites of unsaturation per 1000 carbon atoms by relating the intensity of the infrared absorption vinyl band at 908 cm^{-1} to a calibration curve for standards derived from nuclear magnetic resonance (NMR) measurements, which is the primary measurement technique.

An analytically representative sample of the polyethylene resin is molded into a film with a thickness of 0.4 to 0.5 mm. Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the films have a smooth, consistent surface. The film is placed in the infrared spectrometer and the spectrum is obtained at 2 wavenumber resolution. Using the Agilent DialPath or TumblIR accessories, the film or coupon can be inserted into the infrared beam path between the top and bottom crystals (Figure 1). Both these accessories are unique to Agilent and provide a revolutionary new way to measure thin polymer films or liquids. The horizontal mounting provides a simple, fast and reproducible mechanism to mount the sample by simply laying it down flat and rotating the crystal into position, eliminating errors and providing accurate and reliable answers — fast! The absorbance of the band at 908 cm^{-1} is measured and corrected to a baseline drawn between 950 and 875 cm^{-1}. This absorbance value is divided by the absorbance of a reference band at 2019 cm^{-1} relative to a baseline drawn between 1981 and 2108 cm^{-1}. Substitution of this ratio into the linear regression calibration equation derived from similar measurements on the standards gives the vinyl content in units of number of vinyl groups per 1000 carbon atoms. The vinyl content of a polyethylene sample is primarily determined by the catalyst used to manufacture the resin. Generally, resins made with a chromium catalyst will have significant vinyl content, greater than 0.5 vinyls/1000 carbon atoms, while resins from titanium catalysts typically have low vinyl content, less than 0.5 vinyls/1000 carbon atoms.

Figure 1. The Agilent DialPath transmission cell used for polymer analysis of coupons or films

Apparatus

- Data is obtained using an Agilent Cary 630 FTIR spectrometer equipped with a DialPath or TumblIR sample interface with a 1000 µm path length. Equivalent FTIR spectrometers, such as the mobile or portable Agilent 5500/4500 Series FTIR, can also be used.
- Hydraulic press — with heated platens capable of maintaining 200 °C and a ram force of 25,000 pounds.
- Chase mold — to control thickness (optional).
- Aluminum sheet — 0.05–0.18 mm thick.

Calibration

To perform the calibration, a spectrum is obtained for three films prepared from each standard resin. Determine the area of the analytical absorbance band relative to the baseline at 908 cm^{-1} and the area of the reference band at 2019 cm^{-1} following the same procedure as for samples described in this method. All absorbance values should be less than 1.6 units. Perform a linear least squares regression of the known vinyl content versus the ratio A_{908}/A_{2019} using all data points; do not include the origin as a data point.

The calibration curve and equation obtained for this method is shown in Figure 2.

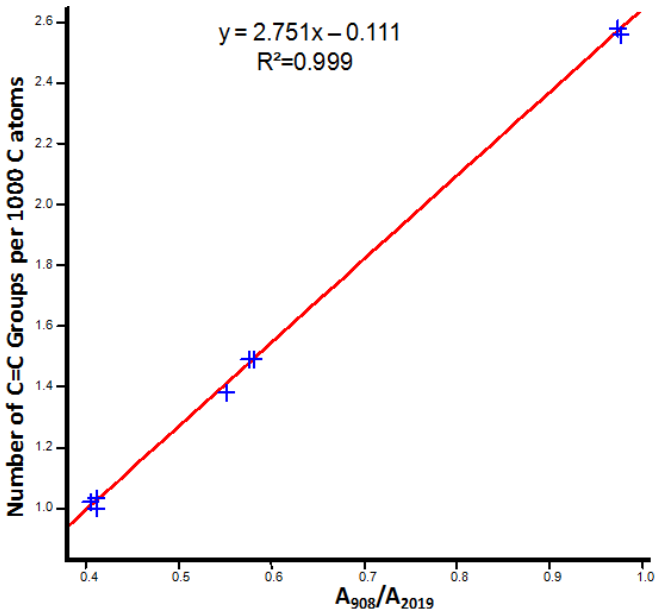


Figure 2. Calibration curve for the number of vinyl C=C groups per 1000 C atoms in polyethylene. The correlation coefficient, R^2, was 0.999 and the 95% confidence interval was ±0.1 C=C per 1000 C atoms.

Vinyl C=C groups per 1000 C atoms = M x (A_{908} / $_{2019}$) + N

Where:

Vinyl C=C groups per 1000 C atoms	= Vinyl C=C groups per 1000 C atoms in the polyethylene
A_{908}	= Peak area absorbance of vinyl group at 908 cm^{-1}
A_{2019}	= Absorbance of polyethylene reference band at 2019 cm^{-1}
M	= Calibration constant
N	= Intercept

The vinyl content of each standard is typically determined by multiple analyses by C^{13} NMR spectroscopy.

Procedure

Sample preparation

Obtain a representative sample of the resin to be analyzed; statistical sampling techniques are recommended (cone and quarter technique, chute splitter, rotary splitter, roto-riffler, and so forth). Molding conditions are not important to the results obtained by this method, as long as the resin is not exposed to temperatures of more than 250 °C for more than 2 to 3 minutes. A typical preparation technique is as follows:

Place the chase mold on a sheet of aluminum and slightly overfill each cavity in the chase with the resin. Another sheet of aluminum is placed on top and the stack is carefully placed in the hydraulic press with the platens heated to 200 °C. The press is closed to apply minimal force for 1 or 2 minutes while the sample melts. The force is increased to at least 25,000 pounds, held for approximately 30 seconds and released. The stack is then removed from the press and allowed to cool on the benchtop or in a cold press. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash.

Once the samples are prepared, each sample is examined for surface defects and checked to ensure that the thickness is between 0.4 and 0.5 mm. Samples with defects or thickness outside of the range are discarded; at least three suitable films are required for the analysis.

Operating conditions

The infrared spectrometer should be turned on and allowed to stabilize for at least 15 minutes prior to analysis. The resolution should be set to 2 wavenumbers or better.

Collect for a minimum of 30 seconds (37 scans) for each of the triplicate film samples.

Method configuration

To determine the vinyl concentration, measure the area under the absorbance band for the vinyl CH wag group at 908 cm^{-1} relative to a baseline drawn between 926 and 898 cm^{-1}. A typical spectrum is shown in Figure 3. The specified peak areas and baseline points can easily be set in an Agilent MicroLab PC FTIR software method. Each peak measurement is called a component and the baseline limits are easily set as shown in Figure 4. The peak type of 'Peak Area with Duel Baseline' is first set. Then parameters for measurement of the area under the reference polyethylene absorbance band at 2019 cm^{-1} relative to a baseline drawn between 2097 and 1987 cm^{-1} (Figure 5) are set. The component is further configured to report the absorbance value to five decimal places as shown in Figures 4 and 5.

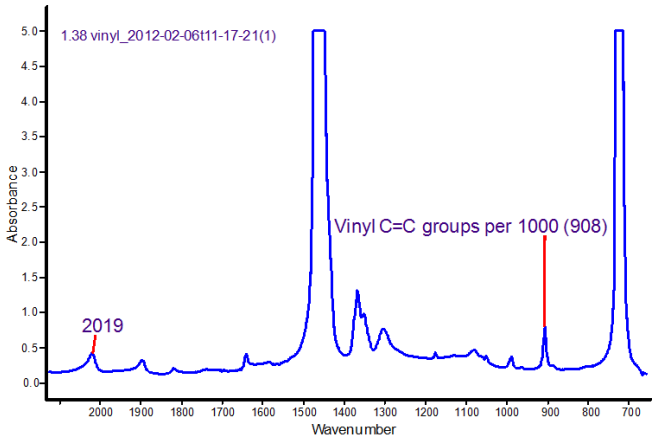


Figure 3. Typical spectrum for the measurement of the vinyl group (CH wag) in polyethylene

A ratio of the analyte band absorbance to the reference band is used for this analysis.

Number C=C per 1000 C atoms = M x [A_{908} / A_{2019}] + N

with M and N as determined in the the Calibration section.

The ratio calibration equation for this analysis is:

Number C=C per 1000 C atoms = 2.751 x [A_{908} / A_{2019}] – 0.111

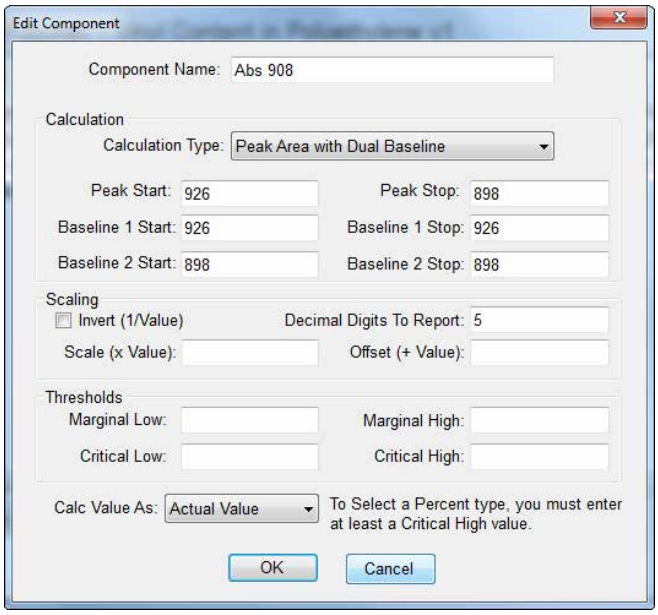


Figure 4. The vinyl peak area absorbance (component) measurement at 908 cm^{-1} in the MicroLab PC FTIR software. The peak start and stop refers to the area under the peak to be integrated. Single point baselines should be set up with the same baseline start and stop points

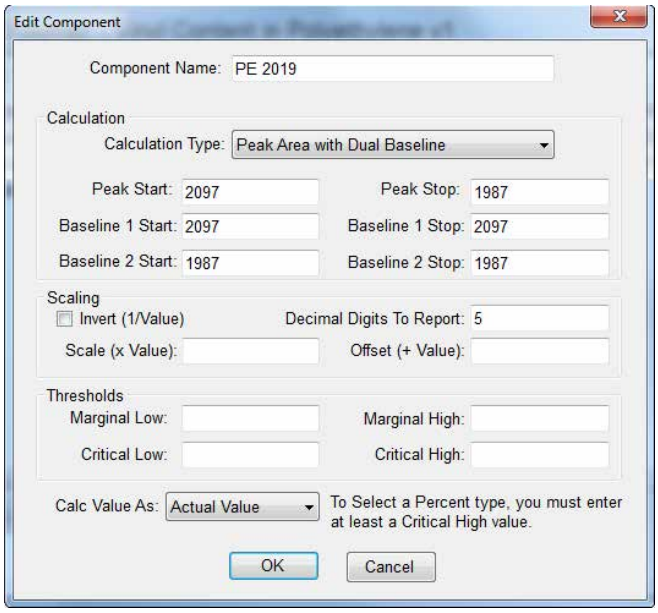


Figure 5. The polyethylene reference peak component addition in the MicroLab PC FTIR software

The MicroLab PC FTIR software makes the peak ratio calculation easy to set up. Simply edit the method by selecting the 'Peak Ratio' calculation type and the peak components that are to be ratioed (Figure 6).

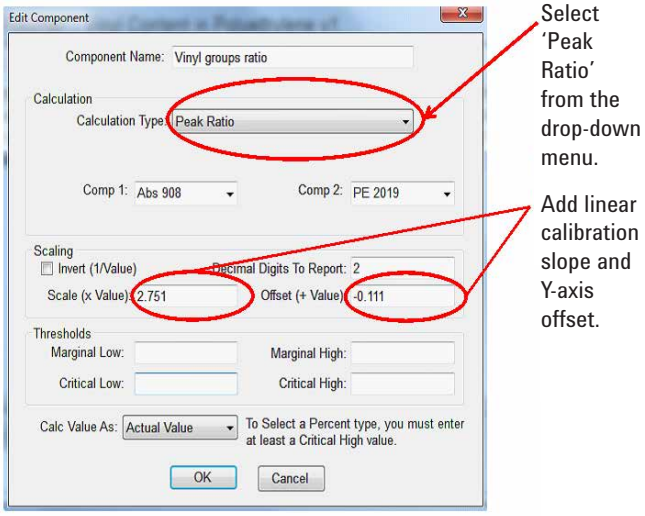


Figure 6. The peak ratio component addition in the MicroLab PC FTIR software. After plotting the calibration data, the resulting linear regression line's slope is entered in the 'Scale' field and the Y-axis offset in the 'Offset' field.

Analysis

With the ratio defined, the new method is ready to be used to obtain at least triplicate measurements of each calibration standard. Unknown polymer coupons should also be run with a minimum of three measurements around the coupon. This process is made simple and convenient with the DialPath or TumblIR transmission cells. Users can see the exact point of measurement in real time, and quickly reposition the sample for the replicate measurements.

Plot the values measured for the ratio relative to the vinyl group concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figure 6. Once the slope and offset values have been entered, the Microlab FTIR software method will report the vinyl group concentration.

The MicroLab PC FTIR software method, Polymer – Vinyl Content in Polyethylene v1, includes the calibration data from Figure 2. This calibrated method is available with the Agilent 5500 and 4500 Series DialPath or TumblIR FTIR spectrometers, as well as the Cary 630 FTIR spectrometers. This method and software performs all the calculations automatically and reports the final value as Number C=C per 1000 C Atoms (Figure 7).

The values obtained from triplicate determinations should be averaged to give the final reported concentration.

Conclusion

This analytical method demonstrates how the Agilent Cary 630 FTIR can be used to easily and accurately measure polymer thin films. The unique sampling capabilities of the DialPath and TumblIR provide a simple mechanism to mount your sample, while the step-by-step method-driven software with color-coded, actionable results guides you through your analysis to ensure that your samples are measured with minimum effort and highest accuracy.

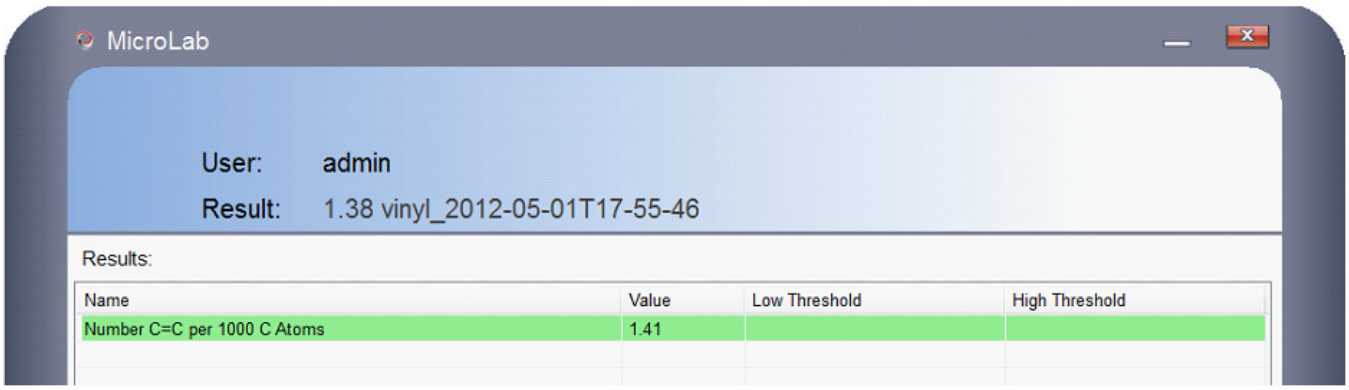


Figure 7. The MicroLab PC FTIR software prediction result for a 1.38 vinyl C=C groups per 1000 C atoms in polyethylene sample

www.agilent.com/chem

Published May 11, 2012
Publication number: 5991-0458EN

Agilent Technologies

Determination of Irganox 1010 in polypropylene by infrared spectroscopy

Analytical method

Polymers

Authors

Dr. Wayne Collins*, John Seelenbinder† and Frank Higgins†

Agilent Technologies
* Wilmington, DE, USA
† Danbury, CT, USA

Scope

This method is for the determination of Irganox 1010 and chemically identical antioxidants in polypropylene where the additive package is known. The method utilizes a characteristic ester carbonyl band associated with the additive that is common in many other additives. Therefore, the total additive package must be known to confirm that other additives present do not contain bands that would interfere with the measurement. The method is typically used for process control of additive addition and is not recommended for filled or pigmented resins. The sample must be pressed into a film or coupon prior to the analysis.

Agilent Technologies

Summary

An analytically representative sample of the polypropylene resin is molded into a 0.5 to 0.7 mm thickness film. Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the films have a smooth, consistent surface. The film is placed in the infrared spectrometer to obtain the spectrum at 4 wavenumber resolution or better. Using the Agilent DialPath or TumblIR accessories, the film or coupon can be inserted into the infrared beam path between the top and bottom crystals (Figure 1). Both these accessories are unique to Agilent and provide a revolutionary new way to measure thin polymer films or liquids. The horizontal mounting provides a simple, fast and reproducible mechanism to mount the sample by simply laying it down flat and rotating the crystal into position, eliminating errors and providing accurate and reliable answers — fast! The absorbance of the additive band is measured at 1745 cm^{-1} and the absorbance is measured for the reference polypropylene band at 4062 cm^{-1} to provide a path length or film thickness correction. To obtain the additive concentration in the sample, the ratio of the additive band to the reference band is substituted into a linear regression calibration equation constructed from measurements of prepared standards with known concentrations of additive. Triplicate films are averaged to obtain a result.

Figure 1. The Agilent DialPath transmission cell used for polymer analysis of coupons or films

Apparatus

- Data is obtained using an Agilent Cary 630 FTIR spectrometer equipped with a DialPath or TumblIR sample interface with a 1000 µm path length. Equivalent FTIR spectrometers, such as the mobile or portable Agilent 5500/4500 Series FTIR, can also be used.
- Film micrometer — capable of measuring 0.5–0.7 mm thickness.
- Hydraulic press — with heated platens capable of maintaining 200 °C and a ram force of 40,000 pounds.
- Chase mold — to control thickness.
- Aluminum sheet — 0.051–0.178 mm thick.
- Scissors.

Calibration

Standards are prepared by blending known amounts of Irganox 1010 with polypropylene powder, and compounding under a nitrogen blanket until thoroughly mixed.

To perform the calibration, prepare and analyze at least three films for each standard resin in accordance with the requirements of this method. Perform a linear least squares regression of the concentration of the analyte versus normalized absorbance using all data points; do not include the origin as a data point.

$$Wt\%\ Irganox\ 1010 = M \times (A_{1745}/A_{4062}) + N$$

Where:

Wt% Irganox 1010	= Weight % of Irganox 1010 in the polypropylene
A_{1745}	= Absorbance of Irganox 1010 at 1745 cm^{-1}
A_{4062}	= Absorbance of polypropylene reference band at 4062 cm^{-1}
M	= Calibration constant
N	= Intercept

The calibration curve for the determination of Irganox 1010 in polypropylene for the standards used in this study is shown in Figure 2.

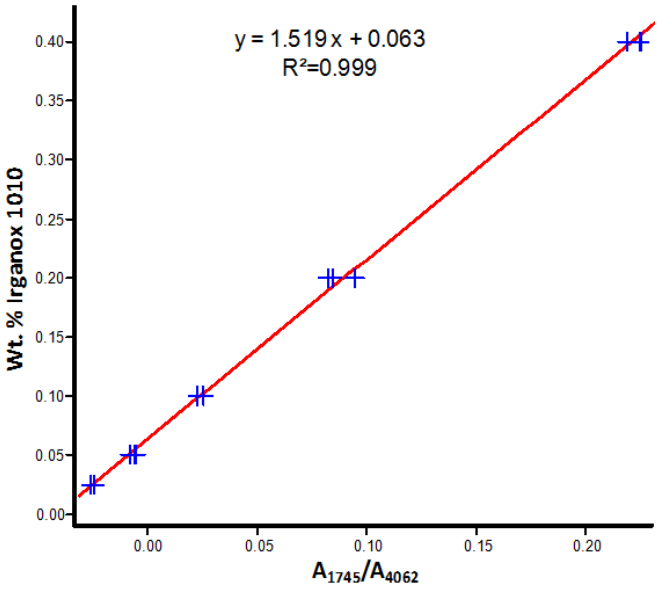


Figure 2. Calibration curve for wt% Irganox 1010 in polypropylene

Procedure

Sample preparation

Molding techniques and conditions used to prepare the sample do not significantly influence the results, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the prepared films have a smooth, consistent surface. A typical preparation procedure is as follows:

Obtain a representative sample of the resin to be analyzed; statistical sampling techniques are recommended (cone and quarter technique, chute splitter, rotary splitter, roto-riffler, and so forth). Place the chase mold on a sheet of aluminum and slightly overfill each cavity in the chase with the resin. Another sheet of aluminum is placed on top and the stack is carefully placed in the press with the platens heated to 200 °C. The press is closed to apply minimal force for 1 or 2 minutes while the sample melts. The force is increased to at least 25,000 pounds, held for approximately 30 seconds, and released. The stack is then removed from the press and allowed to cool on the benchtop. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash. Examine the sample for surface defects and check to ensure that the thickness is between 0.5 and 0.7 mm. Samples with defects or thickness outside of the range are discarded; at least three suitable films are required for the analysis.

Operating conditions

The infrared spectrometer should be turned on for at least 15 minutes prior to analysis. The resolution should be set to at least 4 wavenumbers.

Collect for a minimum of 30 seconds (70 scans) for each of the triplicate film samples.

Method configuration

To determine the additive concentration, measure the area under the absorbance band for Irganox 1010 at 1745 cm^{-1} relative to a baseline drawn between 1775 and 1721 cm^{-1}. The specified peak areas and baseline points can easily be set in an Agilent MicroLab PC FTIR software method. Each peak measurement is called a component and the baseline limits are easily set as shown in Figure 3. The peak type of 'Peak Area with Duel Baseline' is first set. Then parameters for measurement of the area under the reference polypropylene absorbance band at 4062 cm^{-1} relative to a baseline drawn between 4097 and 4010 cm^{-1} (Figure 4) are set. The component is further configured to report the absorbance value to five decimal places as shown in Figures 3 and 4.

A ratio of the analyte band absorbance to the reference band is used for this analysis.

$$\text{Wt\% Irganox 1010} = M \times (A_{1745}/A_{4062}) + N$$

with M and N as determined in the the Calibration section.

The MicroLab PC FTIR software makes the peak ratio calculation easy to set up. Simply edit the method by selecting the 'Peak Ratio' calculation type and the peak components that are to be ratioed (Figure 5).

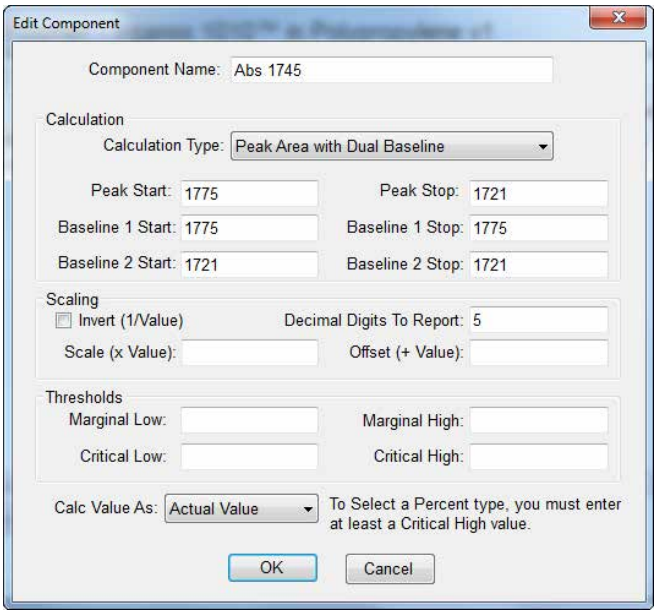


Figure 3. The Irganox 1010 peak area absorbance (component) measurement at 1745 cm^{-1} in the MicroLab PC FTIR software. The peak start and stop refers to the area under the peak to be integrated. Single point baselines should be set up with the same baseline start and stop points.

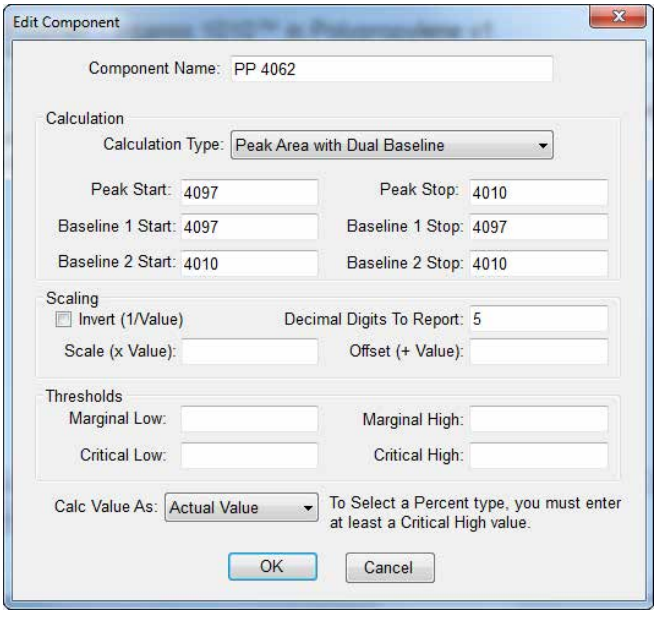


Figure 4. The polypropylene reference peak component addition in the MicroLab PC FTIR software

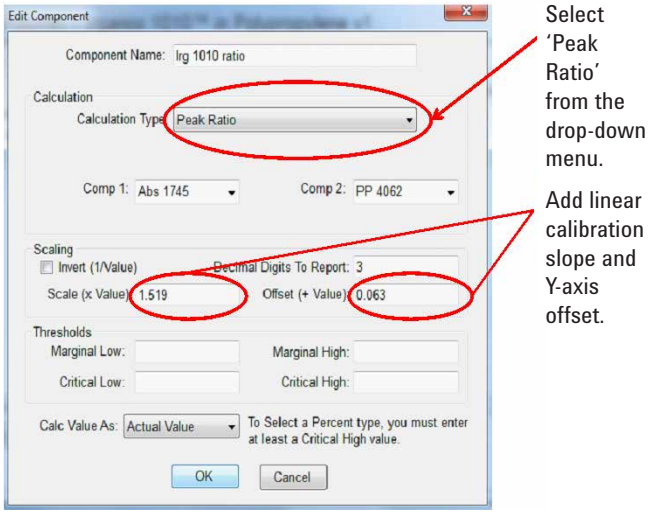


Figure 5. The peak ratio component addition in the MicroLab PC FTIR software. After plotting the calibration data, the resulting linear regression line's slope is entered in the 'Scale' field and the Y-axis offset in the 'Offset' field.

Analysis

With the ratio defined, the new method is ready to be used to obtain at least triplicate measurements of each calibration standard. Unknown polymer coupons should also be run with a minimum of three measurements around the coupon. This process is made simple and convenient with the DialPath or TumblIR transmission cells. Users can see the exact point of measurement in real time, and quickly reposition the sample for the replicate measurements.

Plot the values measured for the ratio relative to the Irganox 1010 concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figure 5. Once the slope and offset values have been entered, the Microlab PC FTIR software method will report the Irganox 1010 concentration.

The MicroLab PC software method, Polymer — Irganox 1010 in Polypropylene v1, includes the calibration data from Figure 2. This calibrated method is available with the Agilent 5500 and 4500 Series DialPath or TumblIR FTIR spectrometers, as well as the Cary 630 FTIR spectrometers. This method and software performs all the calculations automatically and reports the final value as wt% Irganox 1010 in PP (Figure 6).

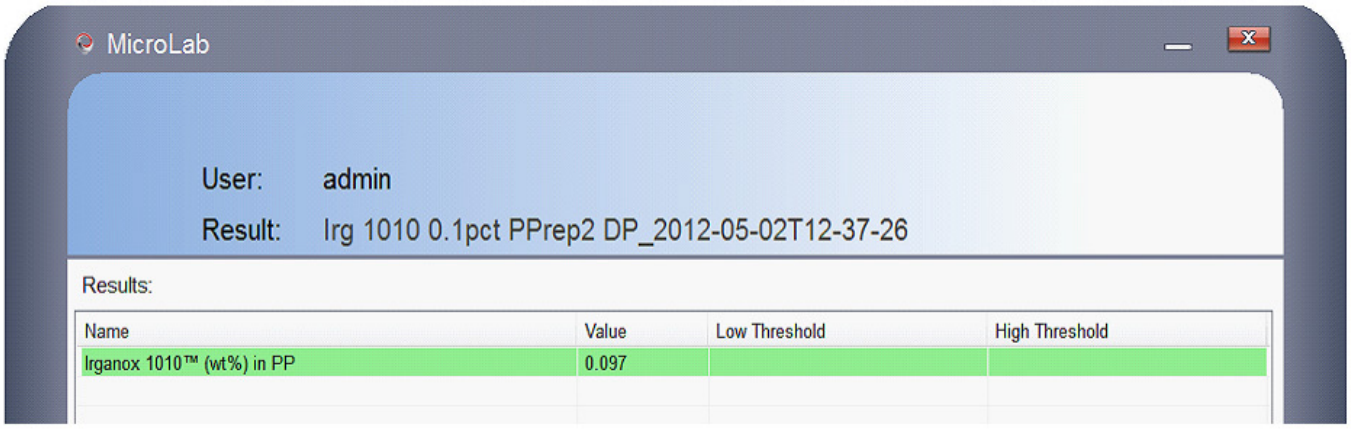


Figure 6. The MicroLab PC FTIR software prediction result for a 0.10 wt% Irganox 1010 in polypropylene sample

The values obtained from triplicate determinations should be averaged to give the final reported concentration.

Conclusion

This analytical method demonstrates how the Agilent Cary 630 FTIR can be used to easily and accurately measure polymer thin films. The unique sampling capabilities of the DialPath and TumbIIR provide a simple mechanism to mount your sample, while the step-by-step method-driven software with color-coded, actionable results guides you through your analysis to ensure that your samples are measured with minimum effort and highest accuracy.

www.agilent.com/chem

Published May 11, 2012
Publication number: 5991-0505EN

Agilent Technologies

Determination of Irganox 3114 in polypropylene by infrared spectroscopy

Analytical method

Polymers

Authors

Dr. Wayne Collins*, John Seelenbinder† and Frank Higgins†

Agilent Technologies
* Wilmington, DE, USA
† Danbury, CT, USA

Scope

This method is for the determination of Irganox 3114 and chemically identical antioxidants in polypropylene where the additive package is known. The method utilizes a characteristic carbonyl band associated with the additive that is common in many other additives. Therefore, the total additive package must be known to confirm that other additives present do not contain bands that would interfere with the measurement. The method is typically used for process control of additive addition and is not recommended for filled or pigmented resins. The sample must be pressed into a film or coupon prior to the analysis.

Agilent Technologies

Summary

An analytically representative sample of the polypropylene resin is molded into a 0.5 to 0.7 mm thickness film. Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the films have a smooth, consistent surface. The film is placed in the infrared spectrometer to obtain the spectrum at 4 wavenumber resolution or better. Using the Agilent DialPath or TumblIR accessories, the film or coupon can be inserted into the infrared beam path between the top and bottom crystals (Figure 1). Both these accessories are unique to Agilent and provide a revolutionary new way to measure thin polymer films or liquids. The horizontal mounting provides a simple, fast and reproducible mechanism to mount the sample by simply laying it down flat and rotating the crystal into position, eliminating errors and providing accurate and reliable answers — fast! The absorbance of the additive's carbonyl band is measured at 1696 cm^{-1} and the absorbance is measured for the reference polypropylene band at 4062 cm^{-1} to provide a path length or film thickness correction. To obtain the additive concentration in the sample, the ratio of the additive band to the reference band is substituted into a linear regression calibration equation constructed from measurements of prepared standards with known concentrations of additive. Triplicate films are averaged to obtain a result.

Figure 1. The Agilent DialPath transmission cell used for polymer analysis of coupons or films

Apparatus

- Data is obtained using an Agilent Cary 630 FTIR spectrometer equipped with a DialPath or TumblIR sample interface with a 1000 µm path length. Equivalent FTIR spectrometers, such as the mobile or portable Agilent 5500/4500 Series FTIR, can also be used.
- Film micrometer — capable of measuring 0.5–0.7 mm thickness.
- Hydraulic press — with heated platens capable of maintaining 200 °C and a ram force of 40,000 pounds.
- Chase mold — to control thickness.
- Aluminum sheet — 0.051–0.178 mm thick.
- Scissors.

Calibration

Standards were prepared by blending known amounts of Irganox 3114 with polypropylene powder, and compounding under a nitrogen blanket until thoroughly mixed.

To perform the calibration, prepare and analyze at least three films for each standard resin in accordance with the requirements of this method. Perform a linear least squares regression of the concentration of the analyte versus normalized absorbance using all data points; do not include the origin as a data point.

$$Wt\%\ Irganox\ 3114 = M \times (A_{1696}/A_{4062}) + N$$

Where:

Wt% Irganox 3114	= Weight % of Irganox 3114 in the polypropylene
A_{1696}	= Absorbance area of the Irganox 3114 band at 1696 cm^{-1}
A_{4062}	= Absorbance area of the polypropylene reference band at 4062 cm^{-1}
M	= Calibration constant
N	= Intercept

The calibration curve obtained for the determination of Irganox 3114 in polypropylene in this study is shown in Figure 2.

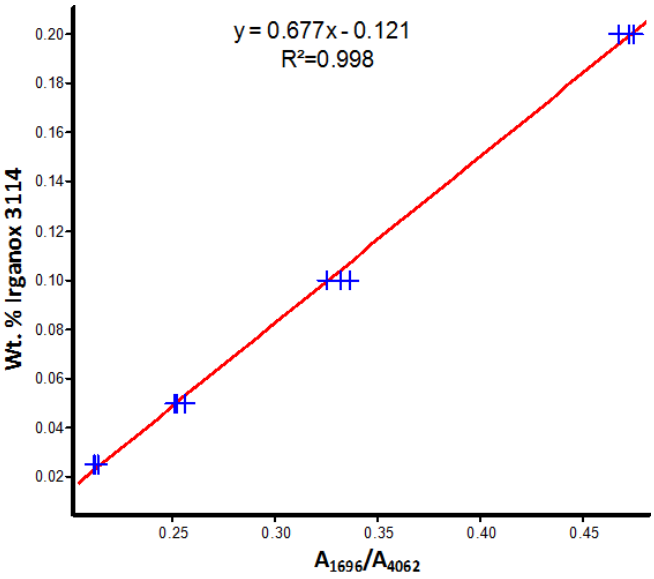


Figure 2. Calibration curve for wt% Irganox 3114 in polypropylene

Procedure

Sample preparation

Molding techniques and conditions used to prepare the sample do not significantly influence the results, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the prepared films have a smooth, consistent surface. A typical preparation procedure is as follows:

Obtain a representative sample of the resin to be analyzed; statistical sampling techniques are recommended (cone and quarter technique, chute splitter, rotary splitter, roto-riffler, and so forth). Place the chase mold on a sheet of aluminum and slightly overfill each cavity in the chase with the resin. Another sheet of aluminum is placed on top and the stack is carefully placed in the press with the platens heated to 200 °C. The press is closed to apply minimal force for 1 or 2 minutes while the sample melts. The force is increased to at least 25,000 pounds, held for approximately 30 seconds, and released. The stack is then removed from the press and allowed to cool on the benchtop. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash. Examine the sample for surface defects and check to ensure that the thickness is between 0.5 and 0.7 mm. Samples with defects or thickness outside of the range are discarded; at least three suitable films are required for the analysis.

Operating conditions

The infrared spectrometer should be turned on for at least 15 minutes prior to analysis. The resolution should be set to at least 4 wavenumbers.

Collect for a minimum of 30 seconds (74 scans) for each of the triplicate film samples.

Method configuration

To determine the additive concentration, measure the area under the absorbance band for Irganox 3114 at 1696 cm^{-1} relative to a baseline drawn between 1717 and 1665 cm^{-1}. The specified peak areas and baseline points can easily be set in an Agilent MicroLab PC FTIR software method. Each peak measurement is called a component and the baseline limits are easily set as shown in Figure 3. The peak type of 'Peak Area with Duel Baseline' is first set. Then parameters for measurement of the area under the reference polypropylene absorbance band at 4062 cm^{-1} relative to a baseline drawn between 4097 and 4010 cm^{-1} (Figure 4) are set. The component is further configured to report the absorbance value to five decimal places as shown in Figures 3 and 4.

A ratio of the analyte band absorbance to the reference band is used for this analysis.

$$\text{Wt\% Irganox 3114} = M \times (A_{1696}/A_{4062}) + N$$

with M and N as determined in the the Calibration section.

The MicroLab PC FTIR software makes the peak ratio calculation easy to set up. Simply edit the method by selecting the 'Peak Ratio' calculation type and the peak components that are to be ratioed (Figure 5).

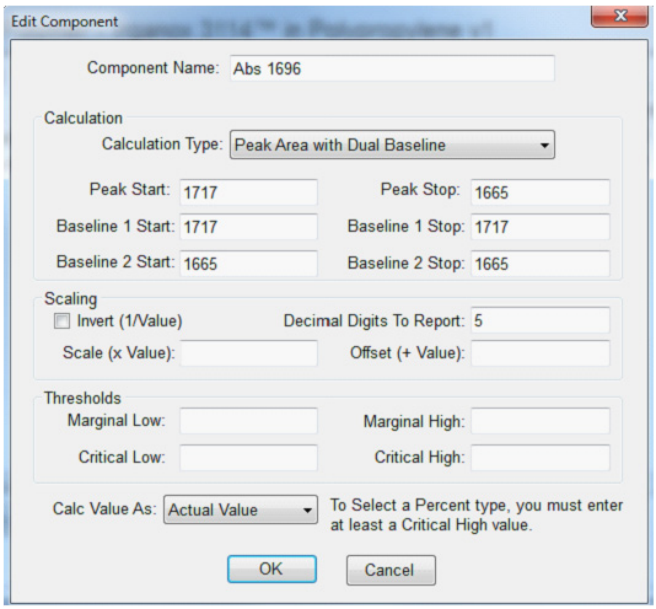


Figure 3. The Irganox 3114 peak area absorbance (component) measurement at 1696 cm^{-1} in the MicroLab PC FTIR software. The peak start and stop refers to the area under the peak to be integrated. Single point baselines should be set up with the same baseline start and stop points.

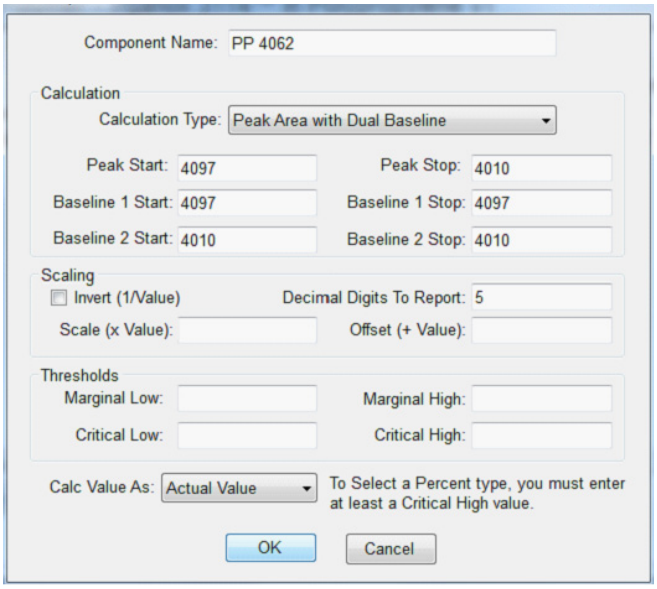


Figure 4. The polypropylene reference peak component addition in the MicroLab PC FTIR software

Analysis

With the ratio defined, the new method is ready to be used to obtain at least triplicate measurements of each calibration standard. Unknown polymer coupons should also be run with a minimum of three measurements around the coupon. This process is made simple and convenient with the DialPath or TumbIIR transmission cells. Users can see the exact point of measurement in real time, and quickly reposition the sample for the replicate measurements.

Plot the values measured for the ratio relative to the Irganox 3114 concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figure 5. Once the slope and offset values have been entered, the MicroLab PC FTIR software method will report the Irganox 3114 concentration.

The MicroLab PC software method, Polymer — Irganox 3114 in Polypropylene v1, includes the calibration data from Figure 2. This calibrated method is available with the Agilent 5500 and 4500 Series DialPath or TumbIIR FTIR spectrometers, as well as the Cary 630 FTIR spectrometers. This method and software performs all the calculations automatically and reports the final value as wt% Irganox 3114 (Figure 6).

The values obtained from triplicate determinations should be averaged to give the final reported concentration.

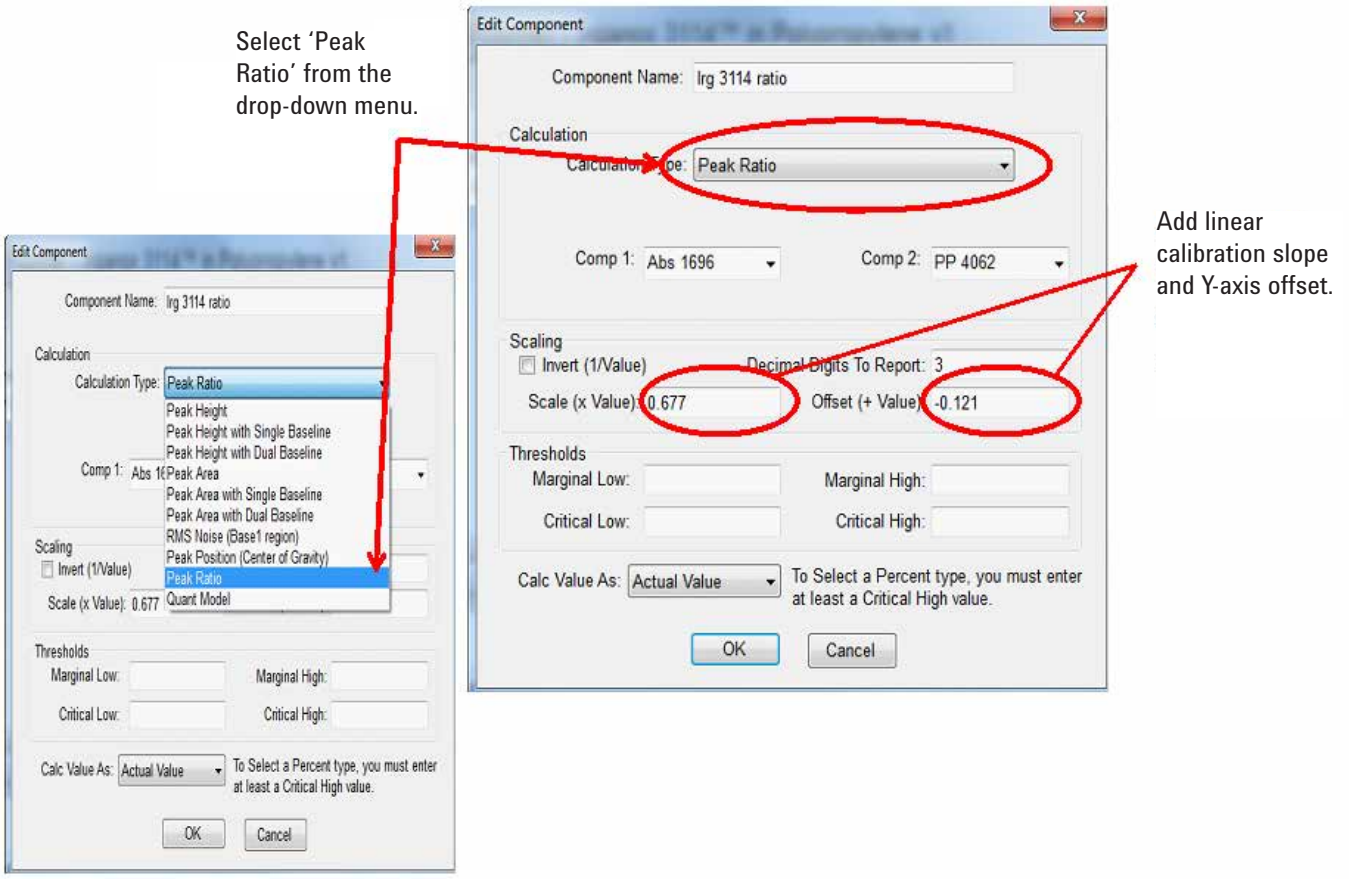


Figure 5. The peak ratio component addition in the MicroLab PC FTIR software. After plotting the calibration data, the resulting linear regression line's slope is entered in the 'Scale' field and the Y-axis offset in the 'Offset' field.

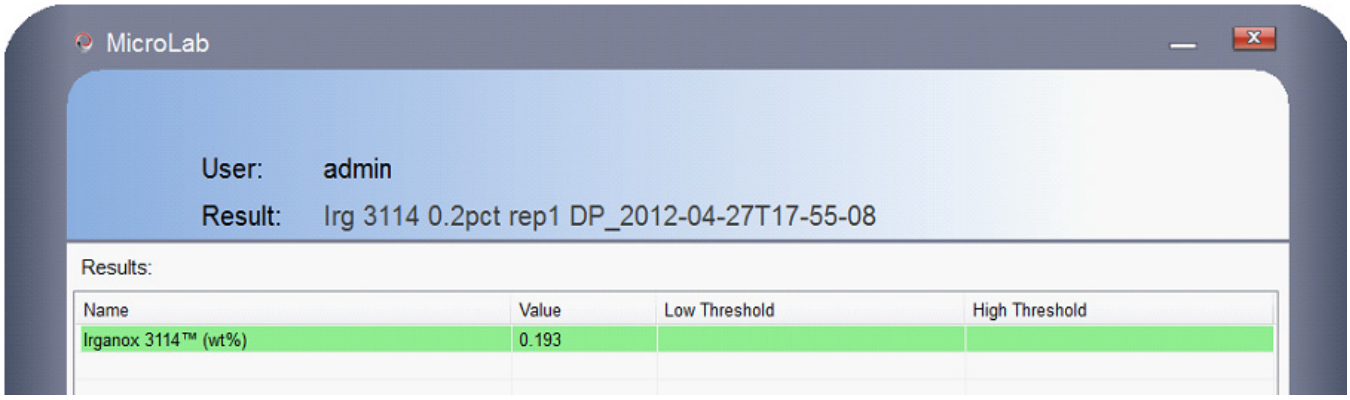


Figure 6. The MicroLab PC FTIR software prediction result for a 0.2 wt% Irganox 3114 in polypropylene sample

Conclusion

This analytical method demonstrates how the Agilent Cary 630 FTIR can be used to easily and accurately measure polymer thin films. The unique sampling capabilities of the DialPath and TumbIIR provide a simple mechanism to mount your sample, while the step-by-step method-driven software with color-coded, actionable results guides you through your analysis to ensure that your samples are measured with minimum effort and highest accuracy.

www.agilent.com/chem

Published May 11, 2012
Publication number: 5991-0455EN

Agilent Technologies

Determination of percent glycerol monostearate in polypropylene by infrared spectroscopy

Analytical method

Polymers

Authors

Dr. Wayne Collins*, John Seelenbinder† and Frank Higgins†

Agilent Technologies
* Wilmington, DE, USA
† Danbury, CT, USA

Scope

This method is for the determination of the glycerol monostearate (GMS) content and chemically identical antistatic additives in polypropylene where the additive package is known. The method utilizes a characteristic ester carbonyl band associated with the additive that is common in many other additives. Therefore, the total additive package must be known to confirm that other additives present do not contain bands that would interfere with the measurement. The method is typically used for process control of additive addition and is not recommended for filled or pigmented resins. The method has been validated over the range of 0.05 to 0.8% GMS content and can be used for either powder or pellet samples. Certain ester-based antioxidants, such as Irganox 1010 and Irganox 3114 have been found to interfere with the determination and therefore a correction factor is necessary for resins containing these additives. The purity of GMS additive for polymers ranges from 40 to 95% monoglyceride content. A correction to account for the purity must be made to determine the quantity of raw additive incorporated into the polymer. The sample must be pressed into a film or coupon prior to the analysis.

Summary

An analytically representative sample of the polypropylene resin is molded into a 0.4 to 0.7 mm thickness film. Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the films have a smooth, consistent surface. The film is placed in the infrared spectrometer to obtain the spectrum at 4 wavenumber resolution or better. Using the Agilent DialPath or TumblIR accessories, the film or coupon can be inserted into the infrared beam path between the top and bottom crystals (Figure 1). Both these accessories are unique to Agilent and provide a revolutionary new way to measure thin polymer films or liquids. The horizontal mounting provides a simple, fast and reproducible mechanism to mount the sample by simply laying it down flat and rotating the crystal into position, eliminating errors and providing accurate and reliable answers — fast! The ester absorbance of the GMS additive band is measured at 1739 cm^{-1} and the absorbance is measured for the reference polypropylene band at 1044 cm^{-1} to provide a path length or film thickness correction. To obtain the additive concentration in the sample, the ratio of the ester GMS band to the reference band is substituted into a linear regression calibration equation, constructed from measurements of prepared standards with known concentrations of additive. This Beer's Law calibration is linear through the 0.05 to 0.8% GMS range, however, non-linearities have been observed due to surface residues. Simply cleaning the film samples with a dry lint-free wipe removes the surface residues. Triplicate films are averaged to obtain a result.

Figure 1. The Agilent DialPath transmission cell used for polymer analysis of coupons or films

Apparatus

- Data is obtained using an Agilent Cary 630 FTIR spectrometer equipped with a DialPath or TumblIR sample interface with a 1000 µm path length. Equivalent FTIR spectrometers, such as the mobile or portable Agilent 5500/4500 Series, can also be used.
- Hydraulic press — with heated platens capable of maintaining 200 °C and a ram force of 25,000 pounds.
- Chase mold — to control thickness (optional).
- Aluminum sheet — 0.05–0.18 mm thick.

Calibration

Standards are prepared by blending known amounts of GMS with polypropylene powder, and compounding under a nitrogen blanket until thoroughly mixed. To perform the calibration, prepare and analyze at least three films for each standard resin in accordance with the requirements of this method. All absorbance values in the calibration and prediction measurements should be less than 1.6 absorbance units. Perform a linear least squares regression of the concentration of the analyte versus normalized absorbance using all data points;

do not include the origin as a data point. Divide the peak height of the GMS ester absorbance band by the peak height of the reference polypropylene absorbance band to normalize the result. The calibration equation obtained for the standards used in this study is:

$$Wt\%\ GMS = M \times (A_{1739}/A_{1044}) + N$$

Where:

Wt% GMS	= Weight % of GMS in the polypropylene
A_{1739}	= Absorbance of GMS at 1739 cm^{-1}
A_{1044}	= Absorbance of polypropylene reference band at 1044 cm^{-1}
M	= Calibration constant
N	= Intercept

The calibration curve for the determination of GMS in polypropylene for the standards used in this study is shown in Figure 2.

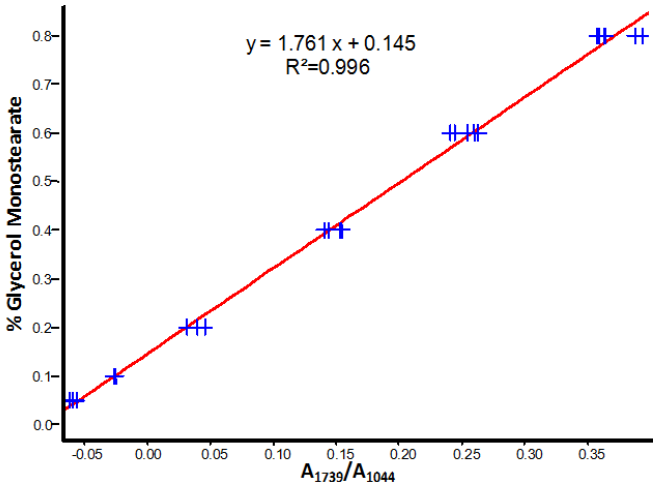


Figure 2. Calibration curve for % GMS in polypropylene.

Procedure

Sample preparation

Molding techniques and conditions used to prepare the sample do not significantly influence the results, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the prepared films have a smooth, consistent surface. A typical preparation procedure is as follows:

Obtain a representative sample of the resin to be analyzed; statistical sampling techniques are recommended (cone and quarter technique, chute splitter, rotary splitter, roto-riffler, and so forth). Place the chase mold on a sheet of aluminum and slightly overfill each cavity in the chase with the resin. Another sheet of aluminum is placed on top and the stack is carefully placed in the press with the platens heated to 200 °C. The press is closed to apply minimal force for 1 or 2 minutes while the sample melts. The force is increased to at least 25,000 pounds, held for approximately 30 seconds, and released. The stack is then removed from the press and allowed to cool on the benchtop. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash. Examine the sample for surface defects and check to ensure that the thickness is between 0.4 and 0.7 mm. Samples with defects or thickness outside of the range are discarded; at least three suitable films are required for the analysis

Operating conditions

The infrared spectrometer should be turned on for at least 15 minutes prior to analysis. The resolution should be set to at least 4 wavenumbers.

Collect for a minimum of 30 seconds (74 scans) for each of the triplicate film samples.

Method configuration

To determine the GMS concentration, measure the peak height absorbance for GMS at 1739 cm^{-1} measured by a vertical intersecting line to a baseline drawn between 1764 and 1722 cm^{-1}. The specified peak height and baseline points can easily be set in an Agilent MicroLab PC FTIR software method. Each peak measurement is called a component and the baseline limits are easily set as shown in Figure 3. The peak type of 'Peak Height with Duel Baseline' is first set. Then parameters for measurement of the peak height polypropylene absorbance band at 1044 cm^{-1} relative to a baseline drawn between 1068 and 949 cm^{-1} (Figure 4) are set. The 'Peak Stop' field is left blank for peak height measurements. The component is further configured to report the absorbance value to five decimal places as shown in Figures 3 and 4.

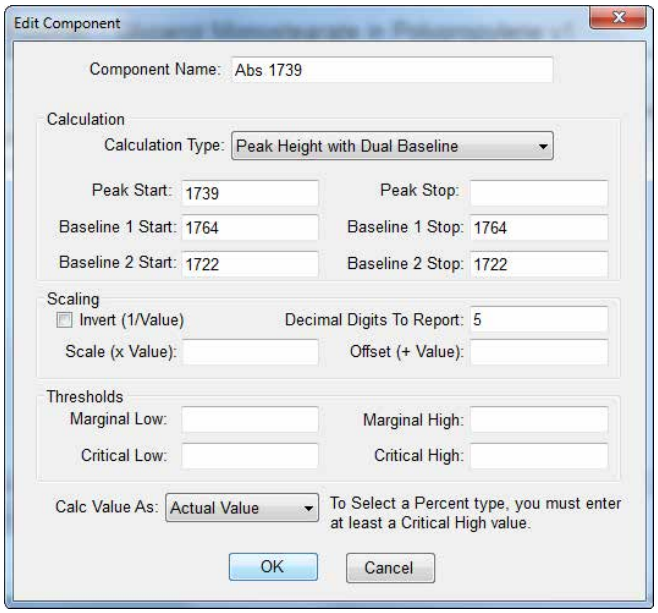


Figure 3. The GMS peak height absorbance (component) measurement at 1739 cm^{-1} in the MicroLab PC FTIR software. The peak start refers to the peak maxima position from which the peak height is measured. Single-point baselines should be set up with the same baseline start and stop points.

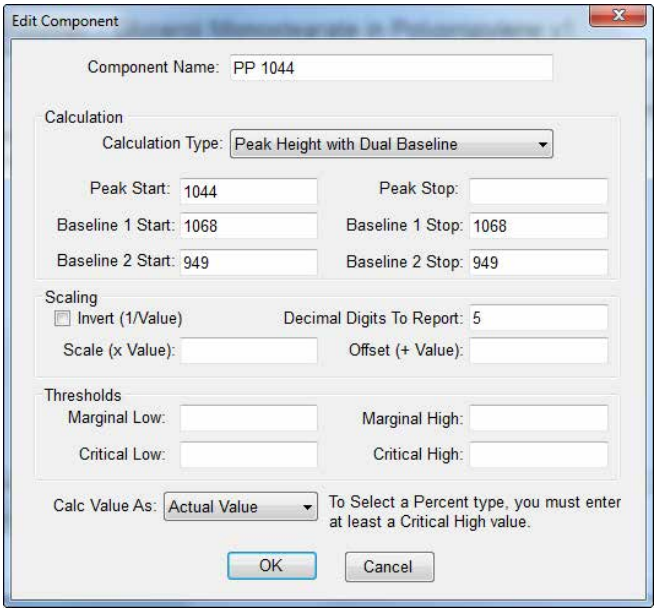


Figure 4. The polypropylene reference peak component addition in the MicroLab PC FTIR software.

A ratio of the analyte to reference absorbance band is used in the calibration for this analysis.

GMS equation:
$Wt\% \text{ GMS} = M \times (A_{1739}/A_{1044}) + N$

GMS resulting calibration values:
$Wt\% \text{ GMS} = 1.761 \times (A_{1739}/A_{1044}) + 0.145$

with M and N as determined in the the Calibration section.

The MicroLab PC FTIR software makes the peak ratio calculations easy to set up. Simply edit the method by adding two new components and selecting the 'Peak Ratio' calculation type. Then add the peak components that are to be ratioed (Figure 5).

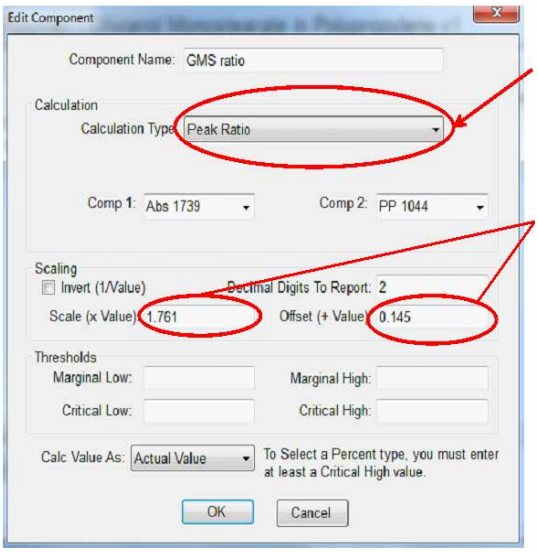


Figure 5. The peak ratio component addition for the calibration in the MicroLab PC FTIR software. After plotting the 0.05– 8% GMS calibration data, the resulting linear regression line's slope is entered in the 'Scale' field and the Y-axis offset in the 'Offset' field.

Analysis

The specimen is placed in the sample compartment and the spectrum is recorded; the typical spectra in the 2200–1500 cm^{-1} range are overlaid in Figure 6. The presence of an absorption band at 1745 cm^{-1} suggests that the resin contains an ester-based antioxidant such as Irganox 1010 or Irganox 3114. If the presence of these antioxidants is confirmed, the GMS measurement must be corrected to compensate for the absorbance of the antioxidants.

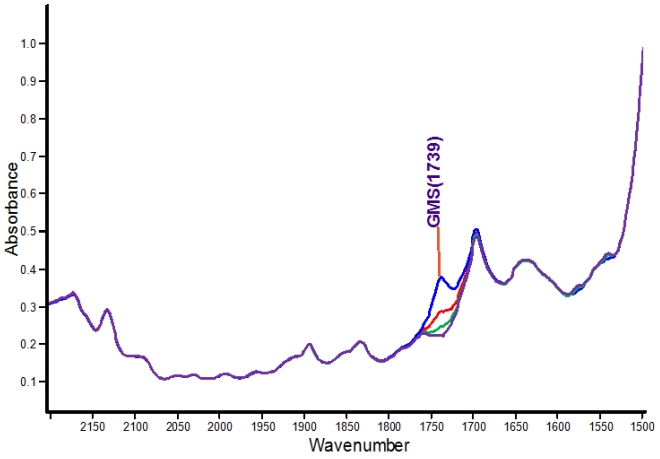


Figure 6. Typical ester carbonyl absorbance for glycerol monostearate in polypropylene

With the ratio defined from the Method Configuration section, the new method is ready to be used to obtain at least triplicate measurements of each calibration standard. Unknown polymer coupons should also be run with a minimum of three measurements around the coupon. This process is made simple and convenient with the DialPath or TumblIR transmission cells. Users can see the exact point of measurement in real time, and quickly reposition the sample for the replicate measurements.

Plot the values measured for the ratio relative to the GMS concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figures 5 and 6. Once the slope and offset values have been entered, the Microlab PC FTIR software method will report the GMS concentration.

The MicroLab PC FTIR software method, Polymer — Glycerol Monostearate in Polypropylene v1, includes the calibration data from Figure 2. This calibrated method is available with the Agilent 5500 and 4500 Series DialPath or TumblIR FTIR spectrometers, as well as the Cary 630 FTIR spectrometers. This method and software performs all the calculations automatically and reports the final value as % Glycerol Monostearate (Figure 7).

The values obtained from triplicate determinations should be averaged to give the final reported concentration.

Conclusion

This analytical method demonstrates how the Agilent Cary 630 FTIR can be used to easily and accurately measure polymer thin films. The unique sampling capabilities of the DialPath and TumblIR provide a simple mechanism to mount your sample, while the step-by-step method-driven software with color-coded, actionable results guides you through your analysis to ensure that your samples are measured with minimum effort and highest accuracy.

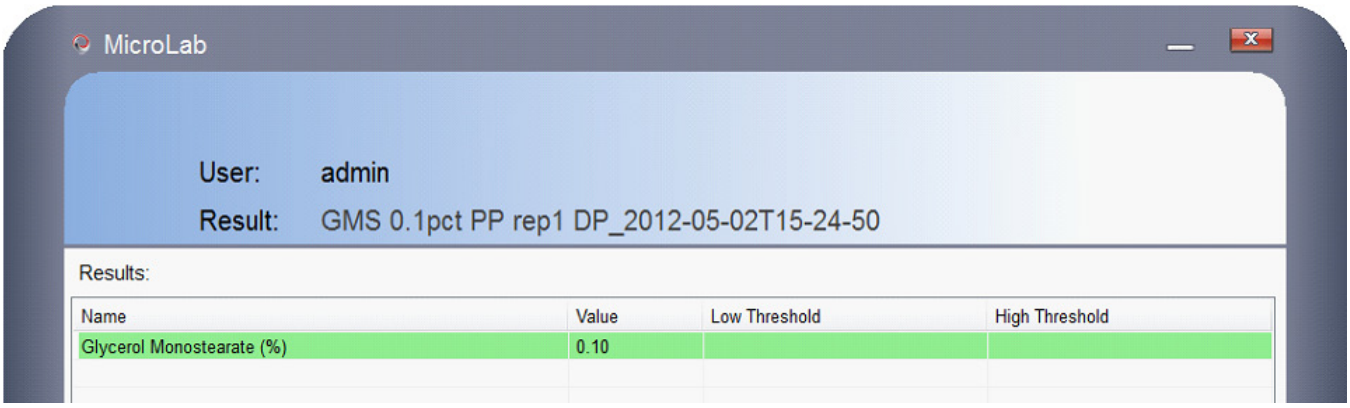


Figure 7. The MicroLab PC FTIR software prediction result for a 0.1% GMS in polypropylene sample

www.agilent.com/chem

Published May 11, 2012
Publication number: 5991-0467EN

Agilent Technologies

Determination of percent ethylene in ethylene-propylene statistical copolymers

Analytical method

Polymers

Authors

Dr. Wayne Collins*, John Seelenbinder† and Frank Higgins†

Agilent Technologies
* Wilmington, DE, USA
† Danbury, CT, USA

Scope

This method is for the determination of the statistical or randomly distributed ethylene content of ethylene-propylene copolymers. The determination is specific for ethylene and cannot be applied for the quantitation of other comonomers. The method has been validated over the range of 0.3 to 3.5% statistical content and can be used for either powder or pellet samples. Certain sorbitol-based clarifiers have been found to interfere with the determination and therefore a correction factor is necessary for resins containing these additives. This method is generally not recommended for quantitation of ethylene in filled or pigmented resins.

Agilent Technologies

Summary

This method describes a procedure for measuring the statistical ethylene contents in ethylene-propylene statistical copolymers. The procedure utilizes an absorption band at 733 cm^{-1} associated with statistically distributed ethylene for a Beer's Law type calculation.

An analytically representative sample of the copolymer resin is molded into a film of thickness between 0.5 and 0.7 mm. Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the films have a smooth, consistent surface. The sample is placed in the infrared spectrometer and the spectrum is obtained at a resolution of 4 wavenumbers or better. Using the Agilent DialPath or TumblIR accessories, the film or coupon can be inserted into the infrared beam path between the top and bottom crystals (Figure 1). Both these accessories are unique to Agilent and provide a revolutionary new way to measure thin polymer films or liquids. The horizontal mounting provides a simple, fast and reproducible mechanism to mount the sample by simply laying it down flat and rotating the crystal into position, eliminating errors and providing accurate and reliable answers — fast! The peak height of the absorbance band at 733 cm^{-1} is determined relative to a baseline drawn between 759 and 703 cm^{-1}. This value is divided by the peak height of the absorbance band at 1044 cm^{-1} relative to a baseline drawn between 1068 and 949 cm^{-1} to give the normalized absorbance at each wavenumber. The random ethylene concentrations can then be determined by comparing these values with a linear regression equation of normalized absorbance versus ethylene content for a set of standards of known ethylene content as determined by C^{13} nuclear magnetic resonance spectroscopy (NMR), which is a primary analytical technique. At least three separate films are analyzed and averaged for each sample analyzed.

Figure 1. The Agilent DialPath transmission cell used for polymer analysis of coupons or films

Apparatus

- Data is obtained using an Agilent Cary 630 FTIR spectrometer equipped with a DialPath or TumblIR sample interface with a 1000 µm path length. Equivalent FTIR spectrometers, such as the mobile or portable Agilent 5500/4500 Series FTIR, can also be used.
- Hydraulic press — with heated platens capable of maintaining 200 °C and a ram force of 25,000 pounds.
- Chase mold — to control thickness (optional).
- Aluminum sheet — 0.05–0.18 mm thick.

Calibration

Standards are prepared by measuring the statistical ethylene content of a series of copolymers covering the desired range using by NMR, which is a primary analytical technique. To perform the calibration, prepare and analyze at least three films for each standard resin in accordance with the requirements of this method. All absorbance values should be less than 1.6 units. Perform a linear least squares regression of the concentration of the analyte versus normalized absorbance using all data points; do not include the

origin as a data point. Divide the peak height of the statistical ethylene absorbance band by the peak height of the reference polypropylene absorbance band to normalize the result. The calibration equation obtained for the standards used in this study is:

$$\% \text{ Stat. ethylene} = M \times (A_{733}/A_{1044}) + N$$

Where:

% Stat. ethylene	= Weight % of statistically distritubed ethylene incorporated into the copolymer
A_{733}	= Peak height of absorbance band of statistical ethylene band at 733 cm^{-1}
A_{1044}	= Peak height of absorbance band of polypropylene reference at 1044 cm^{-1}
M	= Calibration constant
N	= Intercept

The calibration curve for the determination of statistical ethylene in ethylene-propylene copolymers for the standards used in this study is shown in Figure 2.

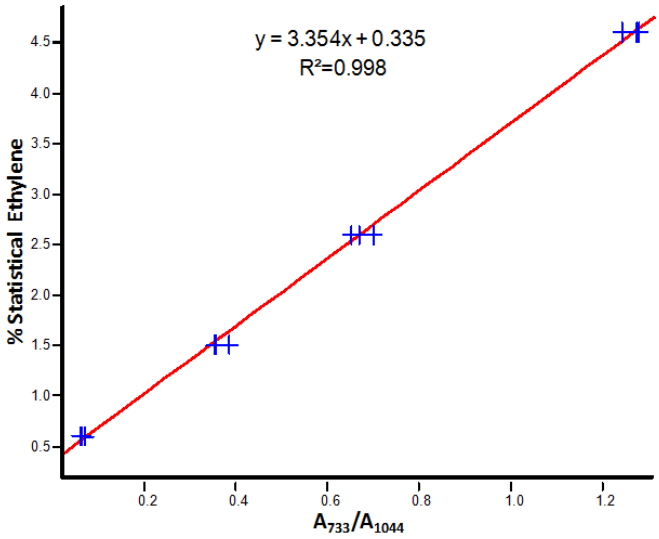


Figure 2. Calibration curve for % statistical ethylene in polypropylene

Procedure

Sample preparation

Obtain a representative sample of the resin to be analyzed; statistical sampling techniques are recommended (cone and quarter technique, chute splitter, rotary splitter, roto-riffler, and so forth). Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes. A typical technique for preparation of these films is as follows:

Place the chase mold on a sheet of aluminum and slightly overfill each cavity in the chase with the resin. Another sheet of aluminum is placed on top and the stack is carefully placed in the press with the platens heated to 200 °C. The press is closed to apply minimal force for 1 or 2 minutes while the sample melts. The force is increased to at least 25,000 pounds, held for approximately 30 seconds and released. The stack is then removed from the press and allowed to cool on the benchtop or in a cold press. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash.

Once the samples are prepared, each sample is examined for surface defects and checked to ensure that the thickness is between 0.5 and 0.7 mm. Samples with defects or thickness outside of the range are discarded; at least three suitable films are required for the analysis.

Operating conditions

The infrared spectrometer should be turned on for at least 15 minutes prior to analysis. The resolution should be set to at least 4 wavenumbers.

Collect for a minimum of 30 seconds (74 scans) for each of the triplicate film samples.

Method configuration

To determine the statistical ethylene concentration, measure the peak height absorbance for statistical ethylene at 733 cm^{-1}, measured by a vertical intersecting line to a baseline drawn between 759 and 703 cm^{-1}. The specified peak height and baseline points can easily be set in an Agilent MicroLab PC FTIR software method. Each peak measurement is called a component and the baseline limits are easily set as shown in Figure 3. The peak type of 'Peak Height with Duel Baseline' is first set. Then parameters for measurement of the peak height polypropylene absorbance band at 1044 cm^{-1} relative to a baseline drawn between 1068 and 949 cm^{-1} (Figure 4) are set. The 'Peak Stop' field is left blank for peak height measurements. The component is further configured to report the absorbance value to five decimal places as shown in Figures 3 and 4.

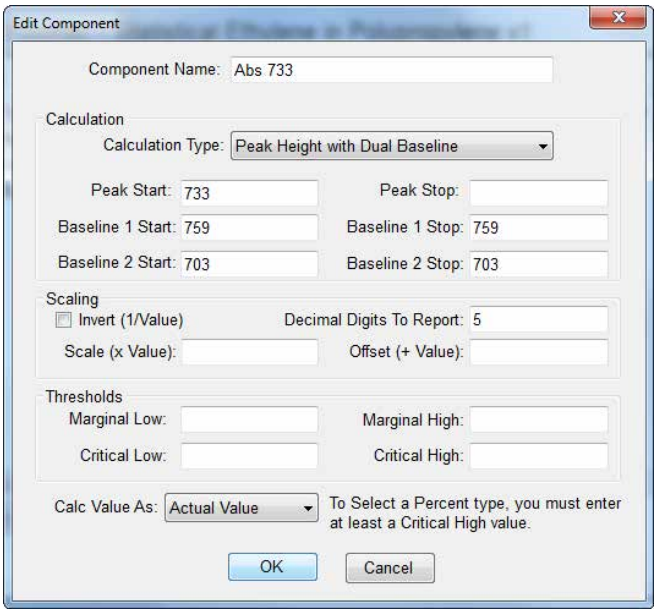


Figure 3. The statistical ethylene peak height absorbance (component) measurement at 733 cm^{-1} in the MicroLab PC FTIR software. The peak start refers to the peak maxima position from which the peak height is measured. Single point baselines should be set up with the same baseline start and stop points.

A ratio of the analyte band absorbance to the reference band is used for this analysis.

$$\% C_2 \text{ (stat.)} = M_s \times (A_{733}/A_{1044}) + N$$

with M and N as determined in the the Calibration section.

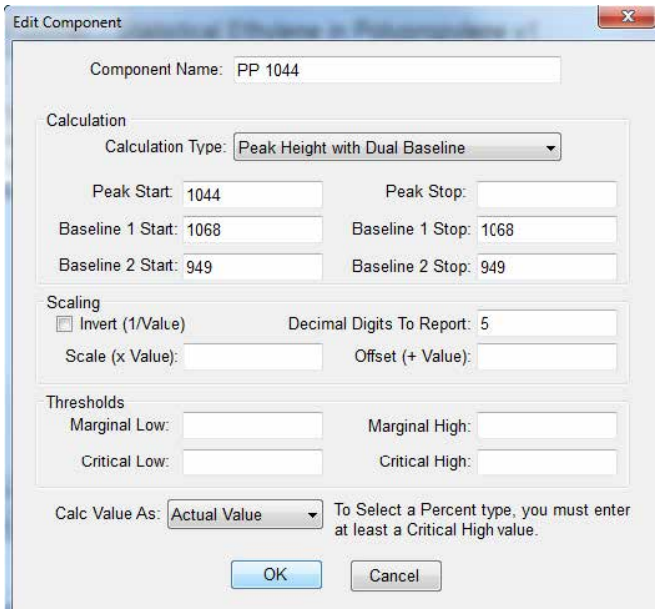


Figure 4. The polypropylene reference peak component addition in the MicroLab PC FTIR software

The MicroLab PC FTIR software makes the peak ratio calculation easy to set up. Simply edit the method by selecting the 'Peak Ratio' calculation type and the peak components that are to be ratioed (Figure 5).

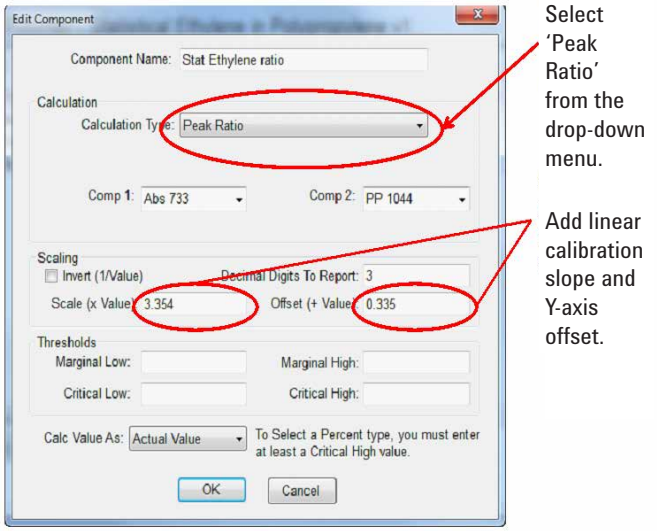


Figure 5. The peak ratio component addition in the MicroLab PC FTIR software. After plotting the calibration data, the resulting linear regression line's slope is entered in the 'Scale' field and the Y-axis offset in the 'Offset' field.

Analysis

The specimen is placed in the sample compartment and the spectrum is recorded; a typical spectrum is shown in Figure 6. The presence of an absorption band at 695 cm^{-1} suggests that the resin contains a sorbitol-based clarifier that can interfere with the statistical ethylene measurement at 733 cm^{-1}. If the presence of this clarifier is confirmed, the statistical ethylene measurement must be corrected to compensate for the absorbance of the clarifier. Certain anti-acid additives can also have an effect on the measurement but are usually ignored since these compounds are present at very low concentrations.

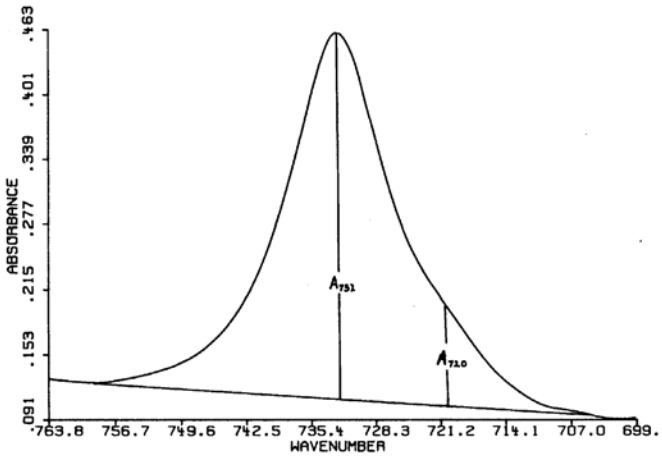


Figure 6. Typical absorption bands for statistical and block ethylene

With the ratio defined from the Method Configuration section, the new method is ready to be used to obtain at least triplicate measurements of each calibration standard. Unknown polymer coupons should also be run with a minimum of three measurements around the coupon. This process is made simple and convenient with the DialPath or TumblIR transmission cells. Users can see the exact point of measurement in real time, and quickly reposition the sample for the replicate measurements.

Plot the values measured for the ratio relative to the statistical ethylene concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figure 5. Once the slope and offset values have been entered, the MicroLab PC FTIR software method will report the statistical ethylene concentration.

The MicroLab PC method, Polymer – Statistical Ethylene in Polypropylene v1, includes the calibration data from Figure 2. This calibrated method is available with the Agilent 5500 and 4500 Series DialPath or TumblIR FTIR spectrometers, as well as the Cary 630 FTIR spectrometers. This method and software performs all the calculations automatically and reports the final value as % statistical ethylene (Figure 7).

The values obtained from triplicate determinations should be averaged to give the final reported concentration.

Conclusion

This analytical method demonstrates how the Agilent Cary 630 FTIR can be used to easily and accurately measure polymer thin films. The unique sampling capabilities of the DialPath and TumblIR provide a simple mechanism to mount your sample, while the step-by-step method-driven software with color-coded, actionable results guides you through your analysis to ensure that your samples are measured with minimum effort and highest accuracy.

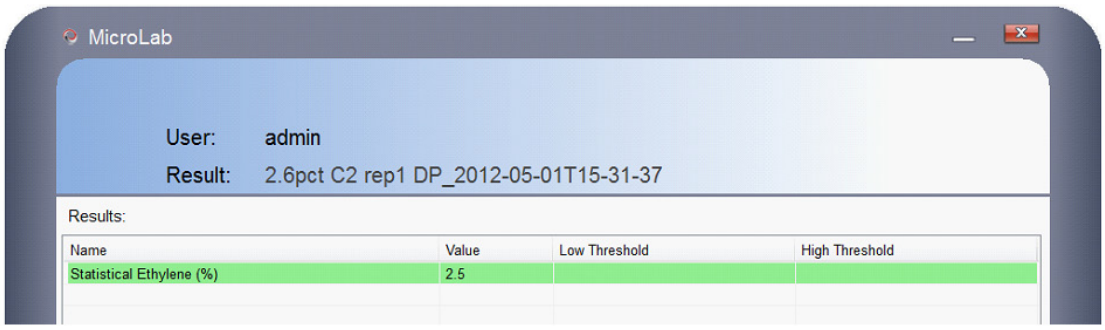


Figure 7. The MicroLab PC software prediction result for a 2.6% statistical ethylene in polypropylene sample

www.agilent.com/chem

Published May 11, 2012
Publication number: 5991-0456EN

Agilent Technologies

PLOT COLUMNS FOR GC/MS

Reduce maintenance costs and extend your capabilities

Most Porous Layer Open Tubular (PLOT) columns are prone to shedding stationary phase particles, which can plug your flow path, damage column switching valves, and contaminate your detector.

In the past, hydrocarbon processing labs have had two options for preventing particle shedding: develop costly, inconvenient workarounds – or avoid using PLOT GC columns altogether.

Now, there's a *better* way: Agilent J&W PLOT PT GC columns

Integrated particle-trapping technology on *both ends* of Agilent PLOT PT GC columns minimizes particle shedding. This reduces downtime, while allowing you to use GC/MS for detailed, qualitative, and quantitative applications.

Back to table of contents ►

Learn more about solutions for the energy and chemical industry at **agilent.com/chem/energy**

Coal-to-Chemical Process Gas Analysis Using Agilent J&W HP-PLOT Q PT and HP-PLOT U PT

Application Note

Energy & Fuels

Author

Yun Zou

Agilent Technologies Shanghai, Ltd.

Abstract

Agilent J&W HP-PLOT Q PT and HP-PLOT U PT GC columns were evaluated for coal-to-chemical process gas analysis by GC/TCD and GC/MS detection. HP-PLOT U PT columns provided excellent peak shapes for the target compounds, especially for polar compounds such as methanol and hydrogen sulfide, although performance for resolving certain hydrocarbon isomers was limited. HP-PLOT Q PT columns were well able to separate polar and nonpolar compounds. GC/MS with an HP-PLOT Q PT column is a useful system for further research of process monitoring or catalyst evaluation.

Introduction

The chemical industry traditionally uses petroleum as its basic raw material, but the use of coal as a feedstock is becoming more attractive as oil prices continue to rise, especially in countries where coal is abundant. Coal-to-olefins (CTO) processes are of particular interest because of the high demand for propylene and ethylene. The first commercial CTO plant in China was started up by the Shenhua Coal to Liquid and Chemical Company at the end of 2010, and at least 10 additional CTO plants are projected to come on stream by 2016 in China. In a typical CTO process, methanol from coal or natural gas is first dehydrated to dimethyl ether (DME). The equilibrium mixture is then converted to light olefins [1]. Current research in this area is focused on developing high-efficiency catalysts and optimizing process conditions for improving yield of olefins [2,3].

Agilent Technologies

GC/MS is a useful tool for analysis of product components after methanol-to-olefins (MTO) reaction or factors affecting catalyst deactivation. Traditional PLOT columns are seldom used for GC/MS analysis, primarily because the stationary phase layer is not mechanically stable and can lead to particle shedding. The Agilent J&W HP-PLOT Q PT and HP-PLOT U PT columns are stabilized with integrated particle trapping technology on both ends of the column to virtually eliminate particle shedding. This allows the columns to be used for valve switching, online, and MS applications [4]. This application note evaluated HP-PLOT Q PT and HP-PLOT U PT GC columns for use in the analysis of coal-to-chemical process gas by GC/TCD and GC/MS.

Experimental

Analyses were performed on an Agilent 7890A GC equipped with a thermal conductivity detector (TCD) and a 7890A GC combined with an Agilent 5975 Series GC/MSD. Sample introduction consisted of a 6-port gas-sample valve connected directly to the split/splitless inlet. A point-of-use gas blending system controlled by auxiliary EPC was used for preparation of low level samples.

The gas mixture was obtained from Beijing AP BAIF Gases Industry Company. The composition of the mixture was referenced to typical coal-to-chemical process gas. To test the performance of the columns, hydrogen sulfide was added to the samples. Table 1 lists the original compounds and concentrations. The concentrations were modified by a point-of-use gas blending system. During analysis, the possibility of air leaking into the sample loop may also have contributed to slight variability in concentration.

Conditions

GC/TCD

Columns:	Agilent J&W HP-PLOT Q PT, 30 m × 0.53 mm, 40 µm (p/n 19095P-QO4PT)
	Agilent J&W HP-PLOT U PT, 30 m × 0.53 mm, 20 µm (p/n 19095P-UO4PT)
Carrier:	Hydrogen, constant flow mode, 40 cm/s, 32 °C
Oven:	32 °C for 5 min, 32 °C to 70 °C at 30 °C/min, 70 °C for 5 min, 70 to 160 °C at 10 °C/min
Injection:	170 °C, split ratio 5:1, 250 µL gas sampling loop
Detector:	TCD at 250 °C

GC/MSD

Columns:	Agilent J&W HP-PLOT Q PT, 30 m × 0.32 mm, 20 µm (p/n 19091P-QO4PT)
	Agilent J&W HP-PLOT U PT, 30 m × 0.32 mm, 10 µm (p/n 19091P-UO4 PT)
Carrier:	Helium, constant flow mode, 35 cm/s, 32 °C
Oven:	32 °C for 5 min, 32 °C to 70 °C at 30 °C/min, 70 °C for 5 min, 70 to 160 °C at 10 °C/min
Injection:	170 °C, split ratio 5:1, 250 µL gas sampling loop
Instrument:	Agilent 7890A GC with gas blending system
MS:	EI, Scan/SIM
Transfer line:	180 °C
MS temperature:	230 °C (source), 150 °C (quad)
Scan mode:	Mass range (10 to 100 amu)

Table 1. Coal-to-chemical process gas sample.

Compound	Concentration (% mol)
Carbon monoxide	19.94
Carbon dioxide	0.81
Methane	1.08
Ethane	0.40
Ethylene	0.43
Propane	0.25
Propylene	0.25
Butane	0.27
Butylene	0.26
Hydrogen sulfide	0.47
Methanol	0.48
Dimethylether	0.94
Hydrogen	Balance gas

Results and Discussion

The conversion of methanol to olefins over a catalyst takes place through a complex network of chemical reactions. In general, at lower temperatures methanol reacts to form dimethyl ether. At higher temperatures, the desired products (olefins) are produced and the selectivity for DME decreases. The variety of components in coal-to-chemical process gas requires the separation of polar and nonpolar compounds.

The gas mixture was analyzed using the GC/TCD system with an HP-PLOT Q PT column and HP-PLOT U PT columns. Figures 1 and 3 show that all polar compounds, such as methanol and hydrogen sulfide, were well separated from hydrocarbons using HP-PLOT Q PT and U PT, but the HP-PLOT Q PT column provided better resolution of hydrocarbon isomers. There were two pairs of coeluting compounds on the HP-PLOT U PT column, namely propylene and propane, and 2-butylene and butane. Since HP-PLOT U PT is a more polar phase, it demonstrated improved inertness and provided better peak shape and response for very polar compounds such as methanol (500 ppm, Figure 3) and hydrogen sulfide (500 ppm, Figure 3), which indicate lower detection limits for these compounds.

The same analytical results were obtained using GC/MS. Figures 2 and 4 show the total ion chromatograms of HP-PLOT Q PT and HP-PLOT U PT GC columns.

Many investigations have been devoted to the study of the effect of reaction conditions on the activity and selectivity of catalysts, or examination of the MTO reaction mechanism. Sometimes the real sample is more complex than the standard gas mixture used in this application note during the MTO reaction. GC/MS is a useful tool for further qualitative and quantitative study. Since the upper temperature limit is quite low (190 °C), backflushing hydrocarbon compounds heavier than C7 is necessary when using HP-PLOT U PT for such investigations. HP-PLOT Q PT is more suitable for use with GC/MS for further identification of unknowns or confirmation of components in process byproducts. This column can elute up to C14 and provide good resolution of polar and nonpolar compounds.

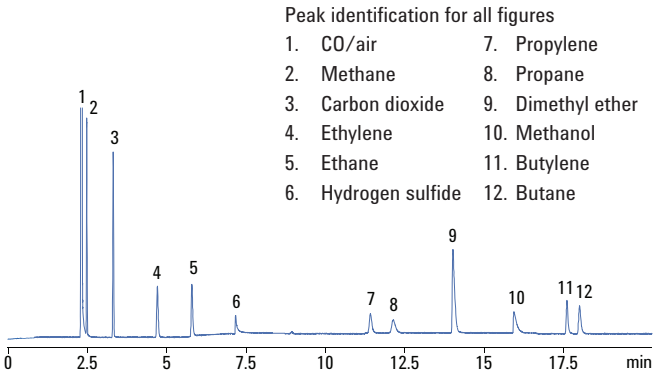


Figure 1. Chromatogram of a gas mix using an Agilent GC/TCD system and Agilent J&W HP-PLOT Q PT column.

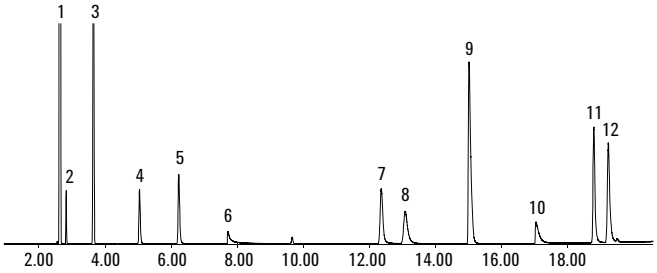


Figure 2. TIC of gas mix using an Agilent GC/MSD system and Agilent J&W HP-PLOT Q PT column.

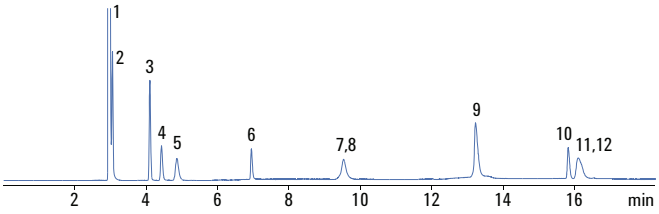


Figure 3. Chromatogram of a gas mix using an Agilent GC/TCD system and Agilent J&W HP-PLOT U PT column.

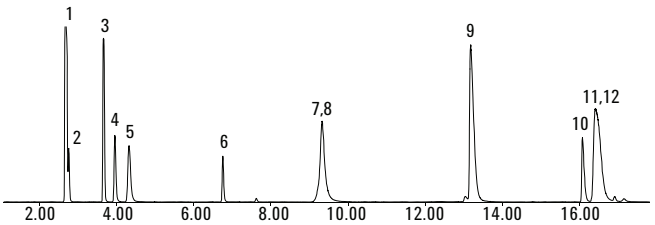


Figure 4. TIC of gas mix using an Agilent GC/MSD system and Agilent J&W HP-PLOT U PT column.

Conclusions

Agilent J&W HP-PLOT Q PT and HP-PLOT U PT columns were evaluated for coal-to-chemical process gas analysis with GC/TCD and GC/MS detection. HP-PLOT Q PT and HP-PLOT U PT columns with integrated particle trapping technology enable worry-free operation with valves and MS detection. HP-PLOT U PT can provide excellent peak shape for even very polar compounds, such as methanol and hydrogen sulfide, but resolution of some hydrocarbon isomers is not as effective as with HP-PLOT Q PT. This Q-type column can provide good resolution for polar and nonpolar compounds and is suitable for GC/MS catalyst evaluation or analysis of the composition of coal-to-chemical process gas.

References

1. C. D. Chang, A. J. Silvestri. *J. Catal*. 47, 249 (1977).

2. H. Q. Zhou, Y. Wang, F. Wei, D. Wang, Z. Wang. *Appl. Catal. A*. 348, 135 (2008).

3. M. Stocker. *Micropor. Mesopor. Mat.* 29, 3 (1999).

4. Anon. Protect your GC system from PLOT column phase shedding. Agilent Technologies, Inc., Publication Number 5991-1174EN (2012).

For More Information

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

www.agilent.com/chem

Printed in the USA
March 26, 2013
5991-2205EN

Agilent Technologies

Agilent J&W PoraBOND Q PT Analyzes Oxygenates in Mixed C4 Hydrocarbon Streams by GC/FID and GC/MSD

Application Note

Energy & Fuels

Authors

Mingji Cao and Zhaoxia Liu
Shanghai SECCO Petrochemical Co., Ltd.
No. 557 Nan Yinhe Road,
Shanghai Chemical Industry Park,
Shanghai 201507, P. R. China

Yun Zou
Agilent Technologies (Shanghai) Co., Ltd.

Abstract

Even trace amounts of oxygenates can cause catalyst poisoning, so monitoring the level of oxygenates in mixed C4 streams is very important in the production of propylene. This application note demonstrates the analysis of trace oxygenates in mixed C4 streams using an Agilent J&W PoraBOND Q PT column with GC/FID and GC/MS detection. The auxiliary qualitative and quantitative analysis by GC/MS allows more effective and reliable process control.

Introduction

Mixed C4 streams, containing butadiene, butenes, and butanes, are coproduced by steam cracking processes [1]. C4 hydrocarbons are used as feedstock for industrial chemicals, rubber, and plastics. Due to the presence of harmful impurities, only a small proportion of valuable components are extracted from the mixed C4 streams and subsequently processed into usable products, while the majority of remaining C4 by-products are flared or used as low-quality, low-value additives. Maximizing the yield of the mixed C4 stream is a major objective for most petrochemical companies. The key to processing C4 streams into value-added products is accurately monitoring impurities.

Agilent Technologies

Based on the mechanism of 2-butene and ethylene disproportionation [2], the process for the production of propylene is one of the effective ways of improving the chemical utilization value of mixed C4. This advanced production technology is mature with good economic returns. The technology can be used with a variety of C4 streams, including mixed C4 produced in steam cracking, raffinate C4 mixtures from MTBE, or butadiene extraction [3]. Fresh C4, plus C4 recycle, are mixed with ethylene and sent through a guard bed to remove trace impurities from the mixed feed. It is crucial that the oxygenate impurities, including dimethyl ether (DME), methanol (MeOH), ethanol (EtOH), methyl tertiary butyl ether (MTBE), and ethyl tertiary butyl ether (ETBE) are thoroughly monitored because trace oxygenates can lead to catalyst poisoning, halting reactions, or lowering yields [4].

Agilent Lowox or GS-OxyPLOT GC columns are designed specifically for the accurate analysis of mg/L or µg/L level oxygenates in complex matrixes [5,6]. They are used successfully to control product quality by GC/FID analysis. However, for process control, the matrix of mixed C4 feed from various routes is sometimes quite complex and will interfere with the qualification analysis of some oxygenates by GC/FID. The alternative GC/MS analysis can offer more identification possibilities but is seldom combined with PLOT columns because the particle layer is not mechanically stable. In this application note, an Agilent J&W PoraBOND Q PT column was used to analyze oxygenates in mixed C4 streams by GC/FID and GC/MS for process monitoring. PoraBOND Q PT columns, with integrated particle traps on both ends, offer greater stability than conventional PLOT columns and enable worry-free operation with MS detection [7].

Experimental

Analyses were performed on an Agilent 7890 Series GC equipped with a flame ionization detector (FID) and a 7890 Series GC combined with an Agilent 5973 Series GC/MSD.

GC/FID conditions

Column:	Agilent J&W PoraBOND Q PT, 30 m × 0.32 mm, 5 µm (p/n CP7351PT)
Sample:	50-100 mg/L oxygenates in mixed C4
Carrier:	Helium, constant flow mode, 35 cm/s, 45 °C
Oven:	45-90 °C at 6 °C/min, 90-240 °C at 15 °C/min, 240 °C for 10 min
Injection:	200 °C, split ratio 30:1, 200 µL gas sampling valve
Detector:	FID at 250 °C
GC:	Agilent 7890A Series

GC/MSD conditions

Column:	Agilent J&W PoraBOND Q PT, 30 m x 0.32 mm, 5 µm (p/n CP7351PT)
Carrier:	Helium, constant flow mode, 39 cm/s, 48 °C
Oven:	48-90 °C at 6 °C/min, 90-240 °C at 15 °C/min, 240 °C for 10 min
Injection:	200 °C, split ratio 5:1, 200 µL gas sampling valve
GC:	Agilent 7890A Series GC
MS:	EI, Scan/SIM
Transfer line:	280 °C
MS temp:	230 °C (source), 150 °C (quad)
Scan mode:	Mass range (10-200 amu)
SIM mode:	See Table 1

Table 1. Typical quantitation ions for target oxygenates.

No.	Compound	CAS no.	Molecular form	Target ion
1	Methanol	67-56-1	CH_4O	31
2	Dimethyl ether	115-10-6	C_2H_6O	45
3	Ethanol	64-17-5	C_2H_6O	31
4	Methyl tert-butyl ether	1634-04-4	$C_5H_{12}O$	73
5	Ethyl tert-butyl ether	637-92-3	$C_6H_{14}O$	59

Results and Discussion

Normally, highly polar stationary phases, such as GS-OxyPLOT and Lowox, are used for the separation of oxygenates in light hydrocarbons with oxygenates eluting well behind the C4 hydrocarbon matrix compounds. This allows these components to be measured accurately at low levels.

The presence of dimers or higher polymers in some mixed C4 streams, however, can interfere with the quantitation of DME by GC-FID. The monitoring of DME is critically important in the production cycle of propylene. Two methods are discussed here. One approach is the choice of a selective column to promote interference-free elution of oxygenates from hydrocarbons.

Figure 1 shows that hydrocarbons are separated according to carbon number on the PoraBOND Q PT column; dimer, such as C8, elutes far from C4. Target oxygenates, including DME, methanol, ethanol, MTBE, and ETBE, achieve good resolution from hydrocarbons. Figure 2 is a chromatogram overlay. Although the content of C3 hydrocarbons is normally not very high in mixed C4 streams, even at the level of 80% C3 hydrocarbons, this does not interfere with the qualitative and quantitative determination of DME. DME can be well resolved from C3 and C4 hydrocarbons.

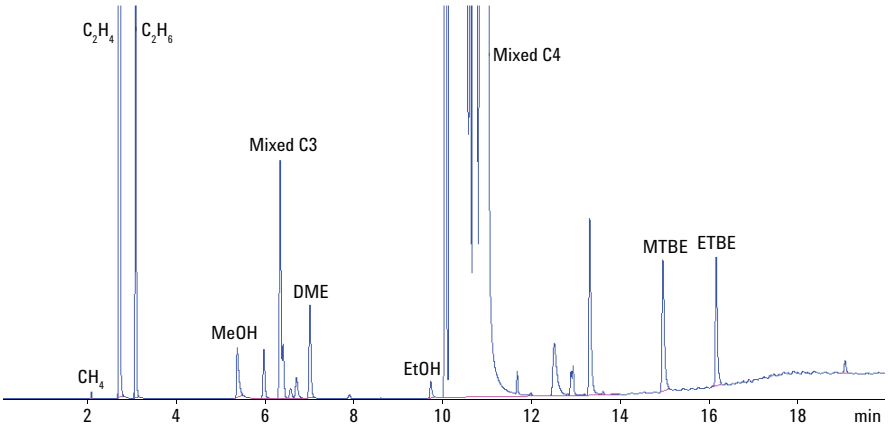


Figure 1. Chromatogram of mixed C4 streams from an etherification process using an Agilent GC/FID system and Agilent J&W PoraBOND Q PT column.

Another solution is the use of highly sensitive and selective GC/MS for identification purposes, as this avoids the detection interference of hydrocarbons. GC/MS is a useful tool for further qualitative and quantitative study on mixed C4 streams. However, traditional PLOT columns are seldom used for GC/MS analysis, primarily because the stationary phase layer is not mechanically stable and can lead to particle shedding as a result. The new PoraBOND Q PT column is stabilized with integrated particle trapping technology on both ends of the column to virtually eliminate particle shedding. This technology expands the applicability of PLOT columns into the MS domain.

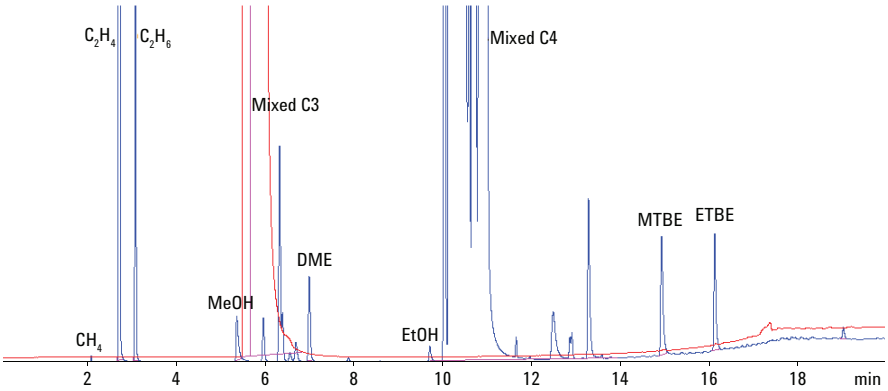


Figure 2. Chromatogram overlay of mixed C4 streams from an etherification process and 80% C3 hydrocarbons using an Agilent GC/FID system and Agilent J&W PoraBOND Q PT column.

GC/MS is a convenient and important tool for routine analysis and process control for further identification of unknowns or confirmation in C4 streams. Figure 3 demonstrates the total ion chromatogram of raffinate C4 mixtures from MTBE. Synchronous SIM/scan was used to monitor ions of interest with high-sensitivity SIM mode and to simultaneously acquire library-searchable scan data in one run. In SIM mode, the method can eliminate air and hydrocarbon interferences to allow for MS identification of the target oxygenates and achieve reliable analysis.

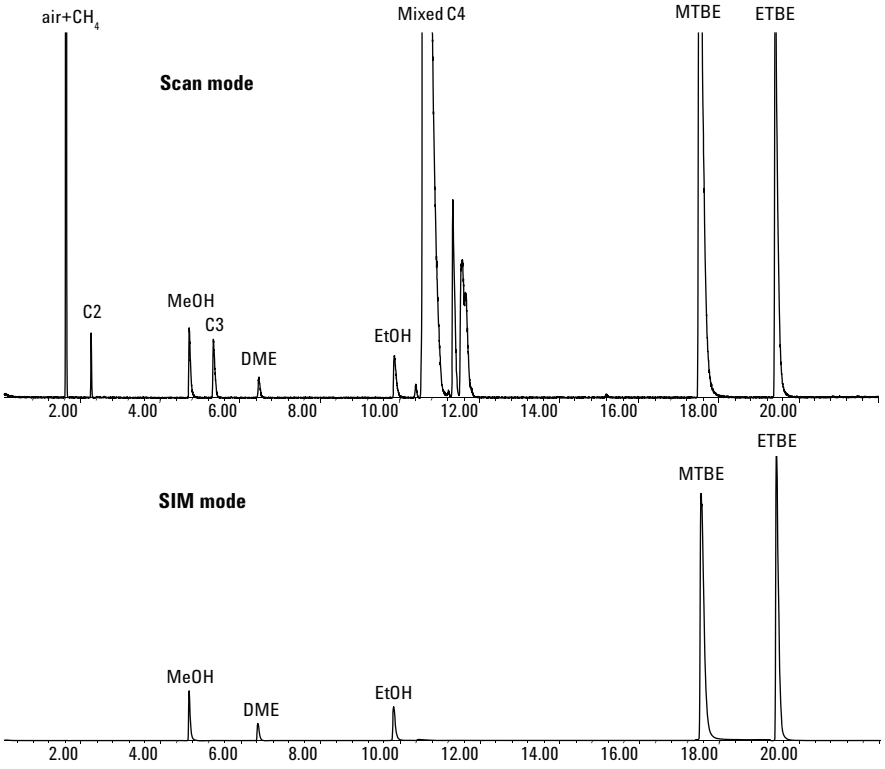


Figure 3. Simultaneous scan (top) and SIM (bottom) analysis of raffinate C4 mixtures from MTBE using an Agilent GC/MS system and an Agilent J&W PoraBOND Q PT column.

Conclusions

This application demonstrates the analysis of oxygenates in mixed C4 streams that are used as feedstock in the production of propylene. The PoraBOND Q PT column with integrated particle trapping technology proves its suitability for quantifying target oxygenates in a challenging C4 matrix using MS detection. In comparison with a standard GC/FID method, the auxiliary qualitative and quantitative analysis from GC/MS can eliminate interfering matrixes. This results in more reliable data for process monitoring or routine analysis and presents opportunities for the possible conversion of more low-value C4 streams into higher value products.

Acknowledgements

The technical support of Chunxiao Wang from Agilent Technologies is gratefully acknowledged.

References

1. A. Beckmann, F. Nierlicha, T. Pöpken, D. Reusch, C. von Scala, A. Tuchlenski. *Chem. Eng. Sci*. 57, 1525 (2002).

2. D. S. Maisel, D.D. Boesiger. In: *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons (2010).

3. Y-j. Zhang, J. Liu. *Chem. Ind*. 29, 32 (2011).

4. C. Changjun, S. Hui, Y. Xiaohong, L. Lei. Chin. *J. Chrom*. 24, 419 (2006).

5. Anon. The Essential Chromatography & Spectroscopy Catalog, 2011-2012. Agilent Technologies, Inc. Publication Number 5990-6674EN (2011).

6. Anon. Agilent J&W GS-OxyPLOT Capillary GC Columns. Agilent Technologies, Inc. Publication Number 5989-6489EN (2007).

7. Anon. Protect your GC system from PLOT column phase shedding. Agilent Technologies, Inc. Publication Number 5991-1174EN (2012).

For More Information

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

www.agilent.com/chem

Printed in the USA
December 6, 2012
5991-1549EN

Agilent Technologies

Analysis of Organic Acids and Alcohols Using the Agilent J&W DB-624UI Ultra Inert GC Column

Application Note

Food Testing & Agriculture

Authors

Pat Sasso and Ken Lynam

Agilent Technologies, Inc.

Abstract

A 26-component mix of aliphatic short chain and aromatic alcohols and carboxylic acids was used to evaluate the recently introduced Agilent J&W DB-624UI column to show acceptable peak shape and resolution. The column was compared to non-Agilent 624 phases. Organic acids had reasonable peak width and peak symmetry for a narrow range of volatilities (C3 through C8) on the DB-624UI column, suggesting it may be possible to analyze these compounds without the need to convert them to methyl esters.

Introduction

Recently, emphasis has been placed on the heart-healthy benefits of long chain omega-3 fatty acids. The accurate quantitation of these acids in various matrixes, ranging from salmon tissue to dietary supplements, typically involves extraction, drying, and derivatization to the methyl esters to permit analysis by gas chromatography. While this technique has gained wide acceptance, the ability to measure organic acids without so much sample preparation has led to the introduction of novel detectors, such as charged aerosol detection coupled to HPLC [1]. The tradeoff is that HPLC columns lack the separation power for closely similar compounds that capillary GC columns can provide. Another problem associated with reversed-phase HPLC is the need to bring samples for injection into an aqueous-friendly environment. GC injection is advantageous because the components of interest possess a nonpolar moiety more easily extracted into GC-friendly nonpolar solvents.

Agilent Technologies

The DB-624UI column acquired its unique phase selectivity over the course of many years, dating back to the original use of the 624 phase for purgeable halogenated hydrocarbons under EPA Method 624 for waste water effluent. By combining sufficient cyanopropyl phenyl with a large percentage of methyl polysiloxane, the column allows GC/MS characterization of previously poorly resolved components with isobaric quantitation ions such as 2-butanone and ethyl acetate [2].

This application note assesses the performance of the DB-624UI GC column against a non-Agilent 624 column for the analysis of organic acids and alcohols, without the need for time-consuming derivatization.

Experimental

An Agilent 6890N GC/FID equipped with an Agilent 7683B Automatic Sampler was used for this series of experiments.

Conditions

Column:	Agilent J&W DB-624UI, 30 m × 0.32 mm, 1.8 µm (p/n 123-1334UI)
Sample:	26-component alcohol and acids mix (C_1 through C_{12}), 100 ng per component on-column
Carrier:	Hydrogen, 38 cm/s, 2.0 mL/min, constant flow mode
Oven:	35 °C (hold 1 min), to 260 °C at 10° C/min (hold 1 min)
Inlet temp:	200 °C
Inlet liner:	Deactivated dual-taper direct connect
Automatic Sampler:	Agilent 7683B, 0.5 µL syringe, 0.01 µL neat, split injection (100:1 ratio)
GC:	Agilent 6890N GC/FID
Detector:	FID at 265 °C

Flow path supplies from Agilent

Vials:	Amber, screw cap (p/n 5182-0716)
Caps:	Blue, screw cap (p/n 5282-0723)
Vial inserts:	250 µL glass with polymer feet (p/n 5181-1270)
Syringe:	0.5 µL (p/n G4513-80229)
Septum:	Advanced Green (p/n 5183-4759)
Inlet liner:	Dual-taper direct connect (p/n G1544-80700)
Magnifier:	20× (p/n 430-1020)

Standards preparation

A 26-component checkout mix at equivalent carbon numbers for FID response was prepared from reagents of ACS grade or better, available from Sigma-Aldrich. To provide approximately similar area responses for all components on the FID detector, methanol was added in slight excess to account for evaporation in the automatic sampler vials over time.

Results and Discussion

EPA 624 columns were purchased from another vendor. Agilent and non-Agilent columns had the same dimensions and film thickness, and all columns were conditioned overnight prior to making any injections. Criteria for evaluation included peak symmetry for 3 different organic acids, peak shape for alcohols, and resolution of the critical pair, phenyl ethanol and nonanol. Elution order was verified separately by GC/MS in EI mode on an Agilent 5975D equipped with an EI 350 °C inert ion source.

Figure 1 shows an analysis of the test mixture on the DB-624UI column. The peak symmetry for the 3 organic acids is acceptable.

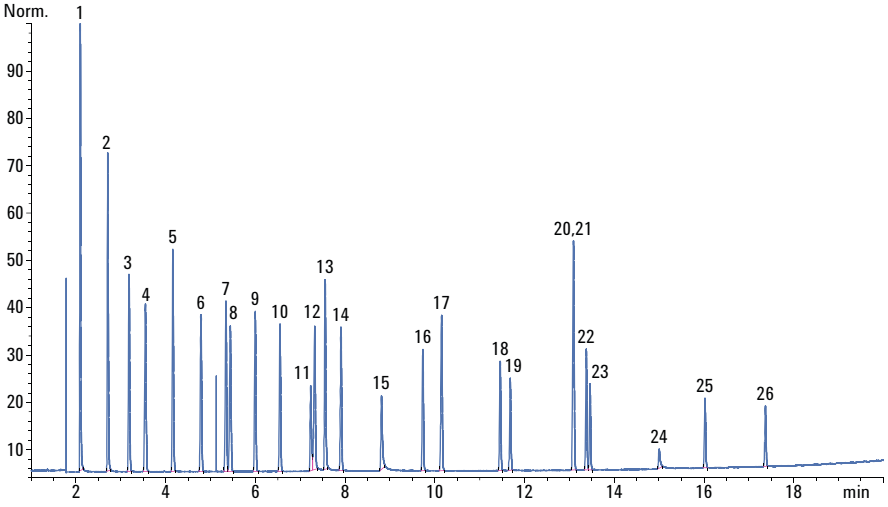


Figure 1. Test mixture showing acceptable peak shape for organic acids on an Agilent J&W DB-624UI GC column.

Table 1 lists the peak symmetry as calculated by the area percent report with performance included. A statistical analysis of 3 replicate injections is provided in Table 2 to demonstrate the reproducible peak symmetry and resolution of the critical pair delivered by the DB-624UI column. It is important to note that under identical temperature programming, 2 non-Agilent columns gave no resolution of the critical pair, leading to the conclusion that not all 624 phases are created equal.

Table 1. Peak width and symmetry for underivatized alcohols and acids following separation on an Agilent J&W DB-624UI GC column.

Component	Peak number	Width	Symmetry
Methanol	1	0.0194	0.6993
Ethanol	2	0.0247	0.7842
Isopropanol	3	0.0293	0.8980
Tert-butanol	4	0.0348	0.9528
1-Propanol	5	0.0299	0.9035
2-Butanol	6	0.0321	0.9521
2-Methyl-1-propanol	7	0.0334	0.9610
2-Methyl-2-butanol	8	0.0367	0.9796
1-Butanol	9	0.0314	0.9466
3.Pentanol	10	0.0323	0.9836
Propanoic acid	11	0.0329	0.5443
3-Methyl-1-butanol	12	0.0354	1.0277
Ethylene glycol	13	0.0309	0.8296
1-Pentanol	14	0.0310	0.9785
Butanoic acid	15	0.0347	0.5953
1-Hexanol	16	0.0312	0.9894
Cyclohexanol	17	0.0342	0.9668
1-Heptanol	18	0.0308	0.9882
1,2-Pentanediol	19	0.0313	0.9390
Benzyl and octanol	20, 21	0.0380	1.0342
Phenyl ethanol	22	0.0321	0.9638
Nonanol	23	0.0305	0.9578
Octanoic acid	24	0.0374	0.6355
Decanol	25	0.0309	0.9398
Undecanol	26	0.0311	0.9527

Table 2. Three replicate injections show reproducible peak symmetry and resolution on an Agilent J&W DB-624UI GC column (serial number USC179032H)

Compound	Avg. symmetry	Std. dev.
Propanoic acid	0.70	0.01
Butanoic acid	1.10	0.03
Octanoic acid	0.87	0.01
	Avg. RS	**Std. dev.**
Phenyl ethanol/nonanol critical pair	3.883	0.021

Figure 2 demonstrates the lack of peak symmetry exhibited by one of the non-Agilent columns. Butanoic acid, also referred to as butyric acid, produced severe tailing on a non-Agilent column, and in replicate injections, it was virtually impossible to integrate properly. This compound can be detected by mammals with good scent detection abilities (such as dogs) at 10 µg/L, whereas humans can detect it in concentrations above 10 mg/L. When butter goes rancid, butyric acid is liberated from the glyceride by hydrolysis, leading to its characteristic unpleasant odor commonly described as acrid.

Figure 3 provides a comparison of the peak symmetry for octanoic acid with the DB-624UI and non-Agilent 624 columns. Symmetry tended to improve as volatility decreased for the DB-624UI column, but the opposite was the case for the non-Agilent column, with octanoic acid eluting so broadly that it appeared to be missing from the sample injections. Octanoic acid, also commonly known as caprylic acid, is present in dairy foods and in palm kernel oil at 6 to 8%, which is the second largest traded edible oil in the world [3].

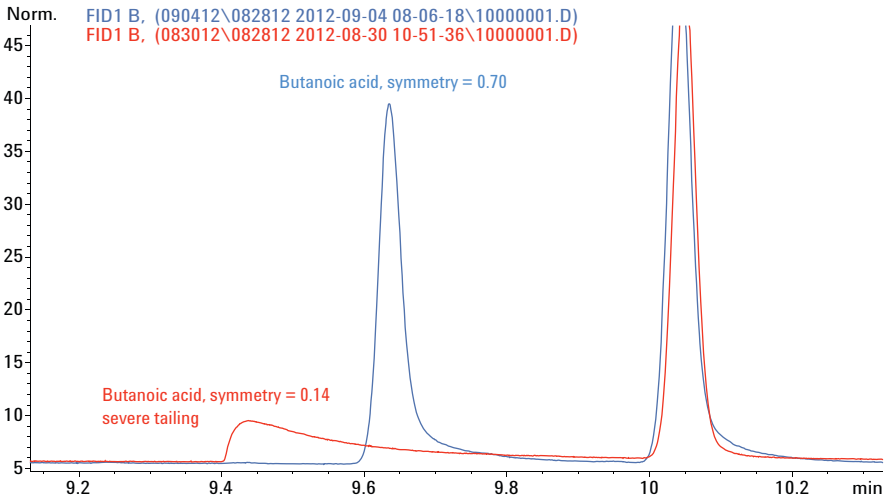


Figure 2. Peak shape for butanoic (butyric) acid on an Agilent J&W DB-624UI GC column (blue) and a non-Agilent 624 column (red).

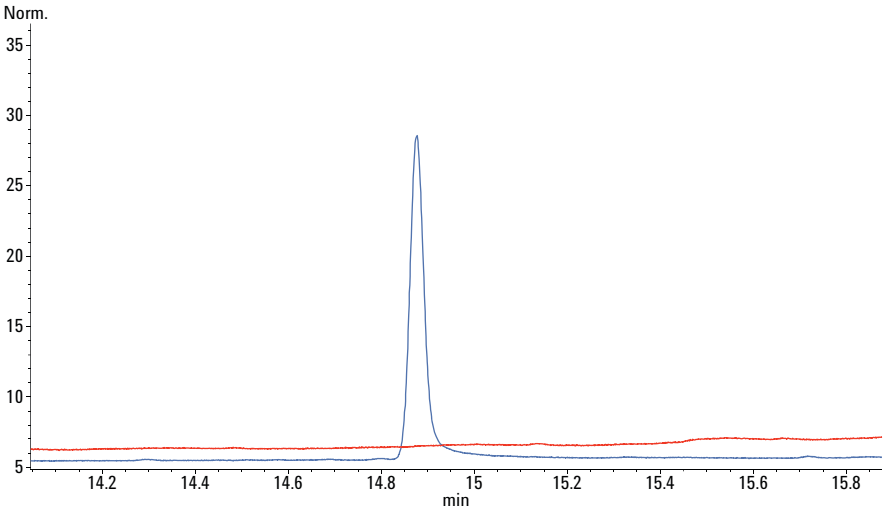


Figure 3. Peak shape for octanoic (caprylic) acid demonstrating complete loss of symmetry on a non-Agilent 624 column (red).

Conclusions

The DB-624 Ultra Inert GC column provided better performance than non-Agilent 624 columns. When considering the potential for time-saving without derivatization, it becomes apparent that this stationary phase can be suitable for the analysis of numerous organic acids. Given that only the Agilent column gave suitable peak symmetry and resolution, the option of analytical work-around procedures, such as foregoing ester derivatization, makes column selection very important to the success of the assay.

References

1. I. Acworth, M. Plante, B. Bailey, C. Crafts. "Quantitation of Underivatized Omega-3 and Omega-6 Fatty Acids in Foods by HPLC and Charged Aerosol Detection". Thermo Fisher Scientific, Inc. Publication Number LPN 2931-02 01/12 (2011).

2. EPA. EPA Method 624 - Purgeables. U.S. Environmental Protection Agency. http://water.epa.gov/scitech/methods/cwa/organics/upload/2007_07_10_methods_method_organics_624.pdf

3. C. Coslett. Facts on Palm Kernel Oil. http://www.ehow.com/facts_5783441_palm-kernel-oil.html

For More Information

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

www.agilent.com/chem

Printed in the USA
November 8, 2012
5991-1441EN

Agilent Technologies

An Alternative Application for a Highly Oxygen-Selective Capillary GC Plot Column

Application Note

Hydrocarbons

Authors

Alejandro Gonzalez
DCG Partnership I, Ltd.
4170A S Main
Pearland, TX 77581
USA

Doris Smith and Ken Lynam
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Abstract

This application note successfully shows selective retention and resolution of low molecular weight sulfur containing species on an Agilent J&W GS-OxyPLOT column. The selective retention for sulfur species enables enough of a retention shift away from hydrocarbon matrices such as base gasoline and n-butane to demonstrate the feasibility of effective quantification of sulfur species in process streams. Using an Agilent J&W GS-OxyPLOT column it is possible to shift the retention of sulfur containing analytes away from a hydrocarbon matrix to achieve effective quantification in the low ppm range.

Agilent Technologies

Introduction

The Agilent J&W GS-OxyPLOT column is highly selective for oxygen-containing species. Most of the initial applications for this column focus on the determination of trace level oxygenates in hydrocarbon matrices [1,2]. Example applications include testing and quantification of species containing oxygen in complex matrixes such as reformulated gasoline and C1-C4 hydrocarbon process streams. ASTM method 7059 is in effect for the analysis of methanol in crude oil by GC [3]. A recently approved method (June 2009, subcommittee D02.D04) D7423 for the analysis of trace oxygenates in light hydrocarbon matrices is also an application of the Agilent J&W GS-OxyPLOT column. Sub 10 ppm quantifications of alcohols, aldehydes and ethers in these feed stocks are important analyses to avoid poisoning of the catalysts used in processing these materials.

Oxygen and Sulfur Chemical Similarity

Chemical species that contain oxygen and sulfur share similar chemical behaviors often undergoing similar reactions to form similar products [4]. Affinity and retention on a highly oxygen selective PLOT column by sulfur-containing species is no exception. This application note demonstrates that the chromatographic behaviors of species containing sulfur on an Agilent J&W GS-OxyPLOT are quite similar to the behaviors demonstrated by oxygen-containing species on the same phase.

Selective retention and resolution of species containing sulfur from complex hydrocarbon matrices can help facilitate trace level analysis of low boiling mercaptans, thiols and sulfides. Monitoring levels of these compounds at low ppm levels has become increasingly important as stack emission and fuel content regulations have stiffened. In hydrocarbon processing, analyses of the sulfur content in feedstocks are used to make processing decisions that hopefully avoid sulfur poisoning of expensive catalysts and enhance refinery throughput.

Experimental

Three different sulfur standards, from liquid to gas, were tested using the Agilent J&W GS-OxyPLOT column.

For the test of a liquid sample, a standard mix of 14 sulfur containing compounds in base gasoline was purchased from Spectrum Quality Standards, Houston TX. Class A volumetric flasks and pipettes were used for dilutions. The liquid sample was analyzed at Agilent Technologies Little Falls Site in Wilmington DE.

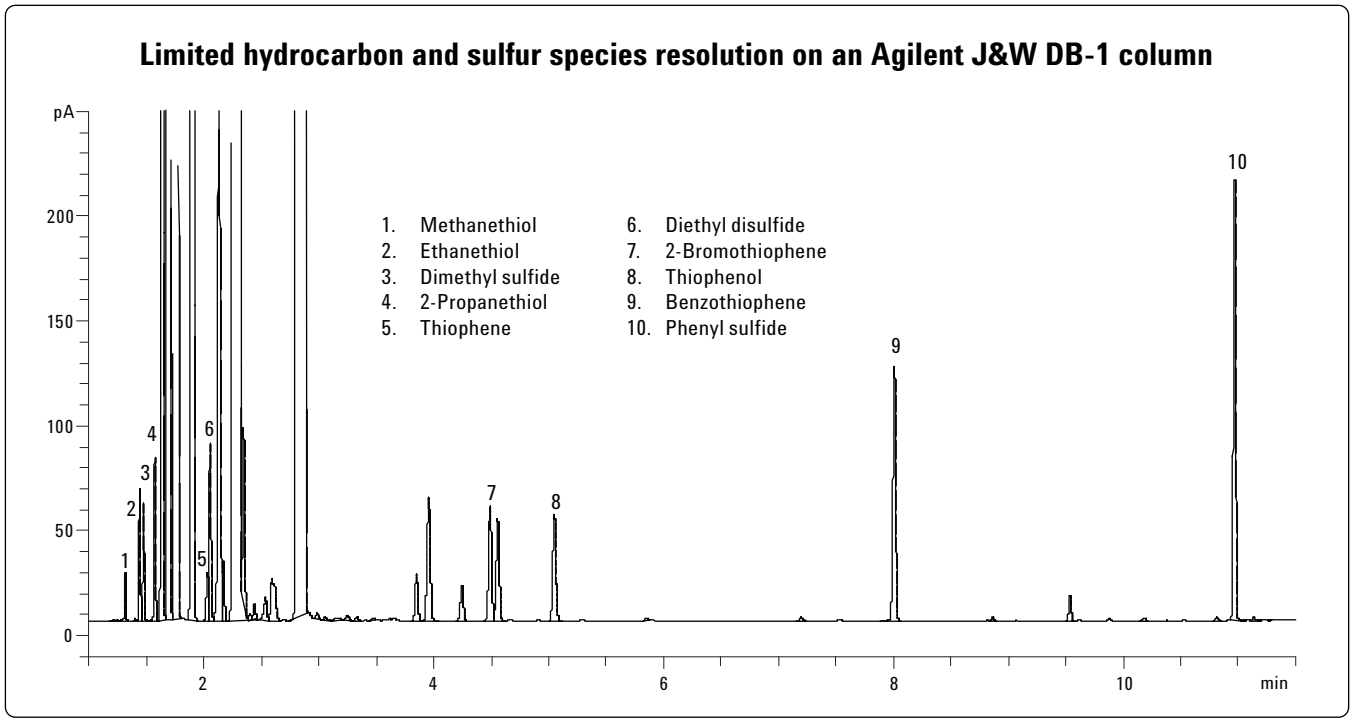
For the test of a gaseous sample, a sulfur mix of 11 sulfur compounds in N_2 was prepared and analyzed in DCG Partnership, Pearland TX.

For the test of a liquefied gas-liquid sample, a sulfur standard mix of 5 sulfur compounds in n-butane was prepared and analyzed in DCG Partnership, Pearland TX.

Chromatographic conditions appear beneath each figure.

Results and Discussion

Figure 1 shows the injection of a liquid sulfur standard in a base gasoline matrix on an Agilent J&W DB-1 column. Most of the sulfur species of interest elute early in the chromatogram along with the hydrocarbon species in the gasoline matrix. This figure illustrates the difficulty in separating sulfur species commonly found in gasoline from hydrocarbons in the gasoline matrix with a primarily boiling point separation mechanism. Higher selectivity and retention for the lighter sulfur species is necessary to resolve the peaks containing sulfur from the hydrocarbon matrix. This type of application is where the selective retention of sulfur species on the Agilent J&W GS-OxyPLOT is most useful.

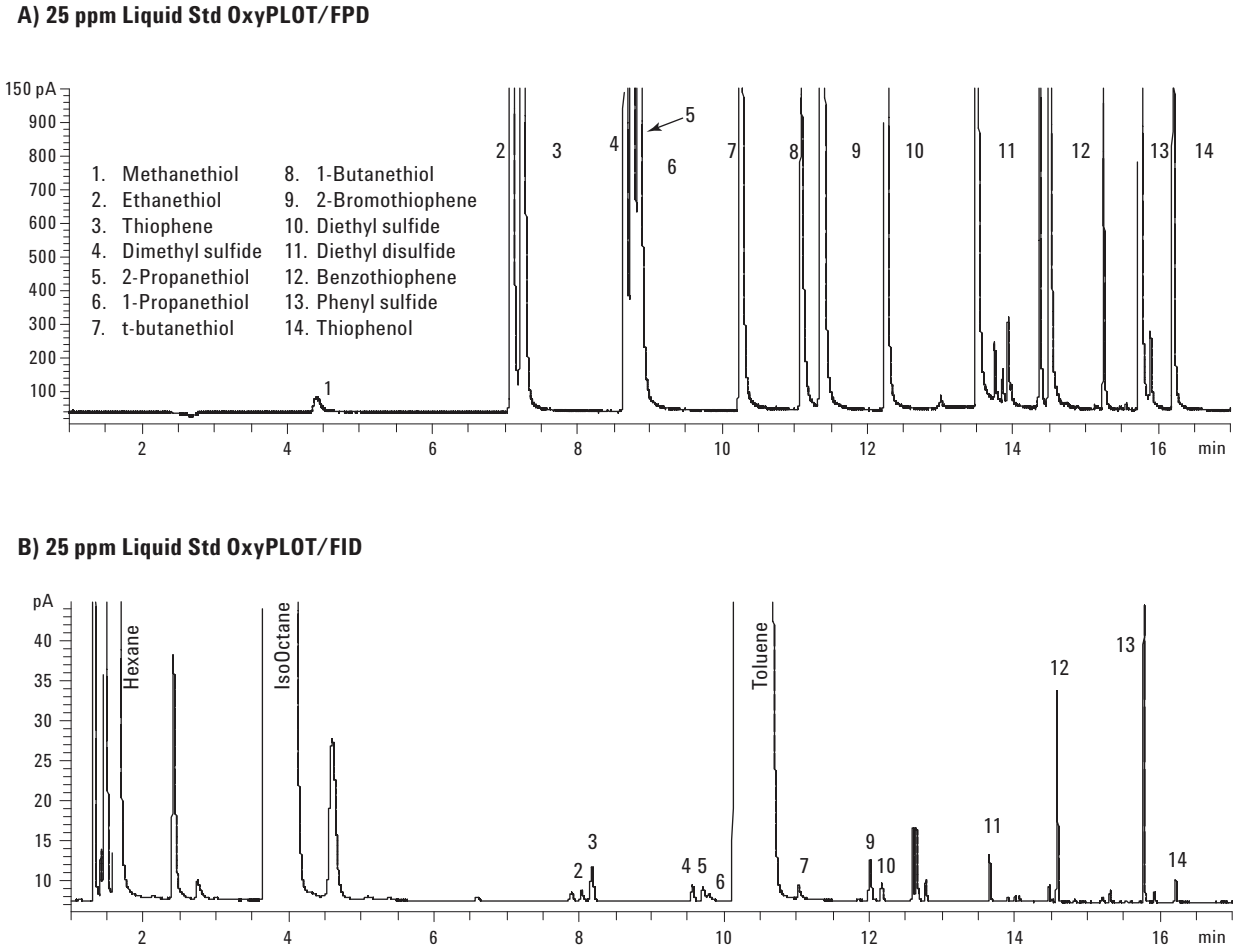


GC:	Agilent 6890N network GC system
Column:	Agilent J&W DB-1 0.53 mm × 25 m, 1.0 µm (Agilent part number 125-102J)
Oven:	60 °C (0.5 min), 10 °C/min to 120 °C, then 20 °C/min to 300 °C (3 min)
Injection:	250 °C, 1 µL, 25:1 split
Carrier:	He, constant flow, 30 cm/s at 60 °C (3.9 mL/min)
Detection:	FID 350 °C, H_2 40 mL/min, Air 450 mL/min, N_2 makeup 30 mL/min

Figure 1. Chromatogram of a liquid sulfur standard mix in base gasoline on an Agilent J&W DB-1 column.

Figure 2 illustrates the selective retention of the sulfur-containing species versus the components in a base gasoline standard. The FPD signal in Figure 2A shows the elution of the sulfur-containing species and helps with peak identification. The FID signal in Figure 2B shows the elution of both the hydrocarbons and the sulfur species as they elute from the Agilent J&W GS-OxyPLOT. Most of the hydrocarbon components of the gasoline matrix, with the exception of toluene, elute early in the chromatogram and are resolved from the sulfur species of interest.

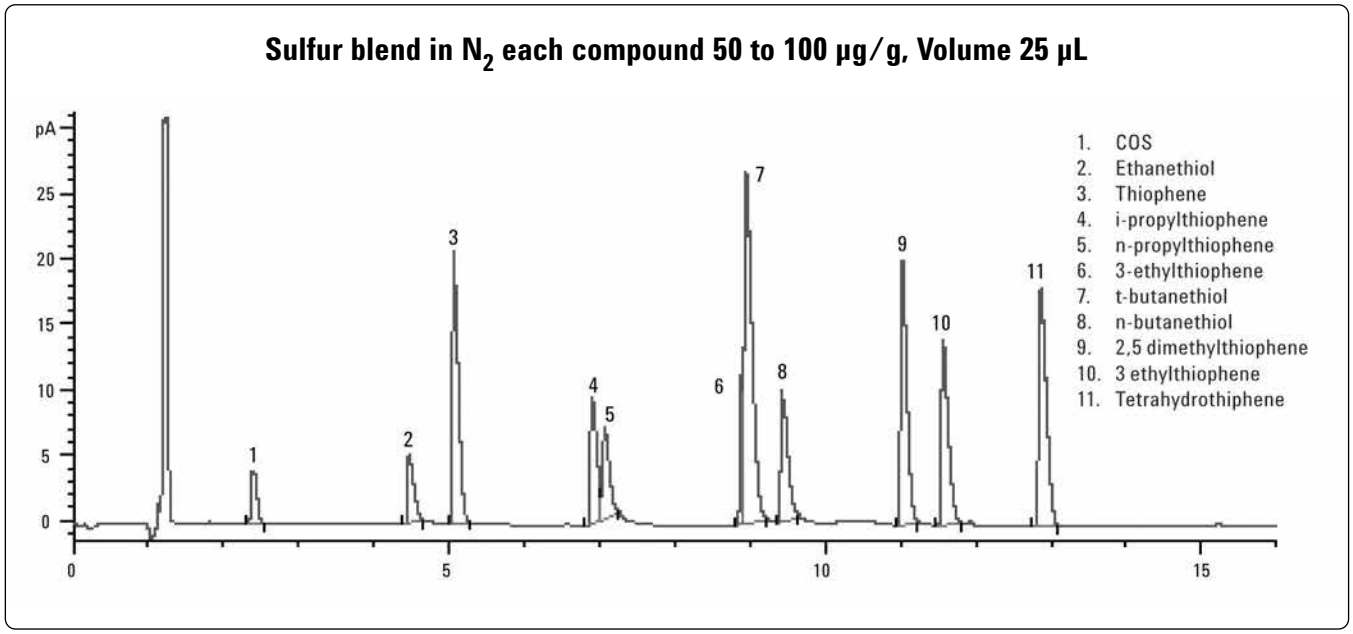
Selective sulfur species resolution from hydrocarbons on an Agilent J&W GS-OxyPLOT



GC:	Agilent 6890N network GC system, Dual Injection
Columns:	Agilent J&W GS-OxyPLOT 0.53 mm × 10 m, 10 µm (Agilent part number 115-4912)
Oven:	40 °C (3 min), 8 °C/min to 110 °C, then 35 °C/min to 300 °C (3 min)
Injection:	250 °C, 1 µL, 25:1 split, gas saver 20 mL/min at 2min
Carrier :	He (Col 1 to FID), 4.7 mL/min constant flow
	He (Col 2 to FPD), 3.15 mL/min constant flow
Detection:	FID 350 °C, H_2 40 mL/min, Air 450 mL/min, N_2 makeup 30 mL/min
	FPD 250°C, H_2 50 mL/min, Air 60 mL/min, N_2 makeup 60 mL/min

Figure 2. Chromatogram of a liquid sulfur standard mix in base gasoline on an Agilent J&W GS-OxyPLOT columns with simultaneous injection. Figure 2a (top) is the FPD signal and Figure 2b (bottom) is the FID signal.

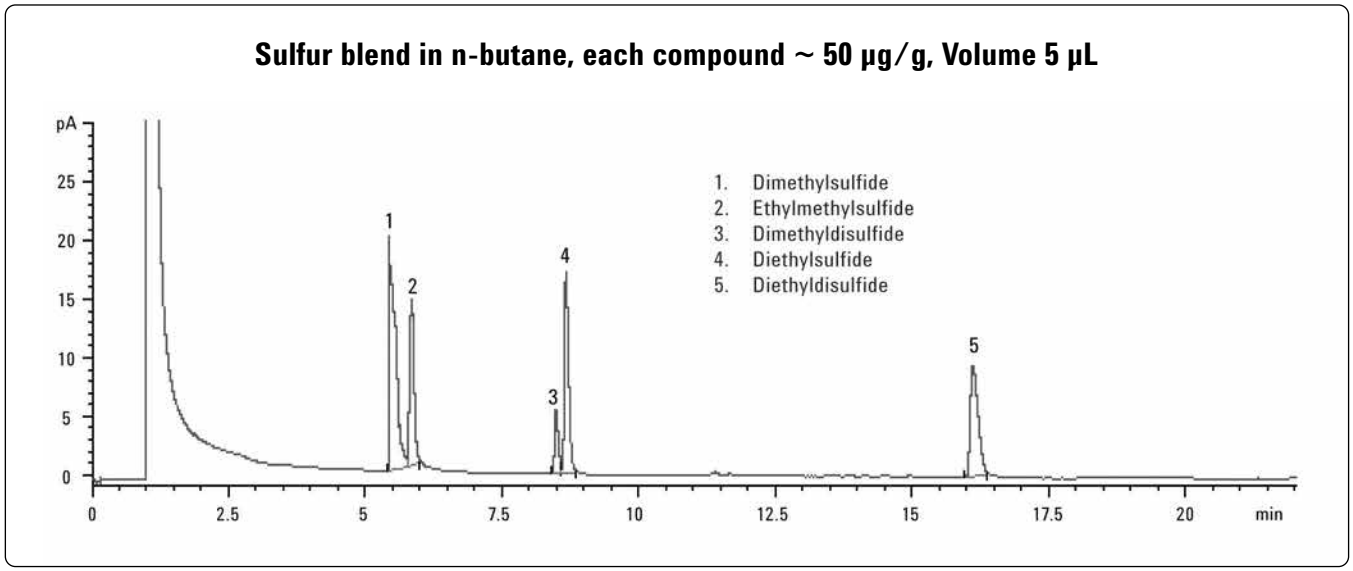
Figure 3 shows the injection of a gaseous sulfur species blend in N_2 on a combination of an Agilent J&W DB-1 connected by a glass insert with an Agilent J&W GS-OxyPLOT. The sulfur species in this sample are well retained. The selective retention of the Agilent J&W GS-OxyPLOT was again useful in separating the sulfur species of interest and achieving retention for these low boiling sulfur compounds.



GC:	Agilent 6890N network GC system
Column:	Agilent J&W DB-1 0.53 mm × 10 m, 0.5 µm (Agilent part number 125-1017)
	+ Agilent J&W GS-OxyPLOT 0.53 mm × 10 m, 10 µm (Agilent part number 115-4912)
Oven:	40 °C (0.1 min), 10 °C/min to 300 °C (5 min)
Injection:	250 °C, 25 µL, 10:1 split
Carrier:	H_2, 0.9 mL/min constant flow
Detection:	FID 250 °C, H_2 30 mL/min, Air 300 mL/min, N_2 makeup 15 mL/min

Figure 3. Chromatogram of a gaseous sulfur standard blend in N_2 on an Agilent J&W GS-OxyPLOT column.

Figure 4 shows an injection of a low molecular weight sulfur standard blend in a liquid n-butane matrix on a combination of an Agilent J&W DB-1 column connected by a glass insert with an Agilent J&W GS-OxyPLOT column. Excellent retention and resolution for the sulfur species from the n-butane were observed. An FID detector was used for this test. Figure 4 shows evidence of overloading of the trace level components in this detector, due to the large sample size. The large volume of injection caused no baseline problem, because of the effective separation away from the non-polar matrix of the analytes.



GC:	Agilent 6890N network GC system
Column:	Agilent J&W DB-1 0.53 mm × 10 m, 0.5 µm (Agilent part number 125-1017)
	+ Agilent J&W GS-OxyPLOT 0.53 mm × 10 m, 10 µm
	(Agilent part number 115-4912)
Oven:	40 °C (0.1 min), 10 °C/min to 300 °C (5 min)
Injection:	250 °C, 5 µL, 10:1 split
Carrier:	H_2, 0.9 mL/min constant flow
Detection:	FID 250 °C, H_2 30 mL/min, Air 300 mL/min, N_2 makeup 15 mL/min

Figure 4. Chromatogram of a liquefied gas-liquid sulfur standard blend in n-butane on an Agilent J&W GS-OxyPLOT.

Conclusions

This application note successfully demonstrates selective retention and resolution of low molecular weight sulfur containing species on an Agilent J&W GS-OxyPLOT column. The selective retention for sulfur species enables enough of a retention shift away from hydrocarbon matrices such as base gasoline and n-butane to suggest that effective quantification of sulfur species in process streams is quite feasible.

The Agilent J&W GS-OxyPLOT column also retained toluene in the base gasoline sample where co-elution was observed between toluene and tert-butanethiol in the liquid standard mix. Potential interferences between analytes of interest and aromatic species are a possibility with the Agilent J&W GS-OxyPLOT column that should be manageable with careful planning and method design.

References

1. A. K. Vickers, "GS-OxyPLOT: A PLOT Column for the GC Analysis of Oxygenated Hydrocarbons," Technical Overview, Agilent Technologies publication 5989-6447EN, March 2007
2. Yun Zou and Min Cai, "Investigation of the Unique Selectivity and Stability of Agilent GC-OxyPLOT Columns," Agilent Technologies publication 5989-8771EN, June 2008
3. Standard Test Method for the Determination of Methanol in Crude Oils by Multi-Dimensional Gas Chromatography, ASTM D7059-04, July 2004
4. Jerry March, "Advanced Organic Chemistry; Mechanisms and Structure," 4th Edition, John Wiley and Sons, 1992

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
August 28, 2009
5990-4493EN

Agilent Technologies

Detailed Hydrocarbon Analysis in Spark Ignition Fuels by ASTM D6730-1 with an Agilent Inert Flow Path

Application Note

Energy & Fuels

Authors

Pat Sasso and Ken Lynam
Agilent Technologies, Inc.

Abstract

Spark ignition engine fuels contain a highly complex mixture of hydrocarbons. Blends include oxygenates such as ethanol, MTBE, ETBE, and t-butanol. These components can be problematic when using ASTM-6730-01 for detailed hydrocarbon analysis, which incorporates the use of a connected tuning column, such as Agilent J&W HP-5ms, in the flow path. The use of an Agilent Ultimate Union with SilTite fittings, in conjunction with Agilent J&W HP-1 PONA or Agilent J&W CP-Sil PONA CB GC columns, provides guaranteed resolution. All critical pairs are resolved, including 2,3,3-trimethylpentane and toluene. Peak symmetry is exceptional, even for alcohols, and installation is worry-free. These Agilent J&W GC columns and simple-to-use fittings meet or exceed all ASTM D6730-01 and Canadian General Standards Board CAN/CGSB 3.0 No. 14.3-99 requirements for detailed hydrocarbon analysis, providing a highly inert flow path with no reactive surfaces.

Agilent Technologies

Introduction

ASTM D6730-01 [1] and Canadian General Standards Board CAN/CGSB 3.0 No. 14.3-99 are two standard methods for detailed hydrocarbon analysis (DHA). Traditionally, choosing columns and connecting fittings for DHA has been challenging, primarily centering on issues of inertness and selectivity. Highly inert columns are required for chromatography of polar compounds with an active hydroxyl group [2], and potentially reactive surfaces in the flow path can result in poor peak symmetry. Additionally, spark ignition engine fuel mixtures injected neat on-column require a 2 to 5 m tuning column of 5% phenyl methyl-siloxane to provide adequate selectivity to separate closely eluting critical pairs such as 2,3,3-trimethylpentane and toluene. Both of these issues have to be overcome as they hinder accuracy and consume time, leading to slower turnaround and reduced precision. Petroleum refining operations need to control blending decisions and product release for distribution channels. Having robust, reliable tools to chromatograph reactive oxygenates enables a laboratory to identify potential instances where line contaminants from inadvertent transfers can lead to disruption and damage to sensitive catalysts or fuel delivery equipment. As an added benefit, suppliers can further safeguard against product liability related to future oxygenate blends such as E15 [3].

Analysis times can be improved significantly by switching to hydrogen as the carrier gas (as much as 20% less time than helium) with no loss in chromatographic performance [4]. J&W HP-1 PONA and J&W CP-Sil PONA CB GC columns meet or exceed all criteria in the standard methods in less time when using hydrogen. These benefits, combined with lower cost, can provide a laboratory with a significant gain in productivity. By leveraging Agilent 6890N GC safety features, including hydrogen carrier shutoff and flame-out shutoff, as well as the gas saver feature to reduce exposure, no unsafe practices are needed. All that is required is to properly vent the split flow so that hydrogen cannot exceed LEL levels in enclosed areas.

Materials and Methods

An Agilent 6890N GC/FID equipped with an Agilent 7683B Automatic Liquid Sampler was used for this series of experiments.

Conditions

Tuning column:	Agilent J&W HP-5ms 15 m × 0.25 mm, 1.0 µm (trimmed to 5 m) (p/n 19091S-231)
Column 2:	Agilent J&W HP-1 PONA, 100 m × 0.25 mm, 0.5 µm (p/n 19091Z-530)
Column 2 (alternative):	Agilent J&W CP-Sil PONA CB, 100 m × 0.25 mm, 0.5 µm (p/n CP7530)
Sample:	Oxy set-up evaluation mix, ASTM D6730 SCE
Carrier:	Hydrogen 38 cm/s, 2.0 mL/min constant flow mode
Oven:	30 °C (hold 8.5 minutes), to 48 °C at 22 °C/min (hold 27 minutes), to 141 °C at 3 °C/min (hold 1 minute), to 275 °C at 1 °C/min (hold 2 minutes)
Inlet temperature:	200 °C
Detector:	FID, 275 °C
GC:	Agilent 6890N Network GC system
Sampler:	Agilent 7683B Automatic Liquid Sampler, 0.5 µL syringe, 0.01 µL neat with split injection 150:1

Flow path supplies

Vials:	Amber screw cap (p/n 5182-0716)
Caps:	Blue screw cap (p/n 5282-0723)
Vial inserts:	100 µL glass/polymer feet (p/n 5181-1270)
Syringe:	0.5 µL (p/n G4513-80229)
Septum:	Advanced Green (p/n 5183-4759)
Inlet liner:	Dual taper direct connect, deactivated (p/n G1544-80700)
Union kit:	Agilent Ultimate Union, deactivated (p/n G3182-61580)
Swaging wrench:	(p/n G2855-60200)
Magnifier:	20× magnifier (p/n 430-1020)

Results and Discussion

Figure 1 demonstrates the ability of Agilent J&W PONA GC columns and Agilent flow path inert connectors to provide peak shapes that meet or exceed the method criteria. Looking at Figure 2 closely, it is clear that the resolution of one particular critical pair (2,3,3-trimethylpentane/toluene) allows the most challenging separations to be achieved in this evaluation mix. The peak symmetry of the light alcohol oxygenates ethanol and t-butanol is seen in Figure 3. Table 1 provides further evidence that Agilent inert flow path supplies deliver the required performance to combat peak asymmetry or changes in selectivity and elution order.

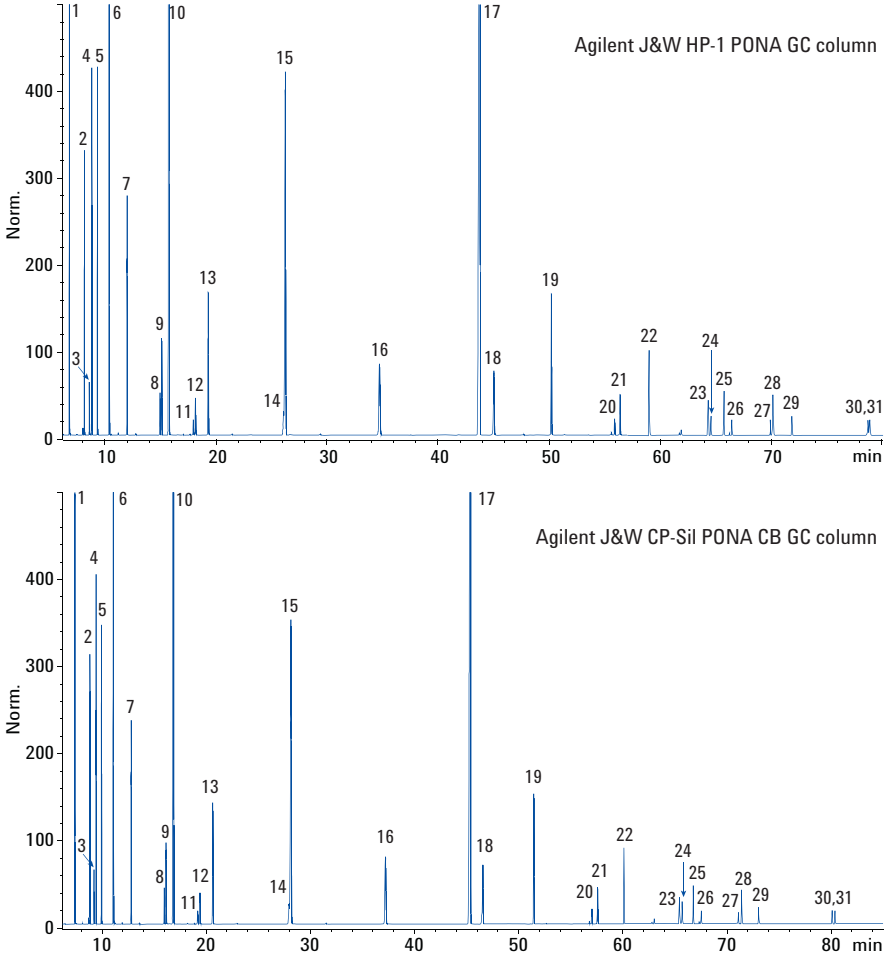


Figure 1. 31-component spark ignition engine fuel test mix with critical pairs resolved on both the Agilent J&W HP-1 PONA and Agilent J&W CP-Sil PONA CB GC columns, 100 m, with a 4 m Agilent J&W HP-5ms tuning column, Ultimate Union connector, and SilTite ferrules.

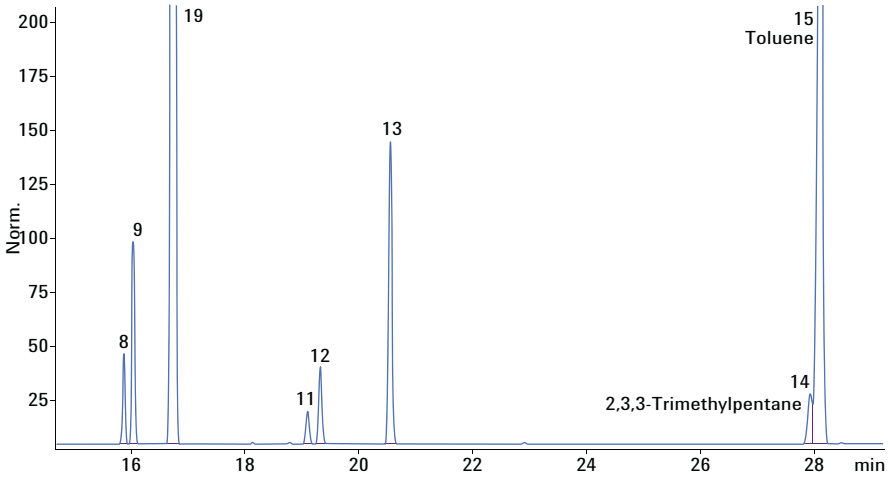


Figure 2. Separation of critical pair 2,3,3-trimethylpentane from toluene on an Agilent J&W CP-Sil PONA CB GC column.

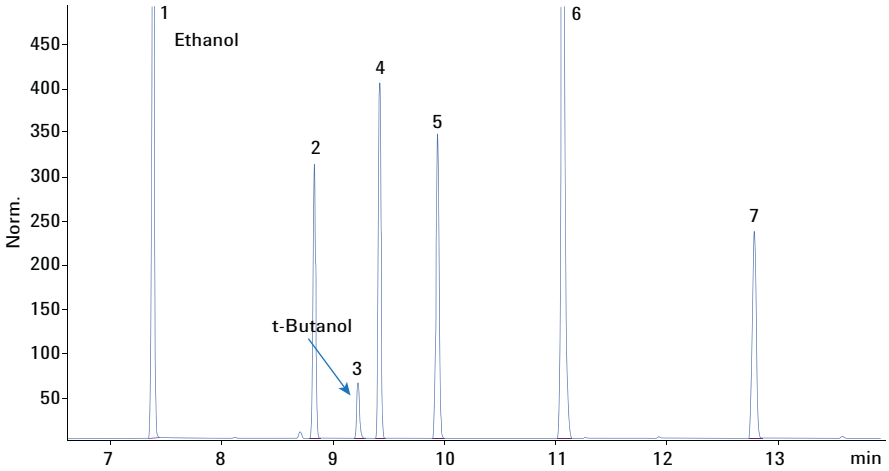


Figure 3. Peak symmetry of light alcohols on an Agilent J&W CP-Sil PONA CB column.

The presence of oxygenates in the test blend allows for a valid comparison to more complex spark ignition engine fuels and shows clearly that Agilent J&W PONA GC columns exhibit exceptional peak symmetry. The calculated symmetry is well within method guidelines and should permit accurate peak integration. The incorporation of the Ultimate Union kit and its associated SilTite ferrules provides confidence that these connectors are properly deactivated and highly inert to fuel components. This allows for more accurate and reliable calculations of oxygenate content and delivers confidence in measurement accuracy for future blends such as E15.

To assess the usefulness of hydrogen as a carrier gas to meet method criteria and deliver shorter chromatographic run times, the identical test mix used to evaluate columns with helium as the carrier was injected on HP-1 PONA and CP-Sil PONA CB GC columns. Hydrogen was plumbed to the GC carrier inlet lines. Figure 1 shows that the system eluted the last critical pair at approximately 78 minutes, versus 96 minutes with helium as the carrier. Time saved on this long run per injection was approximately 18 minutes, or 25%. To provide useful comparisons between different columns, a unified mixture of components was used, as was a neat injection volume to avoid retention drift due to dilution solvent loading [5].

Peak number	Name	Symmetry	Selectivity
1	Ethanol	0.88	1.01
2	C5	0.96	1.20
3	*tert*-Butanol	0.71	1.04
4	2-Methylbutene-2	0.96	1.02
5	2,2-Dimethylbutane	0.93	1.06
6	2,3-Dimethylbutane	0.76	1.11
7	Methyl *tert*-butyl ether (MTBE)	0.97	1.16
8	C6	0.97	1.25
9	1-Methylcyclopentene	0.97	1.01
10	Benzene	1.11	1.04
11	Cyclohexane	0.98	1.14
12	3-Ethylpentane	0.95	1.01
13	1- *tert*-2-Dimethylcyclopentane	0.96	1.06
14	C7	1.29	1.36
15	2,3,3-Trimethylpentane	1.01	1.01
16	Toluene	0.99	1.32
17	C8	1.44	1.22
18	Ethylbenzene	1.23	1.03
19	p-Xylene	0.89	1.00
20	2,3-Dimethylheptane	1.01	1.11
21	C9	0.97	1.11
22	5-Methylnonane	0.97	1.01
23	1,2-Methylethylbenzene	1.00	1.04
24	C10	0.95	1.09
25	C11 (undecane)	0.92	1.00
26	1,2,3,5-Tetramethylbenzene	1.02	1.02
27	Naphthalene	0.97	1.01
28	1,3-di-n-Propylbenzene	0.97	1.06
29	C12 (dodecane)	0.99	1.02
30	1-Methylnaphthalene	1.00	1.10
31	C13 (tridecane)	0.92	1.00

Table 1. Components and their associated peak symmetry factors and selectivity for spark ignition engine fuels. Asymmetry at 10% peak height A_s = B/A (A= width of peak, front to center dropline, B = width of peak, center dropline to back of peak). Selectivity calculated by Agilent ChemStation software.

Conclusions

Spark ignition gasoline blends are complex mixtures of hydrocarbons that in the past have been difficult to analyze because of the presence of active oxygenates. However, it is now possible to construct an extremely inert flow path by using Agilent J&W HP-1 PONA and CP-Sil PONA CB GC columns, Ultimate Unions, and SilTite fittings. This arrangement delivers successful analysis of detailed hydrocarbons, with exceptional selectivity, peak symmetry and critical pair resolution.

References

1. ASTM D6730 - 01(2011) Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100–Meter Capillary (with Precolumn) High-Resolution Gas Chromatography. ASTM International, West Conshohocken, PA, USA (2011). http://www.astm.org/Standards/D6730.htm.

2. Fast Detailed Hydrocarbon Analysis of Naptha Coen Duvekot http://www.chem.agilent.com/Library/applications/SI-01285.pdf

3. E15 ethanol fuel can damage auto engines – compared with typical gasoline. Hydrocarbon Processing, Houston TX, USA (2012). http://www.hydrocarbonprocessing.com/Article/3029925/E15-ethanol-fuel-can-damage-auto-engines-study.html

4. Hydrogen as a Carrier Gas for GC and GC–MS Ronald E. Majors Agilent Technologies Inc. http://www.chromatographyonline.com/lcgc/Column:+Column+Watch/Hydrogen-for-GC-and-GCndashMS/ArticleStandard/Article/detail/

5. J. D. McCurry. “A Unified Gas Chromatography Method for Aromatic Solvent Analysis. Publication Number 5988-3741EN, Agilent Technologies, Inc, Santa Clara, CA, USA (2001). http://www.chem.agilent.com/Library/applications/5988-3741EN.pdf

For More Information

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

www.agilent.com/chem

Printed in the USA
August 16, 2012
5991-0931EN

Agilent Technologies

Natural Gas Analysis: A Simplified Approach for the Analysis of Permanent Gases and Hydrocarbons in Natural Gas by Capillary Chromatography and Deans Switch

Application Note

Authors

Shannon Coleman and Kelly Beard
Agilent Technologies, Inc.
Little Falls, DE, USA

Abstract

A method has been developed for the analysis of permanent gases and hydrocarbons using Agilent Micro-fluidics Capillary Flow Technology (CFT). This has simplified method development and reduced the cost associated with this type of analyzer when compared to using switching valves and packed columns for the analysis of natural gas samples. Capillary columns and CFT allow for improved resolution, more commonly available parts, and allow for increased speed of analysis over packed column methods.

Agilent Technologies

Introduction

Many of the standard methods for natural gas analysis were developed at a time when capillary columns and electronic pressure control were not available. With the advent of newer technologies such as capillary columns, capillary flow technology, more sensitive detectors, and improved flow and pressure control technology, these outdated methods should be revisited. This application note explores alternatives that offer improvements in ease of setup, improved resolution, and improved detection limits. With this in mind we should consider the following topics when designing GC methods.

Many older methods require the use of switching valves and multiple packed columns to obtain the chromatographic results needed. By using capillary columns and Micro-fluidics devices, chromatographic design can often be simplified.

Methods using packed columns were written at a time when operating a GC in flow control mode was not possible. With the advent of accurate electronic flow and pressure control (EPC) modules, users can operate the Agilent 7890 GC in flow control mode, allowing for better control over column flow, often resulting in decreased analysis times. Increasing speed of analysis is often important at a time when there is a global helium shortage resulting in an increased use of alternative carrier gases such as nitrogen.

This technique allows both liquid and gas injection, and is flexible with many types of sample matrixes.

Experimental

Natural gas standard: (p/n 5080-8756)

Table 1. Samples

Compound	Concentration (vol%)
Carbon dioxide	1%
Ethane	9%
Hexane	0.5%
Iso-butane	3%
Iso-pentane	1%
Methane	69%
n-butane	3%
n-pentane	1%
Nitrogen	6%
Oxygen	0.5%
Propane	6%

Table 2. Chromatographic Conditions and Set Points

GC conditions	
Oven	40 °C for 1.5 minutes, then 50 °C/min to 250 °C for 1 minute
Run time	6.7 minutes
SS inlet	Heater: 250 °C Pressure: 33.119 psi Total flow: 193.2 mL/min Split ratio: 45:1 Split flow: 189 mL/min
Column 1	Agilent 19091P-003, HP-Plot Q, 15 m × 320 µm, 20 µm In: Front SS inlet Out: PCM C-1
Column 2	Agilent Restrictor, 0.37 m × 100 µm In: PCM C-1 Out: Front detector TCD
Column 3	Agilent 19091P-MS4, HP-PLOT MoleSieve 5A, 30 m × 320 µm, 12 µm In: PCM C-1 Out: Back detector TCD
Valve	6-port Gas sample valve, 0.25 mL loop Agilent Deans Switch, (p/n G2855B)

Results and Discussion

Traditional configurations for natural gas analysis use packed columns and multiple rotorary valves to perform the analysis. By using a single gas sample inject valve in series with a Micro-fluidics Deans Switch kit (p/n G2855B), a complete natural gas analysis through hexane was obtained in less than 6 minutes with resolution of oxygen and nitrogen. In comparison, the typical single valve GPA 2261 analyzer using packed columns requires 11 minutes to analyze through *n*-pentane, along with reporting a composite air peak instead of resolving oxygen and nitrogen. Other designs such as ASTM D1945 which resolves oxygen and nitrogen, require complex valve configurations and run times longer than 10 minutes.

This system employs a single valve switch for separation of oxygen, nitrogen, and hydrocarbons through hexane. If oxygen and nitrogen resolution is not needed and can be reported as an air composite, this analysis can be accomplished even faster on a single Plot Q column, requiring only an inject valve for introducing sample.

Conclusions

By using a Micro-fluidics Deans Switch kit, the typical natural gas analysis can be simplified.

Analysis can be accomplished in under 6 minutes, including oxygen and nitrogen resolution.

Packed columns can be replaced with more efficient and readily available capillary columns.

In some cases, method development can be simplified by using capillary columns and CFT devices.

For More Information

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

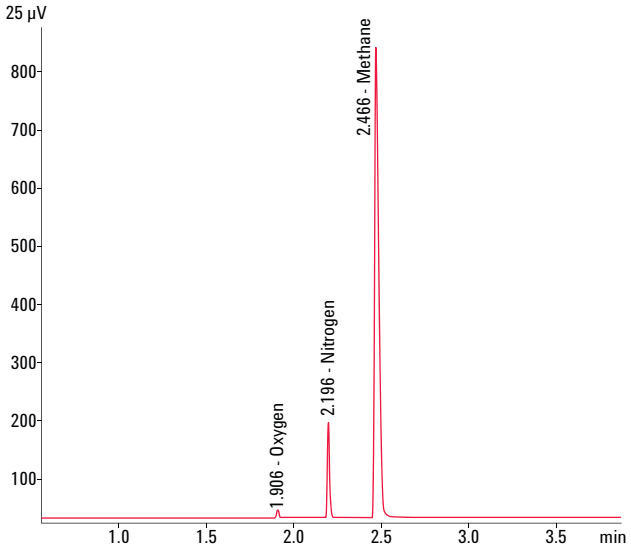


Figure 1. Back TCD signal.

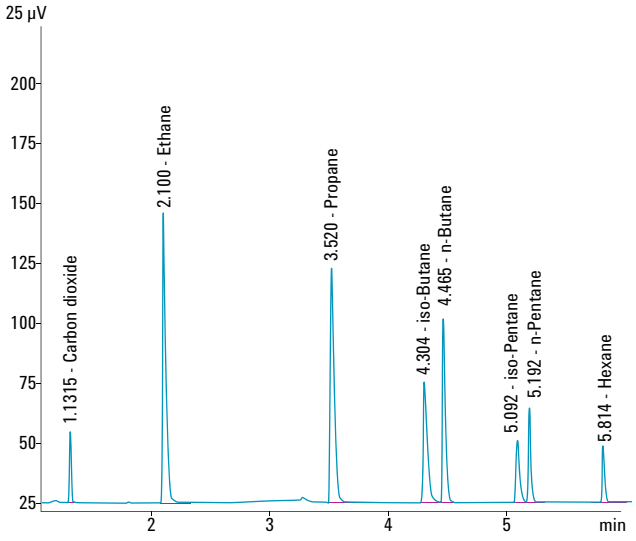


Figure 2. Front TCD signal.

www.agilent.com/chem

Printed in the USA
November 26, 2012
5991-1323EN

Agilent Technologies

BACKFLUSH WITH HYDROGEN CARRIER

Accelerate petroleum biomarker analysis

Petroleum biomarkers, along with other geochemical parameters, are commonly used to derive the unique fingerprints that identify petroleum sources. However, the standard analytical methods for petroleum biomarkers are time-consuming, and rely on high-resolution mass spectrometry.

Agilent Capillary Flow Technology lets you easily make leak-free, in-oven capillary connections that stand up to GC temperature extremes. These connections let you divert your gas flow *pneumatically* – opening the door to techniques such as backflushing, which can improve your results, save time, and maximize resources.

In fact, switching to triple quadrupole mass spectrometry with hydrogen carrier gas and mid-column backflushing can cut your petroleum biomarker cycle time in half *without* selectivity or sensitivity loss.

Back to table of contents ►

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

Application Note

Environmental

Authors

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

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

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

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

Abstract

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

Agilent Technologies

Introduction

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

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

Experimental

Standards and Samples

STANFORD-1 is a new external standard for quantitative biomarker analysis. It is a mixture of pure biomarker standards and paraffin-free saturate fractions from Paleozoic, Mesozoic, Cenozoic, biodegraded, terrestrially-influenced, carbonate/evaporate-sourced, and open-marine sourced petroleum samples. It contains known quantities of most, if not all, commonly used biomarkers and two internal standards, BTI-6 and 5-β cholane, which are useful for quantifying hopane and sterane biomarkers across diverse GC/MS systems.

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

Instruments

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

MS SRM Parameters

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

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

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

Table 2. Analysis Parameters for Precision Experiments*

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

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

Results and Discussion

Backflushing with a Pressure Controlled Tee Configuration

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

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

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

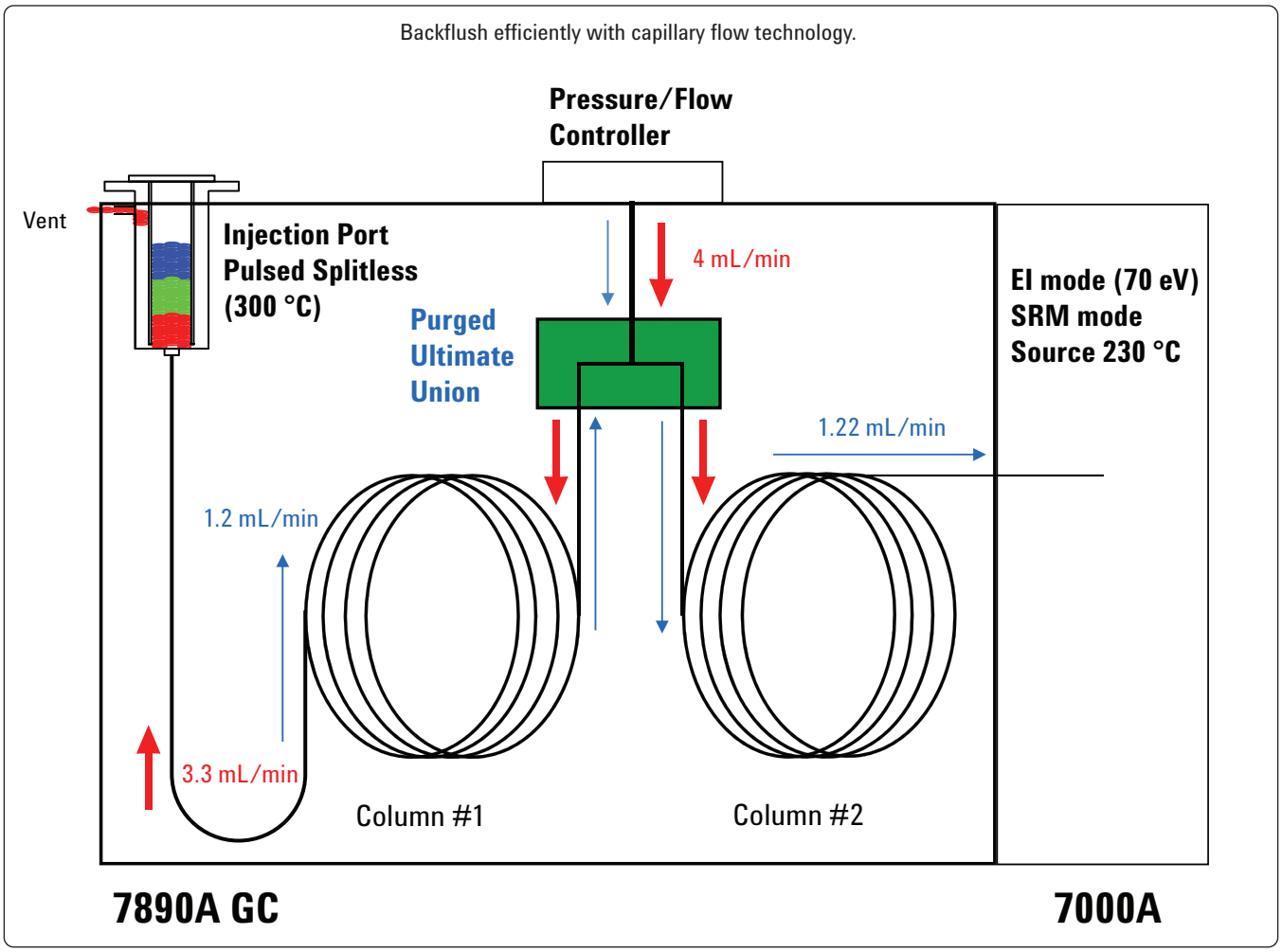


Figure 1. Schematic of the Pressure Controlled Tee GC/MS configuration. The narrower (blue) lines indicate the forward flow during analysis and the thicker (red) lines indicate the backflushing post-run state.

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

Faster Analysis of Biomarkers

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

Backflush for rapid and robust analyses.

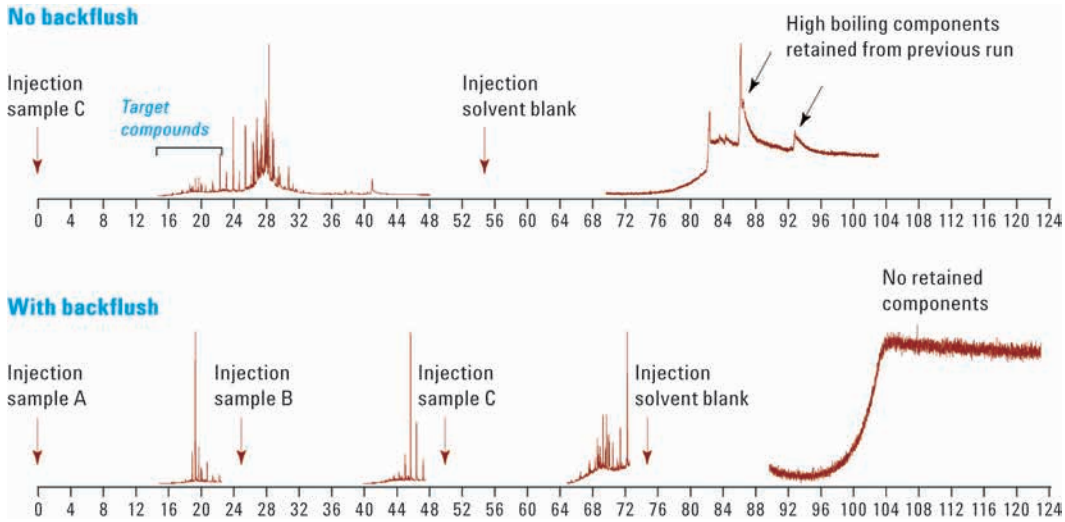


Figure 2. Petroleum samples, including one from Williston Basin source rocks (Sample C) which contains many late eluting, high molecular weight hydrocarbons, were analyzed without (top) and with (bottom) backflushing (40 m configuration). The target compounds comprise a subset of the total number of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

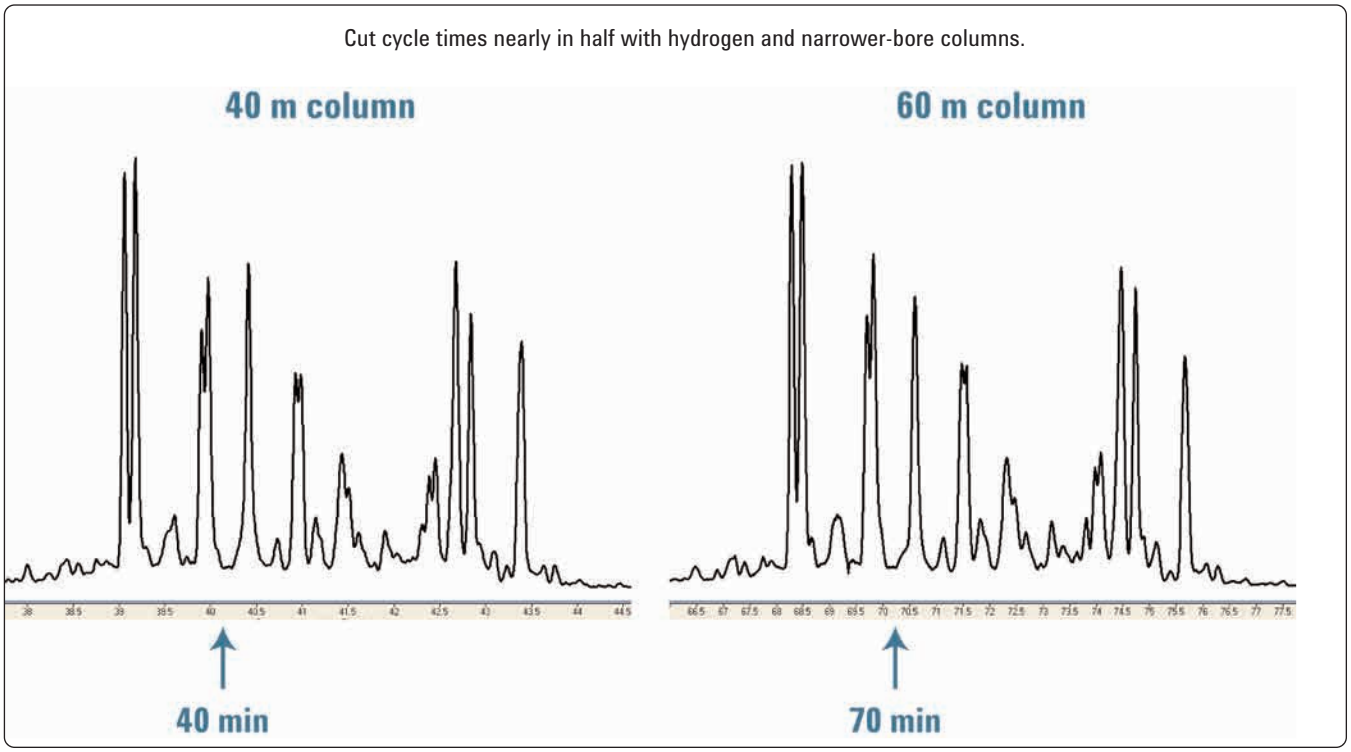


Figure 3. C28 steranes were analyzed using m/z transition 386→217 on either a 60 meter, 0.25 µm column and helium carrier gas, or a 40 meter, 0.18 µm column with hydrogen carrier gas. Employing hydrogen and the smaller bore column reduces analytical time significantly without loss in compound resolution.

Sensitivity, Selectivity and Precision

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

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

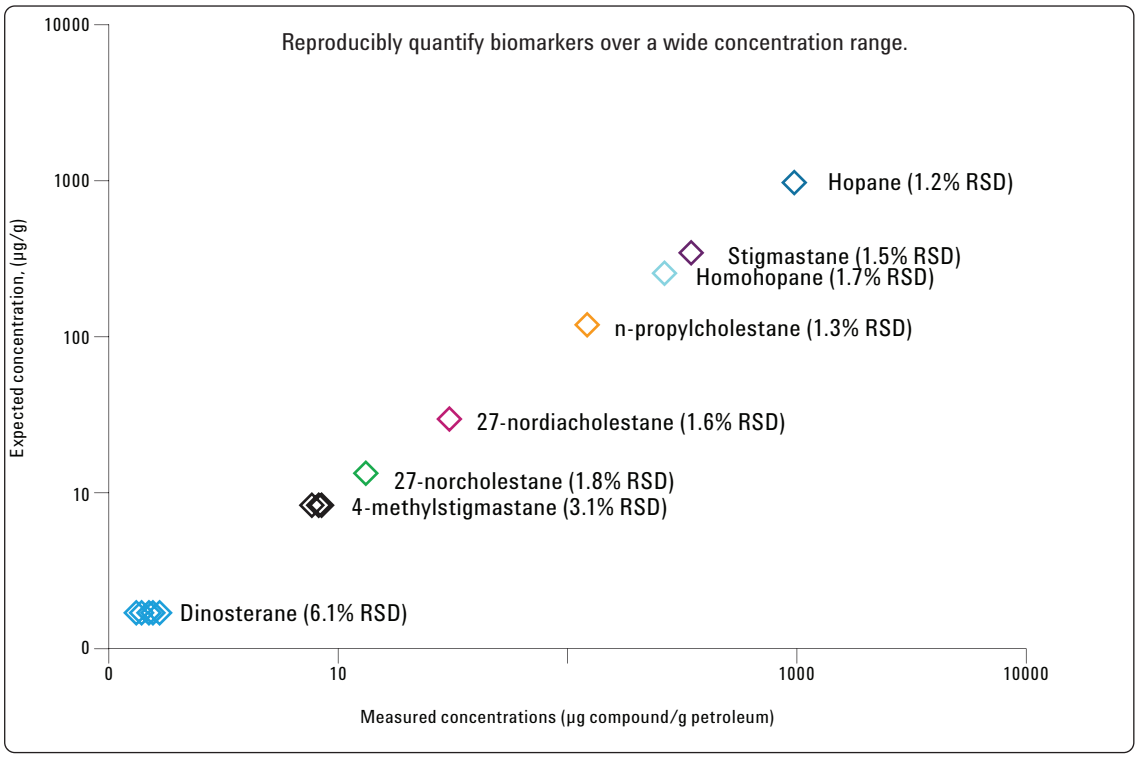


Figure 4a. Precision experiment results for eight biomarkers of widely varying concentrations contained within the STANFORD-1 standard. Ten sequential analyses were performed over a 15 hour period using the 60-m column PCT configuration. See Table 3 for transitions.

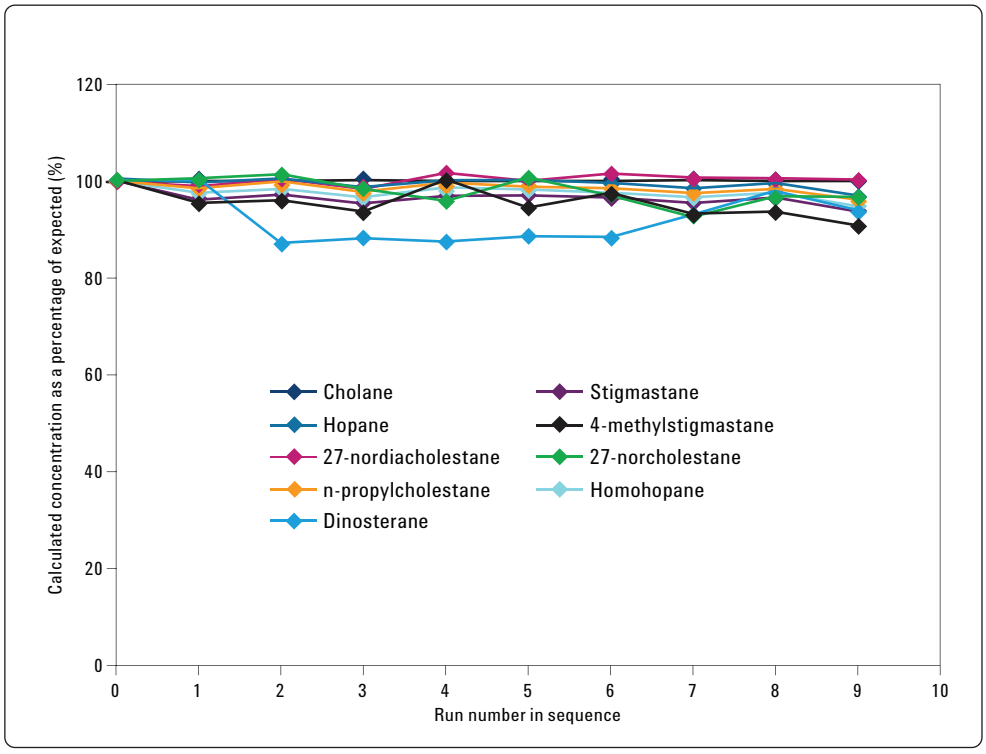


Figure 4b. The data from the analysis described in Figure 4a were plotted as calculated concentration of each biomarker versus the expected concentration over 10 analyses.

Deconvolving Oil Mixtures

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

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

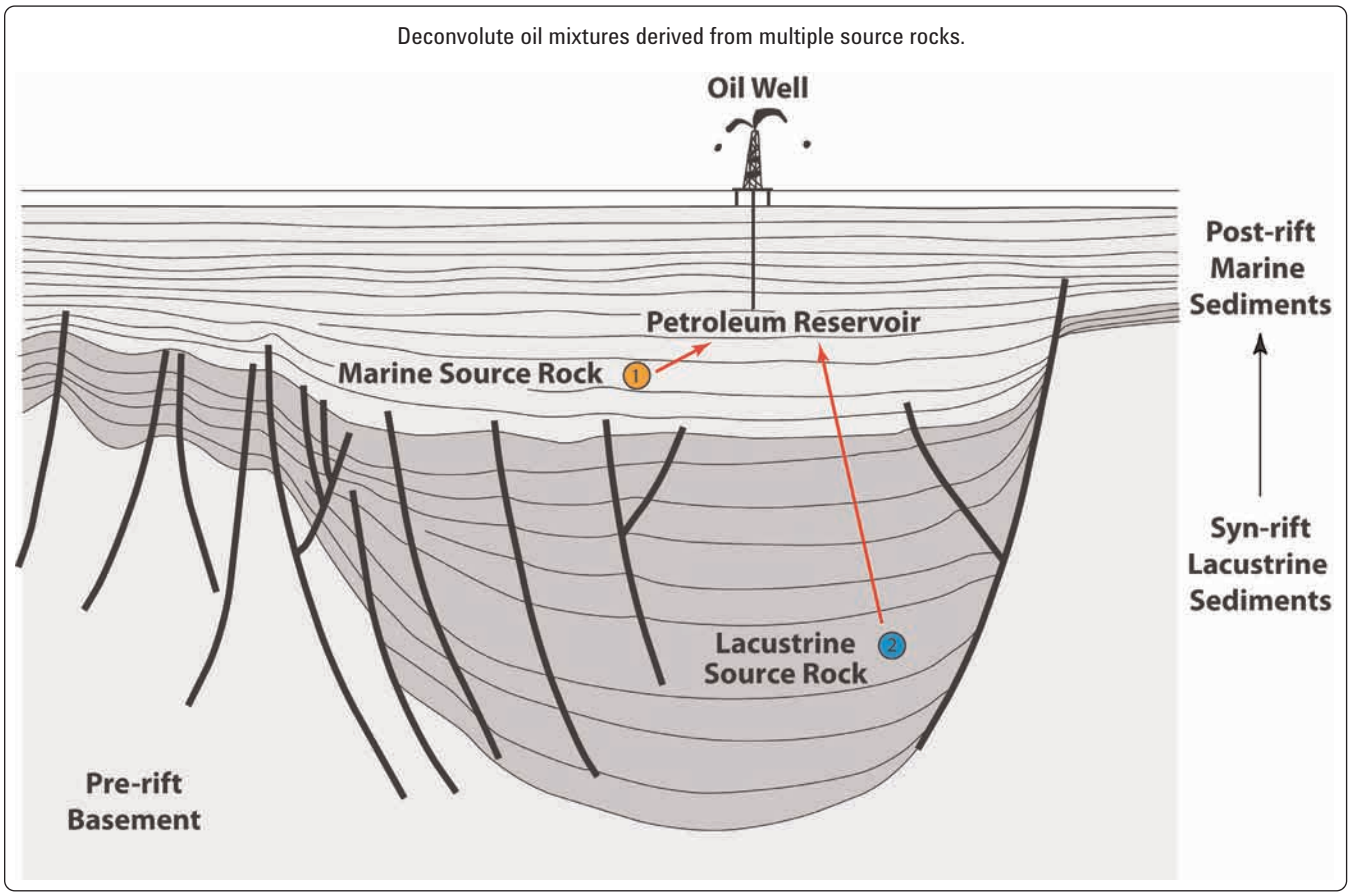


Figure 5. Diagram of an oil deposit containing source rocks from both marine (1) and lacustrine (2) sources.

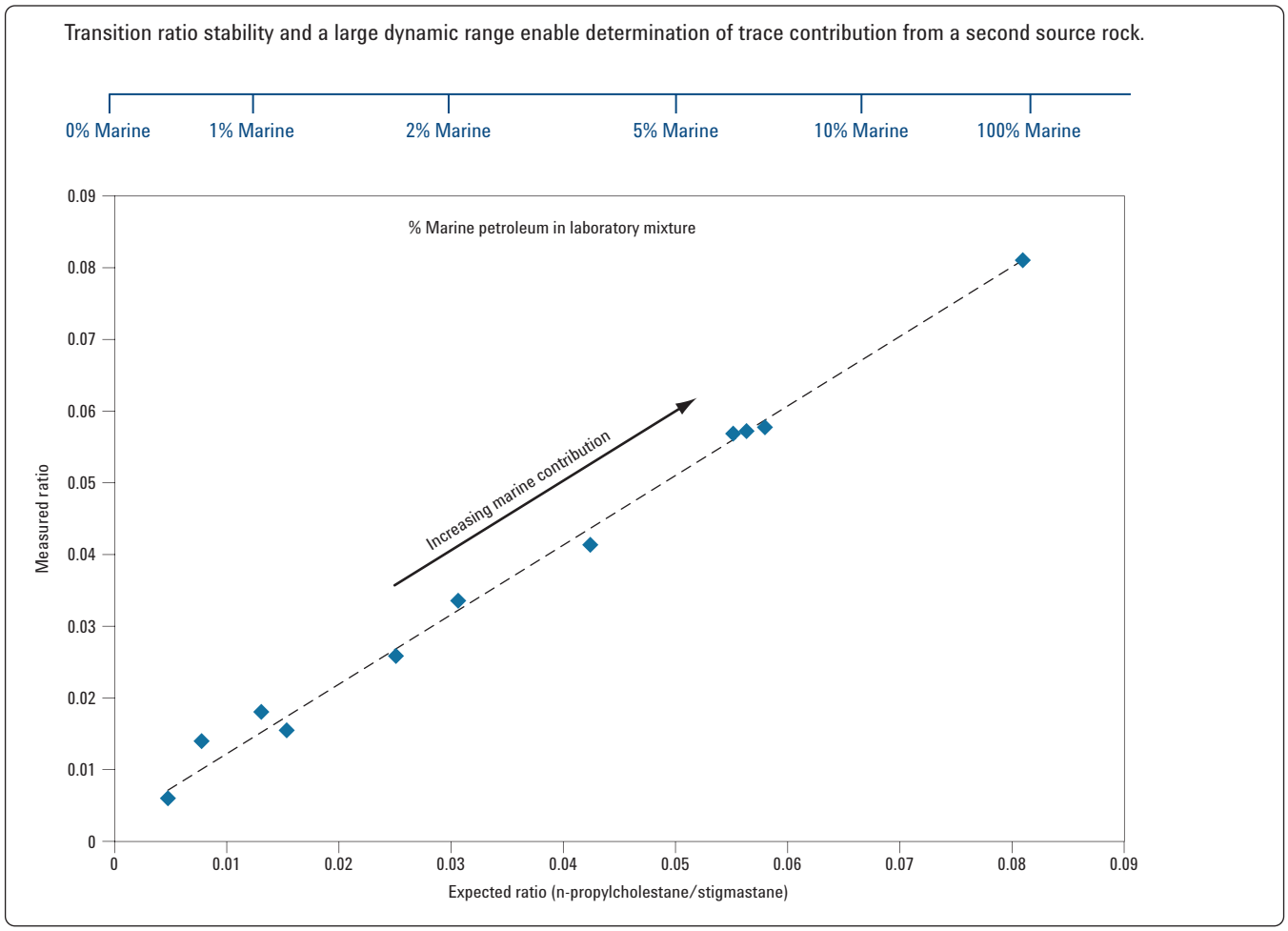


Figure 6. A series of laboratory mixtures consisting of various percentages of a marine petroleum sample in a lacustrine sample were analyzed for stigmastane, a ubiquitous component present in petroleum from both sources, and n-propylcholestane, a compound unique to oil from lacustrine source rock. The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

Conclusions

The Agilent 7000A Triple Quadrupole MS with 7890 GC using backflushing is a viable approach to the routine analysis of petroleum biomarkers, providing increased sensitivity, better selectivity and the potential to greatly reduce analysis time versus traditional GC/MS analysis. Column backflush provides higher sample throughput with lower carryover and source maintenance, and the use of hydrogen carrier gas and narrower bore columns reduces run times nearly two-fold at no significant loss in chromatographic resolution. The SRM speed, linearity, dynamic range and transition ratio stability of the 7000A Triple Quadrupole mass spectrometer enable quantitative characterization for the fingerprinting of petroleum samples and the deconvolution of complex petroleum mixtures.

References

1. Peters, K. E., Walters, C. C. & Moldowan, J. M. 2005. The Biomarker Guide. Volume 2: Biomarkers and Isotopes in Petroleum Exploration and Earth History. Second Edition. (First edition published 1993 by Chevron Texaco.) 1132 pp. total. Cambridge, New York, Melbourne: Cambridge University Press. ISBN 0 521 83763 4.
2. H. Prest, C. Foucault and Y. Aubut, Capillary Flow Technology for GC/MS: Efficacy of the Simple Tee Configuration for Robust Analysis Using Rapid Backflushing for Matrix Elimination, Agilent Technologies Publication 5989-9359EN.
3. H. Prest, Capillary Flow Technology for GC/MS: A Simple Tee Configuration for Analysis at Trace Concentrations with Rapid Backflushing for Matrix Elimination, Agilent Technologies Publication 5989-8664EN.
4. H. Prest, The Pressure Controlled Tee (PCT): Configurations, Installation and Use, Agilent Technologies Technical Document G1472-90001.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
October 15, 2009
5990-4754EN

Agilent Technologies

Capillary Flow Technology for GC/MS: Efficacy of the Simple Tee Configuration for Robust Analysis Using Rapid Backflushing for Matrix Elimination

Application

Environmental

Authors

Harry Prest
Agilent Technologies, Inc.
5301 Stevens Creek Blvd.
Santa Clara, CA 95051
USA

Christian Foucault and Yves Aubut
Agilent Technologies Canada, Inc.
2250 boul Alfred Nobel
St-Laurent, Québec
PQ H4S 2C9 Canada

Abstract

A previous application [1] described a simple Capillary Flow Technology (CFT) arrangement for GC/MS that provides minimal loss in MS signal, rapid backflushing, and quick servicing of the injection port and the head of the GC column without MS venting and operation in constant flow with pulsed injections. This arrangement uses a "tee" or purged union at the midpoint of two capillary GC columns with makeup flow controlled by electronic pressure control (EPC) devices. This application illustrates the improvement in run-to-run response robustness in a biological sample using the pressure-controlled tee (PCT) arrangement.

Introduction

Capillary Flow Technology (CFT) devices offer many opportunities for improvements in analytical quality. From the point of view of GC/MS, one major improvement is the capability of removing the late-eluting or “high-boiling” components that appear in the chromatogram after the last analytes of interest. Typically these are “removed” by increasing the oven temperature and adding additional run time to “boil” these off the column. However, this widely applied practice sends these contaminants off the column and into the MSD ion source. The net outcome is to reduce analyte response due to fouling of the MSD ion source and add analytical time. Ultimately, the result is lowered sample throughput due to long oven cycle times, extensive downtime required for ion source cleaning, and lowered run-to-run analytical quality because of the decreasing compound responses over time. Using the pressure-controlled tee (PCT) arrangement, the previous application [1] demonstrated how to rapidly eliminate these late eluters and shorten run times without substantial loss in signal. This application demonstrates how the PCT can improve the robustness of run-to-run analyte response using a biological sample acquired in positive chemical ionization (PCI) mode as a working example. This is significant for several reasons. First, chemical ionization modes are selective and so “blind” to many contaminants that can be detrimental to the analysis, thus eliminating them is a valuable advance. Secondly, in terms of robustness, the ion source trend is roughly:

Electron Impact Ionization ≥ Positive Chemical Ionization > Electron Capture Negative Ion Chemical Ionization (ECNICI)

Demonstrating enhanced robustness in PCI mode

will indicate the ability to protect the source in the other modes.

Experimental

Figure 1 shows a schematic of the instrument configuration for this analysis. The prior method utilized a single, continuous 50-m column and comparative data was acquired in this typical configuration. For the PCT configuration, two 25-m columns were used, with one ahead and one behind the tee, with the rear injection port controlling the tee flow as in the reference 1. The CFT tee was the Purged Ultimate Union (G3186-60580). All connections to the tee were made with the appropriate ferrules and fittings; most importantly, the MSD transfer-line connection was made with SilTite fittings.

The samples for this example were blood samples prepared for analysis of the lipid peroxidation product, 4-hydroxy-2,3-nonenal (HNE), which is considered an indicator of oxidative stress, and its metabolite, 1,4-dihydroxynonene (DHN). The preparation is extensive, [2] with addition of preservatives and reductive agents, steps for lipid removal, etc., but the resulting sample is still complex. Selective detection utilizing PCI with ammonia was chosen to simplify the detection and improve the quantitative determination. The MSD ion source was operated at 300 °C and the quadrupole at 150 °C and indicative ions were chosen for selected-ion monitoring analysis [2].

Results and Discussion

A reconstructed total ion current (RTIC) chromatogram acquired in full-scan mode using a single continuous 50-m column (without PCT), Figure 2, shows that even with the selective PCI and with the most “gentle” CI reagent gas, the sample still is very complex and the analytes are diminutive compared to the other matrix components. Especially intense are the late-eluting biologicals, which are known to “foul” the column phase; removing these required the oven program to extend to 340 °C and remain there for 3 minutes. This process improved the chromatographic performance by restoring the column phase; but driving these components into the ion source

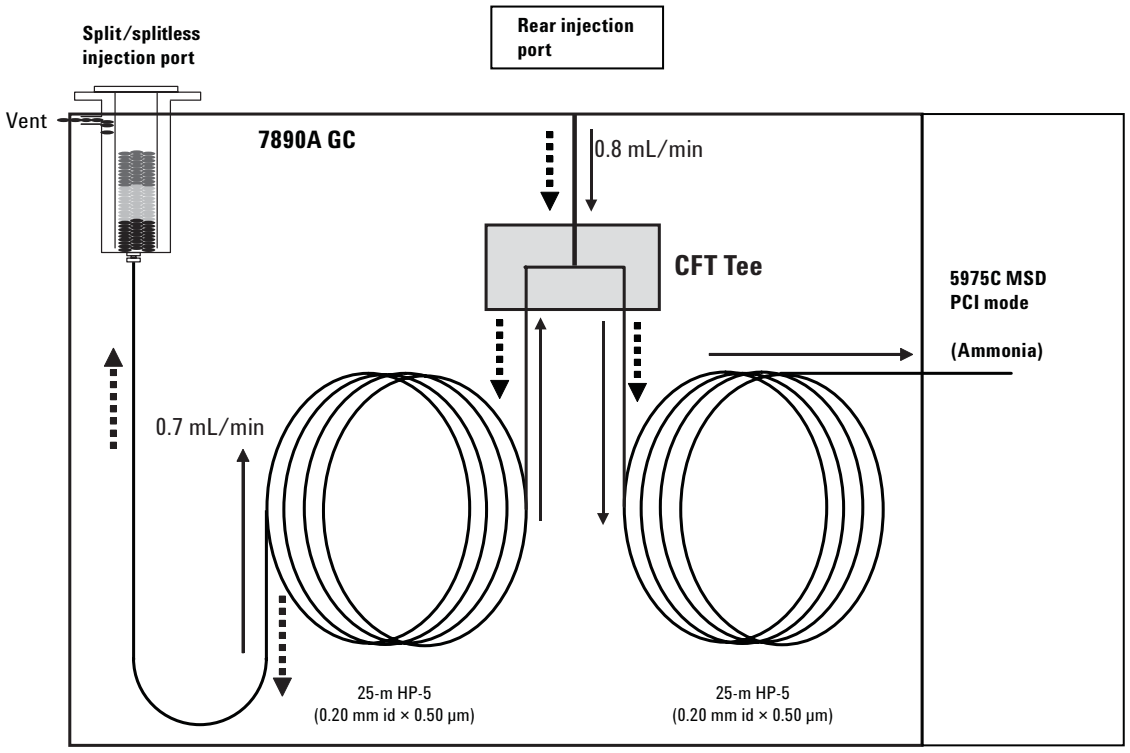


Figure 1. Schematic of pressure-controlled tee configuration for this analysis.

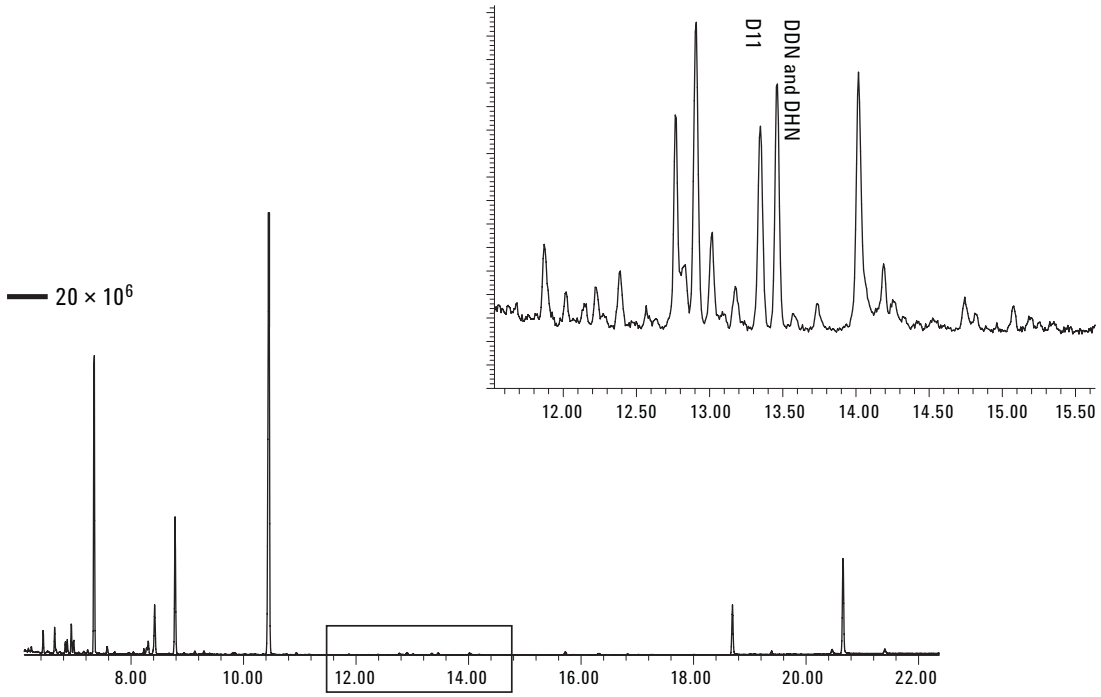


Figure 2. RTIC chromatogram of PCI-NH_3 full-scan acquisition of a typical sample. Note the intense, late-eluting (> 14 min.) components.

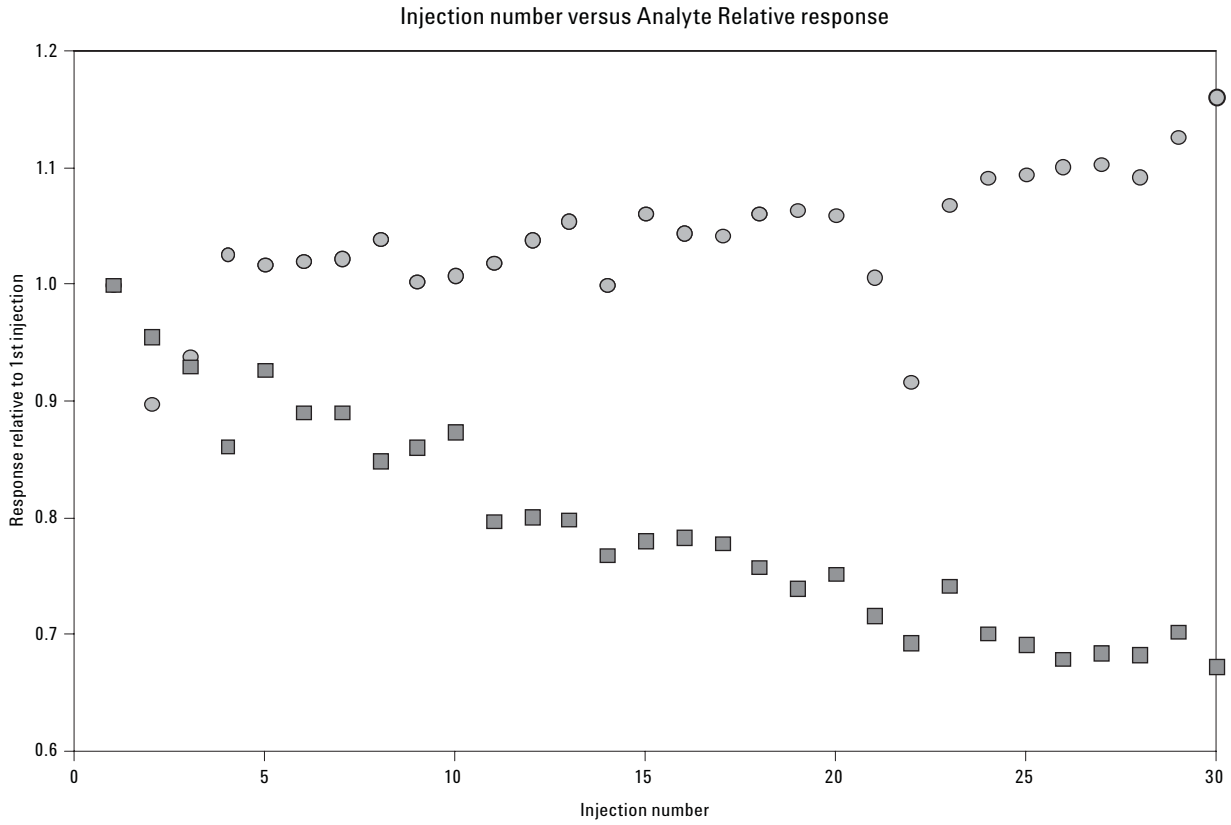


Figure 3. Analyte response versus injection number using the PCT with backflushing (circles) and using a continuous column without backflushing (squares).

rapidly degraded the analyte response. However, using the PCT configuration, these components were removed by backflushing them to the injection port and out the split vent. This improvement is shown in Figure 3. Using a continuous 50-m column configuration (without PCT or backflush), the analyte signal continuously drops and by the thirtieth injection more than 30 percent of the original intensity has been lost. Using the PCT and employing backflushing maintains signal and remains within about 10 percent of the first injection's response. (Some improvement in the PCI signal is seen as the clean source conditions in the course of the injections).

Conclusions

Using backflushing to remove late-eluting, matrix-related components can provide better uniformity in analyte response. This is especially important at trace concentrations, and it is at trace concentrations that the PCT configuration shows less signal loss than other CFT arrangements. Further, the ion source is more susceptible in PCI mode than EI so the improvement is more rapidly revealed. In ECNICI mode it may only take a few injections to lose response and, in this mode, the selectivity is such that many late eluters are invisible. The PCT is expected to be even more valuable in this mode.

Other advantages were found in reduced runtime and improved cycle time. Even with a rather conservative (that is, excessive) backflushing time and temperature (of 4 minutes), run time was shortened by 3.5 minutes and run-to-run cycle times can still be further optimized. The net result is higher sample throughput with higher quality data.

References

1. H. Prest, "Capillary Flow Technology for GC/MS: A Simple Tee Configuration for Analysis at Trace Concentrations with Rapid Back-Flushing for Matrix Elimination," Agilent Technologies publication 5989-8664EN
2. M. Veronneau, B. Comte, and C. Des Rosiers, "Quantitative Gas Chromatographic-Mass Spectrometric Assay of 4-Hydroxynonenal Bound to Thiol Proteins in Ischemic/Reperfused Rat Hearts," *Free Radical Biology & Medicine*, 33(10), p 1380–1388, 2002

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
August 4, 2008
5989-9359EN

Agilent Technologies

Capillary Flow Technology for GC/MS: A Simple Tee Configuration for Analysis at Trace Concentrations with Rapid Backflushing for Matrix Elimination

Application

Environmental, Drug Testing, and Forensics

Author

Harry Prest
Agilent Technologies Inc.
5301 Stevens Creek Blvd.
Santa Clara, CA 95051
USA

Abstract

Capillary Flow Technology devices offer the potential to enhance GC/MSD operation and robustness. In operation, they can allow rapid service of the GC column and inlet, including liner and septum, without venting or subjecting the MSD to air. In terms of robustness, late eluting compoundscan be removed from the column by "backflushing," which forces components to retreat through the column into the injection port before they damage the MSD source or compromise the next analysis. This leads to higher analytical integrity as both the column phase and the MSD can be protected. This application describes a simple arrangement for Capillary Flow Technology devices that provides ventless maintenance features with highly accelerated backflushing and minimal losses in the MSD signal. This solution supports GC analysis in constant flow mode with pressure pulsed injections and is recommended for all MSD users (in both electron impact or chemical ionization modes), including those with diffusion pump systems.

Introduction

The introduction of Electronic Pressure Control (EPC) was a major advance for GC and especially GC/MS analysis. EPC allowed development of the constant flow mode of analysis, which generates chromatographic peaks of consistent width (time) and allows optimization of MS cycle times to meet either qualitative or quantitative requirements. Also, splitless injections gained pressure pulsing or ramped flow modes, which lowered the analytes' residence time in the hot injection port and confined the expansion of the injection solvent (avoiding overfilling of the liner). The power of this approach lead to continued evolution of EPC technology with the present state of the art represented in the new 7890A GC.

The recent addition of Capillary Flow Technology (CFT) devices has reinvigorated and recast Deans switching and other pressure control approaches to GC analysis. One such CFT device, the QuickSwap [1–3], provides two important capabilities to GC/MS:

1) The ability to service and/or replace the entire analytical column or the injection port liner and septum without venting the MSD (yet still retaining high vacuum integrity)

2) The ability to remove from the column late-eluting, highly retained components that elute after the target compounds of analytical interest by reversing the carrier flow direction through the column in what is called “backflushing.” With the oven temperature elevated and the flow reversed, these very high boiling interferences can be pushed off the column into the split vent and thereby prevent degradation of the column phase or the detector.

A schematic representation of the arrangement that makes this possible is shown in Figure 1.

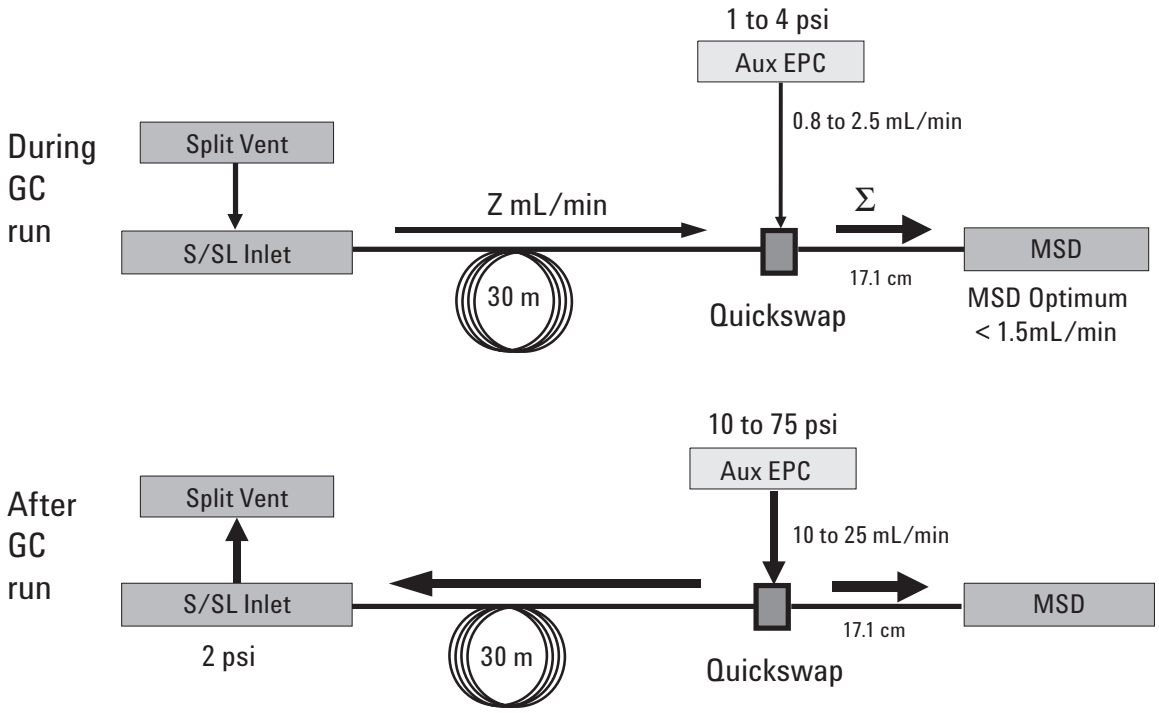


Figure 1. Schematic of QuickSwap arrangement.

Every new approach has a downside and for QuickSwap it is the additional makeup flow required to purge the QuickSwap device during analysis which dilutes the signal in the GC/MSD. This is not an issue for many users since the sensitivity of the MSD is usually more than adequate. However, analysis at trace concentrations has more stringent requirements and maintaining a signal closely comparable to that of a single continuous column is essential.

Another CFT configuration for GC/MSD applications designed specifically for trace GC/MS analysis where customers do not wish to surrender signal is possible using the QuickSwap or any of several other CFT devices. In this alternate configuration, the CFT device is located in the middle of the analytical column, essentially splitting the column in half. For example, a 15-m column preceeds and follows a CFT tee. Schematically this arrangement is illustrated in Figure 2. The auxiliary EPC device adds just enough pressure (flow) to match the flow (pressure) from the first column, so there is little flow addition and therefore less “dilution” and loss in the GC/MSD signal. Backflushing is similarly simple; the pressure or flow is dropped in the first column section while the second section column flow is increased.

Advantages of this pressure controlled tee (PCT) approach are similar to those of QuickSwap, such as:

- Service of injection port liner and septum without venting the MSD
- Column cutback or replacement of the “front” or first column without venting the MSD

But additional advantages of the PCT arrangement over QuickSwap are:

- Minimal or no signal loss (in EI- or CI-MS) is obtained because of the very small additional “makeup” gas flow.
- Constant flow mode and pressure pulsed injections are straightforward.
- This configuration is suitable for diffusion pumped systems and allows backflushing in diffusion pumped systems.
- Backflushing is more rapid and can be initiated earlier.

This application details some configurations and provides an example of backflushing.

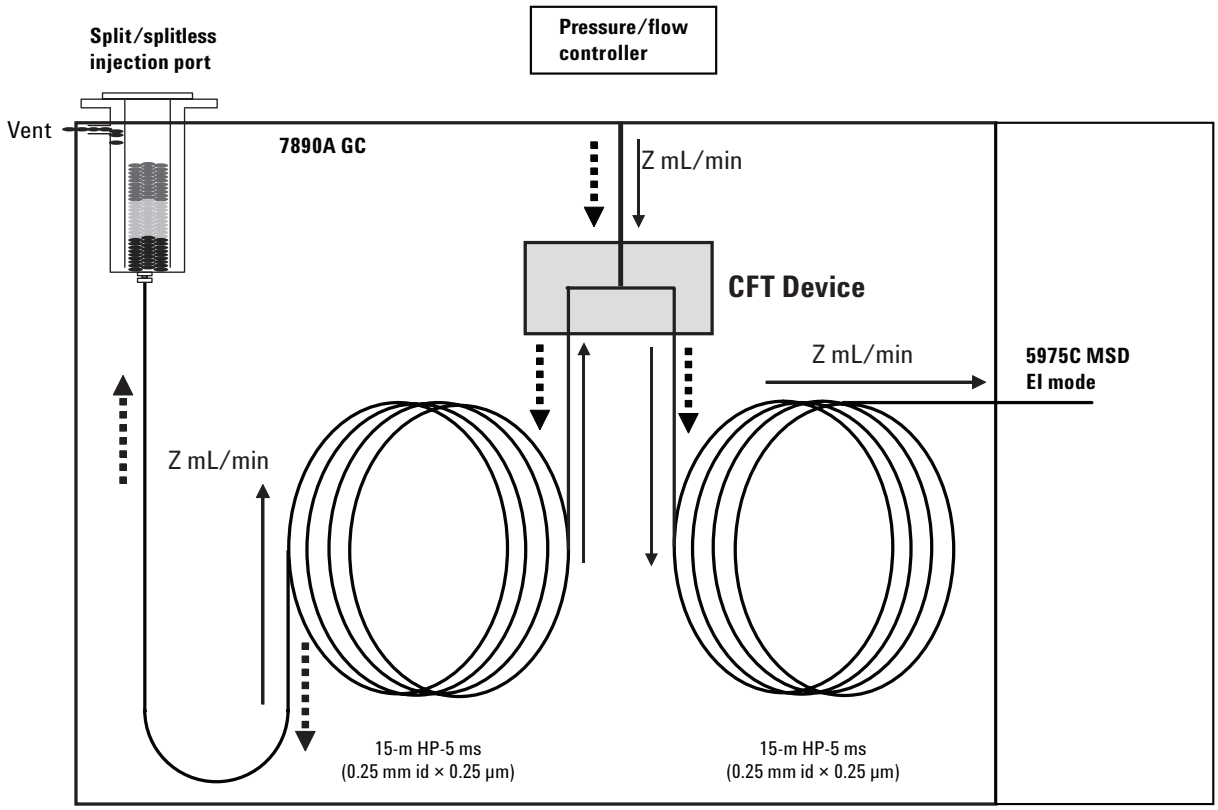


Figure 2. Schematic of pressure controlled tee arrangement for the GC-MSD: solid lines indicate the forward flow during GC/MSD analysis and the dashed lines indicate backflushing flows.

Experimental

A number of devices can be used in this approach and those arrangements will be cited later, but for these experiments the instrument configuration was as follows:

- 7890A GC with split/splitless ports in front and back and a 7683B ALS
- 5975C MSD with performance turbomolecular pump
- 2 HP-5ms 15 m × 0.25 mm id × 0.25 µm film columns (19091S-431)
- CFT device: 2-way unpurged splitter (G3181-60500) with SilTite ferrules and nuts
- CFT GC mounting hardware: dual-wide mounting bracket (G2855-00140) or single-wide mounting bracket kit (G2855-00120)
- Deactivated 0.25 mm id column approximately 1 m long
- 2 CFT blanking plugs (G2855-60570 or as G2855-20550 with G2855-20593)

As an overview of the configuration, the 1-m column was connected to the back injection port and to the first position on the CFT splitter using the appropriate SilTite fittings. (This CFT device has three connection points and is really best thought of as a simple tee reminiscent of glass Y- or T-connectors and will be referred to as a "CFT device" or "CFT tee" from here forward).

One of the 15-m HP-5ms columns was connected at the uppermost position on the CFT tee and the other end through the transfer line into the MSD as usual. The other 15-m HP-5ms column was connected to the midpoint of the CFT device and the front injection port.

In detail, the arrangements were as follows. The CFT tee was attached to the forward position on the mounting hardware on the right side in the GC oven. The 1-m long section of guard column was wound on a spare column cage and hung on the column hanger in the back of the oven. (This could simply be added to one of the 15-m HP-5ms column

cages to avoid the extra cage.) Using a Vespel/graphite ferrule, one end was connected to the back injection port and the other end to the lowest connection of the CFT device with a SilTite ferrule and nut. The other two CFT tee connections were sealed with CFT blanking plugs and the back injection port was pressure tested as described in the 7890A *Advanced User Guide* (part number G3430-90015).

One of the 15-m columns was then hung on the cage carrying the 1-m column and installed with one end through the MSD transfer line. Since this column (column #2) can be expected to have a rather long life as it will be protected by the upstream column, a SilTite ferrule is recommended for the transfer-line seal. These ferrules do not develop leaks as the transfer-line temperature is cycled; however, the Vespel/graphite ferrules can shrink and develop leaks. (Note that if the surface of the transfer line is very worn it may fail to seal well, in which case the Restek *Agilent interface cleaner* [P/N 113450] can be used to resurface the sealing surface if very carefully employed). The other end of this GC column was connected to the uppermost connection on the CFT tee with the SilTite ferrule.

The "upstream" 15-m GC column (column #1) was hung on the other 15-m column cage and installed in the front split/splitless injection port with a Vespel/graphite ferrule, liner, and BTO septum, as usual. The other end was connected to the CFT tee middle post and, after temporarily removing the other connected columns, blanked off and pressure tested as above.

All connections were then re-established to the CFT tee with the 1-m column in the lower position; the front, first column (#1) connected in the middle position; and the rear, second or MSD column (#2) in the uppermost connection. Helium was supplied to both the front and back ports, and a helium leak detector was used to check for any leaks.

A picture of the arrangement is shown in Figure 3.

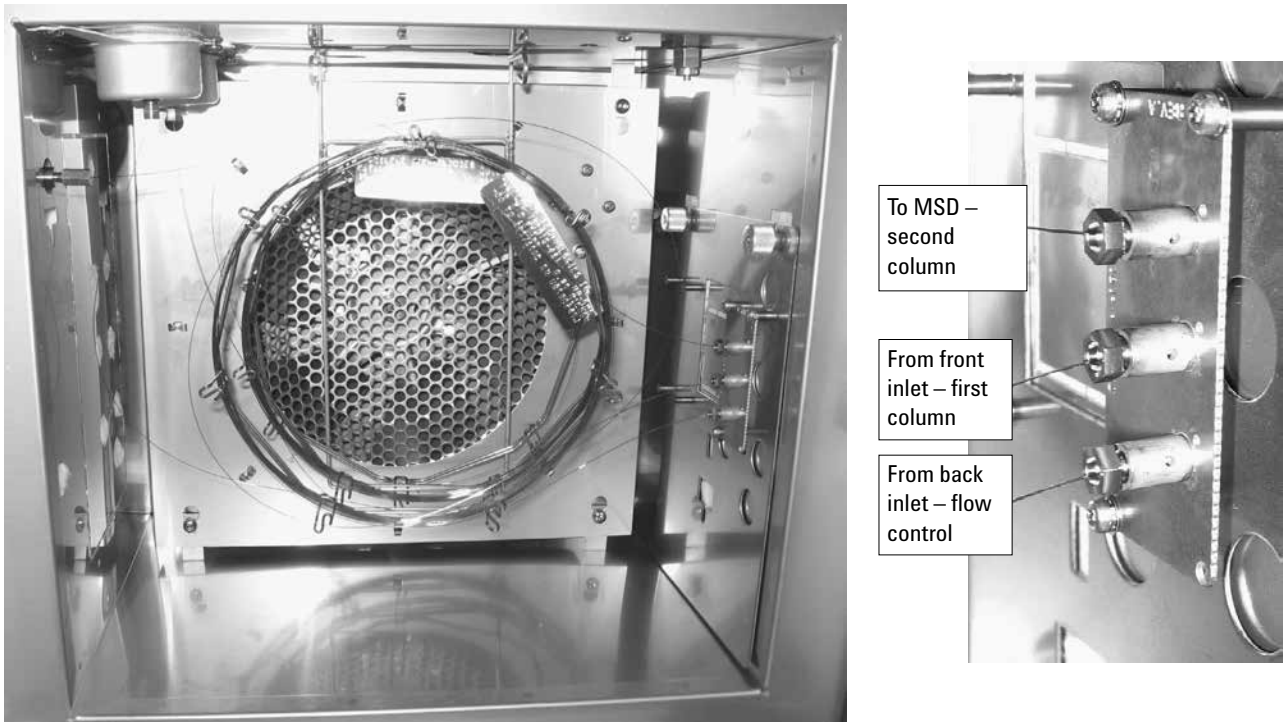


Figure 3. Picture of the installed pressure controlled tee arrangement for the GC/MSD.

GC Configuration

The GC can be configured in several ways. However, for instructional purposes and those of these experiments, the GC was configured as follows:

Column #1:	30 m × 0.25 mm id × 0.25 µm column
Inlet:	Front injection port: pulsed splitless mode, split flow 15 mL/min
Outlet:	MSD (vacuum)
Mode:	Constant flow
Column #2:	15 m × 0.25 mm id × 0.25 µm column
Inlet:	Back injection port: split mode, split flow 15-mL/min
Outlet:	MSD (vacuum)
Mode:	Constant flow

The flows were set to 1.2-mL/min, all zones were left cold, and the MSD power was turned on. With the MSD and GC zones still "cold," the MSD background was checked to be sure *m/z* 28 was decreasing, indicating that the system was tight. Only after there was confidence that there was no leak were other zones brought up to temperature.

Operating with Pressure Pulsed-Splitless Injection

Figures 4A and 4B show screen captures of the 7890A GC configuration for a standard pressure-pulsed splitless injection with constant flow mode operation; they show the front and back injection port parameters. Remember, the arrangement is set up such that the front port, into which the sample will be injected, is configured as if a 30-m column were installed into the MSD. Typical pressure-pulse conditions are set for these parameters: a 25 psi pulse for 0.5 minutes; split flow on at 0.75 minutes at 50-mL/min; with gas saver on at 2 minutes at 15-mL/min. The general rules apply for pressure-pulsed splitless injections: given a particular liner, inlet temperature, injection volume, and solvent, the expansion of the solvent is confined to a fraction of the interior volume (< 0.75) of the liner by the pressure applied.

Figure 4B shows that the back injection port is in split mode, at 120 °C (to remove water background), with split flow and gas saver set at 15-mL/min flow.

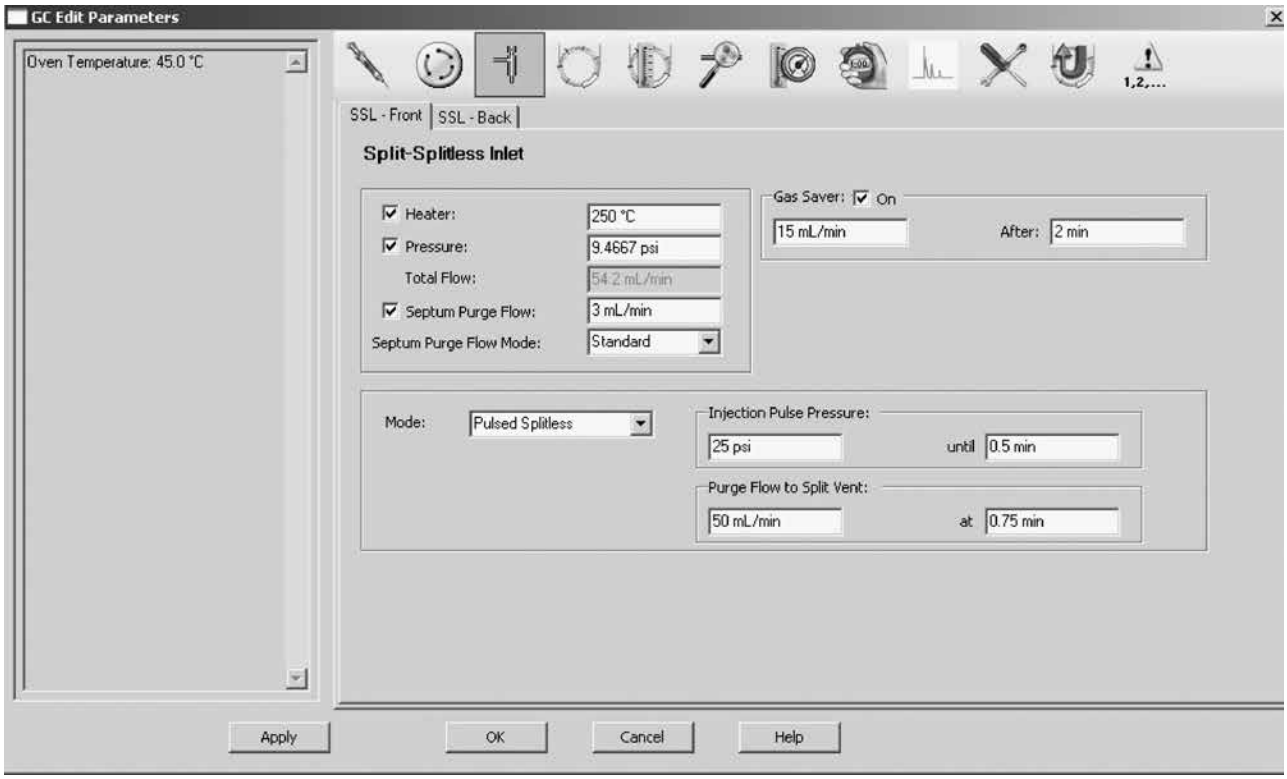


Figure 4A (upper panel). Typical pressure-pulsed splitless injection parameters for constant flow: front injection port.

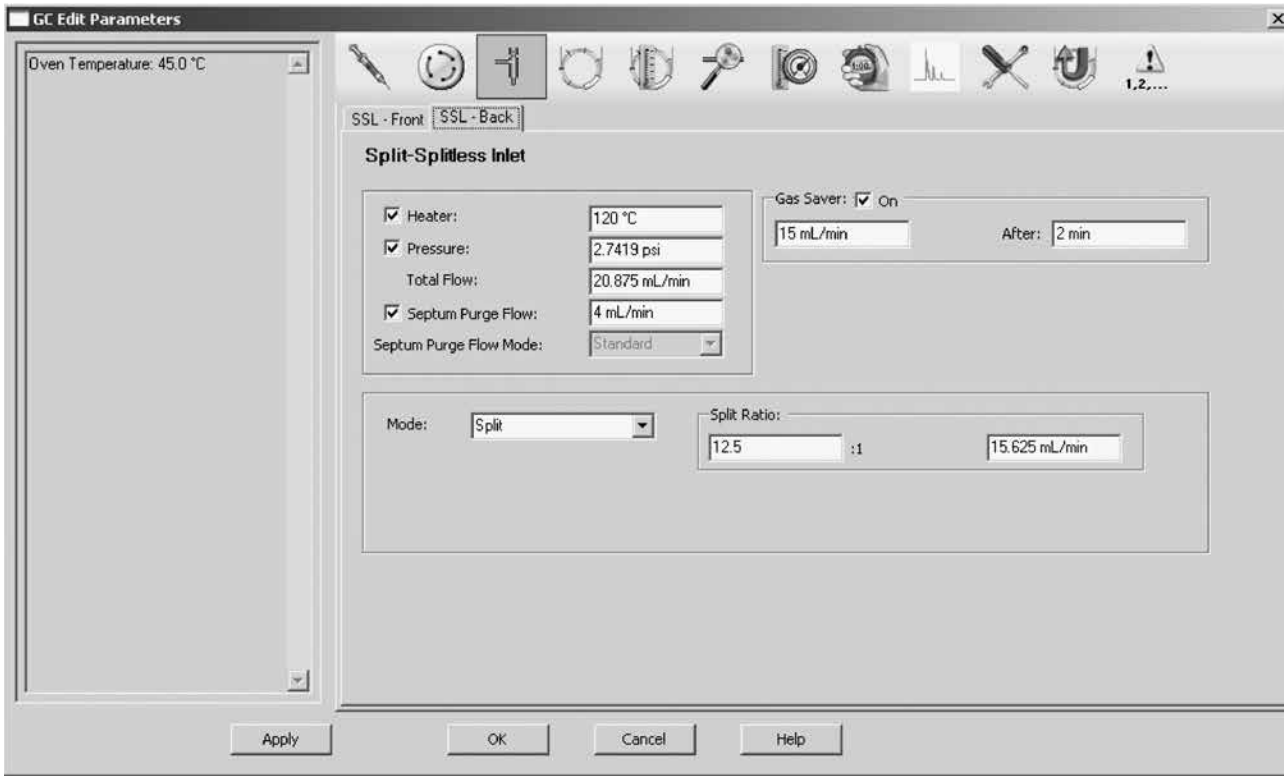


Figure 4B (lower panel). **Typical pressure-pulsed splitless injection parameters for constant flow: back injection port (not used for injection but for column control).**

Figures 5A and 5B show the constant flow mode settings for the two columns. The front column flow is the typical 1.20 mL/min, but the back column flow is slightly higher at 1.25 mL/min to prevent any backflow. Essentially the additional flow is equivalent to an extra meter of column length.

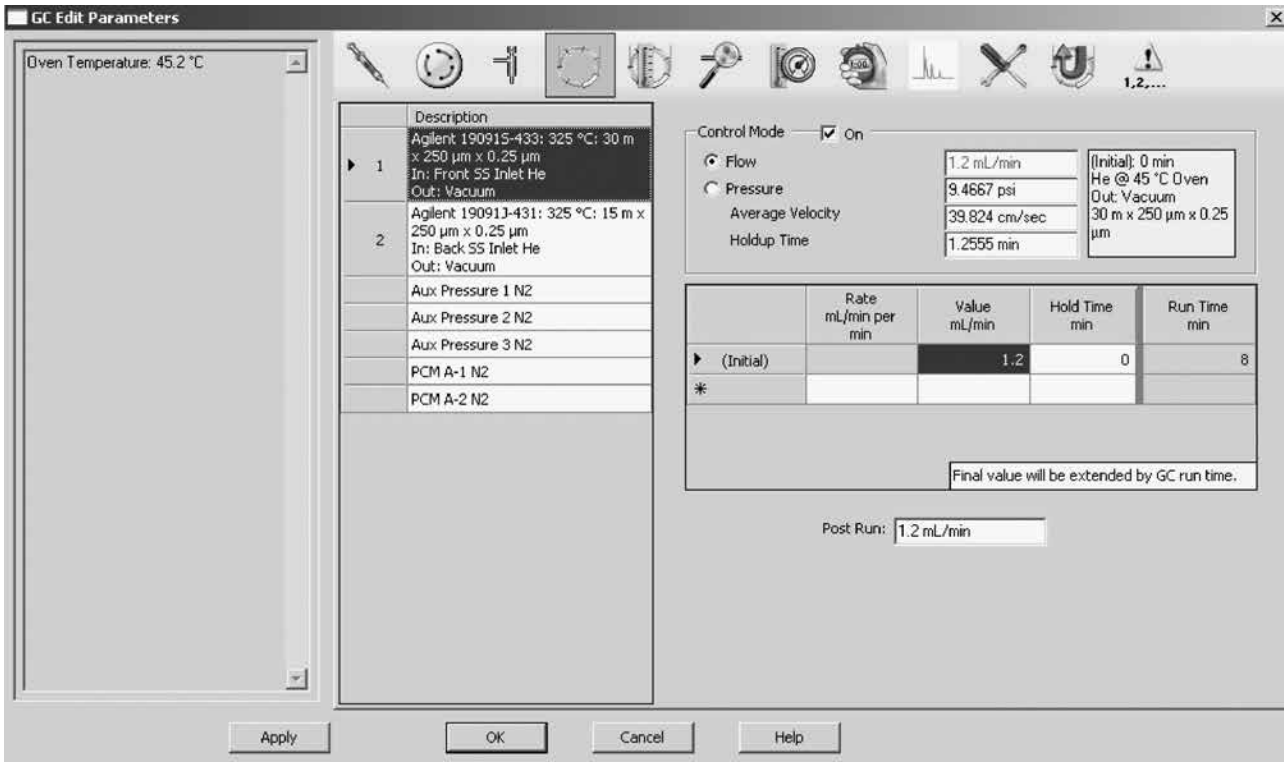


Figure 5A (upper panel). **Typical pressure-pulsed splitless injection parameters for constant flow: First column section (configured as a 30-m column).**

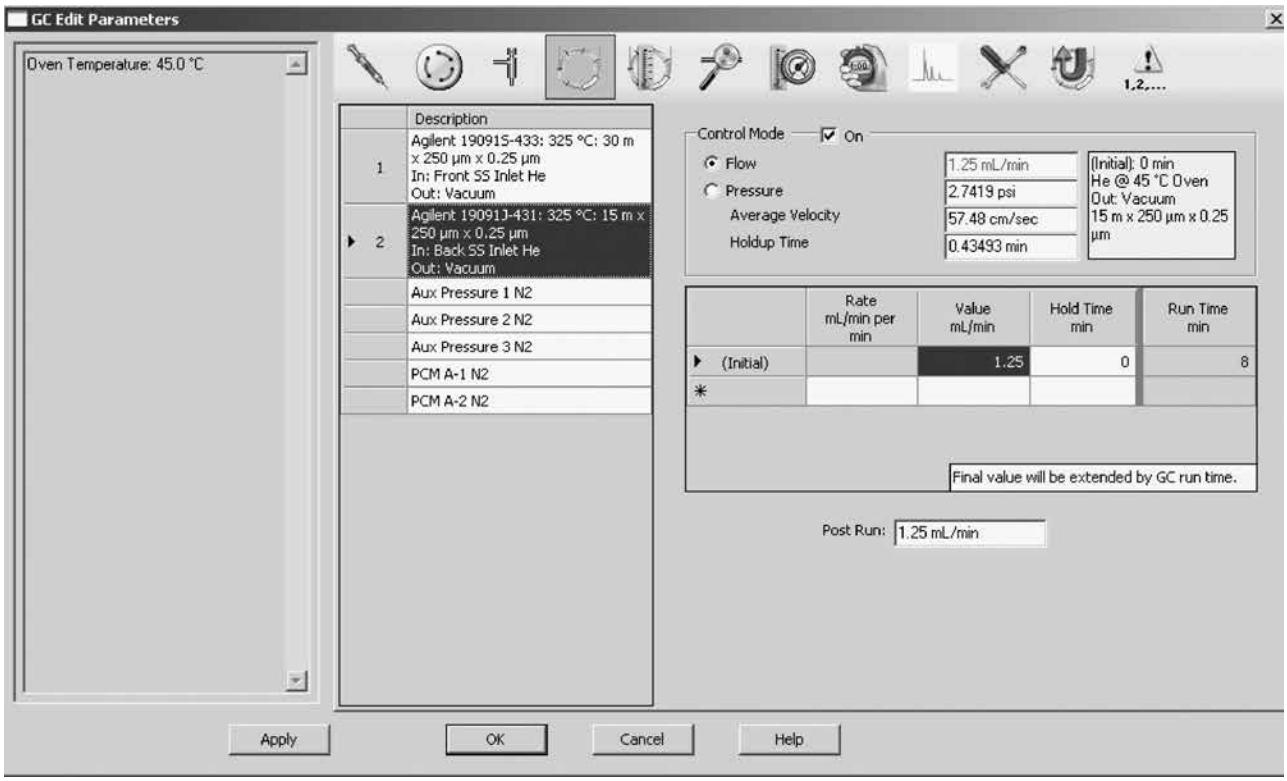


Figure 5B (lower panel). Typical pressure-pulsed splitless injection parameters for constant flow: Second column section (configured as a 15-m column).

Results and Discussion

Figure 6 shows the results for pressure-pulsed splitless injections of octafluoronaphthalene (OFN) at 1-pg/µL acquired in selected ion monitoring (SIM) with the two 15-m column and CFT tee configuration and the standard 30-m continuous column configuration. Both peak height and area remain the same, indicating that there is no loss in signal. This is as expected since no signal dilution is taking place. There is a slight degradation in S/N for the CFT tee results as the background noise is raised by about 35% due to the additional flow controller. The important point is that the signal is preserved at trace levels.

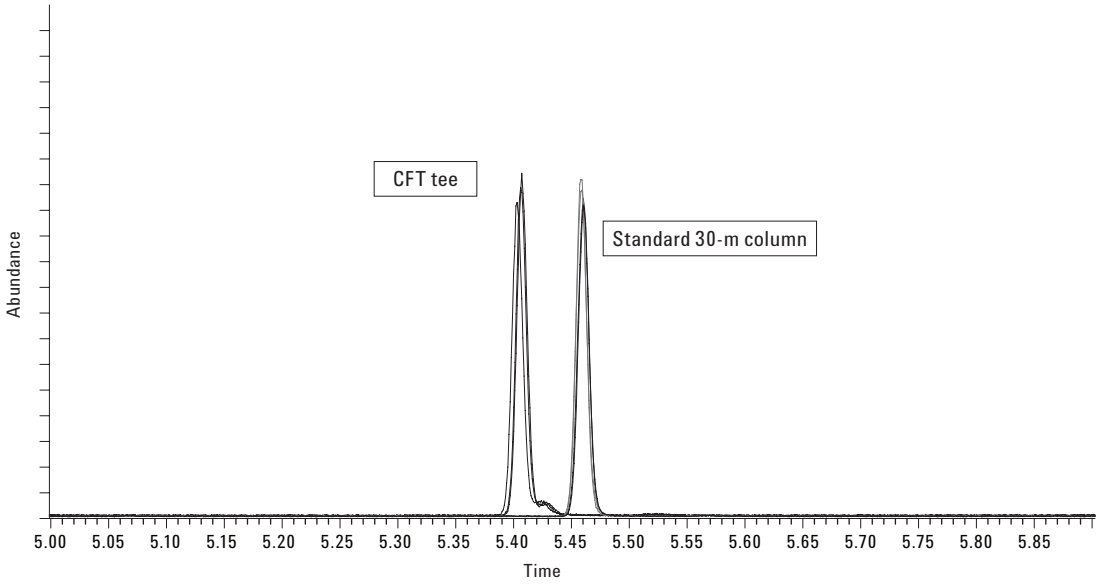


Figure 6. Reconstructed total ion chromatogram (RTIC) of three replicate SIM acquisitions of octafluoronaphthalene using pulsed splitless injection with CFT tee (left profiles) and with a standard 30-m continuous column configuration (right profiles).

Chromatographic Character

Beyond preserving signal, the CFT device should exhibit reasonable chromatographic performance. One indication of chromatographic integrity is the peak shape profiles of the fatty acid methyl esters (FAMEs). The result for GC/MS analysis of a FAMEs standard acquired using a metabolomics method is shown in Figure 7 and suggests very little degradation of chromatography using this PCT. This can be expected as the path is deactivated and the path length in the channels in the PCT relative to the linear velocity suggests a relatively rapid transit through the device.

Another common chromatographic test used in organochlorine pesticide analysis (as in USEPA method 8081) examines degradation of 4,4'-DDT and Endrin. This degradation test was developed to indicate the degree of activity of the injection port by examining the amounts of DDD and DDE products of DDT and the ketone and aldehyde products of Endrin. The situation is complicated here as the degradation products can be generated in both the injection port and the CFT tee. How-

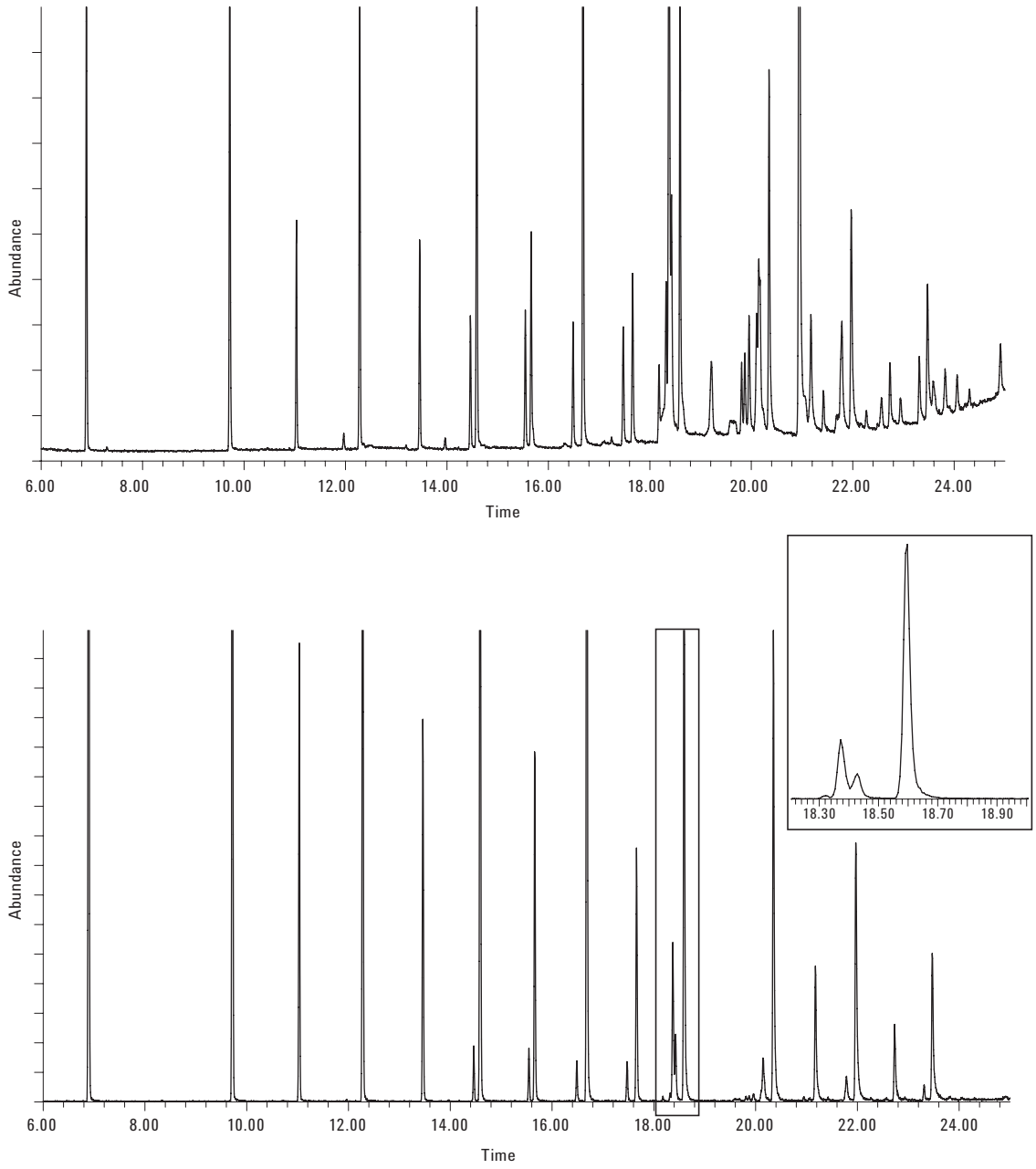


Figure 7. Reconstructed total ion chromatogram (RTIC) of a multicomponent FAMEs standard using pulsed splitless injection with CFT tee (upper) and the reconstructed extracted ion chromatogram (REIC) for *m/z* 74. The enlarged panel is for octadecanoic methyl ester.

ever, because those products formed in the injection port and those formed at the CFT device will have different retention times due to differing lengths of column, the degradation contributions from the two origins should be discernable. By analyzing these known breakdown products in the PCT and then injecting the DDT and Endrin agents themselves, an estimate of the activity contributed by the CFT device can be calculated. The upper panel of Figure 8 presents the reconstructed total ion current (RTIC) for the selected ion monitoring (SIM) signals of the four breakdown products. These were acquired in SIM-scan mode with a single SIM group composed of one or two major ions for each compound so there was no time selection for the compounds' appearance. On the basis of summed areas, the total breakdown for Endrin is less than 13% with the CFT device contributing less than 10% of the total breakdown area or less than 1.2% to the area total. The DDT breakdown is less than 4% for the system; however, the CFT device contributes about 46% of the total observed breakdown and is about double the breakdown generated by the port. It is possible some DDD breakdown is "hidden" under the DDT peak. On the basis of the DDT to DDE contribution from the CFT tee, however, it is likely to increase the breakdown perhaps less than about another 2%. A better study would use on-column injection

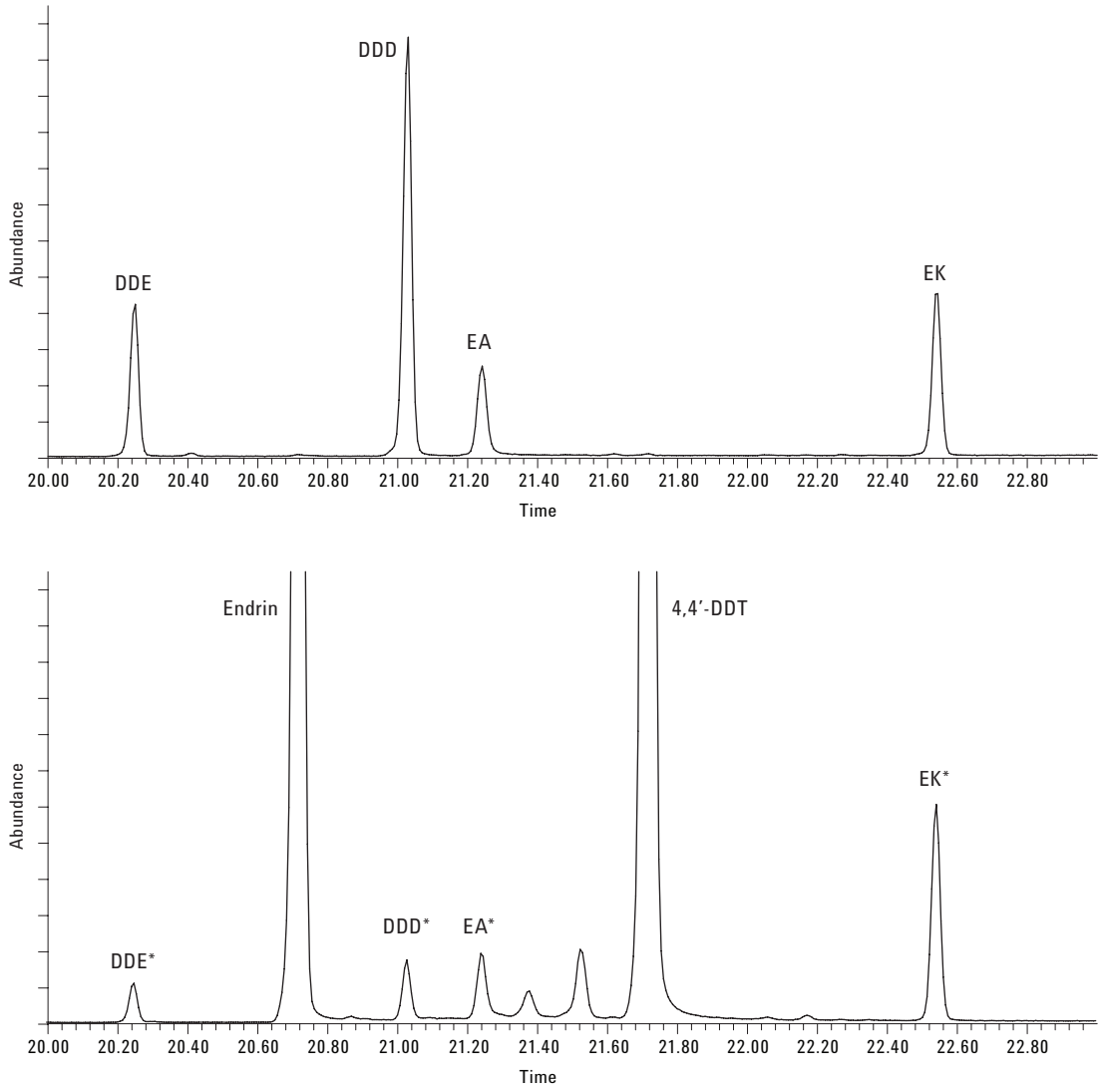


Figure 8. CFT tee activity. A: the REIC of a GC-MS SIM acquisition using pulsed splitless injection with the PCT configuration of the expected degradation products of DDT and Endrin at 0.2 ng on column : 4,4′-DDE (DDE), 4,4′-DDD (DDD), Endrin aldehyde (EA), and ketone (EK). B: REIC for an injection of 2.0 ng of 4,4′-DDT and Endrin identifying degradation products. Those with an asterix (*) are attributed to the injection port and due to the CFT device activity such as; from Endrin (5 as ketone) and from 4,4′-DDT (6 as DDE). Note 7 is tenatively identified as DDMU, source unknown.

of all components, but the verdict is likely the same: the CFT device has some activity but is comparable to that of other elements (for example, in the inlet and liner). It is worth noting that this CFT device has a very long path compared to others (see the *Alternative Configurations* section) and that air intrusion in any part of the system will be a major issue in considering activity problems.

Adding Backflush

Figures 9A, 9B, and 9C show the GC parameters for adding backflush. They are quite simple. The oven temperature can remain the same as the temperature at the end of the oven program or can be raised to the isothermal or programmed temperature limits in Post Run for backflushing. Raising the column temperature during Post Run helps condition the column and removes some column bleed but is not necessary. The front column (column #1) flow is dropped to 0.3 mL/min and the back column (column #2) flow is raised to 4 mL/min.

To quickly estimate the duration of the Post-Run time parameter, notice that the back column (column #2) in Figure 9C cites the column Holdup Time at a given flow. At the 1.25-mL/min shown, the Holdup Time is roughly 0.4 minutes. When the column #2 flow is raised to 4 mL/min, the Holdup Time for back flow through column #1 will be less than this (actually around 0.26 min). But estimating that every 0.4 minute the front 15-m column section would be flushed at least once is very conservative and an adequate approximation. Five to 10 column volumes will flush this front 15-m section in less than 2 to 4 minutes, which is relatively rapid. Choose a time in this range (for example, 3 minutes) and test the effectiveness of the backflush method by injecting a sample and follow this with a solvent blank injected under the non-backflush GC/MSD method. There should be no sign of carryover. Extend this Post-Run time if there is carryover or further raise the Post-Run temperature or both. This is a very conservative approach.

Column or Inlet Servicing and Maintenance

To change the liner, septum, cutback the column, or replace the front 15-m column, simply cool the inlet(s) and increase the flow on the back column (column #2) to 4 mL/min and set the front injection port pressure to OFF. It is worth saving this method (such as SERVICE-Front.M). When the head of the column is removed from the injection port, one can confirm that the carrier is flowing back up the column by immersing the tip in liquid.

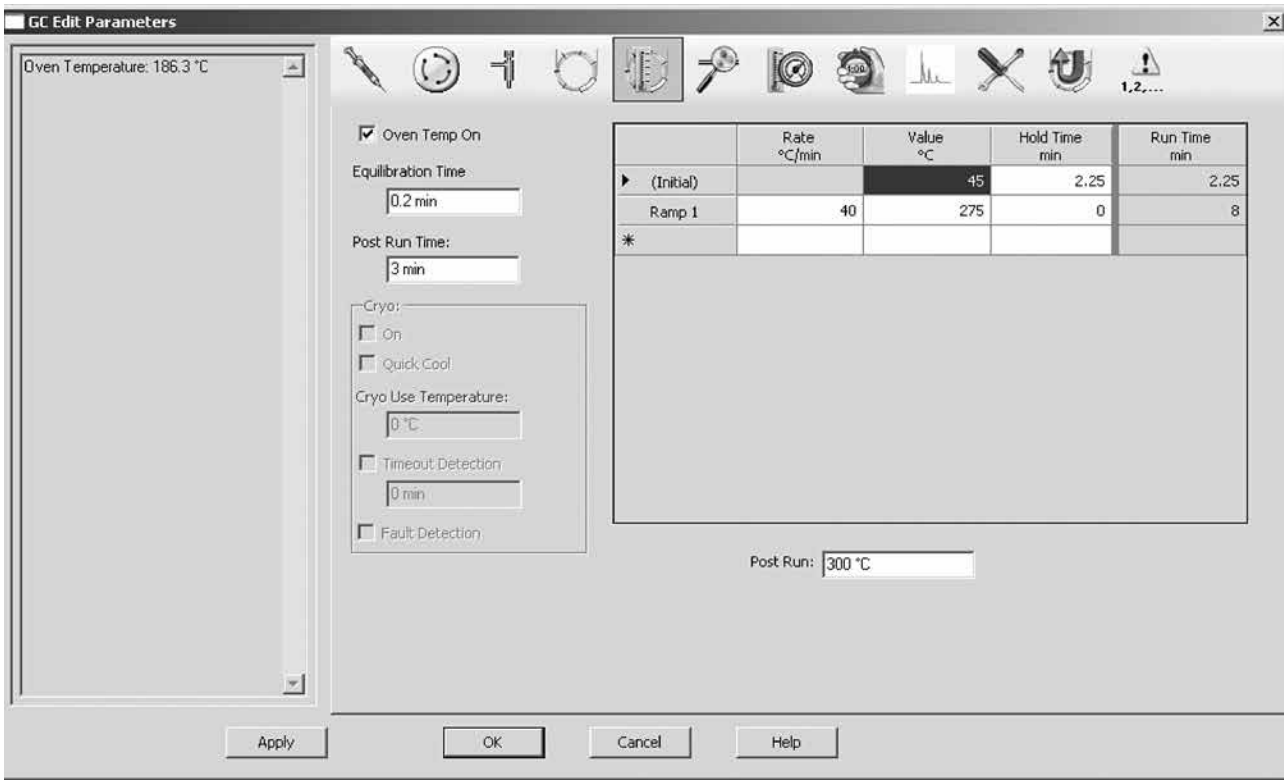


Figure 9A (upper panel). Adding backflushing in Post Run: oven parameters.

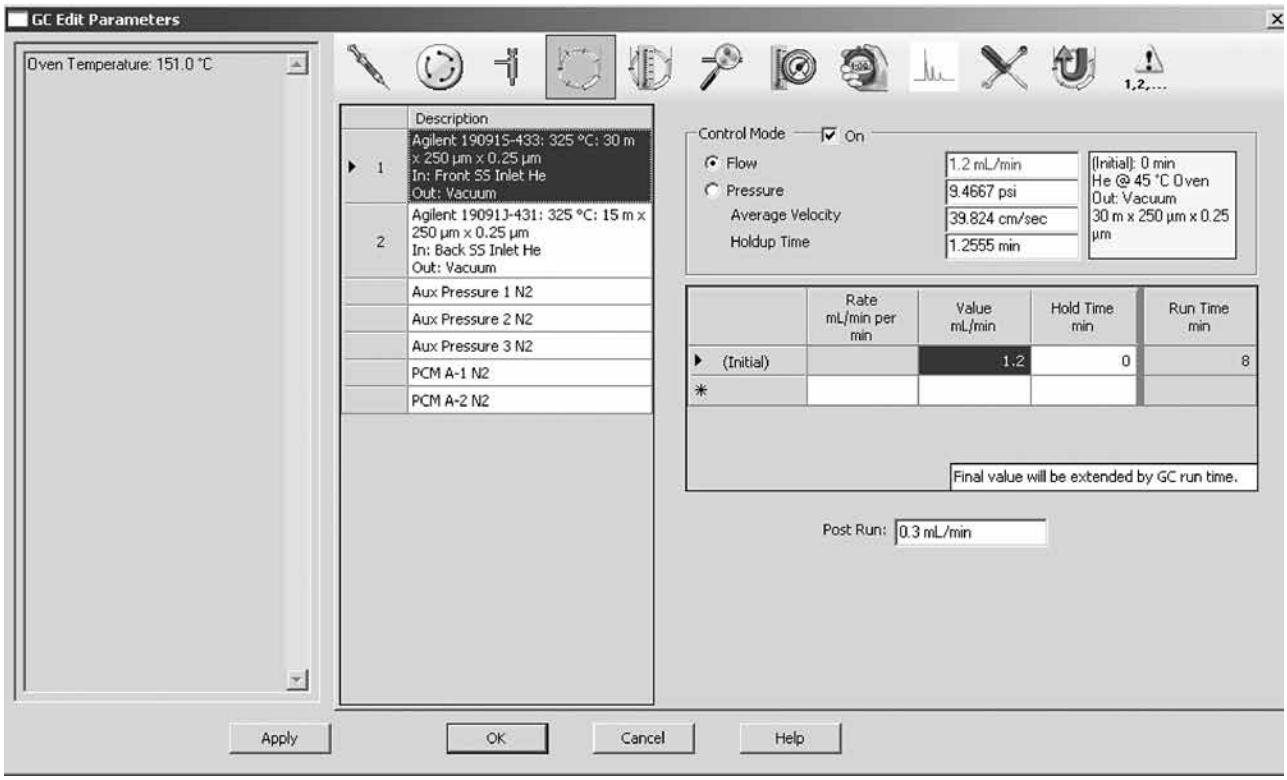


Figure 9B (middle panel). Adding backflushing in Post Run: front column (column #1) parameters.

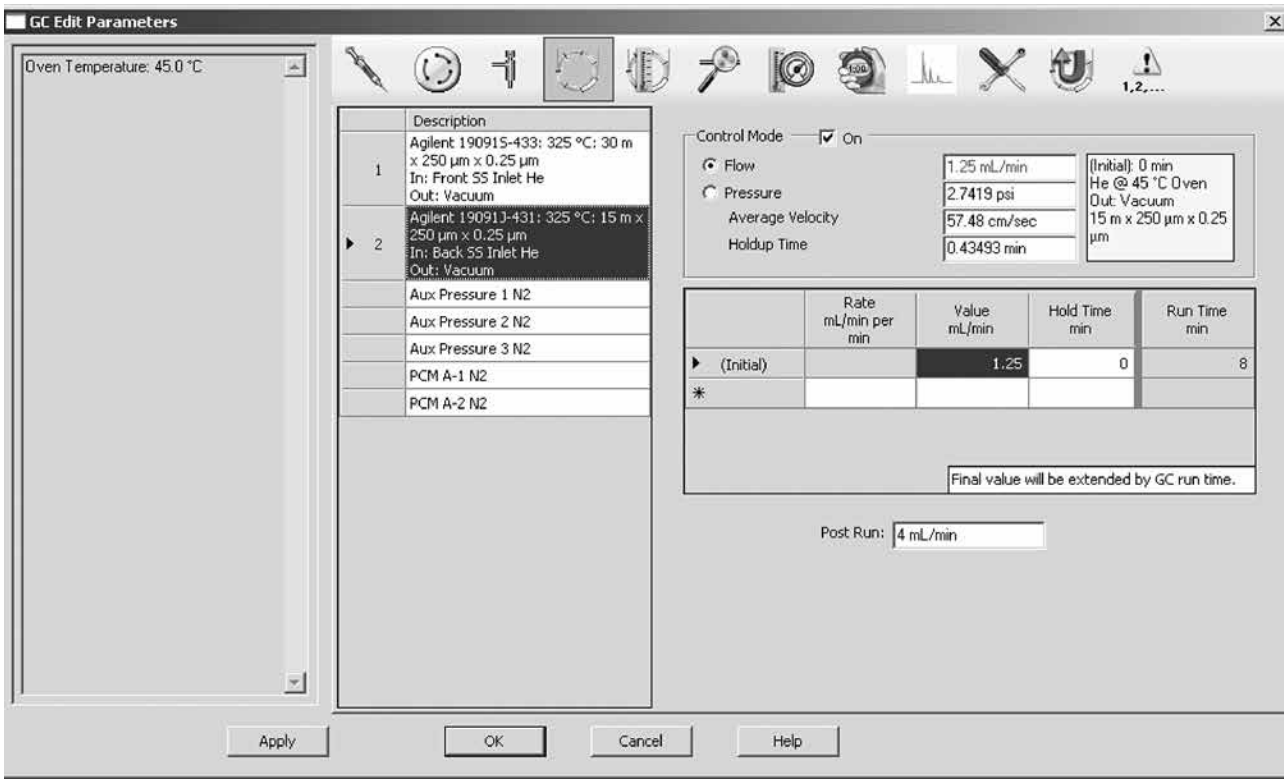


Figure 9C (lower panel). Adding backflushing in Post Run: back column (column #2) parameters.

This backflow also prevents fines from the column cutting from entering the column. Make the necessary service and reattach and reload the analytical method.

If a completely new 15-m column (#1) is installed, it can be conditioned *in situ* by setting up the backflow condition with the oven at the conditioning column temperature.

Advanced Techniques: Concurrent Backflushing

If the fastest possible total analytical time is the highest priority, one will realize that backflush can begin earlier than the elution of the last component. In other words, backflushing can occur during the analytical acquisition, thereby increasing productivity. After the last compound of interest has passed the CFT tee and entered the back 15-m column, the pressure or flow through the earlier 15-m column can be dropped and compounds will cease moving forward and actually begin to retreat. When the last compound elutes, then the flow in the back column can be raised to complete backflushing. This is demonstrated in Figure 10.

The calculations are also very simple. To calculate when the flow (pressure) in the front column (column #1) is to be reduced, simply subtract the Holdup Time (Figure 9C) from the last compound's

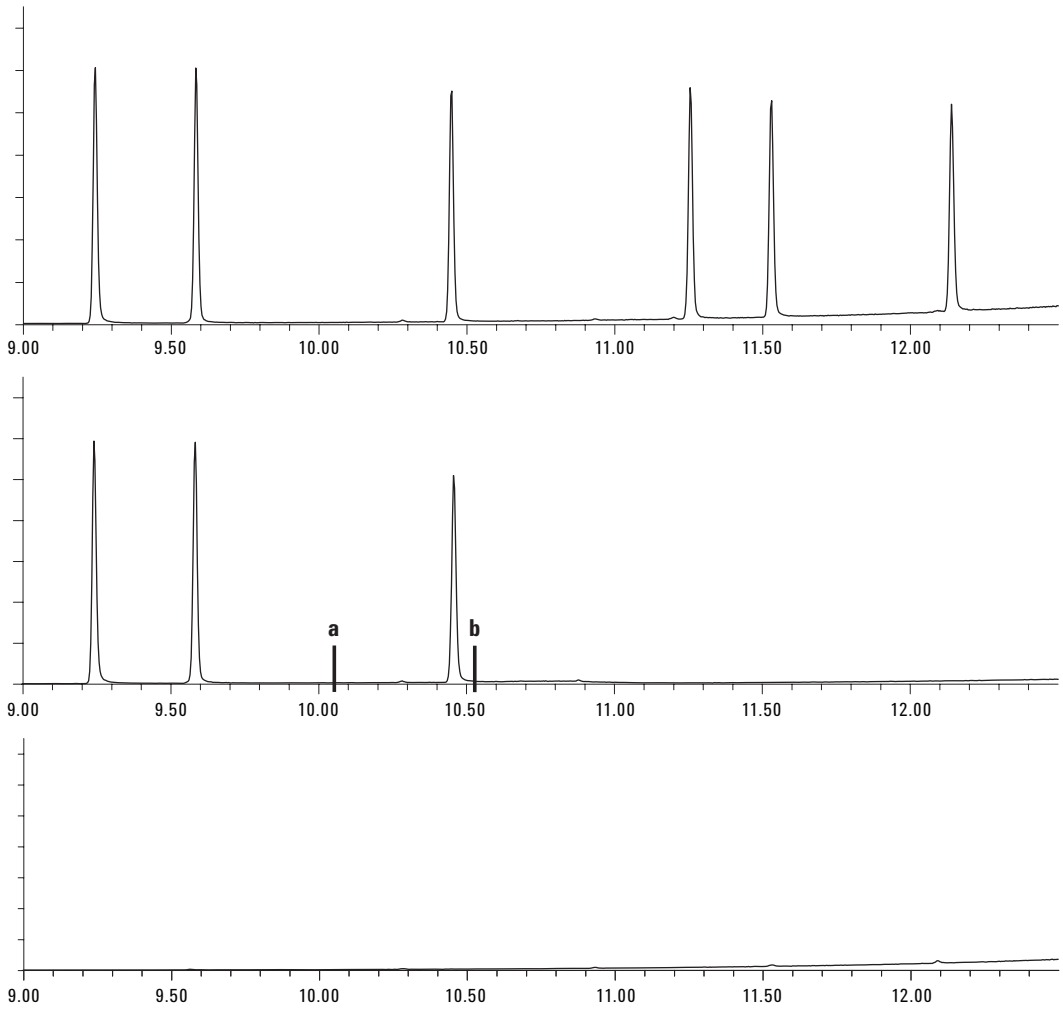


Figure 10. Example of backflushing with flow or pressure control. Upper panel: RTIC of original six-component standard. The third peak is considered the last analyte and the fourth peak the beginning of the late-eluting interferences. Middle panel: RTIC of the same standard with backflushing beginning at 10.1 min (a), where the first 15-m column (column #1) flow is dropped and at (b) where column #2 flow is increased to 4 mL/min. Note that the last analyte is retained but the late eluters never enter the MSD. Lower panel: solvent blank run without backflush after the backflush method which shows no carryover.

elution time. After this last compound has eluted, go into Post Run and set the second 15-m column (#2) flow to 4-mL/min (or the pumping system maximum) with the front column (#1) pressure remaining low and the oven at the final programmed temperature. This can best be accomplished in ramped flow mode or in pressure programming. Do this for two to three column volumes and test with a sample followed by a solvent blank to see if this is sufficient. Experimentation with particular samples will enable setting these requirements more efficiently.

Conclusions

Alternative Configurations

The CFT is very rich and allows many possible arrangements; these are only a few suggestions or alternatives. The CFT tee used here can be replaced by a purged two-way splitter with one channel plugged (G3180-61500) or even the QuickSwap itself can be moved back from the MSD interface and suspended in the oven.

However, the best CFT tee device appears to be the new Purged Ultimate Union (G3186-60580), Figure 11. As the name describes, this is essentially a union with a gas purging line, making it a very low dead volume tee. It occupies very little space and can be suspended from the column cage, the oven wall, or through the upper GC wall. Preliminary tests of this Purged Ultimate Union using DDT and Endrin have shown very little breakdown. Chromatographic behavior is also very good.

Similarly, the carrier control need not be the back injection port split/splitless module; a Pressure Control Module (PCM) or EPC module can be used. Of the two, the Pressure Control Module may be more convenient.

Most importantly, the CFT tee position itself does not need to be exactly in the middle. The best arrangements can be considered on the basis of selection against components and the rapidity of backflushing. In other words, rapid backflushing suggests a shorter upstream column #1. So another arrangement is at the two-thirds mark or a 10-m column, then the CFT tee, and then a 20-m column to create a 30-m analytical column. Here

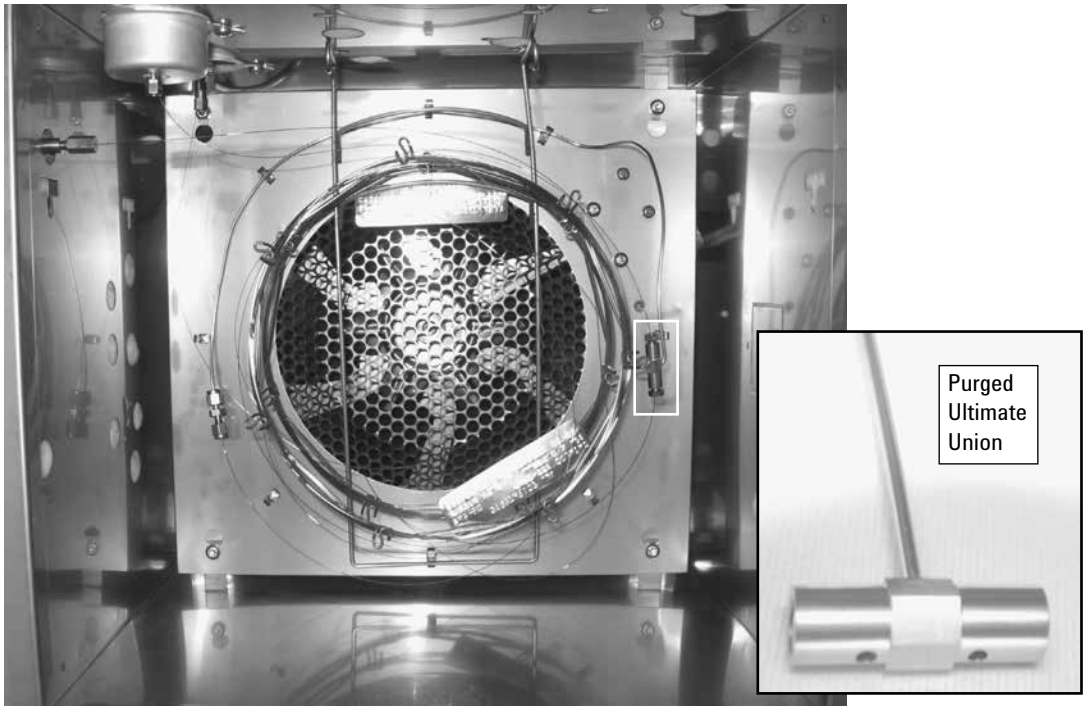


Figure 11. Purged Ultimate Union.

backflushing would be nearly 10 times faster than the arrangement with QuickSwap and more than twice as fast as the 15-m column for the same pressure. This would be the best arrangement for the MSD with a diffusion pump. Also, in terms of analytical time, this approach would provide even higher efficiency since 10 column volumes could be flushed in about 2 minutes. If backflushing begins before the analytical run ends (as shown in Advance Techniques and in Figure 10), then in many cases the Post-Run time would be very short or entirely unnecessary, yet still provide sufficient backflushing. This would further reduce total cycle times.

The joined columns need not match in many aspects. For example, a 0.32-mm id may be the first column and a 0.25-mm id the second column. In this situation it will be better to have the columns configured and described as they actually exist in the 7890A. For example, column #1 inlet is the splitless port and the outlet is the PCM module A; column #2 inlet is the PCM module A and the outlet is the MSD. Considerations of capacity, resolution, robustness, etc., can be entertained in several innovative ways to enhance productivity and data quality.

This solution can also be implemented on the Agilent 6890 GC. Of course, the PCT tee configuration is not confined to the Agilent GC/MS detector, but is suitable for other detection schemes as well.

Future software releases will contain a key command that will allow more functionality and greater ease of use: it will allow the user to apply the IGNORE READY = TRUE condition to the EPC device controlling the CFT tee. This will prevent the pressure pulse or other flow conditions from producing a “not ready” condition for the instrument.

References

1. The 5975C Series GC/MSD, Agilent Technologies publication 5989-7827EN
2. Frank David and Matthew S. Klee, “Analysis of Suspected Flavor and Fragrance Allergens in Cosmetics Using the 7890A GC with Column Backflush,” Agilent Technologies publication 5989-6460EN
3. Frank David and Matthew S. Klee, “GC/MS Analysis of PCBs in Waste Oil Using the Backflush Capability of Agilent QuickSwap Accessory,” Agilent Technologies publication 5989-7601EN

(These references are available in the Literature Library at www.chem.agilent.com.)

Acknowledgements

The author is very grateful to Bruce Quimby, Wes Norman, and Matthew Klee for several informative and encouraging discussions. Also, a special thanks to Wes Norman for providing superb CFT devices tailored to the needs of the GC/MSD and an advance example of the Purged Ultimate Union.

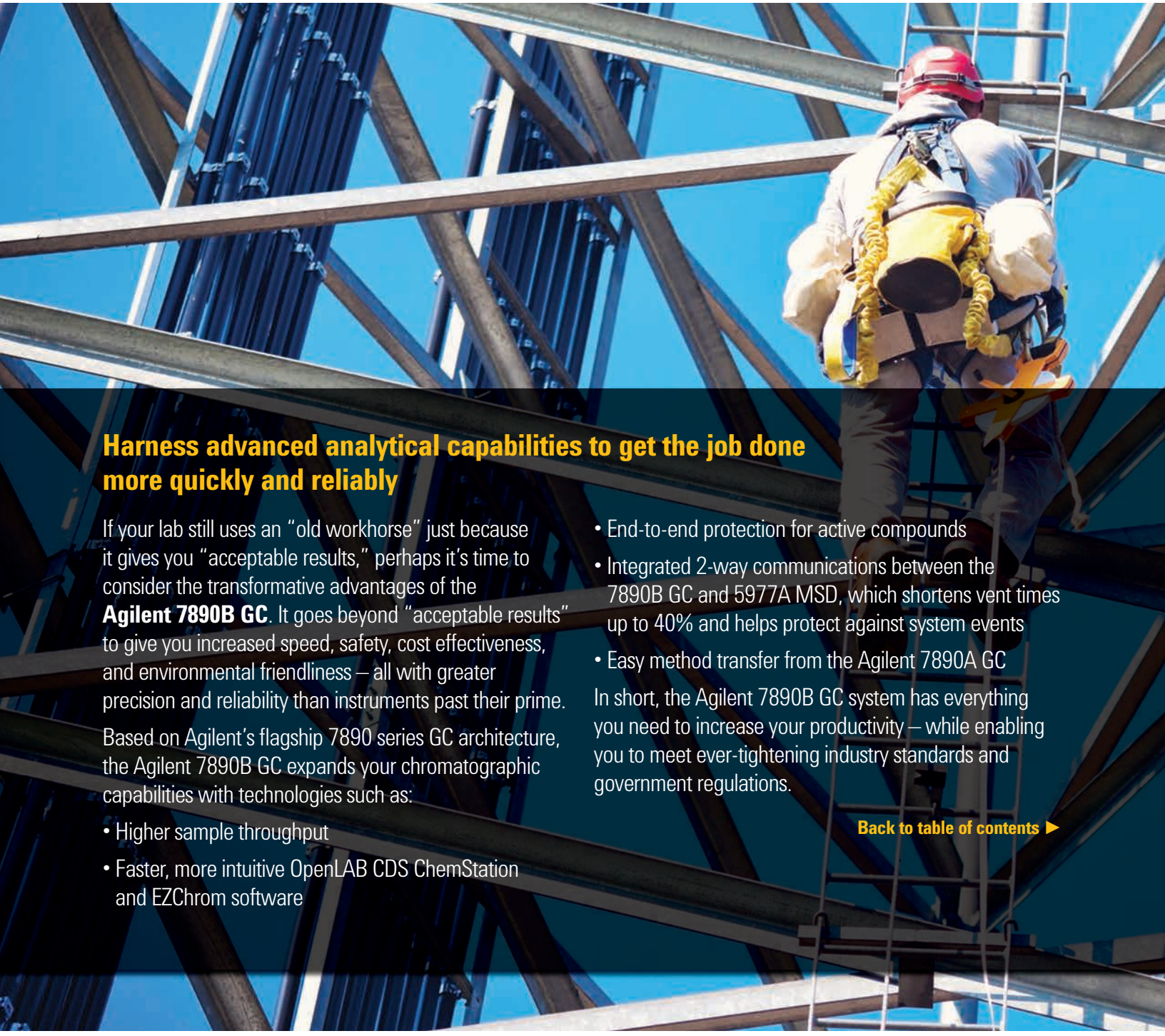
For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
June 24, 2008
5989-8664EN

Agilent Technologies

THE NEW AGILENT 7890B GC



Harness advanced analytical capabilities to get the job done more quickly and reliably

If your lab still uses an "old workhorse" just because it gives you "acceptable results," perhaps it's time to consider the transformative advantages of the **Agilent 7890B GC**. It goes beyond "acceptable results" to give you increased speed, safety, cost effectiveness, and environmental friendliness – all with greater precision and reliability than instruments past their prime.

Based on Agilent's flagship 7890 series GC architecture, the Agilent 7890B GC expands your chromatographic capabilities with technologies such as:

- Higher sample throughput
- Faster, more intuitive OpenLAB CDS ChemStation and EZChrom software
- End-to-end protection for active compounds
- Integrated 2-way communications between the 7890B GC and 5977A MSD, which shortens vent times up to 40% and helps protect against system events
- Easy method transfer from the Agilent 7890A GC

In short, the Agilent 7890B GC system has everything you need to increase your productivity – while enabling you to meet ever-tightening industry standards and government regulations.

Back to table of contents ►

Learn more about solutions for the energy and chemical industry at **agilent.com/chem/energy**

An Improved Flame Photometric Detector for the Analysis of Dibenzothiophenes in Diesel, Distillates, and Feedstocks Using the Agilent 7890B Series GC

Application Note

Hydrocarbon processing industry

Author

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

Abstract

An Agilent 7890B Series GC equipped with a new high temperature Flame Photometric Detector (FPD) was used to determine the sulfur compound distribution of benzothiophenes in heavier fuels and feedstocks such as cycle oils and catalytic cracker feeds. A Capillary Flow Technology (CFT) Deans switch configuration was used to cut selected parts of a HP-1 column separation to a mid-polar DB-17HT column to help minimize quenching and to enhance separation of the sulfur compounds. Identification of many alky dibenzothiophenes in Light Cycle Oil (LCO) and other feedstocks was determined.

Agilent Technologies

Introduction

The distribution of sulfur in various feedstocks is of great importance to the refining industry as processes are adjusted and optimized to meet clean fuel requirements. Sulfur levels in fuels and distillates are being driven lower by environmental regulation. Catalyst optimization for hydrotreating can also benefit from a knowledge of the distribution of dibenzothiophene class sulfur compounds. The new Flame Photometric Detector on the 7890B Series GC with its high temperature capability and improved sensitivity is an ideal, easy-to-use tool for the determination of sulfur in blending stocks such as light cycle oil (LCO). Detail on sulfur content is vital for optimal hydrotreating or hydrocracking conditions where profiling dibenzothiophenes is of particular importance to achieve the lowest sulfur levels in the final products. These include dibenzothiophene, methyl (C1) substituted dibenzothioiphenes, dimethyl (C2) dibenzothiophenes, C3, and C4 dibenzothiophenes. To achieve optimal results, the FPD must be operated at temperatures above 300 °C. A CFT Deans switch system where the Benzothiophene region is cut to a midpolar 30 m × 0.25 mm, 0.15 µm DB17 for additional separation and detection using the FPD was employed. This enhanced separation reduces the possibility for quenching caused by coelution with hydrocarbons.

Experimental

Figure 1 shows a diagram of the system used in this work. In an effort to minimize coelution which will occur with complex hydrocarbon feedstocks, a Deans switch is incorporated so that selected sections of a first dimension separation can be heart cut to undergo a secondary separation on a midpolar column. While this approach will not eliminate coelution, it can be significantly reduced leading to a better determination of sulfur distribution. The FPD can suffer from quenching effects when coelution with hydrocarbons occur. The new FPD+ has excellent sensitivity of 2.5 pg sulfur/second.

Hydrocarbon fuels or feedstocks such as diesel and LCO will elute completely with the configuration shown in Figure 1. When heavier feedstocks are injected, the columns and temperatures used in this work will not permit complete sample elution. Short 0.53 mm id columns with thin stationary phase could be used, however, separation would not be adequate and quenching effects would be severe in the boiling point range of interest for dibenzothiophenes. As with many purged CFT devices, the Deans switch can be backflushed allowing heavy feedstocks to be injected without damaging the higher resolution column sets that are normally used in such configurations. Backflush methods were used when analyzing the gas oil feedstocks. The Multimode inlet (MMI) was used for sample introduction in a temperature programmed split mode. This inlet was also well suited for backflush methods.

Typical parameters for nonbackflush and backflush methods are given in Tables 1 and 2, respectively.

Agilent 7890B Series GC Deans Configuration with the FPD Plus

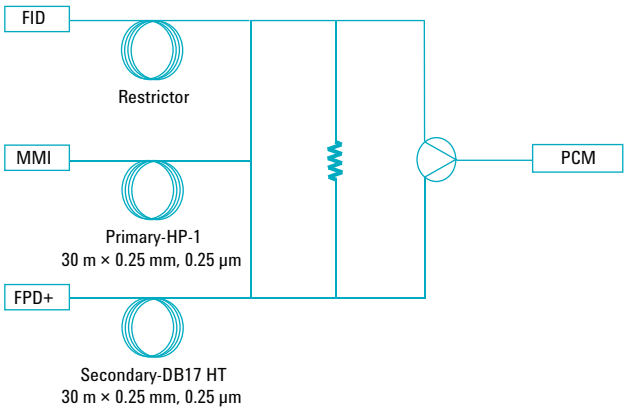


Figure 1. FPD + system with Deans switch.

Table 1. System Parameters

Gas chromatograph	Agilent 7890B Series GC
Injection port	Multimode Inlet (MMI)
MMI program	250 °C (0 minutes) to 350 °C at 50 °C/min
Split ratio	Variable, between 25–150 to 1
ALS	7693A, 1 µL
Oven program	40 °C (0 minutes) to 250 °C (10 minutes) at 10 °C/min, then 15 °C/min to 350 °C (10 minutes)
MMI	1.25 mL/min constant flow, 28.3 psi at 40 °C
PCM A-1	2.20 mL/min constant flow, 20.7 psi
FPD+	Transfer line, 325 °C to 360 °C
	Emission block, 150 °C
	Hydrogen 60 mL/min, Air 60 mL/min, Makeup 60 mL/min
FPD mode	Constant makeup + fuel
FPD data rate	5 Hz
Column 1	30 m × 0.25 mm, 0.25 µm HP-1
Column 2	30 m × 0.25 mm, 0.25 µm DB17-HT
Deans cut windows	18 to 24 minutes, 20 to 24 minutes, various

Table 2. Parameters for a Typical Backflush Method, Parameters not Listed are the Same as in Table 1

Flow program column 1 (MMI)	1.25 mL/min for 27 minutes then 100 mL/min to –3.6 mL/min
Flow program column 2 (PCM A-1)	2.2 mL/min for 27 minutes then 100 mL/min to 4 mL/min
Deans cut windows	23 to 25 minutes, 25 to 26 minutes, various
Sulfur standards	alkylated dibenzothiophenes

Results and Discussion

The FPD has undergone a redesign that enables it to operate at higher temperatures. A two zone heating configuration has been implemented where the emission block and transfer line temperatures are independent. Thermal isolation between these two zones allows the transfer line to be operated up to 400 °C while the emission block is kept at an optimal 150 °C. This makes it possible to analyze heavier feedstocks and distillates than would otherwise be possible. The transfer line is deactivated with an Agilent proprietary process leading to superior inertness which is critical to avoid adsorption or reaction of sulfur compounds with the transfer line wall.

Fuels and distillates analyzed in this work include transportation (highway) diesel, LCOs, and a cracked gas oil. The reactivity of dibenzothiophenes in hydrodesulfurization (HDS) reactions vary widely, making the distribution of these compounds of great interest to process engineers. This information assists in process optimization as well as the certification of final sulfur levels in finished products. Results are presented in order of sample final boiling point beginning with diesel and concluding with a gas oil feedstock having a final boiling point of over 540 °C.

The Deans switch was operated in a different mode that most are familiar with in classic 2D separations. Normally, a very narrow cut window is used to separate a single compound from a complex matrix of interfering compounds on a second column. In this work, wide cut windows of several minutes were typically used in order to transfer a group or class of compounds to the second column. This relied on the collective selectivity of the first and second dimension columns to separate the sulfur species from the hydrocarbons. Some coelution of hydrocarbons cannot be ruled out therefore some hydrocarbon quenching of the sulfur emission is possible. Compounds were identified from retention times by running individual pure standards. Sulfur standards were purchased from Chiron AS, Norway.

Highway Diesel

Highway diesel currently has a total maximum sulfur concentration of 15 ppm in the US. A significant amount of this sulfur can be present as various dibenzothiophenes. A calibration curve was constructed for 4,6 dimethyl dibenzothiophene (15.1% sulfur by weight), the most prominent sulfur species. The FPD shows quadradatic response due to emission from the active S2 species. The square root of area versus ppm of 4,6-dimethyldibenzothiophene linearizes the data and is plotted in Figure 2.

Figure 3 reveals C2 and C3 dibenzothiophenes in a Deans heart cut from 18 to 24 minutes. The bulk of remaining sulfur in highway diesel is represented by these compounds. Earlier cuts do not show any significant sulfur compounds. Based on the 4,6-DM DBT calibration, the sulfur content in this cut is approximately 1.5 ppm. Sulfur distributions in diesel has been extensively studied by a variety of techniques [1].

Light Cycle Oil

Next, light cycle oils were investigated. Two samples were choosen that received different processing and, therefore, expected to show different sulfur levels and compound distribution. Cut windows used for both samples were 18 to 24 minutes designed to capture the majority of dibenzothiophenes. The first sample, LCO1, shows a complex distribution where dibenzothiophene and 4-methy dibenzothiphene are the major species. FID and FPD+ chromatograms are shown in Figures 4A and 4B, respectively. The second sample, LCO2, shown in Figure 5, contains primarily dibenzothiophene and 4 methydibenzothiophene. Sulfur speciation in cycle oils has been widely studied [2,3].

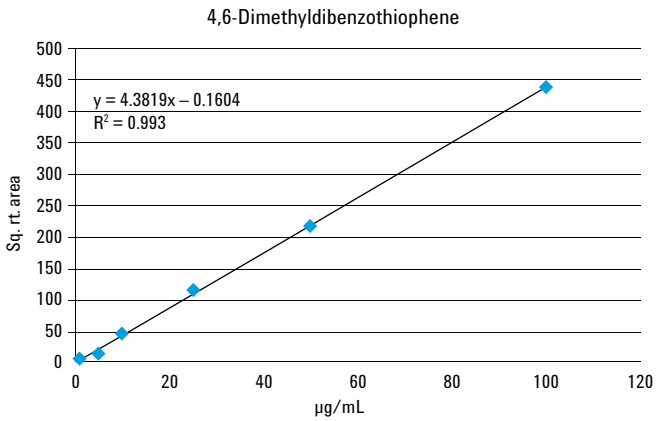


Figure 2. Calibration of 4,6 dimethy dibenzothiophene from 1 to 100 ppm. The split ratio is 25 to 1.

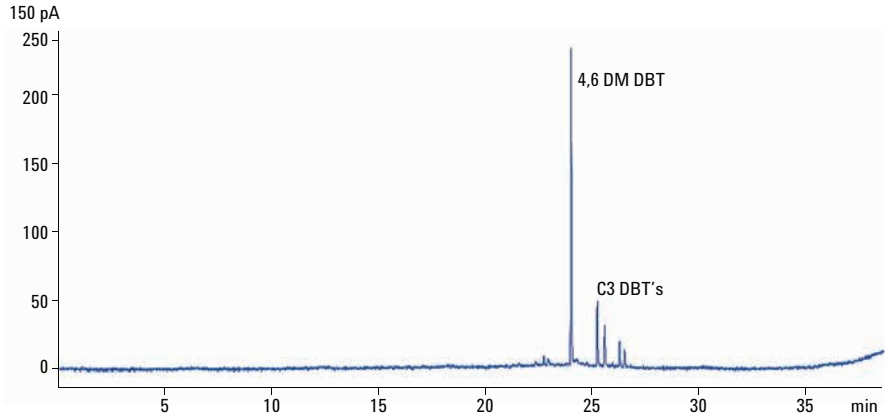


Figure 3. Highway diesel. Deans cut 18 to 24 minutes. Transfer line temperature: 325 °C, FPD emission block temperature: 150 °C.

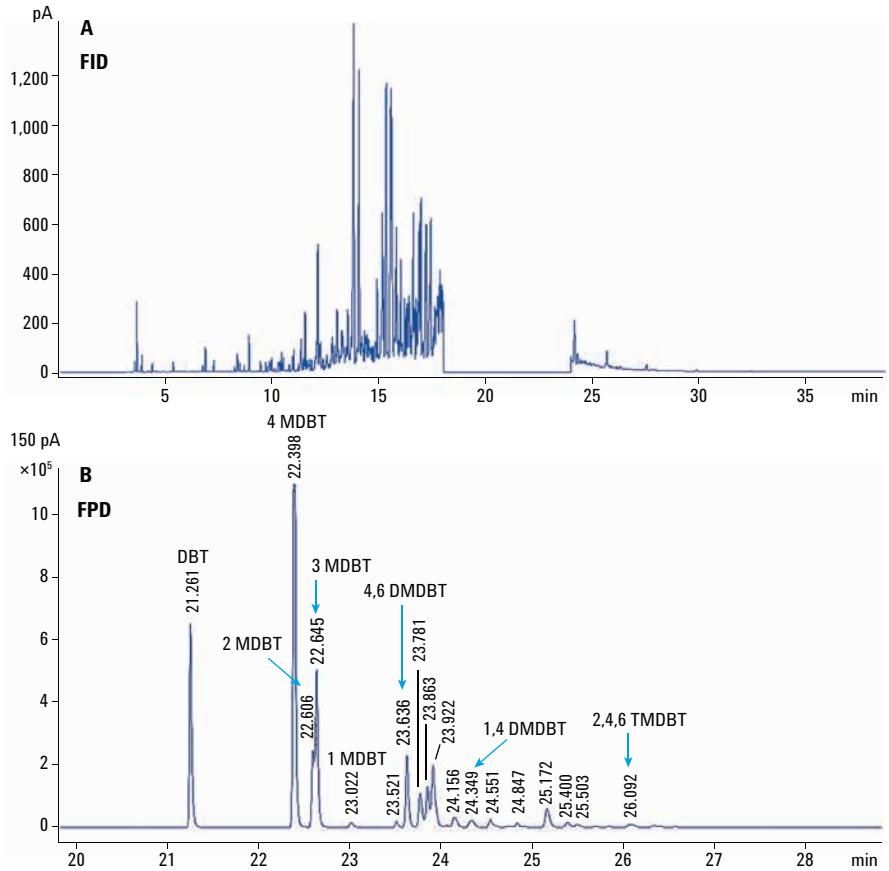


Figure 4. Analysis of substituted Dibenzothiophenes in LCO1 using a CFT Deans switch system and an Agilent 7890B Series GC FPD. Transfer line temperature: 350 °C, FPD emission block temperature: 150 °C. Column 1: 30 m × 0.25 mm, 0.25 µm HP-1ms, Column 2: 30 m × 0.25 mm, 0.15 µm DB-17HT. Deans cut 18 to 24 minutes.

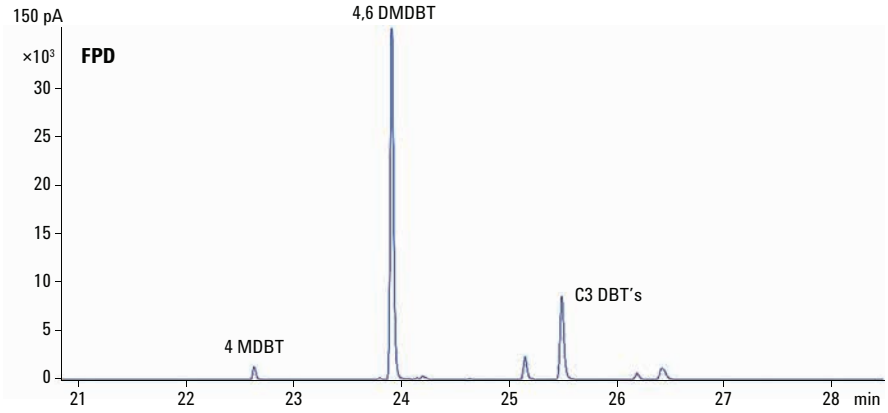


Figure 5. FPD chromatogram of sample LCO2 showing lower levels of dibenzothiophenes. Deans cut: 18 to 24 minutes.

Cracked Gas Oil

As is the case for many CFT devices such as purged unions and purged splitters, the Deans switch can be operated in a backflush mode. Therefore Deans heart cutting and backflushing can be combined in a single analysis. A GC method was developed that incorporates both of these features allowing injection of feedstocks with final carbon numbers of over 50. The gas oil used was first diluted 5 to 1 in toluene prior to injection. Typically, backflush will be programmed to occur at C30 or less to protect the column set and avoid the need for long runs or high tempeature bakeouts. Figure 6 shows the FID chromatogram to illustrate the timing of the heart cut and backflush. An FCC feed, such as the sample used, contains a significant amount of sulfur and shows a very complex distribution of higher molecular sulfur compounds especially in the boiling point ranges selected for this heart cut. This is evident in Figure 7. Benzonaphthothiophenes compounds may also be present in this fraction. Quenching is more likely to occur in this range given the increased coelution possibility. However, a number of compounds can be identified from retention times as shown in Figure 8 where the heart cut is 20 to 24 minutes. Such distributions can be useful to study the effect of steric hendrance caused by alkyl substitution [4]

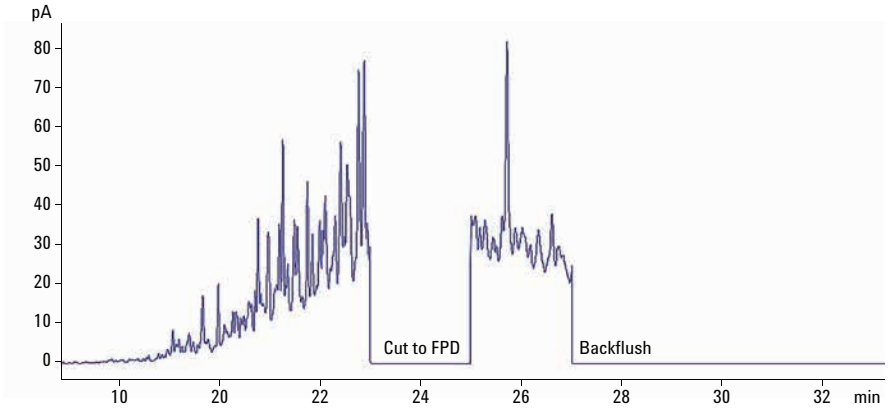


Figure 6. FID chromatogram of a cracked gas oil. Deans cut at 23 to 25 minutes and backflush beginning at 27 minutes are clearly visible.

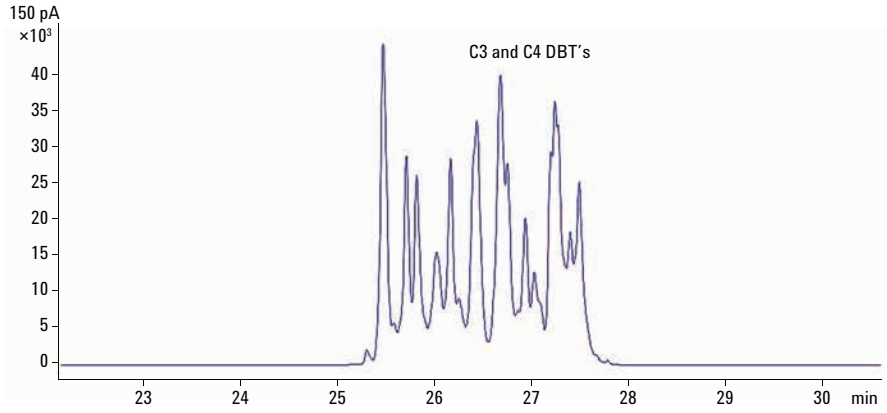


Figure 7. FPD 23 to 25 minute heart cut showing distribution of C3 and C4 alkyl dibenzothiophenes. FPD temperature: 360 °C.

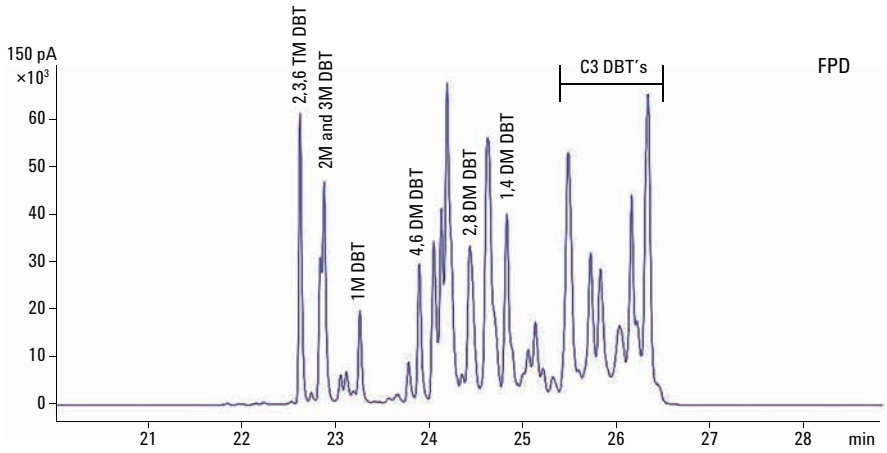


Figure 8. FPD 20 to 24 minute heart cut showing distribution of C2 and C3 alkyl dibenzothiophenes.

Conclusion

The new Flame Photometric Detector available on the Agilent 7890B Series GC is capable of operating at 400 °C which enables a new range of applications particularly for sulfur analysis of fuels, distillates, and feedstocks. To maximize selectivity and minimize coelution, a 2D separation system was used. Heart cuts were made from a nonpolar HP-1 or DB-1 column to a midpolar DB-17HT column. However, other column combinations can certainly be used as desired. CFT enables the Deans switch to be used in a backflush mode. Using backflush with the Deans switch allows heavy distillates and feedstocks with carbon numbers over C50 to be analyzed without damaging the column set with temperatures above 350 °C. Also, runtimes can be kept short with backflush of the heavy fraction. The system can successfully determine the distribution of alkyl dibenzothiophenes in a wide variety of distillates, fuels, and feedstocks.

References

1. X. Ma, K. Sakanishi, I. Mochida, "Hydrodesulfurization Reactiivities of Various Sulfur Compounds in Diesel Fuel", *Ind. Eng. Chem. Res*. 1994, 33, 218-222.

2. S. Shin, H. Yang, K. Sakanishi, I. Mochida, D. Grudoski, J. Shinn, "Inhibition and Deactivaton in Staged Hydrodenitrogenation and Hyudrodesulfurization of Medium Cycle Oil over NiMoS/Al2O3 Catalyst", *Applied Catalysis A: General* 205 ,2001, 101-108

3. V. Thakkar, S. Abdo, V. Gembicki, J. Mc Gehee, "LCO Upgrading, A Novel Approach for Greater Added Value and Improved Returns", UOP LLC, Des Plaines, III, 2005.

4. X. Ma, K. Sakanishi, I. Mochida, "Hydrodesulfurization Reactivities of Various Sulfur Compounds in Vacuum Gas Oil", *Ind. Eng. Chem. Res.*, 1996, 35, 2487-2494.

For More Information

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

www.agilent.com/chem

Printed in the USA
January 28, 2013
5991-1752EN

Agilent Technologies

CLEARLY BETTER INFORMED

Keep current with what's happening in the energy and chemical industries with Agilent Information Pipeline. In each issue, you'll find the latest product news, as well as timely applications and industry developments.

Subscribe now at **agilent.com/chem/pipeline-contactus**

For More Information

Subscribe to Agilent Information Pipeline eNewsletter:
agilent.com/chem/pipeline-contactus

Learn more:
agilent.com/chem/energy

Buy online:
agilent.com/chem/store

Find an Agilent customer center in your country:
agilent.com/chem/contactus

U.S. and Canada
1-800-227-9770
option 3, then option 3 again
agilent_inquiries@agilent.com

In other countries, please call your local Agilent Representative or Agilent Authorized Distributor – visit
agilent.com/chem/contactus

Printed in the USA, December 4, 2013
5991-3592EN

Agilent Technologies