APPLICATIONS

RESTEK

Update . . . >2015

re-published by Chromtech Jan 2016

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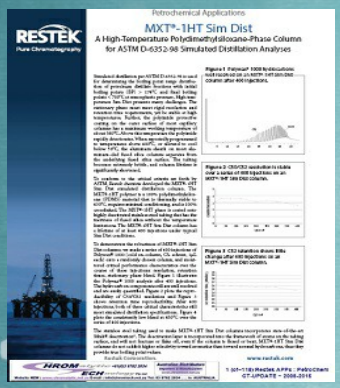

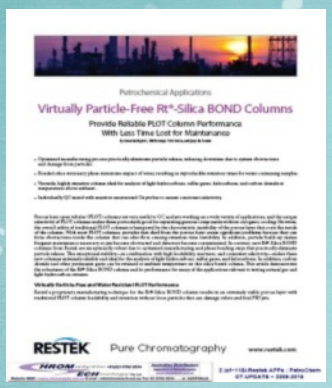

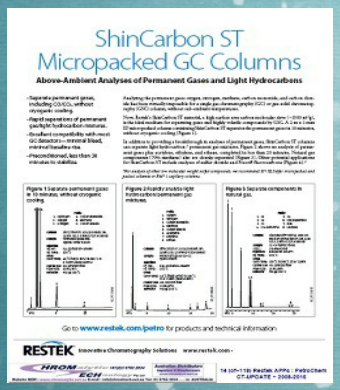

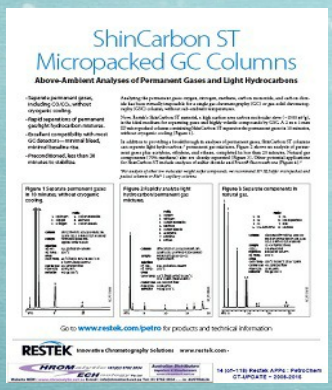

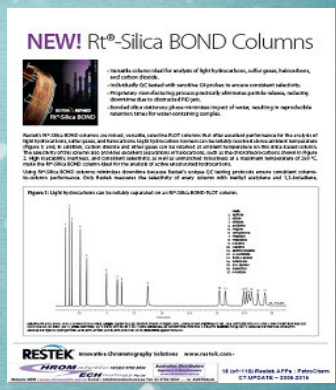

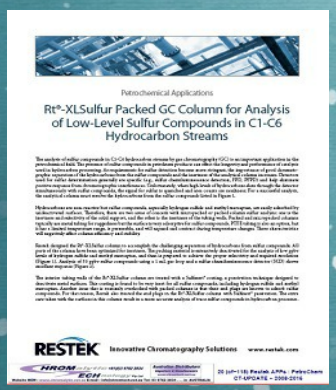

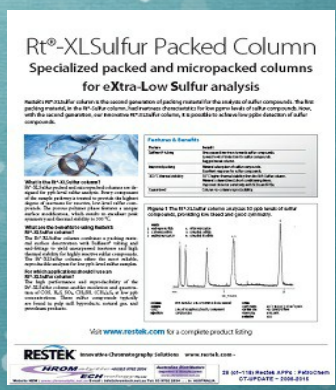

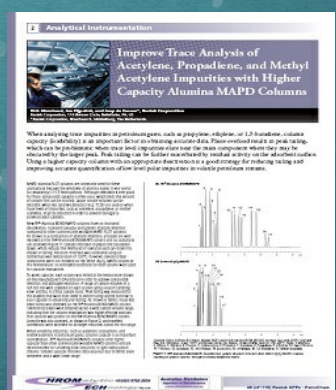

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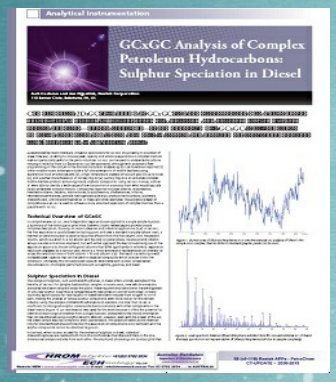

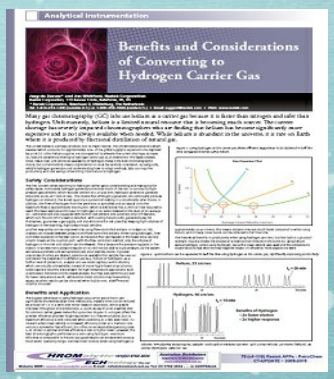

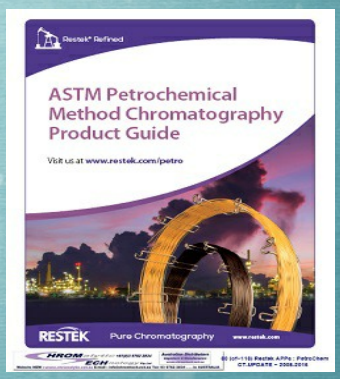

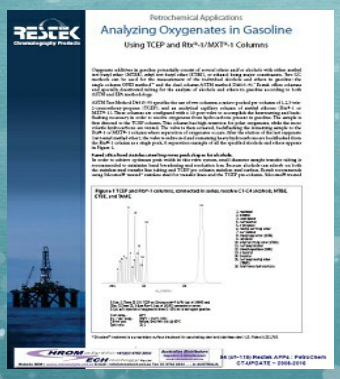

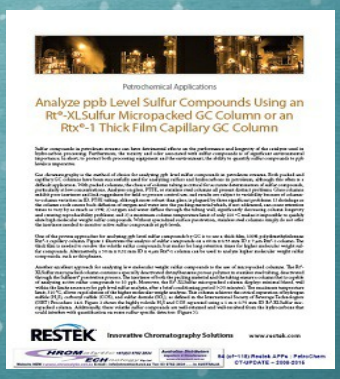

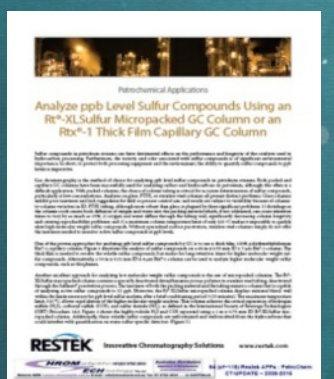

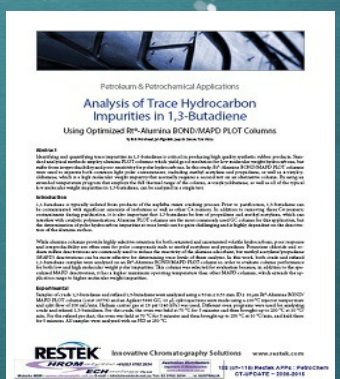

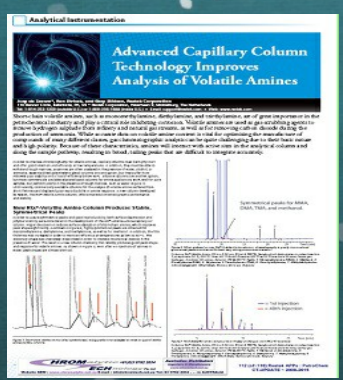

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RESTEK
Pure Chromatography

MXT®-1HT Sim Dist

A High-Temperature Polydimethylsiloxane-Phase Column for ASTM D-6352-98 Simulated Distillation Analyses

Simulated distillation per ASTM D-6352-98 is used for determining the boiling point range distribution of petroleum distillate fractions with initial boiling points (BP) > 174°C and final boiling points < 700°C at atmospheric pressure. High temperature Sim Dist presents many challenges. The stationary phase must meet rigid resolution and retention time requirements, yet be stable at high temperatures. Further, the polyimide protective coating on the outer surface of most capillary columns has a maximum working temperature of about 380°C. Above this temperature the polyimide rapidly deteriorates. When repeatedly programmed to temperatures above 400°C, or allowed to cool below 50°C, the aluminum sheath on most aluminum-clad fused silica columns separates from the underlying fused silica surface. The tubing becomes extremely brittle, and column lifetime is significantly shortened.

To conform to the critical criteria set forth by ASTM, Restek chemists developed the MXT®-1HT Sim Dist simulated distillation column. The MXT®-1HT polymer is a 100% polydimethylsiloxane (PDMS) material that is thermally stable to 430°C, requires minimal conditioning, and is 100% crosslinked. The MXT®-1HT phase is coated onto highly deactivated stainless steel tubing that has the inertness of fused silica without the temperature limitations. The MXT®-1HT Sim Dist column has a lifetime of at least 400 injections under typical Sim Dist conditions.

To demonstrate the robustness of MXT®-1HT Sim Dist columns, we made a series of 400 injections of Polywax® 1000 (cold on-column, CS_2 solvent, 1µL each) onto a randomly chosen column, and monitored critical performance characteristics over the course of these injections: resolution, retention times, stationary phase bleed. Figure 1 illustrates the Polywax® 1000 analysis after 400 injections. The hydrocarbon components still are well resolved and are easily quantified. Figure 2 plots the reproducibility of C50/C52 resolution and Figure 3 shows retention time reproducibility. After 400 injections, both of these critical characteristics still meet simulated distillation specifications. Figure 4 plots the consistently low bleed at 430°C over the series of 400 injections.

Figure 1 Polywax® 1000 hydrocarbons well resolved on an MXT®-1HT Sim Dist column after 400 injections.

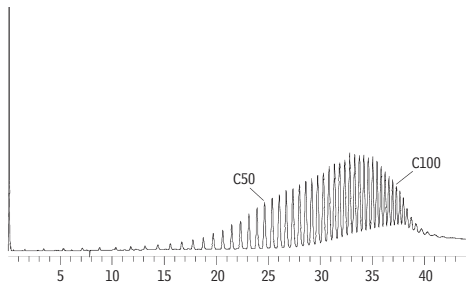


Figure 2 C50/C52 resolution is stable over a series of 400 injections on an MXT®-1HT Sim Dist column.

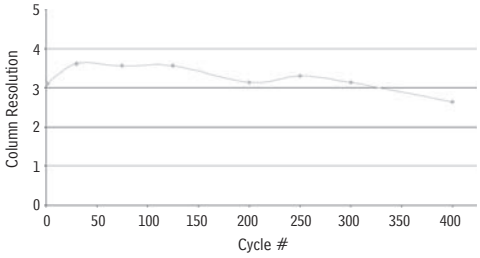
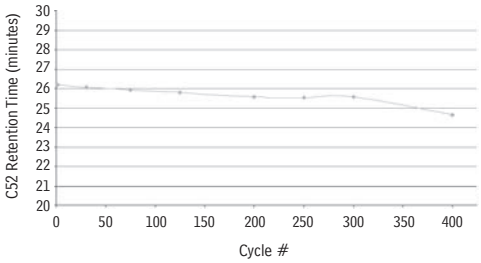


Figure 3 C52 retention shows little change after 400 injections on an MXT®-1HT Sim Dist column.



The stainless steel tubing used to make MXT®-1HT Sim Dist columns incorporates state-of-the-art Siltek® deactivation*. The deactivation layer is incorporated into the framework of atoms on the tubing surface, and will not fracture or flake off, even if the column is flexed or bent. MXT®-1HT Sim Dist columns do not exhibit higher selectivity toward aromatics than toward normal hydrocarbons, thus they provide true boiling point values.

Petrochemical Applications

Virtually Particle-Free Rt®-Silica BOND Columns

Provide Reliable PLOT Column Performance With Less Time Lost for Maintenance

By Amanda Rigdon, Bill Bromps, Tom Vezza, and Jaap de Zeeuw

- Optimized manufacturing process practically eliminates particle release, reducing downtime due to system obstructions and damage from particles.
- Bonded silica stationary phase minimizes impact of water, resulting in reproducible retention times for water-containing samples.
- Versatile, highly retentive column ideal for analysis of light hydrocarbons, sulfur gases, halocarbons, and carbon dioxide at temperatures above ambient.
- Individually QC tested with sensitive unsaturated C4 probes to ensure consistent selectivity.

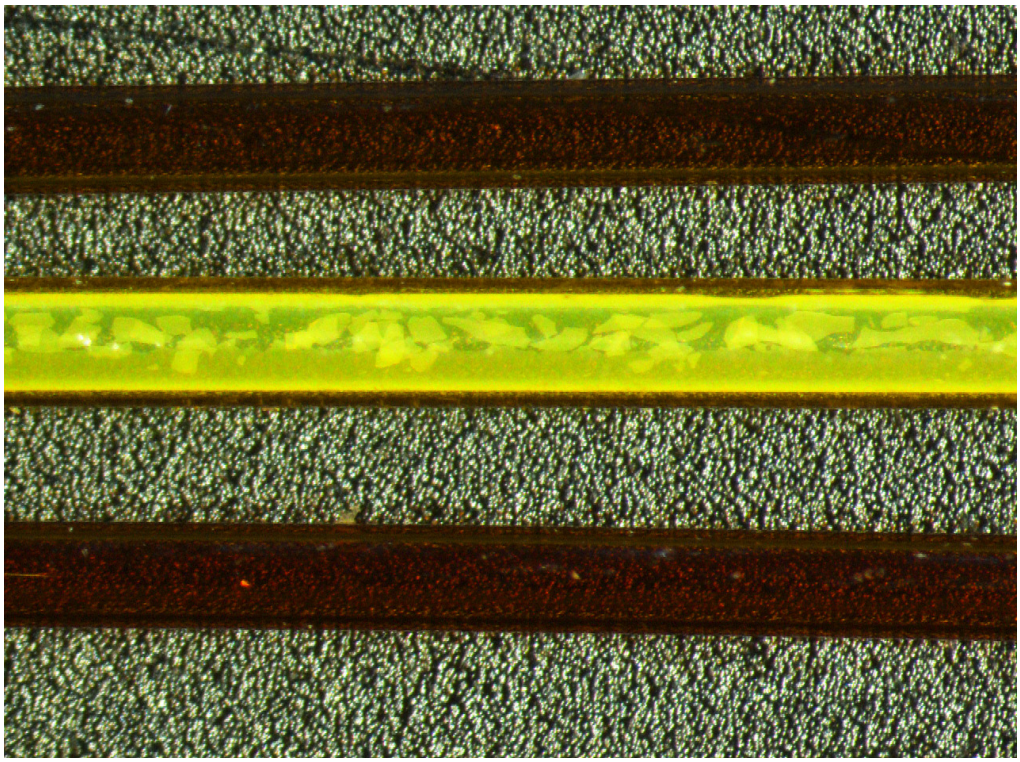
Porous layer open tubular (PLOT) columns are very useful to GC analysts working on a wide variety of applications, and the unique selectivity of PLOT columns makes them particularly good for separating gaseous compounds without cryogenic cooling. However, the overall utility of traditional PLOT columns is hampered by the characteristic instability of the porous layer that coats the inside of the column. With most PLOT columns, particles that shed from the porous layer create significant problems because they can form obstructions inside the column that can alter flow, causing retention time instability. In addition, particle build-up makes frequent maintenance necessary as jets become obstructed and detectors become contaminated. In contrast, new Rt®-Silica BOND columns from Restek are exceptionally robust due to optimized manufacturing and phase bonding steps that practically eliminate particle release. This exceptional stability—in combination with high loadability, inertness, and consistent selectivity—makes these new columns extremely reliable and ideal for the analysis of light hydrocarbons, sulfur gases, and halocarbons. In addition, carbon dioxide and other permanent gases can be retained at ambient temperature on this silica-based column. This article demonstrates the robustness of the Rt®-Silica BOND column and its performance for many of the applications relevant to testing natural gas and light hydrocarbon streams.

Virtually Particle-Free and Water Resistant PLOT Performance

Restek's proprietary manufacturing technique for the Rt®-Silica BOND column results in an extremely stable porous layer with traditional PLOT column loadability and retention without loose particles that can damage valves and foul FID jets.

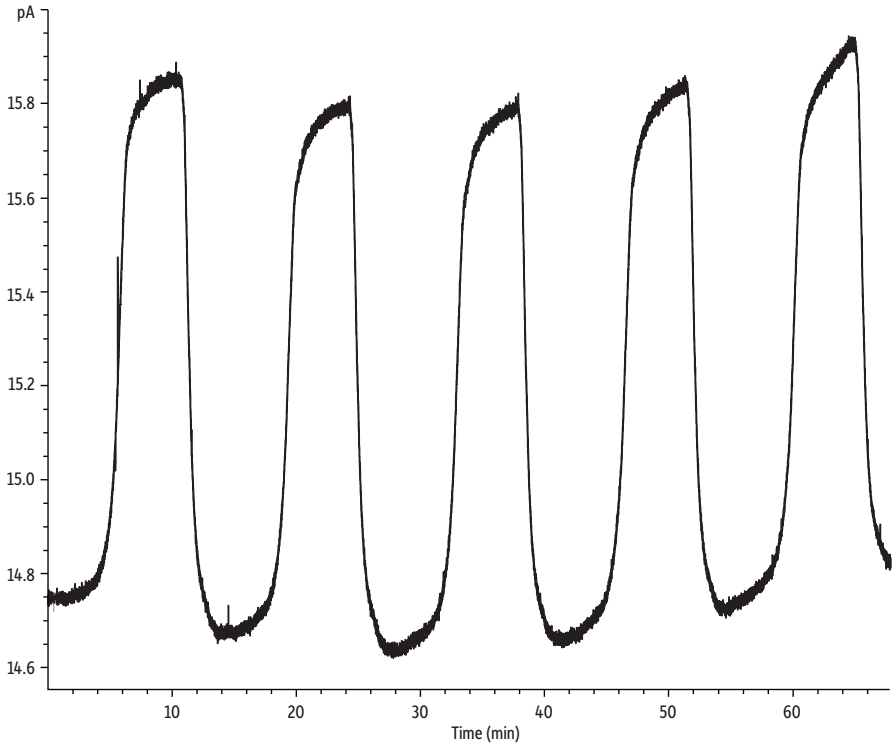
Figure 1 shows a magnified picture of three fused silica columns. The middle column is a traditionally-manufactured PLOT column, the bottom column is a wall-coated open tubular column, and the top column is an Rt®-Silica BOND PLOT column. Note the uneven layer of particles on the middle column, as well as areas where the particles have completely detached from the column wall; this causes irregularities in the internal diameter of the column that can cause retention time instability. In comparison, the Rt®-Silica BOND column looks identical to the wall-coated open tubular column, with no visible shedding of particles or peeling of the coating layer. While the Rt®-Silica BOND column does contain a porous layer, the structure of this layer is extremely fine and well-adhered to the column wall, ensuring virtually particle-free operation over the lifetime of the column.

Figure 1: Traditional PLOT columns (middle) have an uneven coating of particles that can shed, fouling instrument parts. Rt®-Silica BOND columns (top) have a very fine porous layer with no visible particles and look very similar to wall-coated open tubular columns (bottom).



The manufacturing process used to make Rt®-Silica BOND columns results in a PLOT column with high selectivity, retention, and capacity without the particle shedding associated with conventional PLOT columns. This provides improved column robustness and less downtime for maintenance. The particle-free nature of this column is evidenced by a particle-generation experiment in which a column was temperature and pressure ramped multiple times. Changes in temperature cause changes in pressure, which result in particle shedding in traditional PLOT columns. Free particles generate large spikes when they hit the flame ionization detector (FID), interfering with quantification. In addition, the particles themselves can obstruct FID jets and damage valves. Note that no large particle spikes were generated when this experiment was carried out on a brand new Rt®-Silica BOND column (Figure 2).

Figure 2: The Rt®-Silica BOND PLOT column shows no large particle spikes, even with temperature and pressure variation.

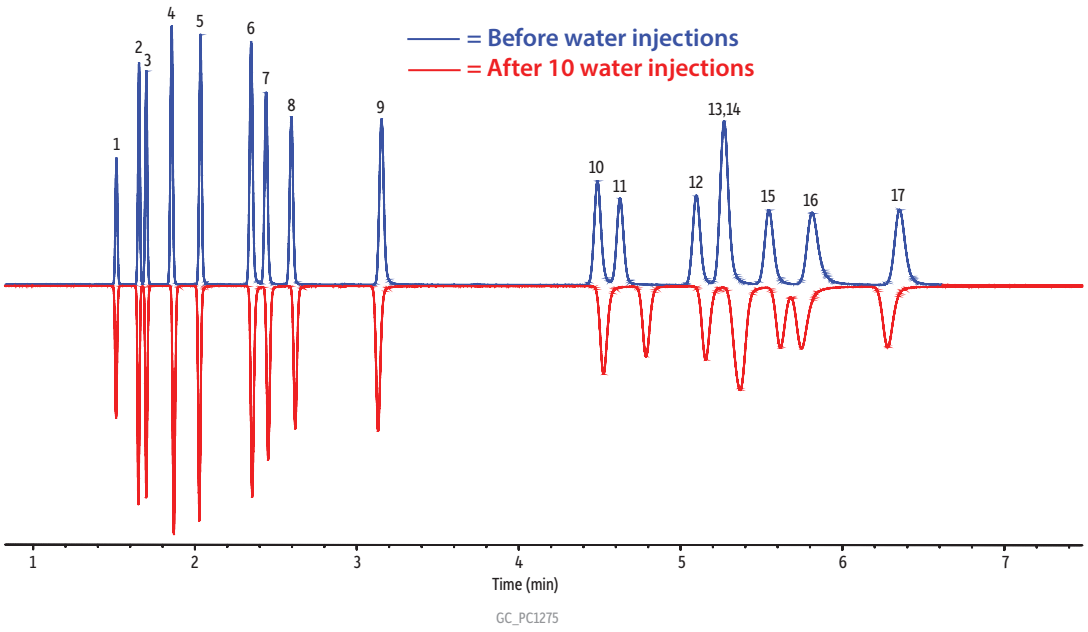


Column	Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785)
Injection	split (split ratio 35:1)
Liner:	Sky® 2.0 mm ID straight inlet liner (cat.# 23313.1)
Inj. Temp.:	250 °C
Oven	
Oven Temp.:	50 °C to 250 °C at 35 °C/min (hold 5 min) to 50 °C at 70 °C/min
Carrier Gas	He, constant flow
Linear Velocity:	114 cm/sec
Detector	FID @ 260 °C
Make-up Gas Flow Rate:	50 mL/min
Make-up Gas Type:	N_2
Hydrogen flow:	40 mL/min
Air flow:	400 mL/min
Data Rate:	10 Hz
Instrument	Agilent 7890A GC

Another benefit of Restek's proprietary manufacturing process for the Rt®-Silica BOND column is that the stationary phase of the column is composed almost entirely of silica. While silica retains water, it does not adsorb it. Some PLOT materials adsorb water, which changes the retention and selectivity of the column. After analyzing samples containing water, these PLOT columns require extensive thermal conditioning (bakeout) to return their original retention and selectivity. Figure 3 shows a mixture of saturated and unsaturated hydrocarbons analyzed on the Rt®-Silica BOND column both before exposure to water and then immediately after 10 large volume water injections. Even under these experimental conditions of extreme overwetting, the retention and selectivity of the column remain very similar and under normal use conditions would be effectively identical. This consistent water-resistant performance allows analysts to save time by minimizing maintenance and eliminating the extensive bakeout periods associated with other PLOT columns.

Figure 3: Repeated water injections have minimal impact on Rt®-Silica BOND column selectivity and retention, meaning, water-containing samples can be analyzed without requiring time-consuming thermal reconditioning.

	Peaks	t_R (min)		Peaks	t_R (min)
1.	Methane	1.514	10.	1-Butene	4.485
2.	Ethane	1.653	11.	Methyl acetylene	4.625
3.	Ethylene	1.698	12.	*trans*-2-Butene	5.096
4.	Acetylene	1.854	13.	1,3-Butadiene	5.267
5.	Propane	2.032	14.	Isobutylene	5.267
6.	Cyclopropane	2.345	15.	*cis*-2-Butene	5.544
7.	Propylene	2.438	16.	iso-Pentane	5.811
8.	Propadiene	2.594	17.	*n*-Pentane	6.352
9.	*n*-Butane	3.151			



Column	Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785)
Sample	Custom hydrocarbon gas standard
Conc.:	1 mole percent in nitrogen
Injection	
Inj. Vol.:	15 µL split (split ratio 35:1)
Liner:	Sky® 2 mm ID straight inlet liner (cat.# 23313.1)
Inj. Temp.:	250 °C
Oven	
Oven Temp.:	120 °C (hold 25 min)
Carrier Gas	He, constant flow
Linear Velocity:	40 cm/sec
Detector	FID @ 260 °C
Make-up Gas	
Flow Rate:	50 mL/min
Make-up Gas	
Type:	N_2
Hydrogen flow:	40 mL/min
Air flow:	400 mL/min
Data Rate:	10 Hz
Instrument	Agilent 7890A GC
Notes	The hydrocarbon mix was first analyzed to generate a baseline reference; then, ten separate 10 µL injections of water were made 1 minute apart using the same method. After the final water injection, the hydrocarbon mix was analyzed again to compare the chromatography before and after the water injections.

Versatile Column for Many Applications

The new Rt®-Silica BOND column combines the retention, capacity, and selectivity of traditional PLOT columns with virtually particle-free, water-resistant performance. The bonded silica surface provides excellent retention for light hydrocarbons (Figure 4), permanent gases, and halocarbons, allowing for easy analysis of impurities in light hydrocarbon streams. In addition to light hydrocarbon analysis, the Rt®-Silica BOND column is especially selective for sulfur compounds in hydrocarbon streams. Figures 5 and 6 illustrate good separation of sulfur compounds in propane and butane, respectively.

Figure 4: Saturated and unsaturated hydrocarbons are resolved and retained well on the Rt®-Silica BOND column.

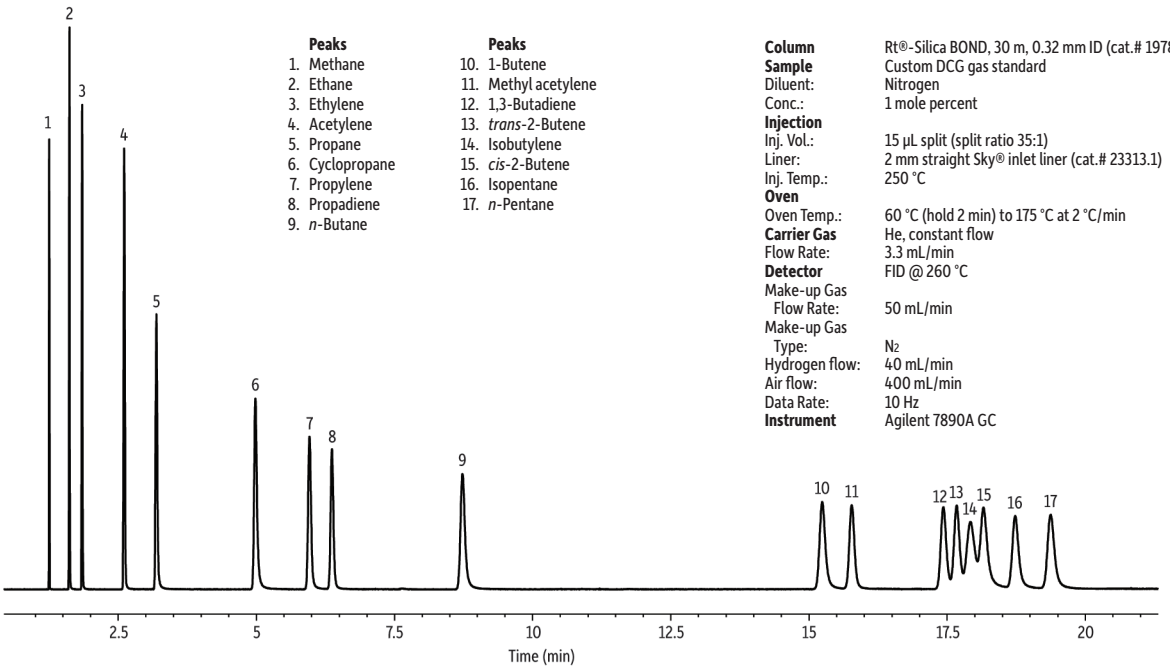


Figure 5: Sulfur Compounds in Propane

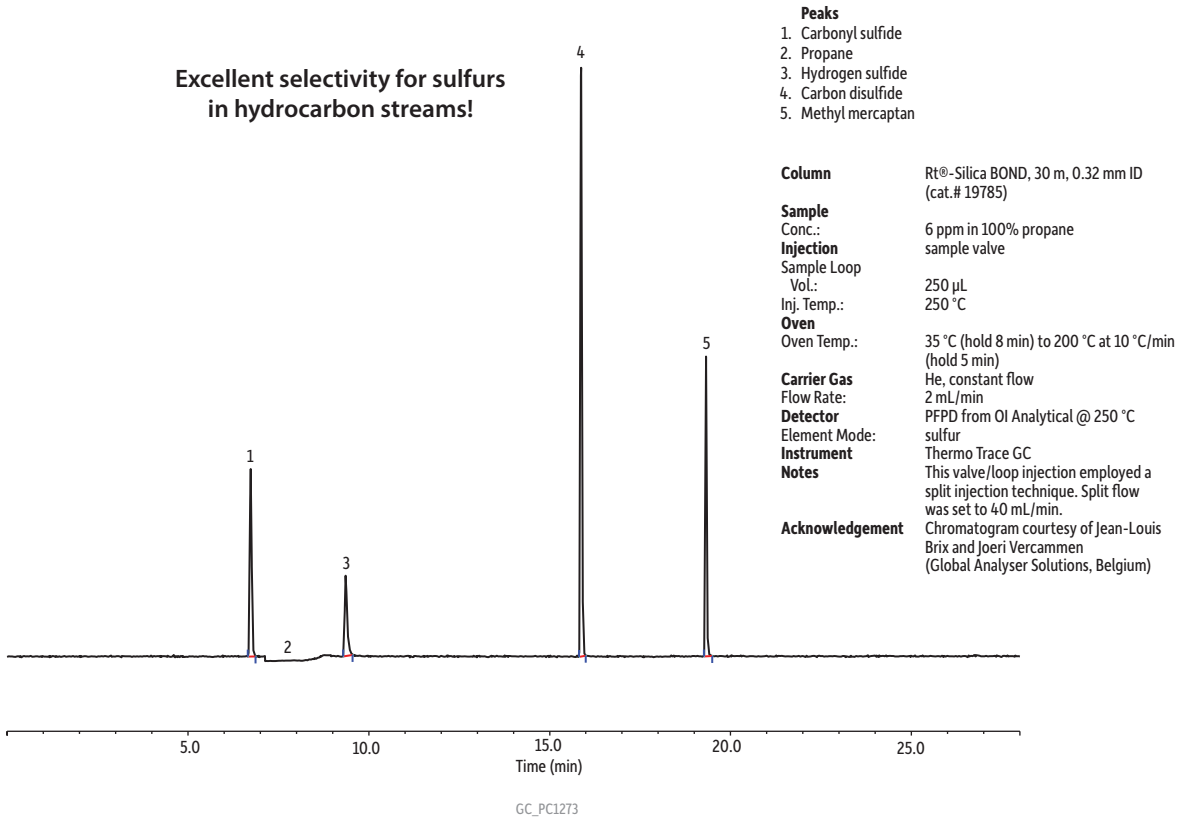
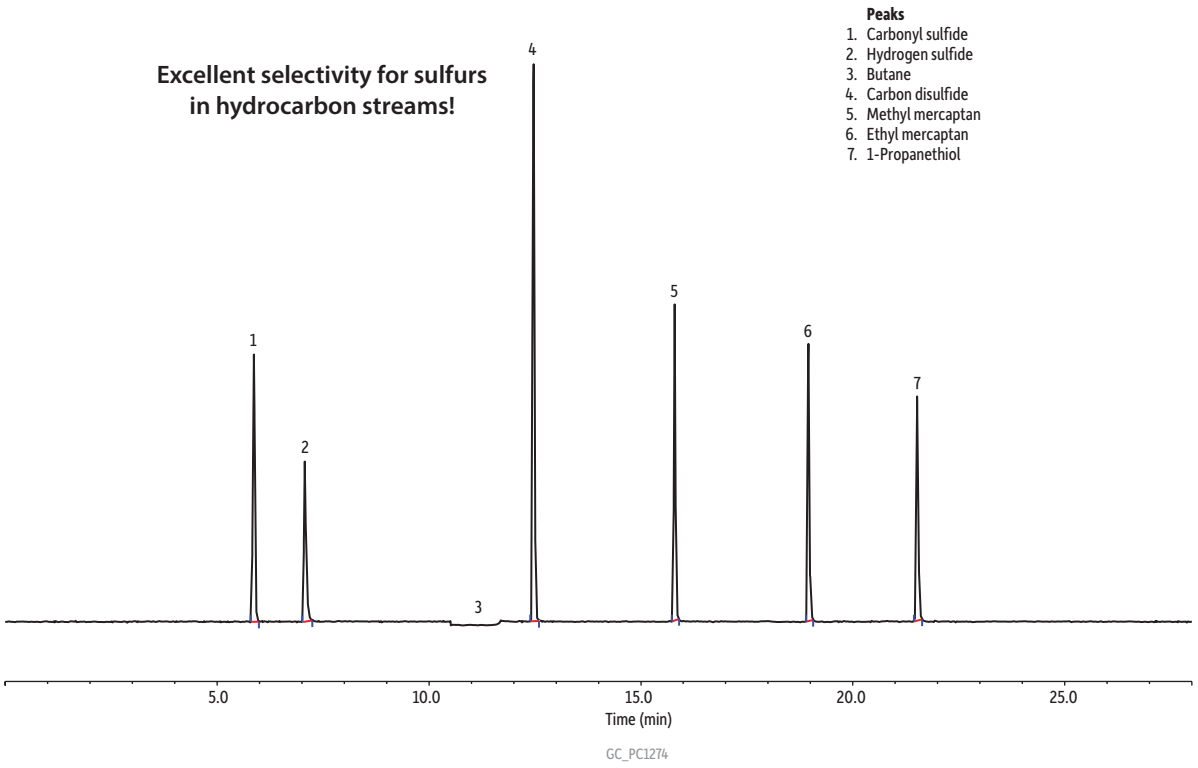


Figure 6: Sulfur Compounds in Butane

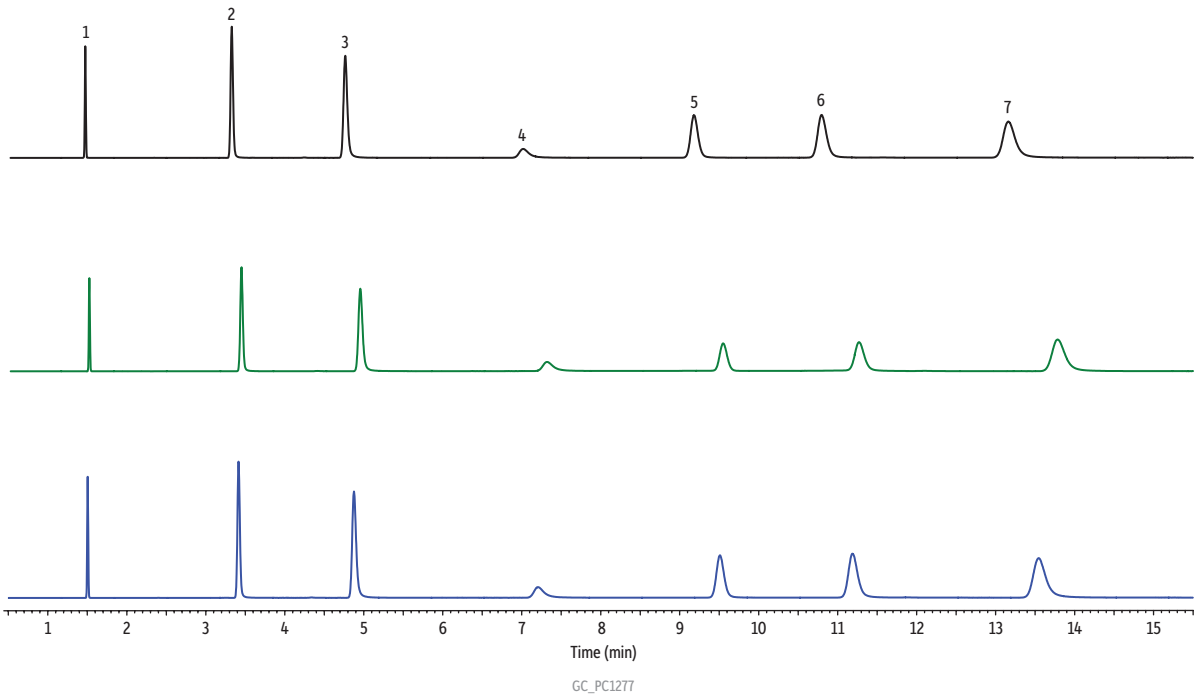


Column	Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785)	**Carrier Gas**	He, constant flow
Sample		Flow Rate:	2 mL/min
Conc.:	6 ppm in 100% butane	**Detector**	PFPD from OI Analytical @ 250 °C
Injection	sample valve	Element Mode:	sulfur
Sample Loop Vol.:	250 µL	**Instrument**	Thermo Trace GC
Inj. Temp.:	250 °C	**Notes**	This valve/loop injection employed a split injection technique. Split flow was set to 40 mL/min.
Oven		**Acknowledgement**	Chromatogram courtesy of Jean-Louis Brix and Joeri Vercammen (Global Analyser Solutions, Belgium)
Oven Temp.:	40 °C (hold 5 min) to 200 °C at 10 °C/min (hold 8 min)		

Rigorous QC Testing Ensures Ultimate Column-to-Column Reproducibility

While column-to-column reproducibility is a must for all analysts, it is especially important in valve, backflushing, or column-switching applications. With this in mind, a special QC test was designed for the Rt®-Silica BOND column. Performance parameters, including efficiency, selectivity (RI), retention (k), and inertness are evaluated for each and every column. While the QC tests from some manufacturers include some of these parameters, the compounds used to measure RI are not well-retained and not sensitive to changes in column selectivity. The RI compounds used in the QC test for the Rt®-Silica BOND are 1,3-butadiene and methyl acetylene, which are not only very sensitive probes for selectivity, but are of high interest to many analysts. Additionally, while some commercially available PLOT columns are not evaluated for inertness, Rt®-Silica BOND column inertness is measured with propylene, which is a more active, unsaturated hydrocarbon. This QC testing ensures the highest level of column-to-column reproducibility available in the industry for PLOT columns. Figure 7 shows QC results from three separate lots of Rt®-Silica BOND columns.

Figure 7: Rigorous QC testing ensures column-to-column reproducibility.



Peaks
1. Methane
2. Propylene
3. *n*-Butane
4. 1,2-Dichlorotetrafluoroethane (CFC-114)
5. Methyl acetylene
6. 1,3-Butadiene
7. *n*-Pentane

Column	Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785)
Sample	Custom gas standard
Diluent:	Nitrogen
Conc.:	1 mole percent each component
Injection	
Inj. Vol.:	15 µL split (split ratio 35:1)
Liner:	Sky® 2.0 mm ID straight inlet liner (cat.# 23313.1)
Inj. Temp.:	250 °C
Oven	
Oven Temp.:	90 °C (hold 20 min)
Carrier Gas	H_2, constant flow
Linear Velocity:	38 cm/sec
Detector	FID @ 260 °C
Instrument	Agilent/HP6890 GC

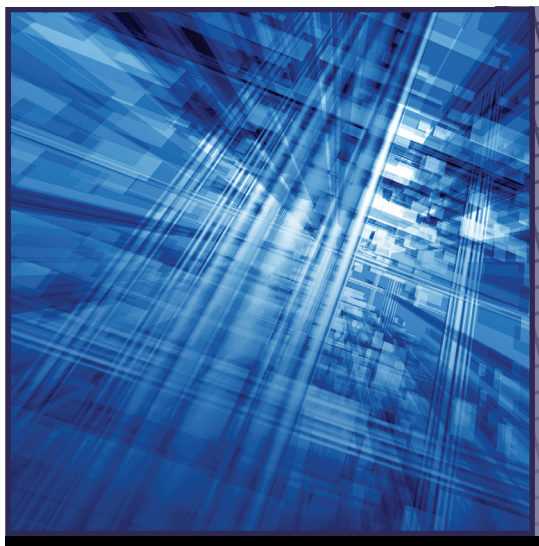
Conclusion

The Rt®-Silica BOND column gives you the retention and capacity you need from PLOT columns, along with virtually particle-free and water-resistant operation. The combination of rugged manufacturing and rigorous QC testing ensures every Rt®-Silica BOND column will provide optimal performance and reliable results for every analysis, while minimizing downtime due to maintenance from particle shedding or time-consuming bakeouts due to water contamination. The column's unique selectivity makes it ideal for analysis of hydrocarbons, halogenated compounds, and sulfur gases.

Pure Chromatography **www.restek.com**

Lit. Cat.# PCAR2069-UNV

Questions about this or any other Restek® product?
Contact us or your local Restek® representative (www.restek.com/contact-us).



Using Micropacked GC Columns for Analyzing Volatiles in Light Hydrocarbon Streams

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Separation of light hydrocarbons and volatile compounds can be done very effectively with adsorption chromatography. Using highly retentive adsorbents in packed columns, unique separations can be obtained at higher temperatures. Additionally, adsorbents are difficult to destroy, resulting in long column lifetimes. Most analysts still employ traditional packed columns for light hydrocarbon analysis, but many adsorbents are also available in micropacked and porous layer open tubular (PLOT) column formats. Recent advances in PLOT column technology indicate that they are a better option when greater efficiency is required, while packed columns still are preferred when higher sample loadability is needed. While both traditional packed and PLOT columns can be used effectively, micropacked columns offer intermediate performance and are a good alternative when both efficiency and sample loadability are desired.

Advantages of Micropacked Columns

Packed columns are made with a wide variety of adsorbent materials, including alumina, molecular sieves, and porous polymers. Columns packed with these adsorbents offer good selectivity and retention for volatile compounds, but they are lower in efficiency than capillary columns. Lower efficiency can lead to broad peaks and less resolution, which can make it difficult to accurately quantify individual analytes in complex mixtures. Many of these adsorbents can also be coated in capillary tubing creating PLOT columns. In PLOT columns, the adsorbent is not packed into the column; instead, it is deposited as a 5–50 µm layer on the internal capillary surface. Since less adsorbent material is used, PLOT columns offer much higher efficiency and better separations can be obtained. However, if greater sample loadability is needed, packed columns are preferred as they are less likely to be overloaded by concentrated samples. Micropacked columns present intermediate characteristics and are a good option for separating components in light hydrocarbon streams.

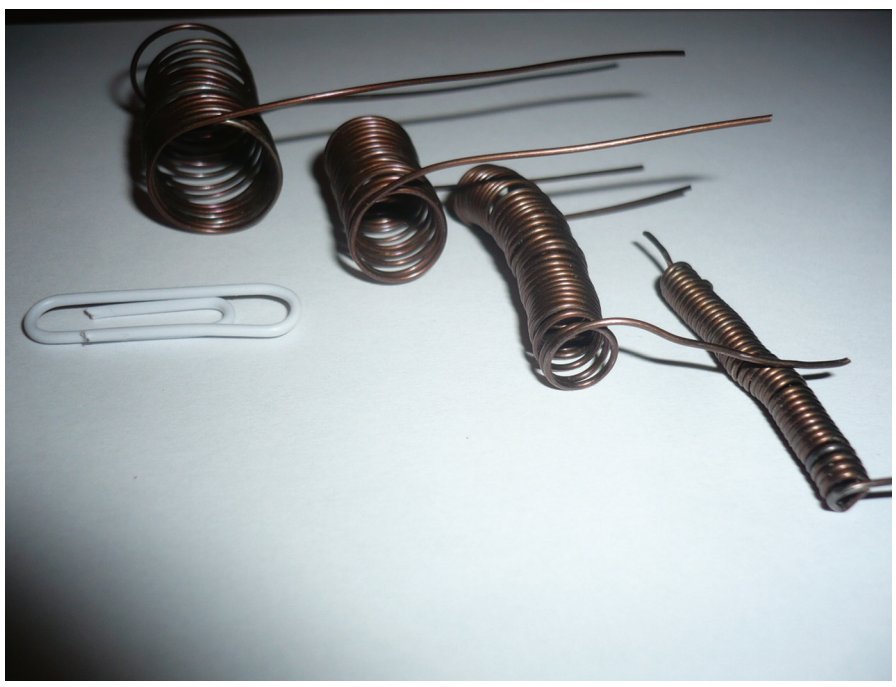


Figure 1: Micropacked columns from Restek can be coiled to fit any GC.

In addition to their balance of efficiency and capacity, micropacked columns are relatively inexpensive, very durable, and easy to install and operate. Micropacked columns from Restek are extremely inert as they are packed in Siltek® treated stainless steel tubing, which can be coiled in extremely small diameters to fit small ovens (Figure 1). In addition, Siltek®-treated, braided-wire end plugs keep packing intact, even under intense pressure surges during valve switching. Standard Restek micropacked columns are 1 meter or 2 meters long and 0.75 mm or 1.00 mm inner diameter (ID). Restek has also recently developed unique 0.53 mm ID micropacked columns, which are available with a variety of adsorbent packings.

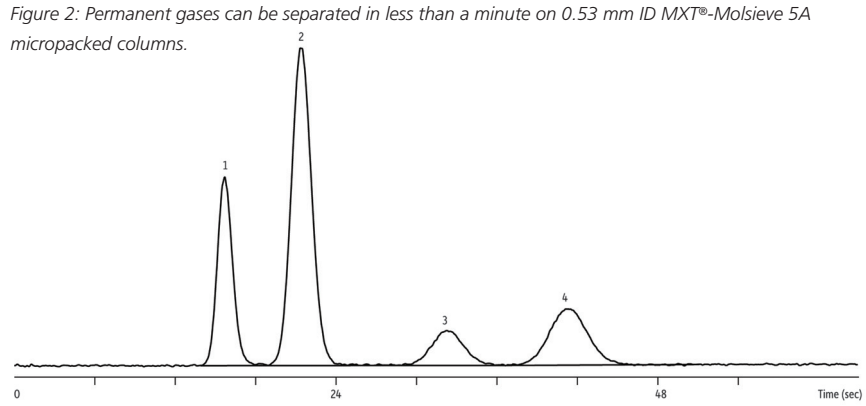
Micropacked Columns for Petrochemical Applications

Molecular sieves and porous polymers are among the most useful adsorbents for petrochemical analyses. For example, permanent gases can be separated to baseline in less than one minute using a 1 m x 0.53 mm MXT®-Molsieve 5A column (Figure 2). The Molsieve 5A adsorbent is highly retentive and selective for gases, so good separation is obtained very quickly and, if greater resolution is desired, this can easily be accomplished by lowering the oven temperature. For example, since the position of carbon monoxide is temperature dependent, it can be moved further away from methane when a lower oven temperature (e.g., 80 °C) is used. Note that 0.53 mm ID MXT® micropacked columns can be installed in any standard capillary instrument using standard 0.8 mm ID ferrules. These columns are operated with flows of 2-5 mL/min and can be used with split injection systems, providing very small injection band broadening.

In addition to molecular sieves, porous polymer adsorbents are also available in a micropacked format. Of the many available types of packing, Rt®-XLSulfur and HayeSep Q adsorbents are among the most interesting for petrochemical testing. The Rt®-XLSulfur is a unique packing designed for ppb level sulfur analysis. This porous polymer phase features a unique surface modification, which results in excellent peak symmetry and thermal stability up to 300 °C. The overlaid sulfur and hydrocarbon chromatograms in Figure 3 show a highly selective separation of light hydrocarbons and sulfur compounds. This is important because even though sulfur-specific detectors are generally used, when high levels of hydrocarbons elute through the detector simultaneously with sulfur compounds, the signal for sulfur is quenched and area counts are nonlinear. Column inertness is also very important as reactive sulfur compounds, such as hydrogen sulfide and methyl mercaptan, are easily adsorbed by undeactivated surfaces, which can result in inaccurate quantification of these catalyst-damaging compounds. Rt®-XLSulfur micropacked columns provide the retention and inertness required for reliable analysis of active sulfur compounds in hydrocarbon streams.

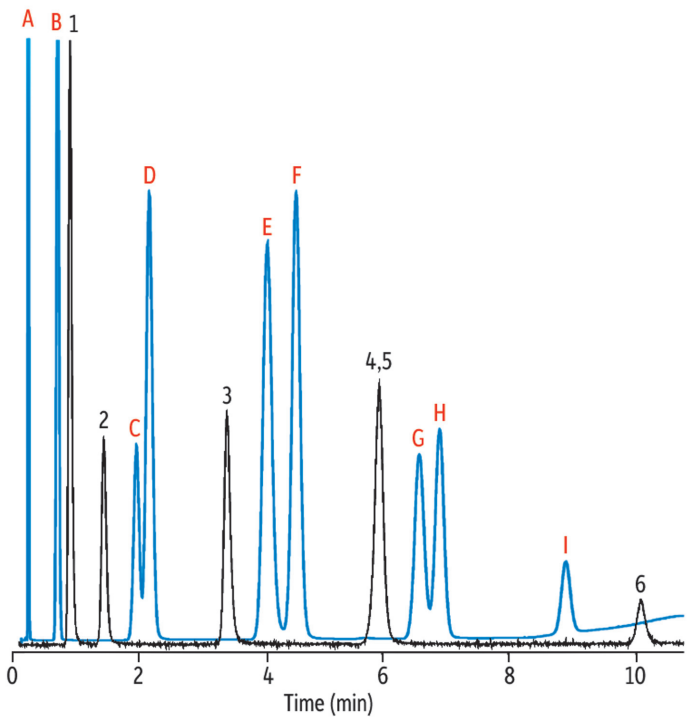
The analysis of solvents on a HayeSep Q micropacked column in Figure 4 provides another example of a successful petrochemical application. Here, a series of solvents was analyzed using GC-FID and the inertness of the Siltek® deactivated tubing allowed even highly polar components, such as alcohols, to be analyzed effectively. In addition to HayeSep Q, HayeSep R, HayeSep S, and HayeSep N packings are also available.

Figure 2: Permanent gases can be separated in less than a minute on 0.53 mm ID MXT®-Molsieve 5A micropacked columns.



Columns: MXT®-Molsieve 5A, 80/100 mesh, 1 m, 0.53 mm ID (cat.# custom); Sample: Permanent gases (2-5% in helium); Injection: 15 µL (split ratio 30:1); Oven: 120 °C, isothermal; Carrier gas: helium, (26 psi, 180 kPa); 1. Oxygen, 2. Nitrogen, 3. Methane, 4. Carbon monoxide.

Figure 3: The Rt®-XLSulfur micropacked column allows accurate low-level quantification of many active sulfur compounds in hydrocarbon streams.

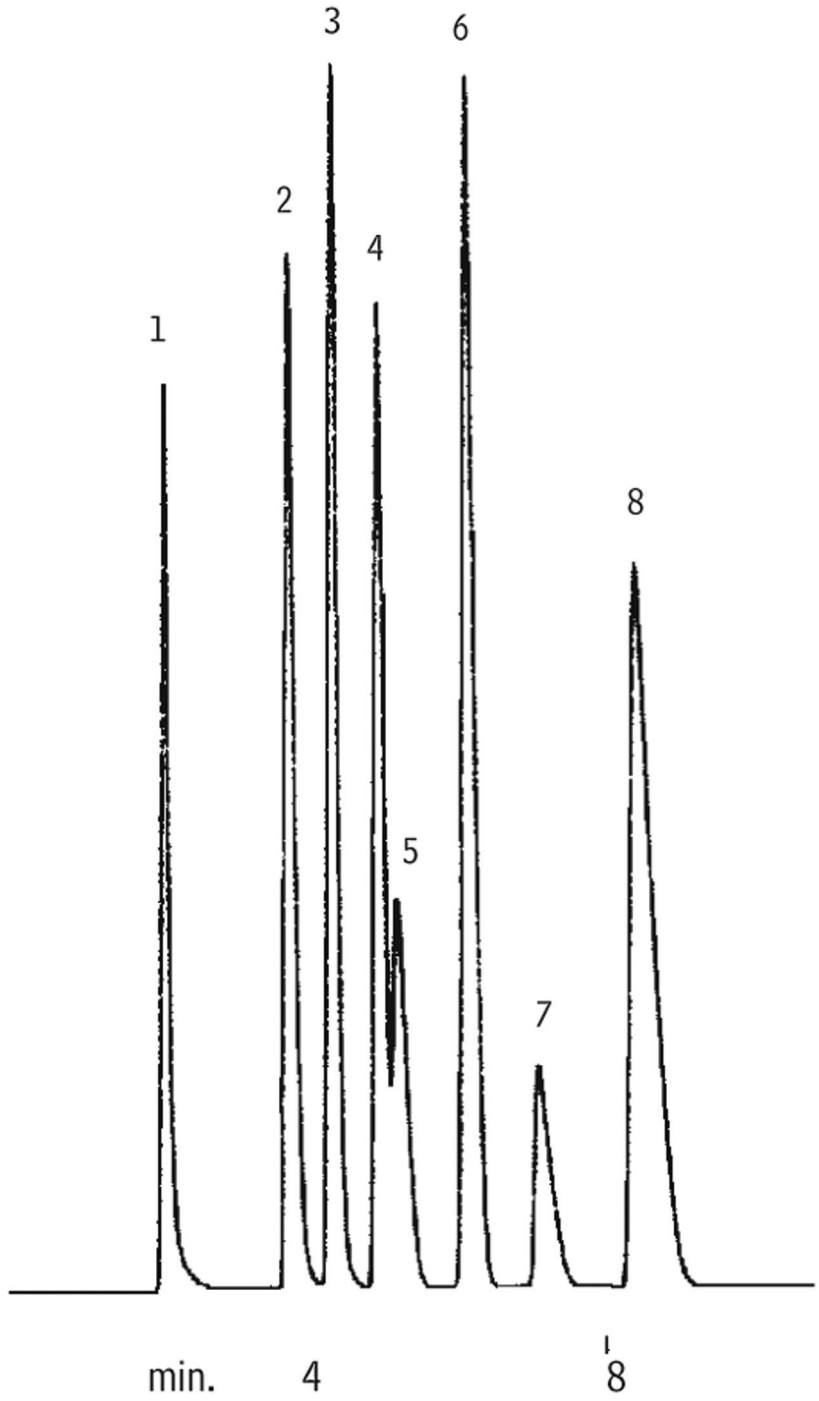


Columns: Rt®-XLSulfur, 1 m, 0.95 mm OD, 0.75 mm ID (cat.# 19806); Sample: sulfur compounds and hydrocarbons, 50 ppb each; Oven: 60 °C to 230 °C at 15 °C/min; Carrier gas: helium, 9 mL/min; Detector: SCD/FID. Sulfur Peaks: 1. Hydrogen sulfide, 2. Carbonyl sulfide, 3. Methyl mercaptan, 4. Ethyl mercaptan, 5. Dimethyl sulfide, 6. Dimethyl disulfide; Hydrocarbon Peaks: A. Methane, B. Ethane, C. Propylene, D. Propane, E. Isobutane, F. Butane, G. Isopentane, H. Pentane, I. Hexane.

Summary

Micropacked GC columns can provide a valuable alternative to traditional packed columns and PLOT columns when intermediate performance is desired. Restek's line of micropacked columns are highly inert and are available with a wide variety of adsorbents. Micropacked columns can provide a useful alternative for petrochemical applications when both high sample loadability and high efficiency are desired. Additionally, the unique 0.53 mm micropacked columns offered by Restek can be used in all standard capillary systems, without any modification of the injector or detector connections.

Figure 4: HayeSep Q micropacked columns are useful for solvents analysis.



Columns: HayeSep® Q, 100/120 mesh, 2 m, 1/16" OD, 1.00 mm ID (cat.# 19017); Sample: Solvent mixture; Injection: 1 µL direct, 200 °C; Oven: 80 °C to 180 °C at 16 °C/min (hold 5 min); Carrier gas: helium, 20 mL/min; Detector: FID, 200 °C. Peaks: 1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. Acetone, 5. Methylene chloride, 6. n-Pentane, 7. Chloroform, 8. n-Hexane.

Stable Sulfur & Mercury Sampling in Refineries

Using Siltek® and Sulfinert® Surface Treated Components

- Reliably sample sulfur and mercury compounds at ppb levels.
- Reduce lab costs—obtain accurate results the first time.
- Detect costly process upsets, improving product yield.

Refinery and natural gas samples often contain trace amounts of sulfur- and mercury-containing compounds, which can interfere with reactions, poison catalysts in petrochemical processes, and damage equipment. Because these compounds quickly react with stainless steel surfaces, accurate determination of these compounds is impossible when samples are collected and stored in untreated sample cylinders. Siltek® and Sulfinert® passivation techniques bond an inert layer into the surface of stainless steel, preventing active compounds from reacting with or adsorbing to the steel.

Accurate Sulfur Sampling

To characterize Sulfinert® surfaces, we tested the stability of 17ppbv standards of sulfur compounds in three Sulfinert® sample cylinders over a 54-hour period. Dimethyl sulfide, which is not adsorbed by stainless steel, was used as an internal standard. The Sulfinert®-treated cylinders were inert to the reactive sulfur compounds over the 54-hour test period (Figure 1). Hydrogen sulfide exhibited greater than 85% recovery; methyl mercaptan, ethyl mercaptan, carbonyl sulfide, and dimethyl disulfide exhibited greater than 90% recovery.

Sulfinert®-treated gas sampling equipment is ideal for collecting and storing samples containing ppb levels of sulfur compounds, such as natural gas or beverage-grade carbon dioxide. Sulfinert® treatment ensures that sulfur compounds or other highly active compounds remain stable during transport from the field to the laboratory.

Stable Mercury Results

Siltek® surface treatment has been used in a wide variety of applications in which an inert surface is of paramount importance. To measure the impact of Siltek® treatment on adsorption of mercury during storage, we compared the performances of 304 grade stainless steel gas sampling cylinders (Swagelok®, Solon OH) with and without Siltek® treatment.

We filled each cylinder with 8µg/m3 of elemental mercury (approximately 1 part per billion) (Spectra Gases, Alpha NJ) and assessed the mercury concentration in each cylinder over time to determine changes in mercury concentration. Detection was achieved by direct interface gas sampling to an atomic adsorption detector. Sample pathway regulator and tubing were Siltek® treated to ensure accurate transfer.

The data in Figure 2 demonstrate that Siltek® treatment provides a stable surface for elemental mercury, and untreated stainless steel does not. Based on these results, we conclude that Siltek® surface treatment for steel or stainless steel components and tubing in CMMS and sorbent tube mercury sampling systems will improve analytical reliability.

Siltek® and Sulfinert® surface treated cylinders and sampling components provide an inert sample path, which prevents adsorption of active compounds and ensures accurate sampling. For more information about these treatments, visit us at www.restekcoatings.com.

Figure 1: Stability of sulfur compounds is remarkable in Sulfinert®-treated cylinders.

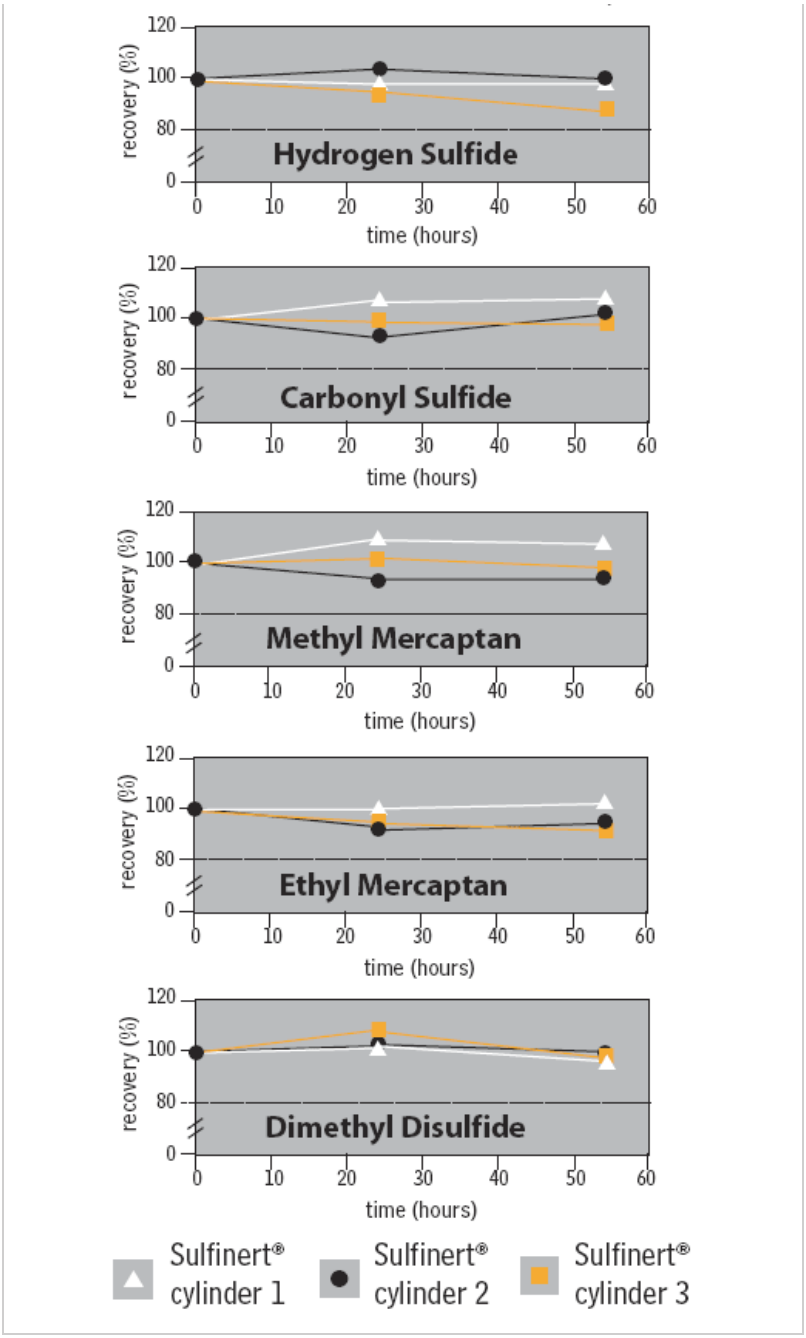
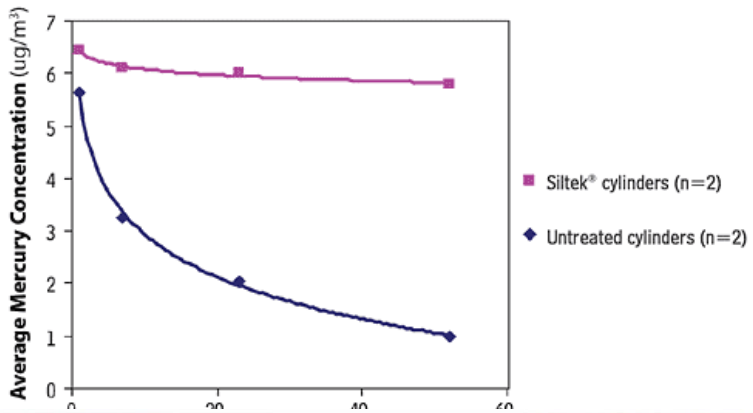


Figure 2: Siltek® treated gas sampling cylinders show very good inertness toward mercury.



Acknowledgement

The authors wish to acknowledge Ted Neeme and Steve Mandel from Spectra Gases for their contributions to this work.

RELATED SEARCHES

sulfur, *mercury*, *passivation*, *siltek*, *sulfinert*, *stability*

ShinCarbon ST Micropacked GC Columns

Above-Ambient Analyses of Permanent Gases and Light Hydrocarbons

- Separate permanent gases, including CO/CO_2, without cryogenic cooling.
- Rapid separations of permanent gas/light hydrocarbon mixtures.
- Excellent compatibility with most GC detectors—minimal bleed, minimal baseline rise.
- Preconditioned, less than 30 minutes to stabilize.

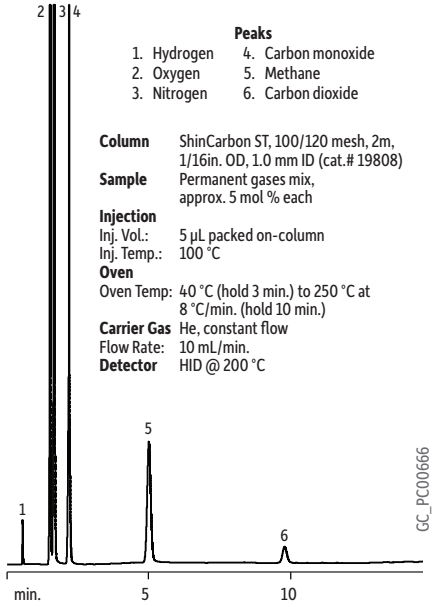
Analyzing the permanent gases oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide has been virtually impossible for a single gas chromatography (GC) or gas-solid chromatography (GSC) column, without sub-ambient temperatures.

Now, Restek's ShinCarbon ST material, a high surface area carbon molecular sieve (~1500 m^2/g), is the ideal medium for separating gases and highly volatile compounds by GSC. A 2 m x 1 mm ID micropacked column containing ShinCarbon ST separates the permanent gases in 10 minutes, without cryogenic cooling (Figure 1).

In addition to providing a breakthrough in analyses of permanent gases, ShinCarbon ST columns can separate light hydrocarbon / permanent gas mixtures. Figure 2 shows an analysis of permanent gases plus acetylene, ethylene, and ethane, completed in less than 20 minutes. Natural gas components (70% methane) also are cleanly separated (Figure 3). Other potential applications for ShinCarbon ST include analyses of sulfur dioxide and Freon® fluorocarbons (Figure 4).*

**For analysis of other low molecular weight sulfur compounds, we recommend Rt®-XLSulfur micropacked and packed columns or Rtx®-1 capillary columns.*

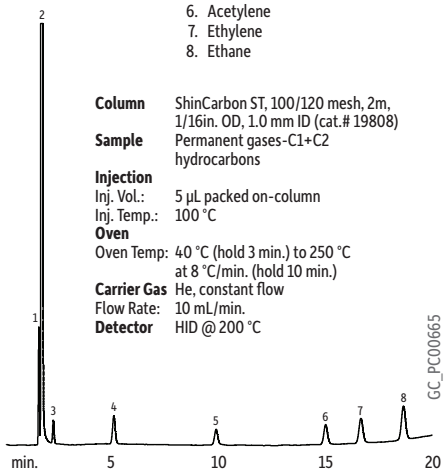
Figure 1 Separate permanent gases in 10 minutes, without cryogenic cooling.



Peaks
1. Hydrogen
2. Oxygen
3. Nitrogen
4. Carbon monoxide
5. Methane
6. Carbon dioxide

Column ShinCarbon ST, 100/120 mesh, 2m, 1/16in. OD, 1.0 mm ID (cat.# 19808)
Sample Permanent gases mix, approx. 5 mol % each
Injection
Inj. Vol.: 5 µL packed on-column
Inj. Temp.: 100 °C
Oven
Oven Temp: 40 °C (hold 3 min.) to 250 °C at 8 °C/min. (hold 10 min.)
Carrier Gas He, constant flow
Flow Rate: 10 mL/min.
Detector HID @ 200 °C

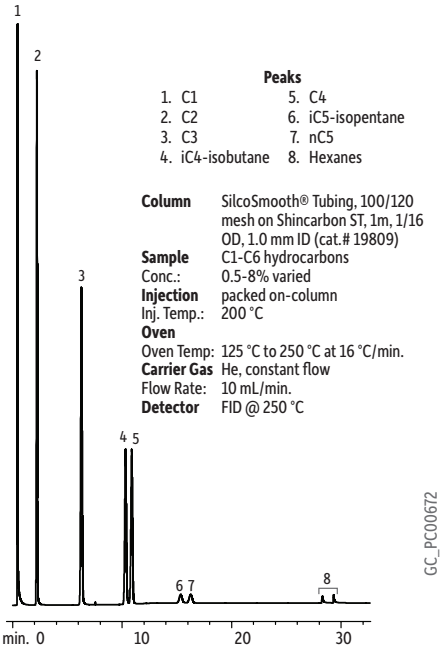
Figure 2 Rapidly analyze light hydrocarbon/permanent gas mixtures.



Peaks
1. Oxygen
2. Nitrogen
3. Carbon monoxide
4. Methane
5. Carbon dioxide
6. Acetylene
7. Ethylene
8. Ethane

Column ShinCarbon ST, 100/120 mesh, 2m, 1/16in. OD, 1.0 mm ID (cat.# 19808)
Sample Permanent gases-C1+C2 hydrocarbons
Injection
Inj. Vol.: 5 µL packed on-column
Inj. Temp.: 100 °C
Oven
Oven Temp: 40 °C (hold 3 min.) to 250 °C at 8 °C/min. (hold 10 min.)
Carrier Gas He, constant flow
Flow Rate: 10 mL/min.
Detector HID @ 200 °C

Figure 3 Separate components in natural gas.



Peaks
1. C1
2. C2
3. C3
4. iC4-isobutane
5. C4
6. iC5-isopentane
7. nC5
8. Hexanes

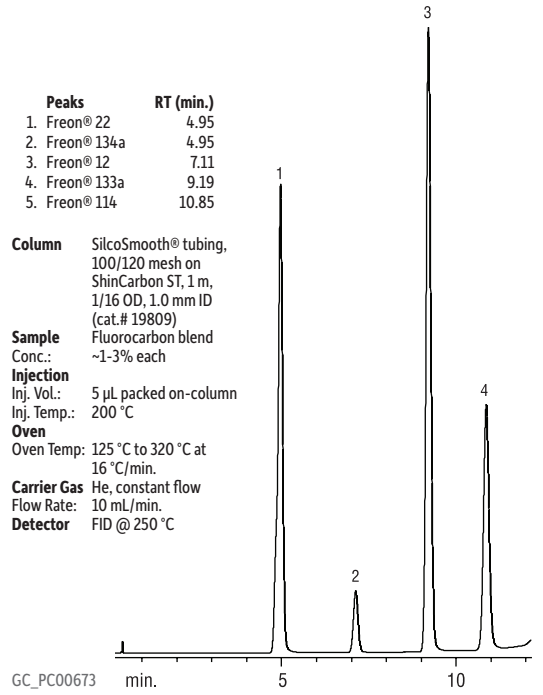
Column SilcoSmooth® Tubing, 100/120 mesh on Shincarbon ST, 1m, 1/16 OD, 1.0 mm ID (cat.# 19809)
Sample C1-C6 hydrocarbons
Conc.: 0.5-8% varied
Injection packed on-column
Inj. Temp.: 200 °C
Oven
Oven Temp: 125 °C to 250 °C at 16 °C/min.
Carrier Gas He, constant flow
Flow Rate: 10 mL/min.
Detector FID @ 250 °C

Go to **www.restek.com/petro** for products and technical information

ShinCarbon ST is a highly stable material. Its 330 °C upper temperature limit minimizes bleed and baseline rise during temperature programming, making the material compatible with most detection systems used for gas analysis, including TCD or HID. All ShinCarbon ST columns are fully conditioned in an oxygen/moisture free environment to prevent contamination. This minimizes stabilization time (less than 30 minutes) when installing a new column which, in turn, minimizes downtime.

The unique properties of ShinCarbon ST make it an ideal packing material for analyses of gases and highly volatile compounds, including permanent gases, low molecular weight hydrocarbons, and Freon® gases. The rapid, above-ambient analyses these columns provide will be a great convenience. Excellent thermal stability of the high surface area carbon, combined with careful conditioning during column manufacture, ensures low-bleed operation and rapid stabilization when installing a new column. Custom-made ShinCarbon ST columns are available on request.

Figure 4 Fluorocarbon analysis completed in 11 minutes on ShinCarbon ST column.



ShinCarbon ST Columns (micropacked)

(SilcoSmooth® Stainless Steel)**

OD	ID	Mesh	1-Meter	2-Meter
1/16"	1.0mm	100/120	19809	19808
0.95mm	0.75mm	100/120	19810	
0.74mm	0.53mm	80/100	19045	19043

**Does not include column nuts and ferrules. Optional installation kits can be ordered separately at www.restek.com

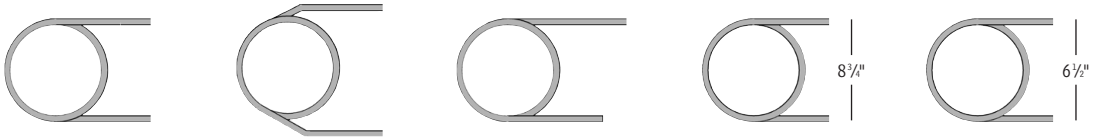
ShinCarbon ST Columns (packed)

(SilcoSmooth® Stainless Steel)*

OD	ID	Mesh	2-Meter
1/8" Silcosmooth	2.0mm	80/100	80486-

*Please add column instrument configuration suffix number to cat.# when ordering. See chart on the next page.

Column Instrument Configurations



General Configuration
Suffix -800

Agilent 5880, 5890, 5987, 6890, 7890:
Suffix -810*

Varian 3700, Vista Series, FID:
Suffix -820

PE 900-3920, Sigma 1,2,3:
Suffix -830

PE Auto System 8300, 8400, 8700
Suffix -840

Note: Initial 2" of column will be empty, to accommodate a needle. For a completely filled column (not on-column) add suffix -901. *-810 suffix also includes 1½" void on detector side.

Installation Kits for Micropacked Columns

Description	qty.	cat.#
Micropacked Column Installation Kit for 1mm ID columns; for valve applications. Kit contains: 1/16" Valco nut (1), 1/16" stainless steel nut (1), 1/16" Vespel/graphite ferrule (1), 1/16" graphite ferrule (1), stainless steel ferrule (1), 1/16" stainless steel front ferrule (1), 1/16" stainless steel back ferrule (1).	kit	21065
Micropacked Column Installation Kit for 1mm ID columns; for direct injections. Kit contains: 1/16" stainless steel nuts (2), 1/16" Vespel/graphite ferrules (2), 1/16" graphite ferrules (2), 1/16" stainless steel front ferrules (2), 1/16" stainless steel back ferrules (2).	kit	21066

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RESTEK®

Lit. Cat.# PCTS1472-UNV

Separate Argon from Oxygen Above Ambient Temperatures

Using an Rt®-Msieve 5A PLOT Column

By Gary Stidsen, GC Columns Product Marketing Manager, and Barry L. Burger, Petroleum Chemist

- Fast, efficient separations at above ambient temperatures.
- High permeability and narrow column diameter mean sharper peaks.
- 100% bonding process eliminates the need for particle traps.

Porous layer open tubular columns—PLOT columns—offer significant advantages over packed gas-solid chromatography (GSC) columns. The open tubular design gives PLOT columns greater permeability, and their narrow diameter ensures sharper peaks. The open construction affords a smaller pressure drop per unit length, so longer columns can be used. This means much higher column efficiency and, therefore, superior resolution. In brief, PLOT columns provide faster and more sensitive analyses than packed GSC columns.

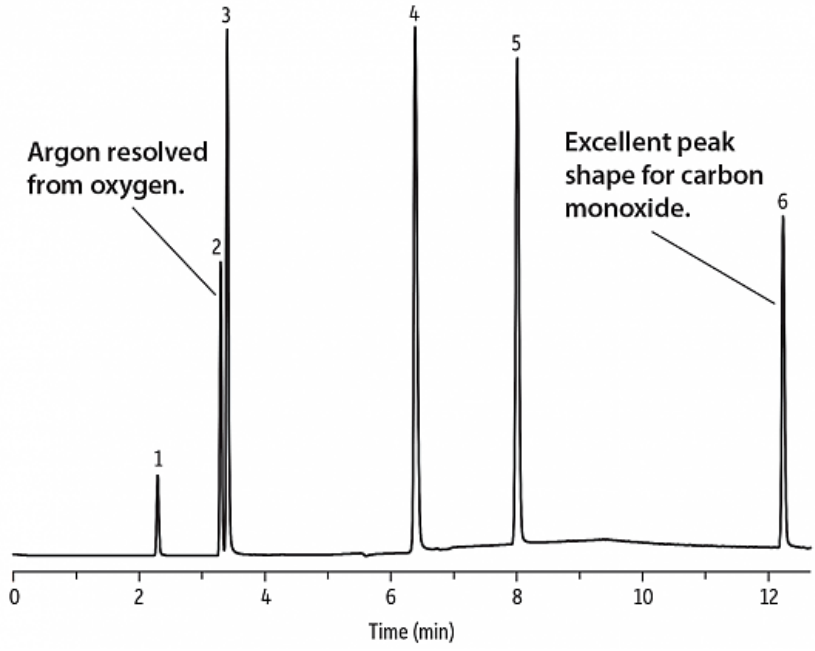
Restek PLOT columns are especially effective for separating mixtures of gaseous analytes. Rt®-Msieve 5A PLOT columns contain molecular sieve 5A particles that are bonded to prevent particle dislocation, thus protecting valves and detection systems from damage. They are designed for fast, efficient separation of argon and oxygen, hydrogen and helium, and other permanent gases, including permanent gases admixed in refinery or natural gas. Finely controlled pore size allows selective adsorption of specific target compounds, ensuring that difficult separations can be made without subambient temperatures.

Figure 1 shows a 30m x 0.53mm ID Rt®-Msieve 5A PLOT column can separate oxygen from argon to baseline, at above ambient temperature, in approximately 4 min. Also, the permanent gases are resolved from methane in the same analysis. Carbon dioxide does not elute from a molecular sieve 5A column, but can be chromatographed on an Rt®-Q-BOND porous polymer column.

If your analyses call for difficult separations of gaseous analytes, and neither conventional packed GC columns nor WCOT capillary columns are providing the separations you want, or if your analyses depend on costly or time-consuming conditions, a Restek PLOT column may be your solution.

Figure 1 Excellent resolution at above ambient temperatures on an Rt®-Msieve 5A PLOT column.

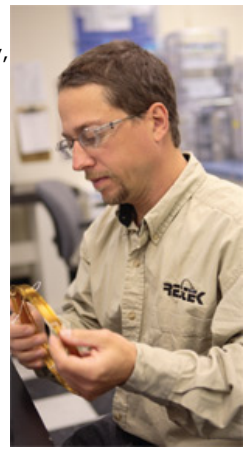
Peaks	Conc. (µg/mL)
1. Hydrogen	40
2. Argon	30
3. Oxygen	50
4. Nitrogen	50
5. Methane	40
6. Carbon monoxide	50



GC_PC00898

Column	Rt®-Msieve 5A, 30 m, 0.53 mm ID, 50 µm (cat.# 19723)
Sample	Permanent gases
Injection	sample valve
Sample Loop Vol.:	5 µL
Valve Name:	6-port Valco valve
Inj. Temp.:	200 °C
Valve Temp.:	Ambient °C
Oven	
Oven Temp.:	27 °C (hold 5 min) to 100 °C at 10 °C/min (hold 5 min)
Carrier Gas	He, constant flow
Flow Rate:	5.0 mL/min
Detector	Valco helium ionization detector @ 150 °C

PLOT Column Advantages



Gas-liquid chromatography (GLC), the most common mode of gas chromatography, has limited application in analyses of gases. Subambient temperatures often are required to achieve a separation, and cryogenic cooling systems are costly and inconvenient.

Gas-solid chromatography (GSC), in which gaseous analytes are adsorbed onto the packing particles, rather than into a surface coating, is far more effective for separating gases. Difficult-to-separate small molecules, such as argon and oxygen, ethane isomers, and many others, can be separated by GSC at above ambient temperatures.

When analyzing gases, PLOT columns offer significant advantages over both GLC and GSC packed columns, including:

- Excellent separations at above ambient temperature; no costly cooling systems required.
- Sharper peaks, due to smaller tubing internal diameters.
- Higher efficiency and greater sensitivity.

RELATED SEARCHES

permanent gases, *argon*, *rt-msieve 5a*, *PLOT*, *GSC*

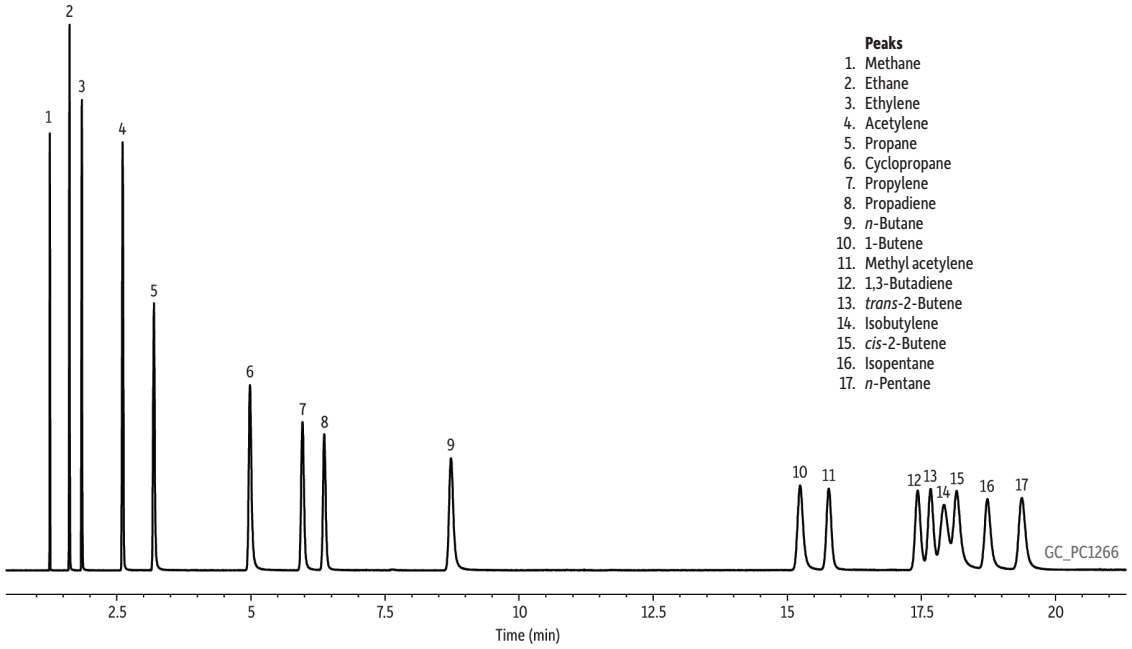
NEW! Rt®-Silica BOND Columns

- Versatile column ideal for analysis of light hydrocarbons, sulfur gases, halocarbons, and carbon dioxide.
- Individually QC tested with sensitive C4 probes to ensure consistent selectivity.
- Proprietary manufacturing process practically eliminates particle release, reducing downtime due to obstructed FID jets.
- Bonded silica stationary phase minimizes impact of water, resulting in reproducible retention times for water-containing samples.

Restek's Rt®-Silica BOND columns are robust, versatile, selective PLOT columns that offer excellent performance for the analysis of light hydrocarbons, sulfur gases, and halocarbons. Light hydrocarbon isomers can be reliably resolved above ambient temperature (Figure 1) and, in addition, carbon dioxide and other gases can be retained at ambient temperature on this silica-based column. The selectivity of this column also provides excellent separations of halocarbons, such as the chlorofluorocarbons shown in Figure 2. High loadability, inertness, and consistent selectivity, as well as unmatched robustness at a maximum temperature of 260 °C, make the Rt®-Silica BOND column ideal for the analysis of active unsaturated hydrocarbons.

Using Rt®-Silica BOND columns minimizes downtime because Restek's unique QC testing protocols ensure consistent column-to-column performance. Only Restek measures the selectivity of every column with methyl acetylene and 1,3-butadiene,

Figure 1: Light hydrocarbons can be reliably separated on an Rt®-Silica BOND PLOT column.



Column: Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785); **Sample**: Custom DCG gas standard; Diluent: Nitrogen; Conc.: 1 mole percent; **Injection:** Inj. Vol.: 15 µL split (split ratio 35:1); Liner: 2 mm straight Sky® inlet liner (cat.# 23313.1); Inj. Temp.: 250 °C; **Oven:** Oven Temp.: 60 °C (hold 2 min) to 175 °C at 2 °C/min; **Carrier Gas:** He, constant flow; Flow Rate: 3.3 mL/min; **Detector:** FID @ 260 °C; Make-up Gas Flow Rate: 50 mL/min; Make-up Gas Type: N_2; Hydrogen flow: 40 mL/min; Air flow: 400 mL/min; Data Rate: 10 Hz; **Instrument:** Agilent 7890A GC

unsaturated C4 hydrocarbons that are more sensitive selectivity probes than the unsaturated C3 hydrocarbon probes that are used by other manufacturers. When only the C3 hydrocarbons are used for QC testing, columns with large shifts in selectivity for the C4 hydrocarbons can be inadvertently released to market because the C3-only testing procedures do not reveal shifts for the C4 compounds. In addition to more rigorous selectivity testing, Rt®-Silica BOND columns are also tested to confirm efficiency and inertness in order to provide optimal peak shape and response for active analytes.

As with all Restek PLOT columns, our proprietary manufacturing process minimizes particle generation, which reduces the problems commonly associated with released particles, such as signal spikes, valve damage, and obstructed FID jets. Even among Restek's highly robust PLOT columns, this column is exceptionally stable. Also, compared to other PLOT columns, the Rt®-Silica BOND column displays outstanding stability in the presence of water due to its unique bonded silica stationary phase. The combination of rugged manufacturing and rigorous QC testing ensures every Rt®-Silica BOND column will provide optimal performance and reliable results for active unsaturated hydrocarbons.

Rt®-Silica BOND Columns

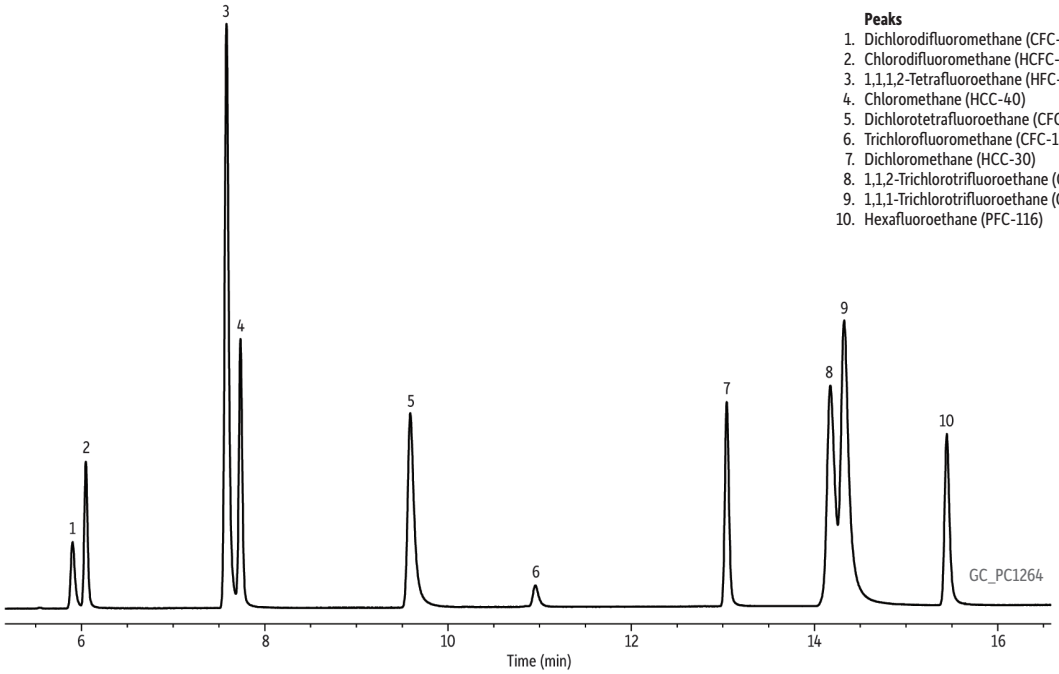
(fused silica PLOT)

Description	temp. limits	qty.	cat.#
15 m, 0.32 mm ID,	-80 to 260 °C	ea.	19784
30 m, 0.32 mm ID,	-80 to 260 °C	ea.	19785
60 m, 0.32 mm ID,	-80 to 260 °C	ea.	19786

similar **phases**

GS-GasPro, CP-SilicaPLOT

Figure 2: The selectivity of Rt®-Silica BOND columns provides good separation of most chlorofluorocarbons.



Column: Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785); **Sample**: Custom Air Liquide gas standard; Conc.: 1,000 ppmv balance nitrogen; **Injection:** Inj. Vol.: 50 µL split (split ratio 10:1); Liner: 2 mm straight Sky® inlet liner (cat.# 23313.1); Inj. Temp.: 250 °C; **Oven:** Oven Temp.: 120 °C (hold 25 min); **Carrier Gas:** He, constant flow; Flow Rate: 2.6 mL/min; **Detector**: FID @ 260 °C; Make-up Gas Flow Rate: 50 mL/min; Make-up Gas Type: N_2; Hydrogen flow: 40 mL/min; Air flow: 400 mL/min; Data Rate: 10 Hz; **Instrument**: Agilent 7890A GC

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RESTEK®

Lit. Cat.# PCTS1972-UNV

Petrochemical Applications

Rt®-XLSulfur Packed GC Column for Analysis of Low-Level Sulfur Compounds in C1-C6 Hydrocarbon Streams

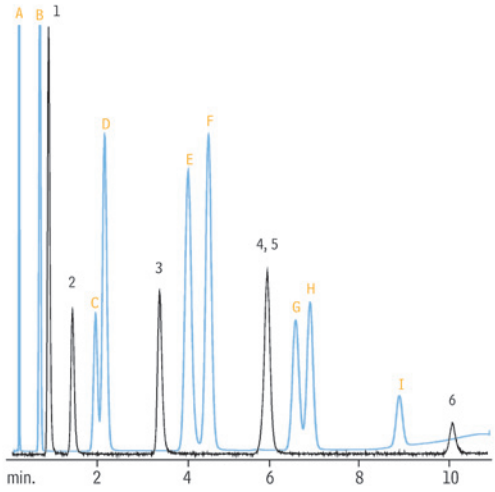
The analysis of sulfur compounds in C1-C6 hydrocarbon streams by gas chromatography (GC) is an important application in the petrochemical field. The presence of sulfur compounds in petroleum products can affect the longevity and performance of catalysts used in hydrocarbon processing. As requirements for sulfur detection become more stringent, the importance of good chromatographic separation of the hydrocarbons from the sulfur compounds and the inertness of the analytical column increases. Detectors used for sulfur determination generally are specific (e.g., sulfur chemiluminescence detection, FPD, PFPD) and help eliminate positive response from chromatographic interferences. Unfortunately, when high levels of hydrocarbons elute through the detector simultaneously with sulfur compounds, the signal for sulfur is quenched and area counts are nonlinear. For a successful analysis, the analytical column must resolve the hydrocarbons from the sulfur compounds listed in Figure 1.

Hydrocarbons are non-reactive but sulfur compounds, especially hydrogen sulfide and methyl mercaptan, are easily adsorbed by undeactivated surfaces. Therefore, there are two areas of concern with micropacked or packed column sulfur analysis: one is the inertness and selectivity of the solid support, and the other is the inertness of the tubing walls. Packed and micropacked columns typically use metal tubing for ruggedness but the surface is very adsorptive for sulfur compounds. PTFE tubing is also an option, but it has a limited temperature range, is permeable, and will expand and contract during temperature changes. These characteristics will negatively affect column efficiency and stability.

Restek designed the Rt®-XLSulfur column to accomplish the challenging separation of hydrocarbons from sulfur compounds. All parts of the column have been optimized for inertness. The packing material is extensively deactivated for the analysis of low ppbv levels of hydrogen sulfide and methyl mercaptan, and then is prepared to achieve the proper selectivity and required resolution (Figure 1). Analysis of 50 ppbv sulfur compounds using a 1 mL gas loop and a sulfur chemiluminescence detector (SCD) shows excellent response (Figure 2).

The interior tubing walls of the Rt®-XLSulfur column are treated with a Sulfinert® coating, a passivation technique designed to deactivate metal surfaces. This coating is found to be very inert for all sulfur compounds, including hydrogen sulfide and methyl mercaptan. Another issue that is routinely overlooked with packed columns is that their end plugs are known to adsorb sulfur compounds. For that reason, Restek also treated the end plugs in the Rt®-XLSulfur column with Sulfinert® passivation. The extra care taken with the surfaces in this column result in a more accurate analysis of trace sulfur compounds in hydrocarbon processes.

Figure 1 The Rt®-XLSulfur micropacked column separates hydrocarbons from sulfur compounds.



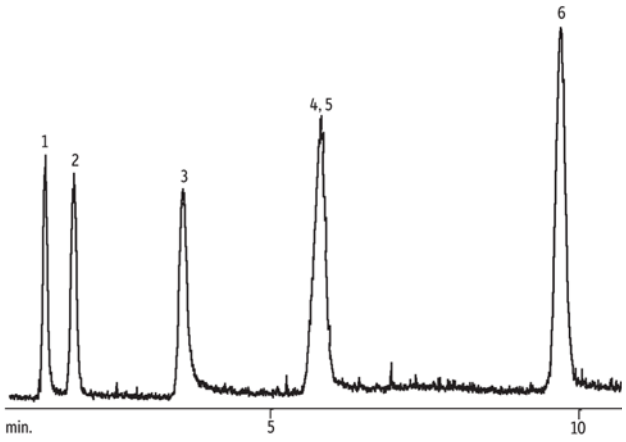
GC_PC00436

Sulfurs
1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Dimethyl sulfide
6. Dimethyl disulfide

Hydrocarbons
A. Methane
B. Ethane
C. Propylene
D. Propane
E. Isobutane
F. Butane
G. Isopentane
H. Pentane
I. Hexane

Column	Rt®-XLSulfur, 1m, 0.95mm OD, 0.75 mm ID (cat.# 19806)
Sample	
Conc.:	50 ppb each
Injection	packed not on-column
Oven	
Oven Temp:	60 °C to 230 °C at 15 °C/min.
Carrier Gas	He, constant flow
Flow Rate:	9 mL/min.
Detector	SCD/FID
Acknowledgement	Sulfur standards courtesy of DCG Partnership 1 Ltd., Pearland, TX.

Figure 2 The Rt®-XLSulfur column is sensitive enough for 50 ppbv sulfur compounds.



GC_PC1221

Peaks
1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Dimethyl sulfide
6. Dimethyl disulfide

Column	Rt®-XLSulfur, 1 m, 0.75 mm ID (cat.# 19806)
Sample	
Conc.:	1 mL of 50 ppbv each sulfur compound
Injection	sample valve
Oven	
Oven Temp:	60 °C to 230 °C at 15 °C/min.
Carrier Gas	He, constant flow
Flow Rate:	9 mL/min.
Detector	SCD

RESTEK®

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Petrochemical Applications

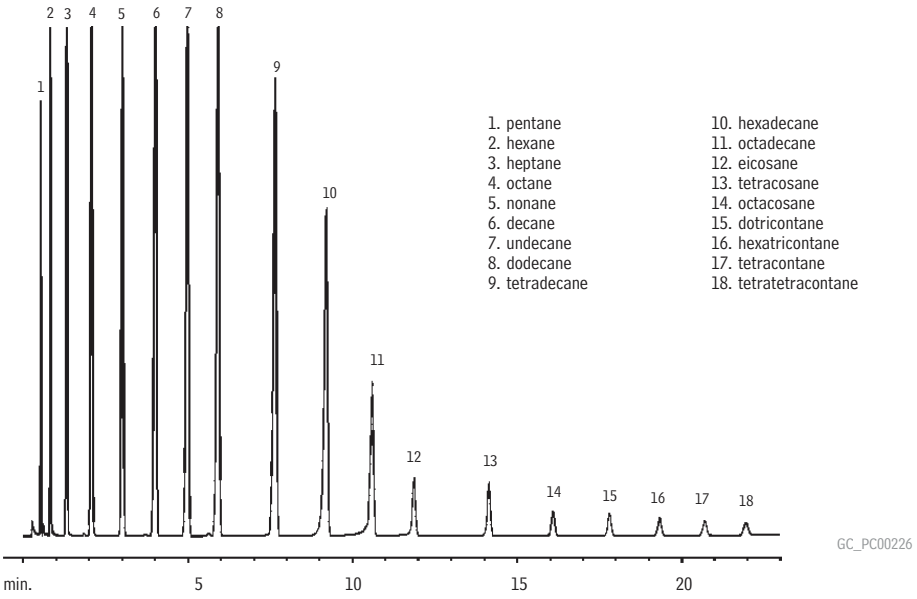
Rtx®-2887 / MXT®-2887

Restek's Capillary GC Columns for Simulated Distillation of Petroleum Fractions

Simulated Distillation (Sim Dist) is an analysis which determines the boiling range distribution of petroleum samples using gas chromatography with temperature programming. Different Sim Dist methods are employed depending upon the boiling range of hydrocarbons in the product to be analyzed. ASTM Test Method D-2887 is most commonly used because its scope specifies petroleum products with a final boiling point less than 538°C (excluding gasoline). This boiling range includes samples such as jet fuel, kerosene, diesel, and gas oil. Although this technique has been in use for many years, using mostly packed columns, ASTM D-2887 permits the use of 0.53mm capillary columns.[1,2] Capillary columns with cross-bonded stationary phases offer several advantages compared to packed columns, including lower column bleed, shorter conditioning times, shorter analysis times, and longer column lifetimes. Although the analysis is, in principle, very simple, there are some important column and instrument parameters which must be optimized to meet the criteria for column resolution, bleed, and peak skewing specified in ASTM Method D-2887.[3]

It is possible to calculate boiling range distribution from GC data since a nonpolar stationary phase operated under temperature programmed conditions will elute hydrocarbons in order of increasing boiling points. The chromatographic system is calibrated by injecting a mixture of *n*-alkanes to cover the hydrocarbon range of the samples. Figure 1 shows the complete analysis of the Simulated Distillation Calibration Mixture in under 23 minutes, using the Rtx®-2887 capillary column. A computer program constructs a calibration curve from the hydrocarbon retention times and their atmospheric boiling points, then uses this curve to calculate the boiling range distribution of the petroleum fractions. Sample area is integrated into area "slices" vs. retention time, then the boiling point for each cumulative area % is determined by the computer program. An example analysis of ASTM Reference Gas Oil #1 appears in Figure 2. Note that it is not desirable to resolve all the components in a single sample when performing Sim Dist, since a typical laboratory distillation used for petroleum analysis generates a limited number of theoretical plates.

Figure 1 Calibration of C5 to C44 standard, using an Rtx®-2887 capillary column (baseline compensated).



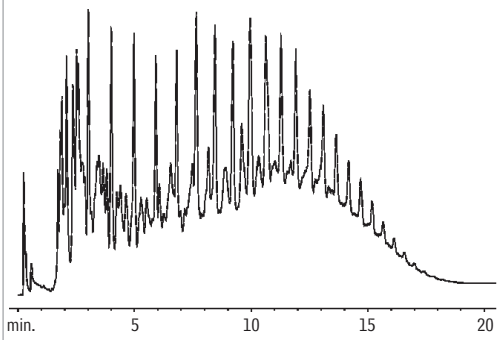
10m, 0.53mm ID, 2.65µm Rtx®-2887 (cat.# 10199)
1.0µL direct injection of a 0.1 to 0.01 wt % hydrocarbon standard in carbon disulfide
Oven temp.: 35°C to 360°C @ 15°C/min. (hold 5 min.)
Inj. & det. temp.: 360°C
Carrier gas: nitrogen
Linear velocity: 112cm/sec. (15mL/min.)

please **note**

Rtx®-2887 and MXT®-2887 columns are both optimized to exceed the resolution and tailing requirements specified in ASTM Method D-2887. The Rtx®-2887 column offers all the benefits of fused silica tubing and greater coating efficiency than metal tubing. Choose the MXT®-2887 column if you operate in a rugged environment, or at higher temperatures, and need the most durable column available.

It is important that the column and chromatographic conditions are set up according to the procedure specified in the ASTM standard.[3] Otherwise, one lab's results will not be comparable with results obtained by other labs. The Rtx®-2887 and MXT®-2887 column dimensions, stationary phase, and stationary phase film thickness are optimized to meet the requirements specified in the current version of the ASTM test method. For example, the resolution for C16/C18 is 8.7, which is within the specified range of 3 to 10 and the skewing factor for heptane is 0.92 which must be greater than 0.5 and less than 2. The Crossbond® methyl silicone stationary phase has increased stability compared to packed columns, resulting in longer column lifetimes and shorter conditioning times when installing a new column. Each column is individually tested with a hydrocarbon mixture to guarantee a stable baseline with low bleed and reproducible retention times. This test assures Rtx®-2887 and MXT®-2887 columns will meet performance requirements specified in ASTM Test Method D-2887.

Figure 2 ASTM Reference Gas Oil #1 on an Rtx®-2887 capillary column (baseline compensated).



10m, 0.53mm ID, 2.65µm Rtx®-2887 (cat.# 70199)
1.0µL direct injection of a 0.1 to 0.01 wt % hydrocarbon standard in carbon disulfide.

Oven temp.:	35°C to 360°C @ 15°C/min. (hold 5 min.)
Inj. & det. temp.:	360°C
Carrier gas:	nitrogen
Linear velocity:	112cm/sec. (15mL/min.)

References:

1. Green L.E., Schumauch L.J., Worman J.C., Anal. Chem., Vol. 36, 1964 p.1512.
2. Green L.E., Hydrocarbon Processing, May 1976 p.506.
3. ASTM Test Method D-2887, 1996 Annual Book of ASTM Standards, Volume 5.02.

References not available from Restek.

Rtx®-2887 Column (fused silica)

(Crossbond® 100% dimethyl polysiloxane—for simulated distillation)

ID	df (µm)	temp. limits	length	cat. #
0.53mm	2.65	-60 to 360°C	10-Meter	10199

MXT®-2887 Column

(Silcosteel® treated stainless steel)*

(Crossbond® 100% dimethyl polysiloxane—for simulated distillation)

ID	df (µm)	temp. limits	length	cat. #
0.53mm	2.65	-60 to 400°C	10-Meter	70199

*Silcosteel® treatment is a proprietary surface treatment for passivating steel and stainless steel. U.S. Patent 6,511,760.

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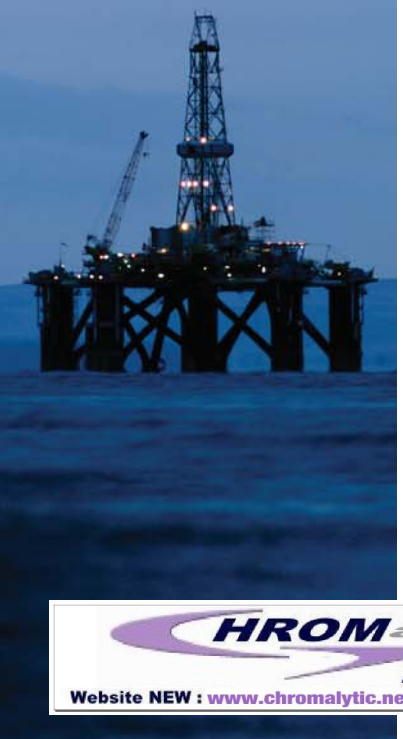


Petrochemical Applications

Rtx®-1 SimDist 2887

A Bonded Packed Column for Simulated Distillation

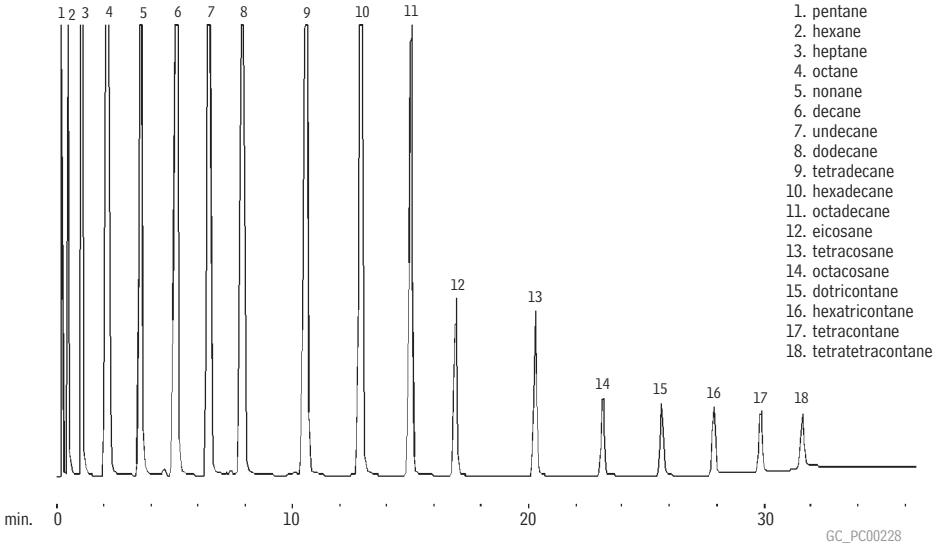
Simulated Distillation (Sim Dist) according to ASTM test methods D2887 or D3710 can be performed using either packed or capillary columns. Advantages of capillary columns are the columns are preconditioned, so they can be used after only minimal conditioning, and the bonded stationary phases exhibit stable baselines and retention times. Many laboratories currently using packed columns would like to take advantage of bonded phases, but do not have GC equipment that can be easily converted for use with capillary columns.

Restek's Rtx®-1 SimDist 2887 bonded packed columns have superior inertness and stability compared to conventional packed columns. These improvements are obtained by preparing the columns with Silcosteel® tubing* and bonding the Rtx®-1 stationary phase to a highly deactivated Silcoport™ support. The column dimensions and packing (1/8" Silcosteel® with 10% Rtx®-1 on Silcoport™) exceed all requirements specified in ASTM Test Methods D2887 and D3710.

Bonded stationary phases require minimal conditioning and give stable baselines and retention times "right from the box." Simulated distillation is a gas chromatographic procedure in which the sample is analyzed using a linear temperature program, so that the retention time of the hydrocarbons are proportional to their boiling points. The sample boiling range distribution is calculated by comparing the sample area and its retention time with that of an alkane calibration standard. In order for the calibration to be valid for sample analysis, it is crucial that retention times be repeatable until the next calibration is performed. Figure 1 is an example of the analysis of the ASTM D2887-01 Calibration Mix (cat.# 31674) illustrating the typical pattern obtained for the alkanes under temperature programmed conditions.

To demonstrate the stability of the Rtx®-1 column, a series of calibration standards were analyzed after only 30 minutes of conditioning at 350°C. Table 1 shows the excellent retention time repeatability obtained with the column, indicating the column is suitable for sample analysis after minimal conditioning.

Figure 1 C5 to C44 calibration on an Rtx®-1 SimDist 2887 bonded packed column after only 30 minutes conditioning.



25" x 1/8" x 2mm ID Rtx®-1 SimDist 2887 (cat.# 80000)
1.0µL direct injection, 1–12% (w/w) each component
Oven temp.: 35°C to 350°C @ 10°C/min. (hold 5 min.)
Inj. & det. temp.: 350°C
Carrier gas: helium @ 25mL/min.
FID sensitivity: 256 x 10^{-11} AFS

cat.# 31674 (1% each listed analyte in CS_2) and cat.# 31675 (5% each, neat) meet requirements of ASTM D2887-01.

*Silcosteel® treatment is a proprietary surface treatment for passivating steel and stainless steel. U.S. Patent 6,511,760.

Column bleed is another important consideration for selecting a Sim Dist column. The baseline must be stable and free of any artifacts during the temperature program up to 350°C. Although baseline subtraction is permitted in the method, this compensation will produce errors if the baseline is not consistent. Conventional packed columns require up to 14 hours of conditioning and frequent updating of the baseline compensation run because the stationary phase is not bonded. Rtx®-1 columns, however, exhibit stable and reproducible baselines with just 30 minutes of conditioning. This results in fewer baseline blanks and less frequent calibration, increasing laboratory productivity.

Table 1 Retention time repeatability for calibration after only 30 minutes conditioning.

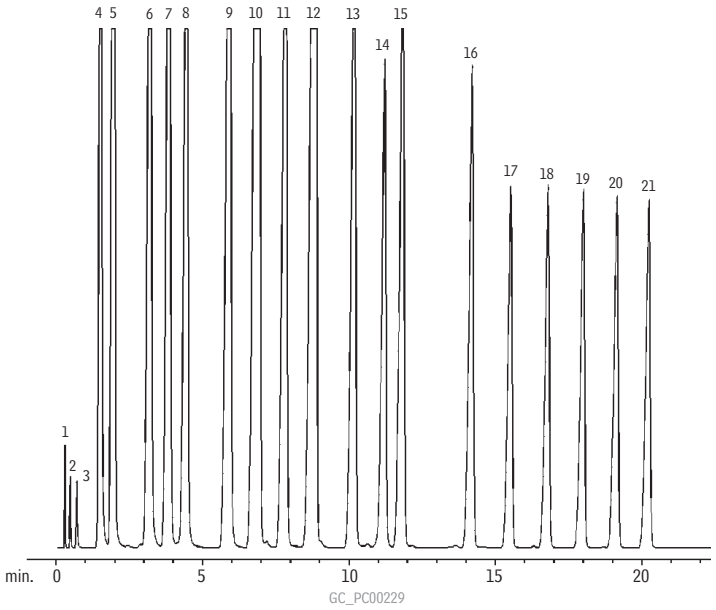
Hydrocarbon	Min Rt	Max Rt	Avg. RT	Stand. Dev.
C_5	0.241	0.243	0.242	0.001
C_6	0.493	0.497	0.495	0.002
C_{10}	5.746	5.765	5.752	0.005
C_{20}	18.482	18.491	18.486	0.004
C_{28}	25.093	25.103	25.098	0.004
C_{40}	32.160	32.171	32.166	0.004
C_{44}	34.316	34.328	34.326	0.007

Rtx®-1 SimDist 2887 Packed Columns also can be used for gasoline range simulated distillation.

Simulated distillation of gasoline range hydrocarbons according to ASTM method D3710-93 also can be performed using the Rtx®-1 SimDist 2887 packed column. Figure 2 shows the analysis of ASTM D3710 calibration mix with the addition of *n*-propane, 2-methyl propane, *n*-butane, *n*-hexadecane, and *n*-heptadecane. To achieve baseline separation of *n*-propane, 2-methyl propane, and *n*-butane, the GC oven was cooled to -30°C with liquid nitrogen. Figure 3 shows the analysis of a composite gasoline sample under the same run conditions. Other volatile petroleum fractions, such as kerosene and jet fuel, also can be analyzed with this column.

Figure 2 Rtx®-1 SimDist 2887 packed columns also can be used for ASTM D-3710 analysis.

1. *n*-propane
2. 2-methyl propane
3. *n*-butane
4. 2-methylbutane
5. *n*-pentane
6. 2-methylpentane
7. *n*-hexane
8. 2,4-dimethylpentane
9. *n*-heptane
10. toluene
11. *n*-octane
12. *p*-xylene
13. *n*-propylbenzene
14. *n*-decane
15. *n*-butylbenzene
16. *n*-dodecane
17. *n*-tridecane
18. *n*-tetradecane
19. *n*-pentadecane
20. *n*-hexadecane
21. *n*-heptadecane



25" x 1/8" OD x 2mm ID Rtx®-1 SimDist 2887 (cat.# 80000)
D-3710 Calibration Mix, C3, C4, C16, & C17 added
Oven temp: -30°C to 250°C @ 10°C/min.
Inj./det. temp.: 250°C / 300°C
Carrier gas: helium @ 25mL/min.
FID sensitivity: 256 x 10^{-11} AFS

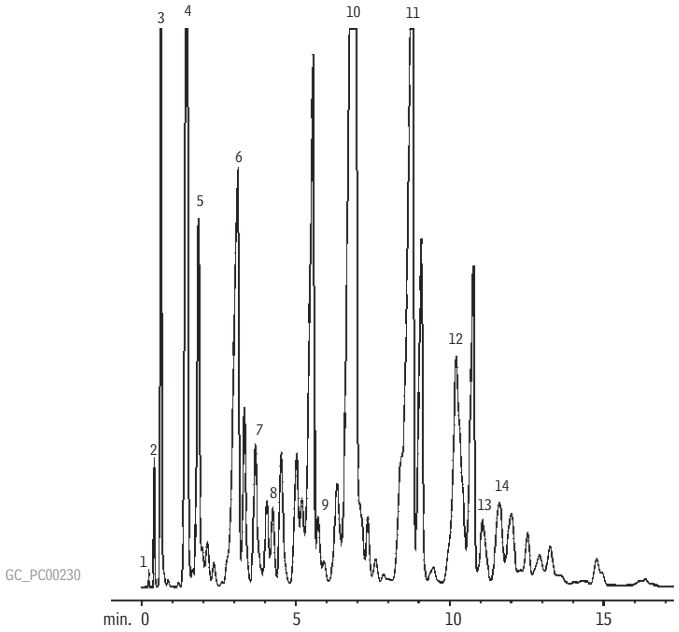
Bonded stationary phases have longer column lifetimes and lower bleed.

The Rtx®-1 stationary phase is bonded to the diatomite particles, resulting in an immobilized coating which is resistant to solvents and lower in bleed than conventional packings. Since the packing is preconditioned, there is no need for extended conditioning. Extended conditioning can greatly decrease column lifetime. Figure 4 shows a conventional non-bonded methyl silicone column after only 170 temperature cycles, demonstrating higher bleed and more tailing than the Rtx®-1 Sim Dist column. Although actual column lifetimes depend upon the system and type of samples analyzed, the bonded stationary phase should have a longer lifetime than its nonbonded equivalent.

Rtx®-1 SimDist columns have polarity equivalent to OV®-101 and UCW-982.

In order for a stationary phase to be acceptable for ASTM methods, the column must not exhibit selective retention for aromatic hydrocarbons compared to aliphatic hydrocarbons. This is an important test because if the polarity of a column is different, the boiling point results will demonstrate a bias, especially for highly aromatic samples. The "polarity" of the bonded Rtx®-1 column was compared with OV®-101 and UCW-982, two of the most common stationary phases currently used for simulated distillation. The calculated boiling points for aromatics, compared to the published boiling points, appear in Table 2. All three silicone columns tested are essentially identical in that they elute aromatics at a slightly lower temperature than alkanes. This confirms the polarity of the Rtx®-1 column is equivalent, and the boiling range values obtained will agree with values from OV®-101 and UCW-982 columns.

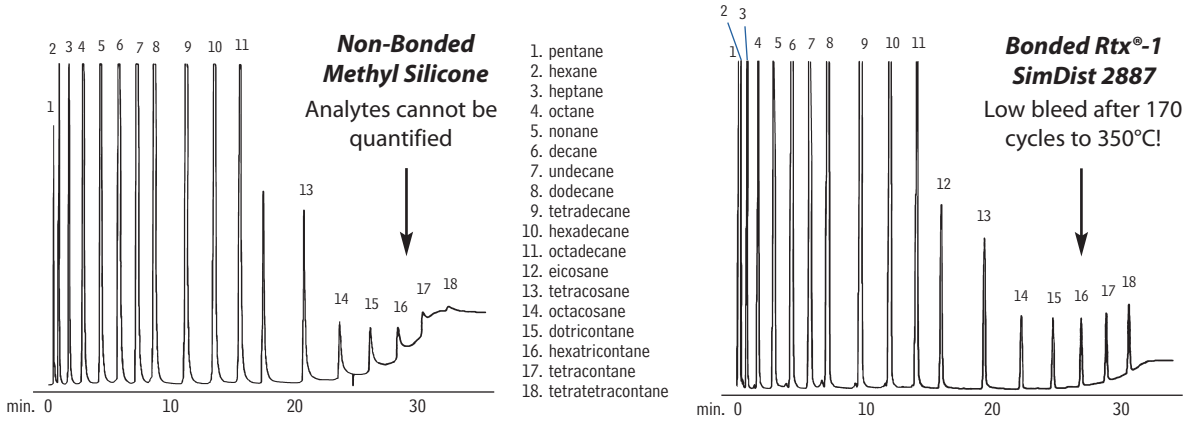
Figure 3 Simulated distillation of gasoline using the Rtx®-1 SimDist 2887 packed column.



1. *n*-propane
2. 2-methyl propane
3. *n*-butane
4. 2-methylbutane
5. *n*-pentane
6. 2-methylpentane
7. *n*-hexane
8. 2,4-dimethylpentane
9. *n*-heptane
10. toluene
11. *p*-xylene
12. *n*-propylbenzene
13. *n*-decane
14. *n*-butylbenzene

25" x 1/8" OD x 2mm ID Rtx®-1 SimDist 2887, (cat.# 80000)
1.0µL direct injection of unleaded gasoline (ASTM D-2887)
Oven temp: -30°C to 250°C @ 10°C/min.
Inj./det. temp.: 250°C/300°C
Carrier gas: helium @ 25mL/min.
FID sensitivity: 256 x 10^{-11} AFS

Figure 4 Bonded packed columns exhibit lower bleed and longer lifetimes.



1. pentane
2. hexane
3. heptane
4. octane
5. nonane
6. decane
7. undecane
8. dodecane
9. tetradecane
10. hexadecane
11. octadecane
12. eicosane
13. tetracosane
14. octacosane
15. dotricontane
16. hexatricontane
17. tetracontane
18. tetratetracontane

25" x 1/8" x 2mm ID Rtx®-1 SimDist 2887 (cat.# 80000)
1.0µl direct injection, 1–12% (w/w) each component
Oven temp.: 35°C to 350°C @ 10°C/min. (hold 5 min.)
Inj. & det. temp.: 350°C
Carrier gas: helium @ 25mL/min.
FID sensitivity: 256 x 10^{-11} AFS

cat.# 31674 (1% each listed analyte in CS_2) and cat.# 31675 (5% each, neat) meet requirements of ASTM D2887-01.

Rtx®-1 is an excellent choice for Sim Dist using packed columns.
Simulated distillation is one of the most common GC analyses performed in the petroleum laboratory. ASTM test methods D2887 and D3710 can be performed with either packed or capillary columns, but until now the benefits of bonded phases were available only to capillary users. The Rtx®-1 packed column uses a bonded stationary phase which is immobilized on Silcoport™-a specially deactivated support. The columns are prepared using Silcosteel® tubing for inertness unavailable with conventional metal tubing. Rtx®-1 bonded packed columns require minimal conditioning and give stable baselines and retention after only 30 minutes of operation at 350°C. If your laboratory has been looking for a better Sim Dist analysis, Restek's Rtx®-1 SimDist 2887 packed columns are the answer.

Table 2 Comparison of bonded and conventional packed columns indicates no polarity differences.

Aromatic Hydrocarbons	Published BP[1] (°C)	Rtx®-1	UCW-982	OV®-101
benzene	80	81.3	82	80.3
p-xylene	139	138.6	140.2	137.7
naphthalene	218	204.6	206.9	204.3
acenaphthylene	280	252.7	255.6	252.2
anthracene	342	304.1	307.2	303.4
chrysene	447	385.6	389.2	384.9
dibenzo(a,h)anthracene	524	452.3	455.7	450.4

Column Configurations


General Configuration
Suffix -800


Agilent 5880, 5890, 5987, 6890:
Suffix -810


Varian 3700, Vista Series, FID:
Suffix -820

PE 900-3920 Sigma 1,2,3:
Suffix -830

PE Auto System 8300, 8400, 8700 (Not On-Column):
Suffix -840

See our general catalog for custom configurations

Note: Initial 2" of column will be empty, to accommodate a needle. For a completely filled column add suffix -901.

Bonded Packed Column Stainless Steel Tubing

- Short conditioning times.
- Low bleed levels.
- Higher sensitivities.
- Longer column lifetimes.
- Unsurpassed inertness for active compounds.

Bonded Phase on 100/120 Silcoport™ W	Stainless Steel Tubing L (ft.)	OD (in.)	ID (mm)	cat.#*	Silcosteel®-Deactivated Stainless Steel Tubing L (m)	OD (in.)	ID (mm)	cat.#*
3% Rtx®-1	6	1/8	2.1	80441-	2	1/8	2	80401-
10% Rtx®-1	6	1/8	2.1	80442-	2	1/8	2	80405-
20% Rtx®-1	6	1/8	2.1	80443-	2	1/8	2	80409-
Rtx®-1 SimDist 2887**	25"	1/8	2.1	80450-	25"	1/8	2	80000-

*Please add configuration suffix number to cat.# when ordering.
**Application specific column.

ASTM D2887-01 Calibration Mix (20 components)

To facilitate the ASTM International guideline and help petroleum analytical laboratories in determining petroleum product boiling range applications, Restek introduced two chemical standards designed specifically for ASTM Method D2887-01. The mixture prepared at 1% w/w in carbon disulfide is for convenient laboratory use.

n-pentane (C5)
n-hexane (C6)
n-heptane (C7)
n-octane (C8)
n-nonane (C9)
n-decane (C10)
n-undecane (C11)
n-dodecane (C12)
n-tetradecane (C14)
n-pentadecane (C15)
n-hexadecane (C16)
n-heptadecane (C17)
n-octadecane (C18)
n-eicosane (C20)
n-tetracosane (C24)
n-octacosane (C28)
n-dotriacontane (C32)
n-hexatriacontane (C36)
n-tetracontane (C40)
n-tetratetracontane (C44)

1% weight each in carbon disulfide, 1g solution/ampul*
cat. # 31674 (ea.)

5% w/w, 1g /ampul**
cat. # 31675 (ea.)

No data pack available.
*This standard may only be shipped by FedEx™ ground, and only within the US.
**The 5% w/w blend of neat hydrocarbons can be shipped overnight in the US and can be shipped to our international customers.

D2887 Calibration Mix (17 components)

Compound	Concentration (% w/w)	Compound	Concentration (% w/w)
n-hexane (C6)	6	*n*-octadecane (C18)	5
n-heptane (C7)	6	*n*-eicosane (C20)	2
n-octane (C8)	8	*n*-tetracosane (C24)	2
n-nonane (C9)	8	*n*-octacosane (C28)	1
n-decane (C10)	12	*n*-dotriacontane (C32)	1
n-undecane (C11)	12	*n*-hexatriacontane (C36)	1
n-dodecane (C12)	12	*n*-tetracontane (C40)	1
n-tetradecane (C14)	12	*n*-tetratetracontane (C44)	1
n-hexadecane (C16)	10		

Packaged 1mL/ampul
cat. # 31222 (ea.)

No data pack available.

D3710-95 Calibration Mix (16 components)

Compound	Concentration (% w/w)	Compound	Concentration (% w/w)
n-pentane (C5)	8	*n*-pentadecane (C15)	2
n-hexane (C6)	6	2-methylbutane	10
n-heptane (C7)	10	2-methylpentane	6
n-octane (C8)	5	2,4-dimethylpentane	6
n-decane (C10)	4	toluene	12
n-dodecane (C12)	4	*p*-xylene	14
n-tridecane (C13)	2	*n*-propylbenzene	5
n-tetradecane (C14)	2	*n*-butylbenzene	4

Packaged 1mL/ampul
cat. # 31223 (ea.)

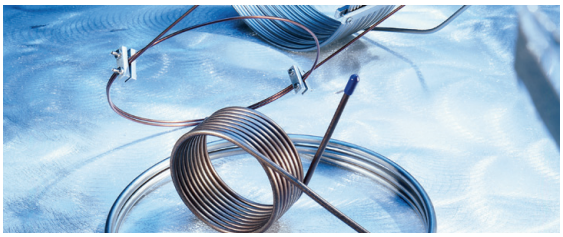
No data pack available.

Lit. Cat.# 59570A

Rt®-XLSulfur Packed Column

Specialized packed and micropacked columns for eXtra-Low Sulfur analysis

Restek's Rt®-XLSulfur column is the second generation of packing material for the analysis of sulfur compounds. The first packing material, in the Rt®-Sulfur column, had inertness characteristics for low ppmv levels of sulfur compounds. Now, with the second generation, our innovative Rt®-XLSulfur column, it is possible to achieve low ppbv detection of sulfur compounds.



What is the Rt®-XLSulfur column?
Rt®-XLSulfur packed and micropacked columns are designed for ppb-level sulfur analysis. Every component of the sample pathway is treated to provide the highest degree of inertness for reactive, low-level sulfur compounds. The porous polymer phase features a unique surface modification, which results in excellent peak symmetry and thermal stability to 300 °C.

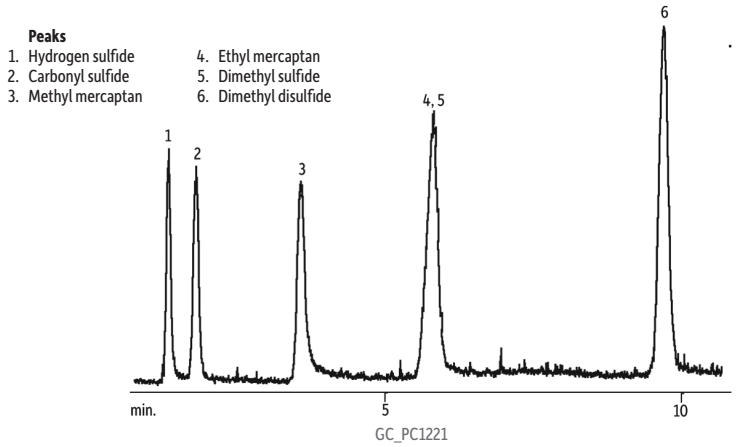
What are the benefits to using Restek's Rt®-XLSulfur column?
The Rt®-XLSulfur column combines a packing material surface deactivation with Sulfinert® tubing and end-fittings to yield unsurpassed inertness and high thermal stability for highly reactive sulfur compounds. The Rt®-XLSulfur column offers the most reliable, reproducible analyses for low ppb-level sulfur samples.

For which applications should I use an Rt®-XLSulfur column?
The high performance and reproducibility of the Rt®-XLSulfur column enables resolution and quantitation of COS, H_2S, SO_2, CH_3SH, $(CH_3)_2S_2$ at low ppb concentrations. These sulfur compounds typically are found in pulp mill byproducts, natural gas, and petroleum products.

Features & Benefits

Feature	Benefit
Sulfinert® tubing	Unsurpassed inertness towards sulfur compounds. Lowest level of detection for sulfur compounds. Rugged metal column.
Improved packing	Minimal adsorption of sulfur compounds. Excellent response for sulfur compounds.
300 °C thermal stability	50 °C higher thermal stability than the Rt®-Sulfur column. Minimal column bleed, short conditioning times. Improved detector sensitivity with SCDs and FPDs.
Guaranteed	Column-to-column reproducibility.

Figure 1 The Rt®-XLSulfur column analyzes 50 ppb levels of sulfur compounds, providing low bleed and good symmetry.



Column	Rt®-XLSulfur, 1 m, 0.75 mm ID (cat.# 19806)	**Oven**	
Sample		Oven Temp:	60 °C to 230 °C at 15 °C/min.
Conc.:	1 mL of 50 ppbv each sulfur compound	**Carrier Gas**	He, constant flow
Injection	sample valve	Flow Rate:	9 mL/min.
		Detector	SCD

Visit **www.restek.com** for a complete product listing

Commonly Asked Questions

- What is Sulfinert® treatment?

Sulfinert® treatment is a metals passivation coating for low-level sulfur storage and transfer. The Sulfinert® coating is rugged, durable, and thermally stable to 360 °C. Like Silcosteel® treatment, Sulfinert® coating is incorporated into the framework of atoms on the surface of stainless steel. Holding studies have proven Sulfinert® coating to be non-adsorptive and unreactive to low ppb-levels of sulfur compounds.

- What is the Rt®-XLSulfur column made of?

The Rt®-XLSulfur column is made with Sulfinert® tubing and end-fittings, and is packed with a porous polymer having a unique surface modification that results in excellent inertness to ppb levels and thermal stability to 300 °C.

- What other areas should be addressed to improve the response of sulfur compounds?

To achieve the highest degree of inertness for ppb-level sulfur analysis, each part of the sample pathway must be optimized. In addition to the Rt®-XLSulfur analytical column, we also recommend deactivation of the inlet system. The use of Sulfinert® sample cylinders, sample loops, and transfer line tubing will provide ultra-high sensitivity and reproducibility for low-level sulfur analysis.

Rt®-XLSulfur Packed/Micropacked Columns

- Optimized columns for low pbbv sulfur analyses.
- Eliminate the need for PTFE tubing.
- Column and end-fittings are Sulfinert® treated for maximum inertness.

Rt®-XLSulfur Columns (packed)*

OD	ID	1-Meter	2-Meter
1/8"	2.0mm	80484-	80485-
3/16"	3.2mm	80482-	80483-

*Please add column instrument configuration suffix number to cat.# when ordering. See chart on this page.

Rt®-XLSulfur Columns (micropacked)**

OD	ID	1-Meter	2-Meter
1/16"	1.0mm	19804	19805
0.95mm	0.75mm	19806	19807

**Does not include column nuts and ferrules. Optional installation kits can be ordered separately.

For More Information on Sulfur Analysis:

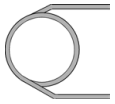
Visit **www.restek.com** and download these free application notes.

Rt®-XLSulfur Packed GC Column for Analysis of Low-Level Sulfur Compounds in C1-C6 Hydrocarbon Streams (lit. cat.# PCAN1498-UNV)

Analyze Sulfur Compounds at ppb Levels, Using an Rt®-XLSulfur Micropacked GC Column or an Rtx®-1 Thick Film Capillary GC Column (lit. cat.# PCAN1499-UNV)

Column Instrument Configurations

General Configuration:
Suffix -800



Agilent 5880, 5890, 5987, 6890, 7890:
Suffix -810*

Varian 3700, Vista Series, FID:
Suffix -820

PE 900-3920, Sigma 1,2,3:
Suffix -830

PE Auto System 8300, 8400, 8700:
Suffix -840

See www.restek.com for additional configurations.

Note: Initial 2" of column will be empty, to accommodate a needle.
For a completely filled column (not on-column) add suffix -901.
*-810 suffix also includes 1½" void on detector side.

Contact your Restek representative and order yours today!

Visit **www.restek.com/Contact-Us** to find a distributor or representative.

RESTEK®

Lit. Cat.# PCTS1500A-UNV

www.restek.com

Restek's PLOT Column Family —
The Benchmark For Performance!

- Innovative bonding process minimizes particle release.
- More consistent flow means stable retention times.
- Outstanding peak symmetry improves impurity analysis.

Next Generation of Porous Layer Open Tubular (PLOT) Columns

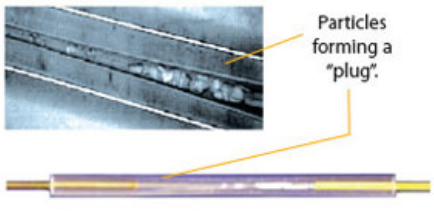
- Stabilized particle layers improve robustness and reproducibility of retention and flow.
- Compatible with valve switching and Deans switching systems.
- Highly efficient, reproducible analyses; ideal for permanent gases, solvents, and hydrocarbons.
- Innovative manufacturing procedure reduces particle generation and improves performance of PLOT columns.
- Wound on a 7"-diameter, 11-pin cage unless otherwise noted.

Porous layer open tubular (PLOT) columns are very beneficial for solving application problems, especially for the analysis of volatile compounds. PLOT columns have a unique selectivity, allowing for the separation of volatile compounds at ambient temperature. Due to the adsorption mechanism of the stationary phases used in PLOT columns, permanent gases and light hydrocarbons can be resolved at ambient temperature; columns can then be programmed to higher temperatures to elute higher boiling compounds.

Traditional PLOT Columns Offer Poor Stability

The traditional PLOT column is built with a 5–50 µm layer of particles adhered to the tubing walls. Because this layer of particles generally lacks stability, PLOT columns must be used very carefully, as particle release is common and can cause unpredictable changes in retention time and flow behavior. Traditional PLOT columns also must generally be used in conjunction with particle traps to prevent the contamination of valves, injectors, and GC detectors. Detectors contaminated with particles typically generate electronic noise, which shows up chromatographically as a spike in the baseline. In extreme cases, detector flow can be obstructed by particle buildup. Particles can also affect valves by becoming lodged in the valve and causing leaks or restricting flow. Figure 1 shows an example of blockage caused by particle accumulation inside a Press-Tight® connector.

Figure 1: Particles released from traditional PLOT columns can cause blockages.



Restek® PLOT Columns Offer Improved Stability to Minimize Particle Release

PLOT Columns Available In:

Fused Silica
Rt® Column Phases:
- Rt®-Alumina BOND/MAPD
- Rt®-Alumina BOND/Na_2SO_4
- Rt®-Alumina BOND/KCl
- Rt®-Alumina BOND/CFC
- Rt®-MSieve 5A
- Rt®-Silica BOND
- Rt®-Q-BOND
- Rt®-QS-BOND
- Rt®-S-BOND
- Rt® -U-BOND

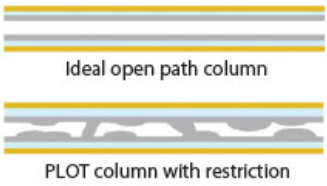
Metal
MXT® Column Phases:
- MXT®-Alumina BOND/MAPD
- MXT®-Alumina BOND/Na_2SO_4
- MXT®-MSieve 5A
- MXT®-Q-BOND
- MXT® -S-BOND

Restek has developed technology and procedures to manufacture PLOT columns with concentric stabilized adsorption layers. These next generation PLOT columns show a constant flow behavior (permeability) and have significantly improved mechanical stability, resulting in easier operation, better chromatography, and reduced particle release. Greater particle stability means more reproducible retention times, virtually no spiking, and longer column lifetimes. This innovative Restek® stabilization chemistry is currently applied to all fused silica and metal PLOT columns featured here.

Consistent Flow Restriction Factor (F) Guarantees Reproducible Flow

Thick layers of particles are difficult to deposit in a homogeneous layer, and in traditionally manufactured PLOT columns, this results in variable coating thicknesses. The positions where the layer is thicker act as restrictions and affect flow (Figure 2). Depending on the number and intensity of these restrictions, traditional PLOT columns often show greater variation in flow restriction than wall coated open tubular (WCOT) columns. In practice, conventional PLOT columns with the same dimensions can differ in flow by a factor of 4 to 6 when operated at the same nominal pressure. For applications where flow is important, such as with Deans switching, the nonreproducible flow behavior of most commercially available PLOT columns is a problem.

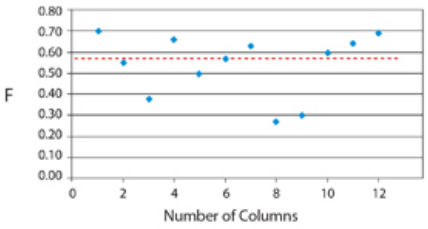
Figure 2: Inconsistent coating thicknesses result in restrictions that cause significant variation in flow.



In order to measure flow restriction reproducibility, Restek introduced a new factor: the flow restriction factor (F). This factor is based on the retention time of an unretained marker compound, as measured on both coated and uncoated tubing using the same backpressure setting (Equation 1). For quality control purposes, methane is used as the marker when evaluating porous polymer columns, and helium is used for testing molecular sieve 5A columns.

Flow restriction factor determination can be used to assess both the degree of column restriction and the reproducibility of the column coating process. Figure 3 shows typical results for PLOT columns manufactured using a conventional process. Because of the difference in flow restriction, individual columns have very different flow characteristics. In contrast, Figure 4 shows results for columns made using our Rt®-QS-BOND (bonded porous polymer) PLOT column process. Clearly, our manufacturing process results in greater consistency in both column coating thickness and flow restriction, which results in more stable retention times and better performance in Deans and related flow switching techniques. Flow restriction factors are specified on the certificate of analysis (CofA) included with every Restek® PLOT column, and the values are listed on the report.

Figure 3: Traditional PLOT columns show significant flow variability, indicating inconsistent column coating thicknesses.



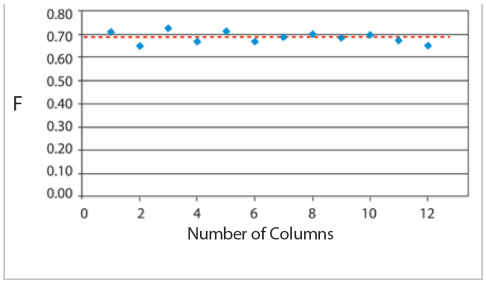
Equation 1: Flow restriction factor (F) is used to demonstrate coating consistency.

$$F = \frac{t_{R1} \text{ of unretained component (uncoated tubing)}}{t_{R2} \text{ of unretained component (coated column)}}$$

t_R = retention time

Note: F values will always be <1 as the coated column always has more restriction than the uncoated column.

Figure 4: PLOT columns from Restek offer consistent flow restriction, giving more reproducible results column to column.



Restek's PLOT columns are exceptionally robust, featuring concentric stabilized coating layers. They allow for more consistent gas flows and are recommended for applications sensitive to variation in retention time or flow. These PLOT columns are a significant advance in technology and are ideal for efficient, reproducible analyses of permanent gases, solvents, and hydrocarbons.

PLOT Column Phase Cross-Reference: Similar Selectivity

Restek® Rt® and MXT® Columns	Porous Layer	Supelco	Alltech	Agilent (J&W, Varian, Chrompack)	Quadrex
Alumina BOND/Na_2SO_4	Aluminum oxide	Alumina-Sulfate	AT-Alumina	GS-Alumina, CP-Al_2O_3/NA_2SO_4	—
Alumina BOND/KCl	Aluminum oxide	Alumina-Chloride	—	GS-Alumina KCl, HP PLOT Al_2O_3, CP-Al_2O_3/KCl	—
Alumina BOND/CFC	Aluminum oxide	unique product			
Alumina BOND/MAPD	Aluminum oxide	—	—	Select Al_2O_3 MAPD	—
Msieve 5A	Molecular sieve 5A	Molsieve 5A	AT-Molesieve	HP PLOT Molesieve, CP-Molesieve 5A	PLT-5A
Q-BOND	100% Divinylbenzene	Supel-Q-PLOT	AT-Q	HP PLOT Q ,CP-PoraPlot Q, PoraBond Q	—
QS-BOND	Intermediate polarity porous polymer	—	—	GS-Q	—
S-BOND	DVB vinylpyridine polymer	—	—	CP-PoraPlot S	—
U-BOND	DVB ethylene glycoldimethylacrylate polymer	—	—	HP PLOT U, CP-PoraPlot U, CP-PoraBond U	—
Silica BOND	Bonded silica	—	—	CP Silica PLOT, GS-GasPro	—

®

Rt -Alumina BOND Columns

Restek Rt -Alumina BOND columns are highly selective for C1–C5 hydrocarbons and separate all saturated and unsaturated hydrocarbon isomers above ambient temperatures. The reactivity of the aluminum oxide stationary phase is minimized, by deactivation with inorganic salts like KCl or Na_2SO_4, to improve column response for polar unsaturates, such as dienes, and the column's sensitivity (or response) ensures linear and quantitative chromatographic analysis for these compounds. Strong bonding mimimizes particle generation and release, which allows valve switching with minimal risk to the injection or detection systems. And because they are stable up to at least 200 °C, Rt -Alumina BOND columns can be regenerated to restore full efficiency and selectivity by conditioning at their maximum temperature if water is adsorbed. High capacity and loadability give you exceptionally symmetrical peaks, making these columns ideal for volatile hydrocarbon separations at percent levels, as well as impurity analyses at ppm concentrations. Restek Rt -Alumina BOND PLOT columns are manufactured on fused silica tubing; select phases are also available on metal MXT tubing.

To ensure reproducible retention times and predictable flow behavior column to column, each Rt -Alumina BOND column is extensively tested. A hydrocarbon test mix confirms proper phase retention and selectivity. To calculate k (retention or capacity factor), which is a measure of phase retention, 1,3-butadiene is used, while selectivity is measured using retention indices for propadiene and methyl acetylene. The resolution of *trans*-2-butene and 1-butene is also verified and, to measure efficiency, plates per meter are checked using 1,3-butadiene.

Rt -Alumina BOND/Na_2SO_4 Columns (fused silica PLOT)

tech tip

Traces of water in the carrier gas and samples will affect the retention and the selectivity of alumina. If exposed to water, the retention times will shorten. The column can be regenerated by conditioning for 15–30 minutes at 200 °C under normal carrier gas flow. Periodic conditioning ensures excellent run-to-run retention time reproducibility.

Unless noted, the maximum programmable temperature for an Rt -Alumina BOND column is 200 °C. Temperatures higher than the stated maximum temperature can cause irreversible changes to the porous layer adsorption properties.

(Na_2SO_4 deactivation)

- Acetylene and propadiene elute after butanes.
- Best separation for butene isomers (impurities in butene streams).
- Methyl acetylene elutes after 1,3-butadiene.
- Cyclopropane (impurity in propylene) elutes well before propylene.
- Stable to 200 °C.
- Also available on metal MXT® tubing!

ORDER NOW

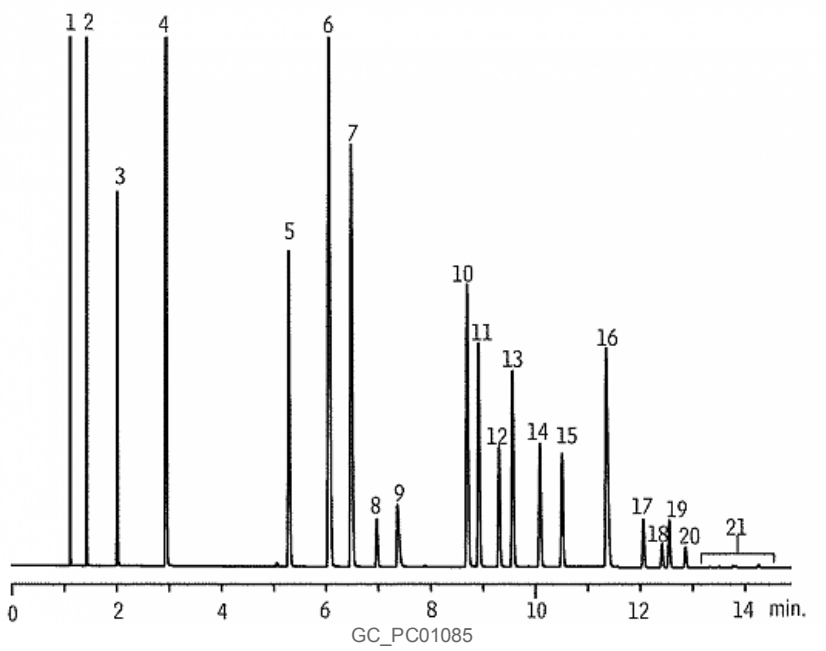
similar phases

GS-Alumina, CP-Al_2O_3/Na_2SO_4, Alumina-Sulfate, AT-Alumina

Refinery Gas on Rt®-Alumina BOND (Na_2SO_4)

Peaks
1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. Isobutane
7. *n*-Butane
8. Propadiene
9. Acetylene
10. *trans*-2-Butene

Peaks
11. 1-Butene
12. Isobutylene
13. *cis*-2-Butene
14. iso-Pentane
15. *n*-Pentane
16. 1,3-Butadiene
17. *trans*-2-Pentene
18. 2-Methyl-2-butene
19. 1-Pentene
20. *cis*-2-Pentene
21. Hexanes



GC_PC01085

Column	Rt®-Alumina BOND/Na_2SO_4, 50 m, 0.53 mm ID, 10 µm (cat.# 19756)
Sample	Refinery gas
Injection	
Inj. Vol.:	10 µL split
Liner:	Taper (2 mm) (cat.# 20795)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	80 ml/min
Oven	
Oven Temp.:	45 °C (hold 1 min) to 200 °C at 10 °C/min (hold 3.5 min)
Carrier Gas	H_2, constant pressure (8.0 psi, 55.2 kPa)
Linear Velocity:	74 cm/sec @ 45 °C
Detector	FID @ 200 °C

did you know?

Restek draws our own fused silica tubing and applies our own proprietary stationary phases. By fully managing our production streams, we are able to ensure unparalleled reliability and stability.

Rt®-Alumina BOND/KCl Columns (fused silica PLOT)

(KCl deactivation)

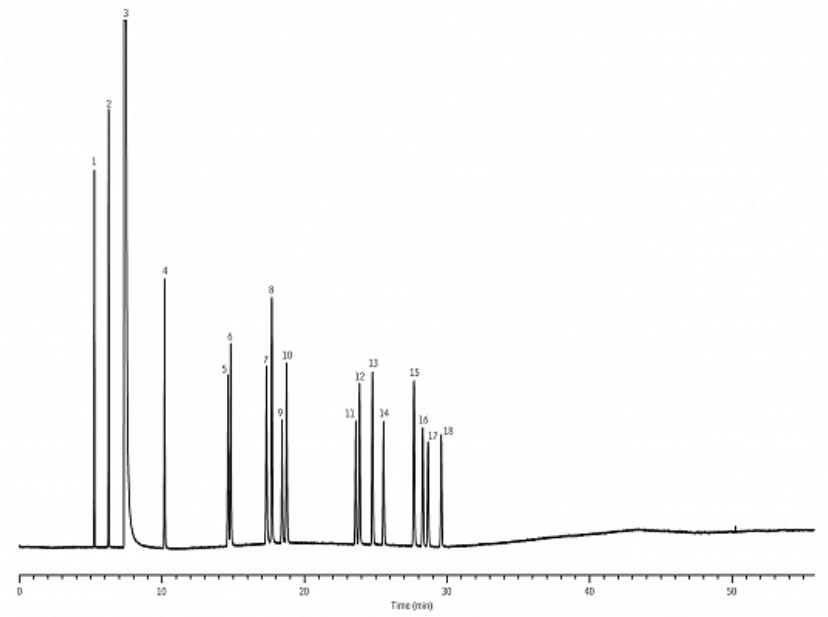
- Restek's lowest polarity alumina column.
- Low moisture sensitivity reduces the need for frequent regeneration.
- Acetylene elutes before *n*-butane.

- Methyl acetylene (impurity in 1,3-butadiene) elutes before 1,3-butadiene.
- Stable to 200 °C.

ORDER NOW

Ethylene and C1-C5 Hydrocarbons by ASTM D6159-97 on Rt®-Alumina BOND/KCl, Rtx®-1

Peaks	Peaks
1. Methane	10. *n*-Butane
2. Ethane	11. *trans*-2-Butene
3. Ethylene	12. 1-Butene
4. Propane	13. Isobutylene
5. Cyclopropane	14. *cis*-2-Butene
6. Propylene	15. iso-Pentane
7. Acetylene	16. Methylacetylene
8. Isobutane	17. *n*-Pentane
9. Propadiene	18. 1,3-Butadiene



GC_PC01110

Column	Rt®-Alumina BOND/KCl *, 50 m, 0.53 mm ID, 10 µm (cat.# 19760)
Sample	Ethylene gas plus C1 through C5 hydrocarbons
Injection	
Inj. Vol.:	1 µL split
Liner:	2 mm splitless (cat.# 20712)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	60 ml/min
Oven	
Oven Temp.:	35 °C (hold 2 min) to 190 °C at 4 °C/min (hold 15 min)
Carrier Gas	He, constant pressure (8.0 psi, 55.2 kPa)
Linear Velocity:	25.4 cm/sec @ 35 °C
Detector	FID @ 200 °C
Make-up Gas Type:	N_2
Data Rate:	20 Hz
Instrument	HP5890 GC
Notes	* Rt®-Alumina BOND/KCl, 50 m, 0.53 mm ID, 10.0 µm (cat.# 19760) in series with an Rtx®-1, 30 m, 0.53 mm ID, 5.0 µm (cat.# 10179) connected using a universal Press-Tight® connector (cat. # 20401) (conditions as per ASTM D6159-97)

Rt®-Alumina BOND/CFC Columns (fused silica PLOT)

- Improved inertness for chlorofluorocarbon (CFC) compounds.
- Highly selective alumina-based column, separates most CFCs.
- High retention and capacity for CFCs.
- Stable to 200 °C.

The Alumina BOND/CFC adsorbent is ideal for retaining volatile halogenated compounds, especially CFCs (chlorinated fluorocarbons) like Freon® products. It offers high selectivity, allowing a wide

similar phases

GC-Alumina KCl, HP-PLOT Al_2O_3/KCl, CP-Al_2O_3/KCl, Alumina-Chloride

did you know!

All Restek® PLOT columns come standard on a 7"-diameter, 11-pin cage. Metal MXT® columns are also available coiled to 3.5" diameter by adding the suffix -273 to the part number. If you need more information, please call your local Restek® representative.

tech tip

Especially when valve switching or backflushing is used, Restek recommends using particle traps to help prevent detector spikes and valve rotor scratches.

Visit www.restek.com/plot for specialized PLOT column particle

column is thoroughly deactivated to reduce the reactivity of alumina. Even though there is still some residual reactivity for some mono- or disubstituted CFCs, the majority of these compounds can be accurately quantified from main stream processes or in impurity analyses.

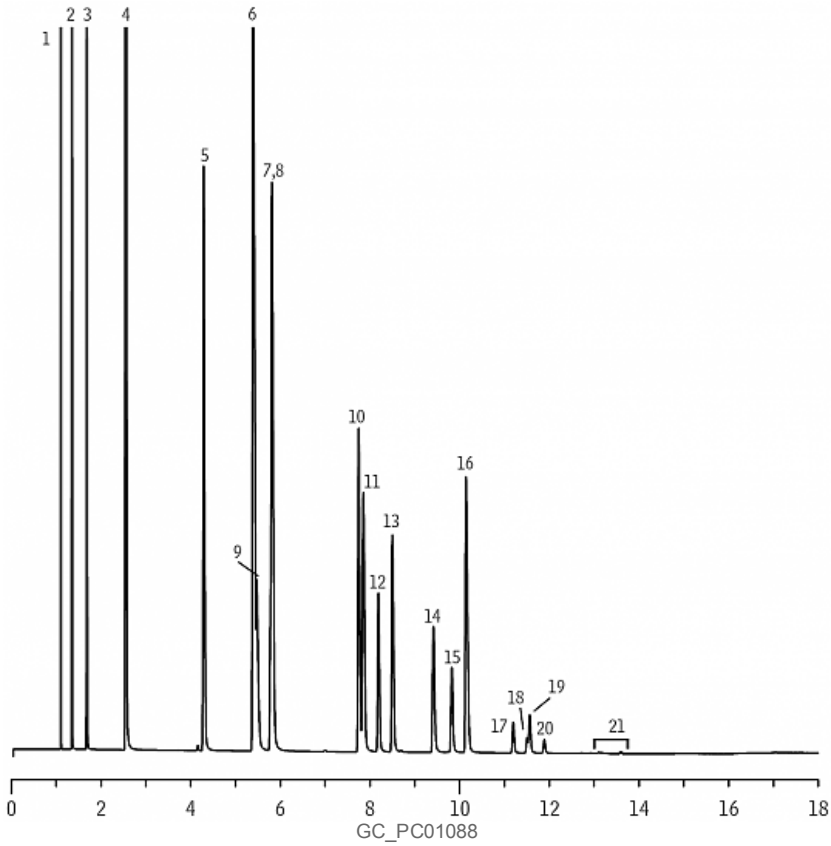
traps.

ORDER NOW

Impurity Analysis of 1,1,1,2-Tetrafluoroethane (CFC-134a) on Rt®-Alumina BOND/CFC

Peaks
1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. Isobutane
7. *n*-Butane
8. Propadiene
9. Acetylene
10. *trans*-2-Butene

Peaks
11. 1-Butene
12. Isobutylene
13. *cis*-2-Butene
14. Isopentane
15. *n*-Pentane
16. 1,3-Butadiene
17. *trans*-2-Pentene
18. 2-Methyl-2-butene
19. 1-Pentene
20. *cis*-2-Pentene
21. Hexanes



Column	Rt®-Alumina BOND/KCl, 50 m, 0.53 mm ID, 10 µm (cat.# 19760)
Sample	Refinery gas standard
Injection	
Inj. Vol.:	10 µL split
Liner:	Taper (2 mm) (cat.# 20795)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	80 mL/min
Oven	
Oven Temp.:	45 °C (hold 1 min) to 200 °C at 10 °C/min (hold 3.5 min)
Carrier Gas	H_2, constant pressure (8.0 psi, 55.2 kPa)
Linear Velocity:	74 cm/sec @ 45 °C
Detector	FID @ 200 °C
Make-up Gas Type:	N_2
Data Rate:	20 Hz
Instrument	HP5890 GC

Rt®-Alumina BOND/MAPD Columns (fused silica PLOT)

- Optimized deactivation produces maximum response when analyzing trace levels of acetylene, methyl acetylene, and propadiene.
- Stable response factors make this column ideal for process type applications where recalibration must be

did you know?

All Restek PLOT columns come standard on a 7"-diameter, 11-pin cage. Metal MXT® columns are also

minimized.

- High loadability reduces peak tailing and improves separations.
- Extended temperature range up to 250 °C for fast elution of high molecular weight (HMW) hydrocarbons and accelerated column regeneration following exposure to water.
- Stable to 250 °C.
- Also available on metal MXT® tubing!

Restek's R&D chemists have optimized the deactivation technology applied to our Rt®-Alumina BOND/MAPD column for improved analysis of trace concentrations of polar hydrocarbons like acetylene, methyl acetylene, and propadiene in hydrocarbon streams containing higher levels of C1-C5 hydrocarbons. Our alumina PLOT deactivation produces an incredibly inert column that offers superior reproducibility and stable response factors to maximize the number of analyses before recalibration is required. Its high sample capacity reduces peak tailing, thereby improving the separation of target compounds. In addition, a 250 °C maximum operating temperature lets you more quickly elute hydrocarbons up to dodecane and reduces regeneration time when the column is exposed to water from samples or carrier gases.

ORDER NOW

available coiled to 3.5" diameter by adding the suffix -273 to the part number. If you need more information, please call your local Restek® representative.

similar phases

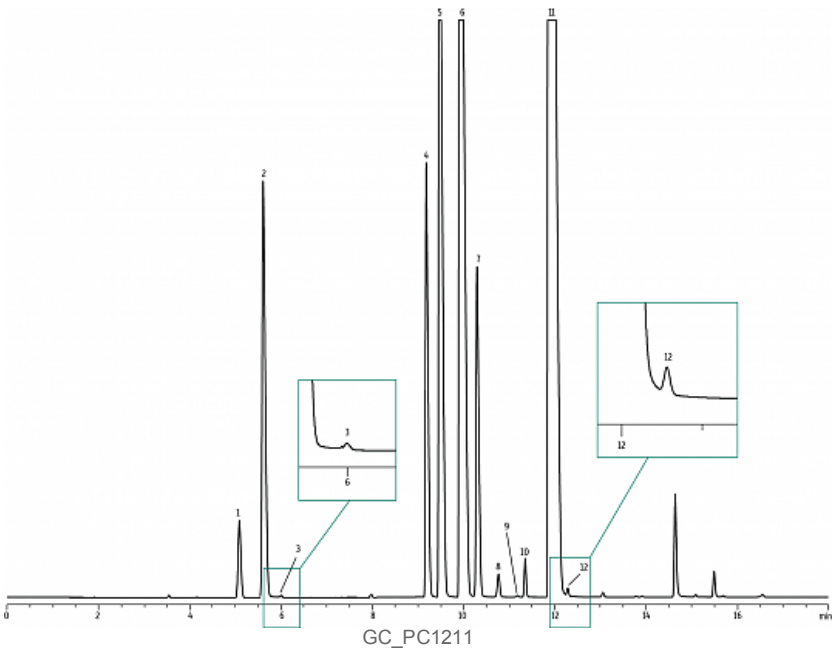
Select Al_2O_3 MAPD

1,3-Butadiene on Rt®-Alumina BOND/MAPD (Purity Analysis)

Rt®-Alumina BOND/MAPD PLOT columns are made specifically for the analysis of petrochemicals and downstream products such as ethylene, propylene, butylenes, and butadiene.

Peaks

1. Isobutane
2. *n*-Butane
3. Propadiene
4. *trans*-2-Butene
5. 1-Butene
6. Isobutene
7. *cis*-2-Butene
8. Isopentane
9. *n*-Pentane
10. 1,2-Butadiene
11. 1,3-Butadiene
12. Methyl acetylene



GC_PC1211

Column	Rt®-Alumina BOND/MAPD, 50 m, 0.53 mm ID, 10.0 µm (cat.# 19778)
Sample	Crude 1,3-butadiene
Injection	
Inj. Vol.:	10 µL split

also available

Metal MXT® PLOT Columns

Split Vent Flow Rate:	100 mL/min
Oven	
Oven Temp.:	70 °C (hold 5 min) to 200 °C at 10 °C/min (hold 0 min)
Carrier Gas	He, constant pressure (20 psi, 137.9 kPa)
Detector	FID @ 250 °C
Make-up Gas Flow Rate:	30 mL/min
Make-up Gas Type:	N_2
Data Rate:	20 Hz
Instrument	HP5890 GC

Molecular Sieve 5A PLOT Columns

Restek's molecular sieve 5A PLOT columns are designed for efficient separation of argon/oxygen and other permanent gases, including carbon monoxide. Special coating and deactivation procedures ensure chromatographic efficiency and the integrity of the porous layer coating. Molecular sieves have very high retention, allowing separations of permanent gases at temperatures above ambient. Our deactivation technology also allows carbon monoxide to elute as a sharp peak. Additionally, our unique immobilization process guarantees that the uniform particles remain adhered to the tubing—even after continuous valve cycling.

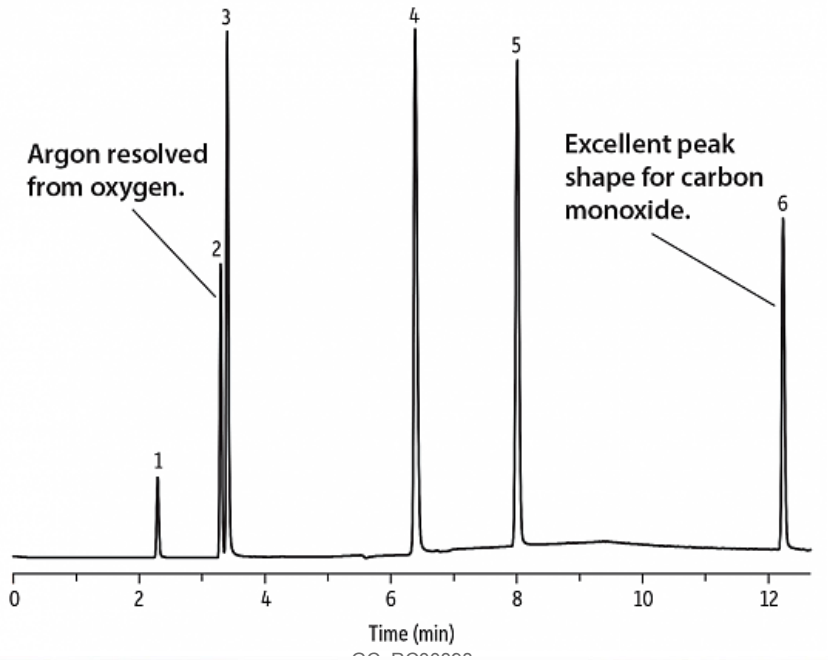
Rt®-Msieve 5A Columns (fused silica PLOT)

- Improve accuracy with sharp, symmetrical peaks for argon, oxygen, and carbon monoxide.
- Easily separate permanent gases at temperatures above ambient.
- Restek® PLOT technology reduces particle release, improving flow reproducibility and reducing downtime for maintenance.
- Stable to 300 °C.
- Also available on metal MXT® tubing!

ORDER NOW

Separation of Argon/Oxygen and Other Permanent Gases on Rt®-Msieve 5A

Peaks	Conc. (µg/mL)
1. Hydrogen	40
2. Argon	30
3. Oxygen	50
4. Nitrogen	50
5. Methane	40
6. Carbon monoxide	50



did you know?

Rt®-Msieve 5A PLOT columns are designed for efficient separation of Ar/O_2 and other permanent gases, including CO.

similar phases

HP PLOT Molesieve, CP-Molsieve 5A, Molsieve 5A, AT-Molsieve, PLT-5A

tech tip

Because molecular sieve materials are very hydrophilic, they will adsorb water from the sample or carrier gas. Water contamination can have a detrimental effect on peak symmetry and can reduce the resolution of all compounds. If water contamination occurs, reactivate your Rt®-Msieve 5A PLOT column by conditioning at 300 °C with dry carrier gas flow for 3 hours.

Column	Rt®-Msieve 5A, 30 m, 0.53 mm ID, 50 µm (cat.# 19723)
Sample	Permanent gases
Injection	sample valve
Sample Loop Vol.:	5 µL
Valve Name:	6-port Valco valve
Inj. Temp.:	200 °C
Valve Temp.:	Ambient °C
Oven	
Oven Temp.:	27 °C (hold 5 min) to 100 °C at 10 °C/min (hold 5 min)
Carrier Gas	He, constant flow
Flow Rate:	5.0 mL/min
Detector	Valco helium ionization detector @ 150 °C

also available

Metal MXT® PLOT Columns

Porous Polymer Columns

Porous polymers are unique, highly retentive stationary phases with a wide application range that are able to elute both polar and nonpolar compounds. They are very hydrophobic, so water has no impact on retention times and even elutes as a good chromatographic peak. The Q-BOND is our most nonpolar and widely used porous polymer column; functional groups can be added to increase polarity (i.e., QS-, S-, and U-BOND). The process used to manufacture porous polymer PLOT columns causes the particles to adhere strongly to the walls of the tubing, so there is virtually no particle generation. You get reproducible performance from column to column, including selectivity and flow.

Our porous polymer PLOT columns are not moisture sensitive, making them ideal for applications where moisture is of major concern.

Rt®-Q-BOND Columns (fused silica PLOT)

100% divinylbenzene

- Nonpolar PLOT column incorporating 100% divinylbenzene.
- Excellent for analysis of C1 to C3 hydrocarbons as well as isomers and alkanes up to C12.
- High retention for CO_2 simplifies gas analysis; CO_2 and methane separated from O_2/N_2/CO. (Note: O_2/N_2/CO not separated at ambient temperature.)
- Use for analysis of oxygenated compounds and solvents.
- Maximum temperature of 300 °C.
- Also available on metal MXT® tubing!

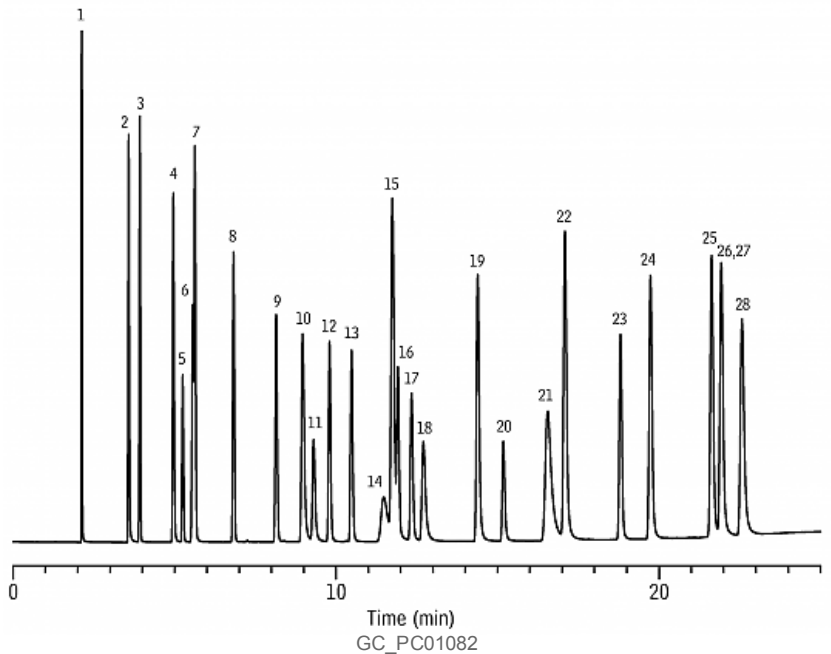
similar phases

HP PLOT Q, CP-PoraPLOT Q, CP-PoraBOND Q, Supel-Q-PLOT, AT-Q

ORDER NOW

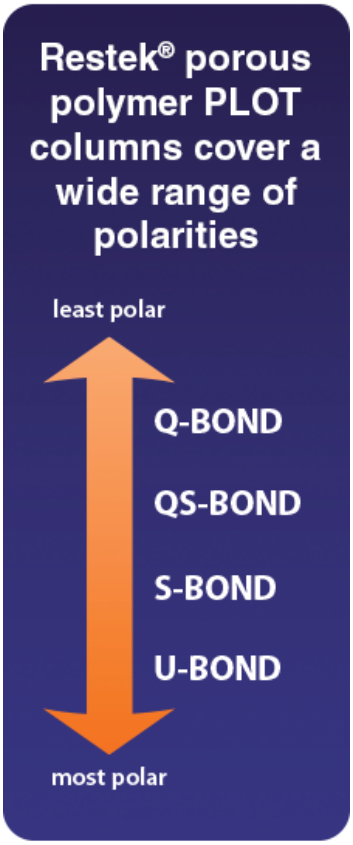
Solvent Mixture on Rt®-Q-BOND

Peaks		Peaks	
1. Methanol		15. Benzene	
2. Ethanol		16. 1,2-Dimethoxyethane	
3. Acetonitrile		17. Trichloroethylene	
4. Acetone		18. 1,4-Dioxane	
5. Dichloromethane		19. Pyridine	
6. 1,1-Dichloroethene		20. Dimethylformamide	
7. Nitromethane		21. Methylcyclohexane	
8. *trans*-1,2-Dichloroethylene		22. Toluene	
9. *cis*-1,2-Dichloroethylene		23. 2-Hexanone	
10. Tetrahydrofuran		24. Chlorobenzene	
11. Chloroform		25. Ethylbenzene	
12. Ethyl acetate		26. *m*-Xylene	
13. 1,2-Dichloroethane		27. *p*-Xylene	
14. 1,1,1-Trichloroethane		28. *o*-Xylene	



GC_PC01082

Column	Rt®-Q-BOND, 30 m, 0.53 mm ID, 20 µm (cat.# 19742)
Sample	Solvent mixture
Injection	
Inj. Vol.:	1.0 µL split
Liner:	Splitless taper (4 mm) (cat.# 20798)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	100 ml/min
Oven	
Oven Temp.:	120 °C to 240 °C at 5 °C/min (hold 5.0 min)
Carrier Gas	H_2, constant pressure (4.2 psi, 29.0 kPa)
Linear Velocity:	40 cm/sec @ 120 °C
Detector	FID @ 240 °C



Rt®-QS-BOND Columns (fused silica PLOT)

porous divinylbenzene homopolymer

- Intermediate polarity porous polymer PLOT column incorporating low 4-vinylpyridine.
- Separates ethane, ethylene, and acetylene to baseline.
- Stable to 250 °C.

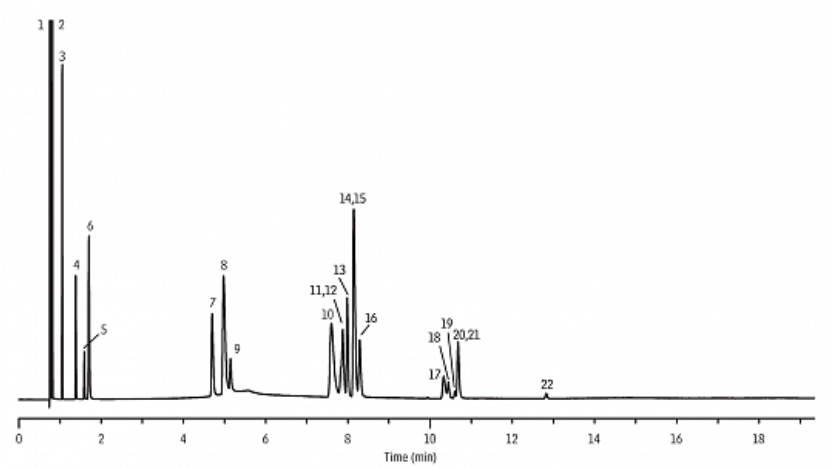
ORDER NOW

similar phases

GS-Q

Refinery Gas Mixture on Rt®-QS-BOND

Peaks	Peaks
1. Air	12. 1-Butene
2. Methane	13. 1,3-Butadiene
3. Carbon dioxide	14. *n*-Butane
4. Ethylene	15. *cis*-2-Butene
5. Acetylene	16. *trans*-2-Butene
6. Ethane	17. Isopentane
7. Propylene	18. 1-Pentene
8. Propane	19. 2-Methyl-2-butene
9. Propadiene	20. *n*-Pentane
10. Isobutane	21. *cis*-2-Pentene
11. Isobutylene	22. *n*-Hexane



GC_PC01143

Column	Rt®-QS-BOND, 30 m, 0.53 mm ID, 20 µm (cat.# 19738)
Sample	Refinery gas standard
Injection	
Inj. Vol.:	20 µL split
Liner:	2 mm (cat.# 20712)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	35 mL/min
Oven	
Oven Temp.:	40 °C (hold 2 min) to 225 °C at 15 °C/min (hold 5 min)
Carrier Gas	He, constant pressure (11.5 psi, 79.3 kPa)
Linear Velocity:	68 cm/sec @ 40 °C
Detector	TCD @ 225 °C
Make-up Gas Type:	He
Data Rate:	20 Hz
Sensitivity Mode:	He/H_2
Instrument	HP5890 GC

Rt®-S-BOND Columns (fused silica PLOT)

porous divinylbenzene homopolymer

- Midpolarity porous polymer PLOT column, incorporating high 4-vinylpyridine.
- Use for the analysis of nonpolar and polar compounds.
- Stable to 250 °C.
- Also available on metal MXT® tubing!

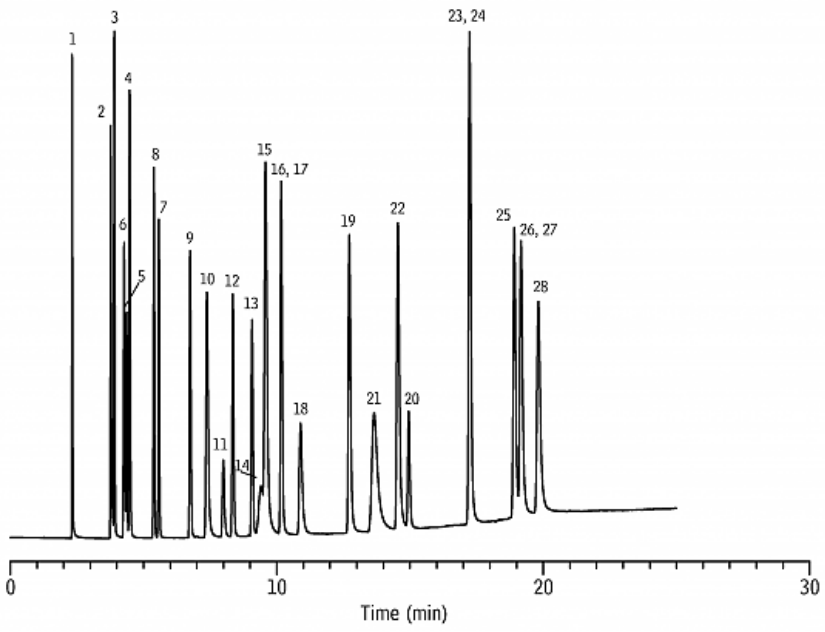
ORDER NOW

similar phases

CP-PoraPLOT S

Solvent Mixture on Rt®-S-BOND

Peaks	Peaks
1. Methanol	15. Benzene
2. Ethanol	16. 1,2-Dimethoxyethane
3. Acetonitrile	17. Trichloroethylene
4. Acetone	18. 1,4-Dioxane
5. Dichloromethane	19. Pyridine
6. 1,1-Dichloroethene	20. Dimethylformamide
7. Nitromethane	21. Methylcyclohexane
8. *trans*-1,2-Dichloroethylene	22. Toluene
9. *cis*-1,2-Dichloroethylene	23. 2-Hexanone
10. Tetrahydrofuran	24. Chlorobenzene
11. Chloroform	25. Ethylbenzene
12. Ethyl acetate	26. *m*-Xylene
13. 1,2-Dichloroethane	27. *p*-Xylene
14. 1,1,1-Trichloroethane	28. *o*-Xylene



GC_PC01080

Column	Rt®-S-BOND, 30 m, 0.53 mm ID, 20 µm (cat.# 19746)
Sample	Solvent mixture
Injection	
Inj. Vol.:	1.0 µL split
Liner:	Taper (4 mm) (cat.# 20798)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	100 ml/min
Oven	
Oven Temp.:	120 °C to 220 °C at 5 °C/min (hold 5.0 min)
Carrier Gas	H_2, constant pressure (4.2 psi, 29.0 kPa)
Linear Velocity:	40 cm/sec @ 120 °C
Detector	FID @ 220 °C

Rt®-U-BOND Columns (fused silica PLOT)

divinylbenzene ethylene glycol/dimethylacrylate

- Restek's highest polarity porous polymer column.
- Polar PLOT column, incorporating divinylbenzene ethylene glycol/dimethylacrylate.
- Highly inert for the analysis of polar and nonpolar compounds.
- Ideal for trace H_2S, COS, and mercaptans in hydrocarbon streams.
- Stable to 190 °C.

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also available!

Metal MXT® PLOT Columns

similar phases

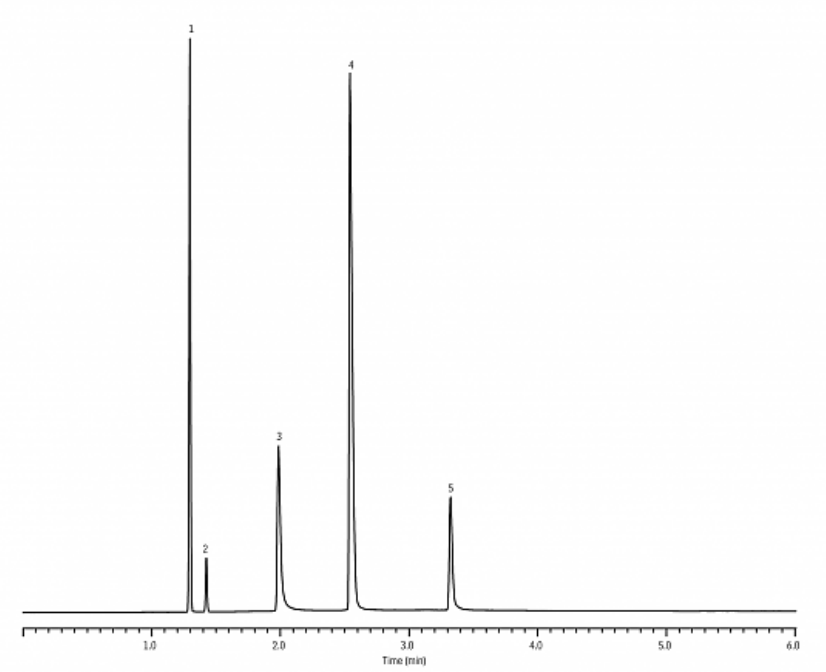
HP-PLOT U, CP-PoraPLOT U, CP-PoraBOND U

Formaldehyde on Rt®-U-BOND

Excellent peak shape for highly polar analytes

Peaks

1. Air
2. Carbon dioxide
3. Formaldehyde
4. Water
5. Methanol



GC_CH01137

Column	Rt®-U-BOND, 30 m, 0.53 mm ID, 20 µm (cat.# 19750)
Sample	Formaldehyde (manual headspace)
Injection	
Inj. Vol.:	10 µL split (split ratio 10:1)
Liner:	2 mm split Precision® liner w/wool (cat.# 20823)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	40 mL/min
Oven	
Oven Temp.:	100 °C (hold 1 min) to 150 °C at 25 °C/min (hold 3 min)
Carrier Gas	He, constant pressure (7.7 psi, 53.1 kPa)
Linear Velocity:	39 cm/sec @ 100 °C
Detector	TCD @ 200 °C
Make-up Gas Type:	He
Data Rate:	20 Hz
Sensitivity Mode:	He/H_2
Instrument	HP5890 GC

Rt®-Silica BOND Columns (fused silica PLOT)

- Versatile column ideal for analysis of light hydrocarbons, sulfur gases, halocarbons, and carbon dioxide.
- Individually QC tested with sensitive C4 probes to ensure consistent selectivity.
- Proprietary manufacturing process practically eliminates particle release, reducing downtime due to obstructed FID jets.
- Stable to 260 °C.

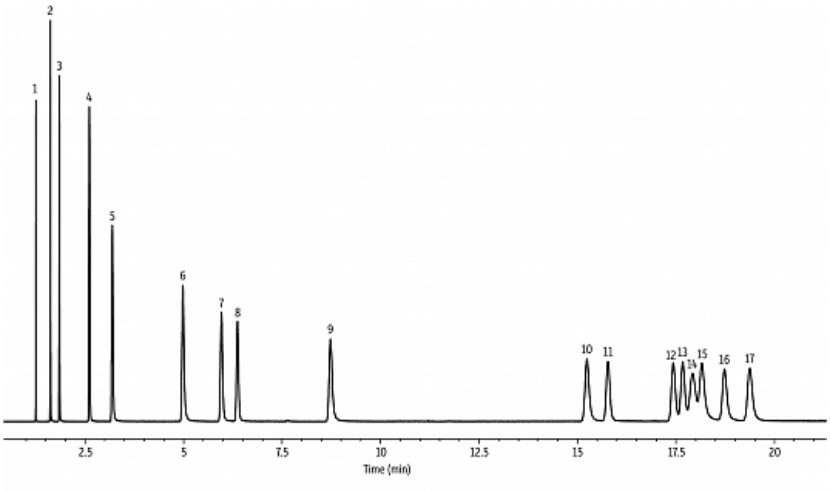
ORDER NOW

similar phases

GS-GasPro, CP-SilicaPLOT

Saturated and Unsaturated Hydrocarbons on Rt®-Silica BOND PLOT Column

Peaks	Peaks
1. Methane	9. *n*-Butane
2. Ethane	10. 1-Butene
3. Ethylene	11. Methyl acetylene
4. Acetylene	12. 1,3-Butadiene
5. Propane	13. *trans*-2-Butene
6. Cyclopropane	14. Isobutylene
7. Propylene	15. *cis*-2-Butene
8. Propadiene	16. Isopentane
	17. *n*-Pentane



GC_PC1266

Column	Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785)
Sample	Custom DCG gas standard
Diluent:	Nitrogen
Conc.:	1 mole percent
Injection	
Inj. Vol.:	15 µL split (split ratio 35:1)
Liner:	2 mm straight Sky® inlet liner (cat.# 23313.1)
Inj. Temp.:	250 °C
Oven	
Oven Temp.:	60 °C (hold 2 min) to 175 °C at 2 °C/min
Carrier Gas	He, constant flow
Flow Rate:	3.3 mL/min
Detector	FID @ 260 °C
Make-up Gas Flow Rate:	50 mL/min
Make-up Gas Type:	N_2
Hydrogen flow:	40 mL/min
Air flow:	400 mL/min
Data Rate:	10 Hz
Instrument	Agilent 7890A GC

Metal MXT® PLOT Columns

Advantages of metal MXT® PLOT columns include:

- Can be made in small coil diameters—perfect for tight spaces.
- Rugged material withstands rough handling and shock.
- Designed for robust performance in process GCs and field instruments.
- Available in 3.5"-coil diameter or 7"-diameter, 11-pin cage.

Restek® chemists have developed technology that allows many of our popular PLOT columns to be made on Siltek®-treated stainless steel. These columns have the same characteristics and performance as fused silica PLOT columns, but offer additional benefits for process GCs and field applications as they are virtually unbreakable and can be coiled into very small diameters.

MXT®-Msieve 5A

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MXT®-Alumina BOND/MAPD

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MXT®-S-BOND

ORDER NOW

MXT®-Alumina BOND/Na_2SO_4

ORDER NOW

MXT®-Q-BOND

ORDER NOW

MXT® Low Dead Volume Connector Kits for Metal Columns

- Connect a guard column/transfer line to an MXT® stainless steel column.
- Low thermal mass tracks rapid oven temperature programming.
- Stainless steel ferrules and nuts.
- Available in “Y” and union configurations.

Each kit contains the MXT® union, two 1/32-inch ferrules and nuts.

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RESTEK Pure Chromatography

Restek Corporation, U.S., 110 Benner Circle, Bellefonte, PA 16823

Resolve Benzene and Toluene in Spark Ignition Fuels Containing Ethanol

Using a Modified ASTM D3606-10 Method D3606 Column Set

- ★ **Complete resolution of benzene from ethanol**—no compromising coelutions.
- ★ **Easy, accurate quantification of aromatics.**
- ★ **Fully conditioned column set**.
- ★ **Each set is tested for method applicability and includes chromatogram.**

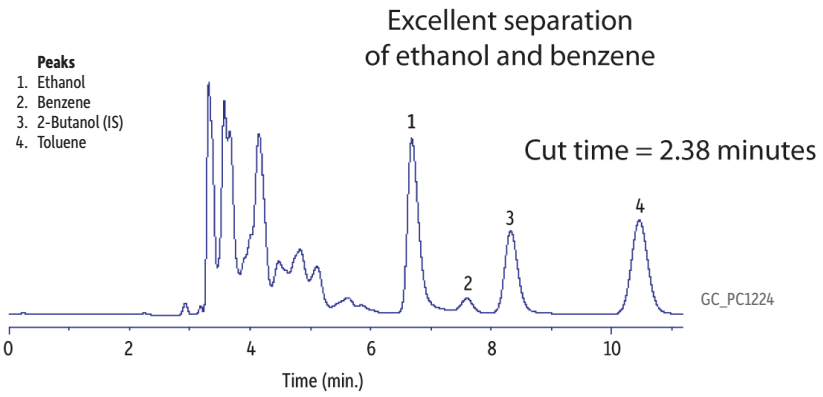
Laboratories analyzing reformulated spark ignition fuels that contain ethanol for the determination of benzene and toluene must use a modified ASTM D3606-10 method to prevent the coelution of ethanol and benzene. This method modification is also a requirement of the U.S. EPA. The benzene range of determination is 0.1 to 5% by volume, and the toluene range is 2 to 20% by volume. The primary challenge in this analysis is twofold: the tailing of the ethanol peak, and the retention time shift of the aromatics towards ethanol, specifically benzene merging quickly into the ethanol peak and preventing accurate quantification.

Restek has resolved these issues by developing a D3606 column set for this modified ASTM D3606-10 application. Column 1 is a 6' x 1/8" nonpolar Rtx®-1 phase, which separates components by boiling point. After the elution of *n*-octane (C8), Column 1 is backflushed to prevent heavier compounds from entering Column 2, the main analytical column. The light compounds pass into Column 2, a 16' x 1/8" column packed with a proprietary polymer that fully resolves the aromatics compounds.

To demonstrate the performance of this column set, a gasoline sample was analyzed using a GC equipped with a thermal conductivity detector (TCD). Helium was used as the carrier gas at 20 mL/min. in the constant flow mode. The data in Figure 1 show that the aromatic compounds are fully resolved, and can easily be quantified using the internal standard, 2-butanol.

This column set is fully conditioned. Only a brief (10 min.) carrier gas purge at ambient temperature, followed by a 1 hour hold at 165 °C, is required. If your laboratory has been struggling with ASTM method D3606-10 for reformulated fuels containing ethanol, Restek's column set is the solution.

Gasoline Containing Ethanol on D3606 Application Column Set by ASTM D3606-10 (Modified)



Column	D3606 application column (2 column set). Column 1: 6' (1.8 m), 1/8" OD, 2.0 mm ID, nonpolar Rtx®-1; Column 2: 16' (4.9 m), 1/8" OD, 2.0 mm ID, proprietary packing material (cat.# 83606-800)
Sample	Ethanol-containing gasoline with internal standard (IS)
Diluent:	
Injection	sample valve
Sample Loop Vol.:	1.5 µL
Valve Temp.:	150 °C
Oven	
Oven Temp:	135 °C (hold 12 min.)
Carrier Gas	He, constant flow
Flow Rate:	20.0 mL/min.
Detector	TCD @ 200 °C
Notes	2.38 minute backflush (must be determined for each GC system).

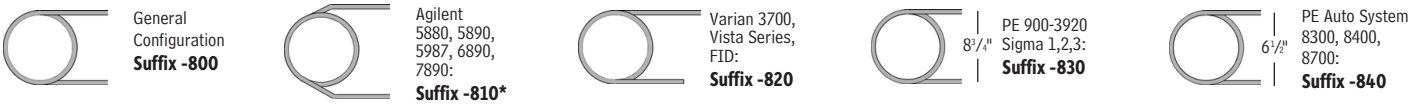
D3606 Application Column (2 column set)

Description	cat.#*
D3606 Application Column (2 column set)**	
Column 1: 6' (1.8m), 1/8" OD, 2.0mm ID, nonpolar Rtx-1	83606-
Column 2: 16' (4.9m), 1/8" OD, 2.0mm ID, proprietary packing material	

*Please add column instrument configuration suffix number to cat.# when ordering. See chart on this page.
**The column set is designed to accommodate both valve injection and/or syringe injection. Column 1 is configured with a 2" inlet void to facilitate on-column injection. The inlet is identified on both column 1 and column 2. Note: The inlet of column 2 is identified for proper orientation for connection to the valve.

Visit **www.restek.com/D3606standards** for a list of our certified reference materials.

Column Configurations



See our website for custom configurations

Note: Initial 2" of column will be empty, to accommodate a needle. For a completely filled column (not on-column) add suffix -901.
*-810 suffix also includes 1 1/2" void on detector side.

Visit **www.restek.com/petro** for more products and technical resources.

RESTEK®

Lit. Cat.# PCTS1408-UNV

www.restek.com

New D3606 Column Set Outperforms TCEP Columns for Benzene Analysis

Barry Burger, Petroleum Chemist and Jan Pijpelink, Petrochemical Market Development Manager, Restek Corporation
110 Benner Circle, Bellefonte, PA 16823, USA. Tel: 1-800-356-1688 E-mail: support@restek.com Web: www.restek.com

Demand for finished gasolines containing ethanol continues to increase, as these fuels reduce greenhouse gas emissions and can be used to help control air pollution. Ethanol is a cost-effective additive for production; however, its presence significantly complicates the analysis of benzene, a regulated carcinogen which is added to increase octane levels. Accurate benzene and toluene analysis is critical because incorrect data can result in inaccurate octane levels and out-of-specification product. Toluene analysis is straightforward, but benzene is extremely difficult to separate from ethanol on the 1,2,3-tris(2-cyanoethoxy) propane (TCEP) column listed in ASTM method D3606. A new D3606 column set developed by Restek separates benzene and ethanol completely and more reliably than TCEP columns, resulting in tighter control and more accurate results for refineries and contract laboratories.

Independent Testing Shows New D3606 Column Set Outperforms TCEP

It is widely recognised that TCEP columns often fail to adequately separate ethanol and benzene (*Figure 1*). Additionally, ethanol frequently shows considerable tailing on TCEP columns, further complicating the integration of benzene. Both these effects combine to make accurate benzene quantification on TCEP columns a substantial challenge. In contrast, the new D3606 column set developed by Restek reliably provides excellent separation of benzene and ethanol, allowing accurate benzene quantification (*Figure* 2). Ethanol/benzene resolution values are typically greater than 3.00, allowing easy integration of benzene and more accurate quantification than is typically obtained on TCEP columns.

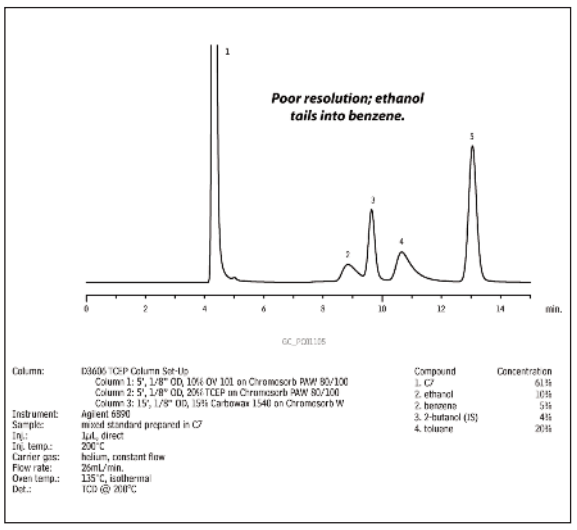


Figure 1 TCEP columns often fail to adequately resolve benzene from ethanol, resulting in poor quantitative results.

Since ethanol and benzene are easily resolved on the D3606 column set, a third column is not needed, resulting in simpler installation than the 3 column configuration described in Appendix X1 of the method (modifications for resolving benzene from ethanol). Each set is composed of 2 columns: column 1 is packed with nonpolar 100% dimethyl polysiloxane Rtx®-1 polymer (6' [1.8m], 1/8" OD, 2mm ID), and column 2 is packed with a new proprietary polymer (16' [4.9], 1/8" OD, 2mm ID). Column 1 separates components by boiling point and is backflushed after the elution of n-octane (C8) to prevent the heavier compounds from entering column 2, the main analytical column. The proprietary polymer used in column 2 allows the complete separation of aromatic compounds and reliably resolves ethanol

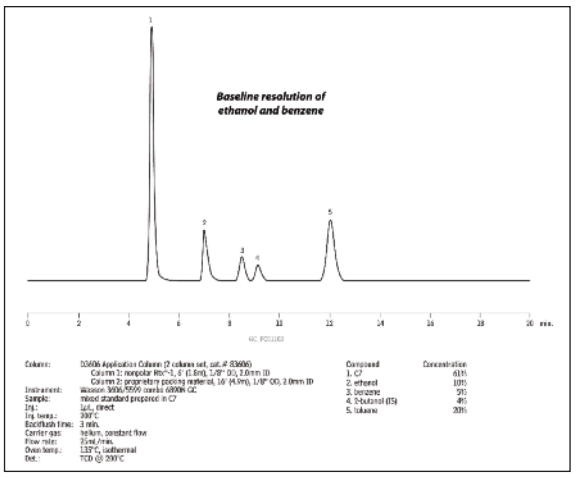


Figure 2 Restek's new D3606 column set accurately and reliably separates benzene from ethanol, improving quantitative accuracy.

Following extensive in-house testing, D3606 column sets were sent to refineries for independent analysis by beta testers and excellent results were obtained from all test sites (*Figures 3 and* 4). Linearity was assessed using calibration curves for benzene and toluene and correlations of 0.99999 and 1.00000, respectively, were obtained. Additionally, beta testers reported that repeatability was excellent and that overall reliability exceeded typical TCEP column performance. Both in-house testing and results from independent testers demonstrate that Restek D3606 column sets substantially outperform TCEP columns and provide more accurate and reliable data for quantifying benzene.

Reliable Performance Guaranteed

In addition to inadequate resolution of ethanol and benzene, TCEP columns show poor thermal stability. This results in short column lifetimes, making TCEP columns a relatively expensive choice in terms of cost-per-injection and downtime required for frequent column changes. In comparison, Restek's D3606 column set is stable to 165°C and exhibits very low bleed, allowing accurate integration and quantification of both benzene and toluene.

Reliable performance is assured, as all D3606 column sets are individually tested for method applicability and a quality test chromatogram is included with each set. D3606 column sets are fully conditioned and ready to use after a short conditioning period (30 minutes at 160°C), resulting in minimal downtime, increased productivity, and lower

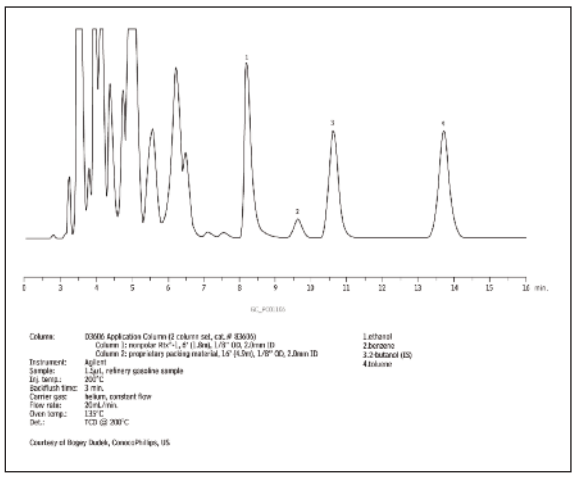


Figure 3 Ethanol and benzene are reliably resolved in refinery gasoline by beta testers using Restek's new D3606 column set.

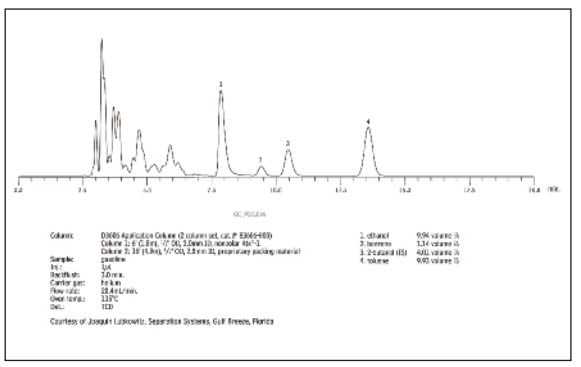


Figure 4 Ethanol and benzene are reliably resolved in commercial gasoline by beta testers using Restek's new D3606 column set.

Conclusion

The new D3606 column set developed by Restek offers substantial performance improvements compared to TCEP columns. New D3606 columns reliably resolve benzene from ethanol, allowing more accurate quantitation.

Additionally, these column sets are individually tested for method applicability and have higher thermal stability than TCEP columns—resulting in a more reliable, cost-effective column option for refineries.

Improve Trace Analysis of Acetylene, Propadiene, and Methyl Acetylene Impurities with Higher Capacity Alumina MAPD Columns

Rick Morehead, Jan Pijpelink, and Jaap de Zeeuw*, Restek Corporation
Restek Corporation, 110 Benner Circle, Bellefonte, PA, US
*Restek Corporation, Weerhaan 9, Middelburg, The Netherlands

When analysing trace impurities in petroleum gases, such as propylene, ethylene, or 1,3-butadiene, column capacity (loadability) is an important factor in obtaining accurate data. Phase overload results in peak tailing, which can be problematic when trace level impurities elute near the main component where they may be obscured by the larger peak. Peak tailing can be further exacerbated by residual activity on the adsorbent surface. Using a higher capacity column with an appropriate deactivation is a good strategy for reducing tailing and improving accurate quantification of low level polar impurities in volatile petroleum streams.

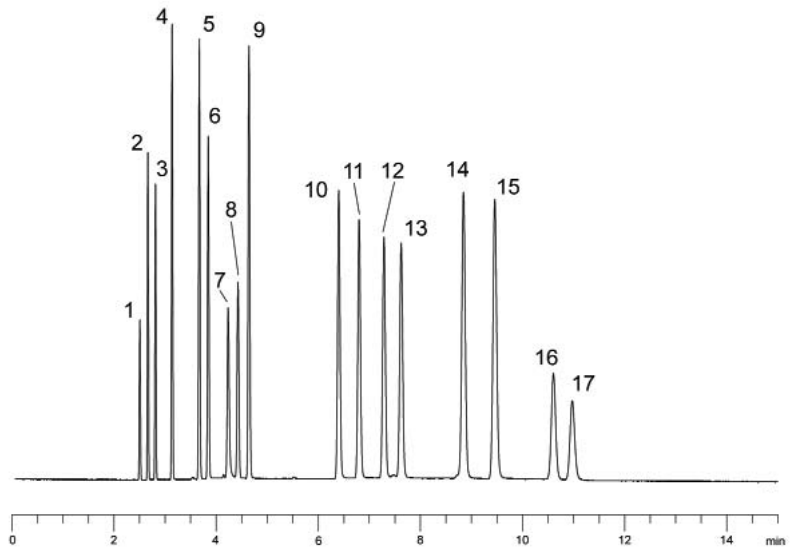
MAPD alumina PLOT columns are commonly used for these applications because the selectivity of alumina makes it very useful for separating C1-C5 hydrocarbons. Although selectivity is very good for these compounds capacity is often poor, which limits the amount of sample that can be injected. Larger sample volumes can be desirable when less sensitive detectors (e.g. TCDs) are used or when trace levels of impurities, such as acetylene, propadiene, or methyl acetylene, must be detected in order to prevent damage to polymerisation catalysts.

New Rt®-Alumina BOND/MAPD columns have an improved deactivation, increased capacity, and greater absolute retention compared to other commercially available MAPD PLOT columns. As shown in a comparison of absolute retention, all peaks are well resolved on the Rt®-Alumina BOND/MAPD column and no coelutions are observed (Figure 1). Greater retention increases the separation space, which reduces the likelihood of coelution and can lessen the impact of tailing. Absolute retention was compared using an isothermal oven temperature of 130°C; however, several critical compounds were not resolved on the Select Al_2O_3 MAPD column at this temperature, so optimized conditions for each column were used for capacity evaluations.

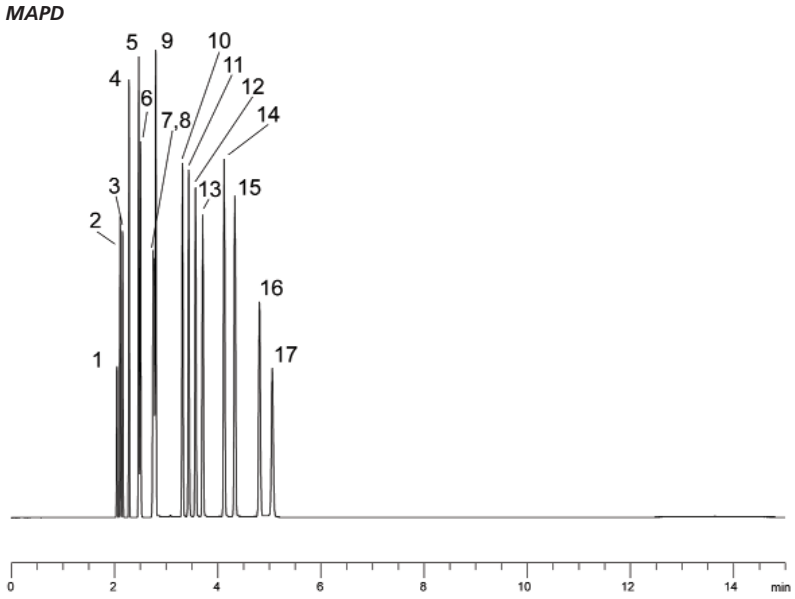
To assess capacity, each column was tested at the temperature shown on the manufacturer's QA protocol in order to achieve comparable retention and adequate resolution. A range of sample volumes of a QA test mix were analysed on each column using a 6-port sampling valve and 5µL to 250µL sample loops. Peak tailing was measured for the analytes that were most likely to exhibit tailing and be sensitive to poor capacity in actual impurity testing. As shown in Table I, much less peak tailing was observed on the Rt®-Alumina BOND/MAPD column. Symmetrical peaks were obtained across a wide sample volume range, indicating that the column deactivation was highly effective and also that capacity was greater on the Rt®-Alumina BOND/MAPD column. Linearity was also assessed, as shown in Figure 2, and excellent correlations were achieved for all target impurities across the test range.

When analysing impurities, such as acetylene, propadiene, and methyl acetylene in petroleum gases, column capacity is an important consideration. Rt®-Alumina BOND/MAPD columns offer higher capacity than other commercially available MAPD columns and are recommended for analysing polar impurities in light hydrocarbon streams. Greater capacity improves data accuracy due to better peak symmetry and a wide linear range

1A. Rt®-Alumina BOND/MAPD



1B. Select Al_2O_3 MAPD



Columns: 50m x 0.53mm ID x 10µm; Sample: PLOT column QA test mix (DCG# 547267); Injection: 5µL, split, 200°C; Split vent flow rate: 80mL/min.; Oven: 130°C, isothermal; Carrier gas: helium, (4.4psi, 30kPa); Detector: FID, 200°C. Peaks: 1. Methane, 2. Ethane, 3. Ethylene, 4. Propane, 5. Cyclopropane, 6. Propylene, 7. Acetylene, 8. Propadiene, 9. n-Butane, 10. trans-2-Butene, 11. 1-Butene, 12. Isobutene, 13. cis-2-Butene, 14. Isopentane, 15. n-Pentane, 16. 1,3-Butadiene, 17. Methyl acetylene.

***Figure 1:** Rt®-Alumina BOND/MAPD columns have greater absolute retention than Select Al_2O_3 MAPD columns, ration space.*

Rt®-Alumina BOND/MAPD (130°C)

Tailing Factor (USP)			
Sample Size (µL)	**Propadiene**	**Acetylene**	**Methyl Acetylene**
5	1.038	1.227	1.083
10	1.040	1.219	1.130
25	1.058	1.248	1.216
50	1.085	1.292	1.388
100	1.094	1.316	1.546
250	1.177	1.481	2.224

Select Al_2O_3 MAPD (100°C)

Tailing Factor (USP)			
Sample Size (µL)	**Propadiene**	**Acetylene**	**Methyl Acetylene**
5	1.073	1.298	1.908
10	1.098	1.478	2.743
25	1.165	1.902	4.555
50	1.304	2.580	6.871
100	1.448	3.241	9.208
250	1.979	4.882	15.476

Table I: *Higher capacity is also demonstrated by comparing peak symmetry. Rt®-Alumina BOND/MAPD columns produce more symmetrical peaks, even when more material is injected.*

2. Rt® - Alumina BOND/MAPD Linearity

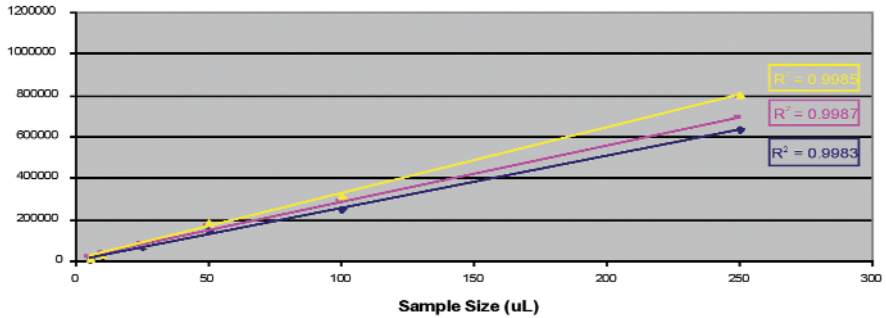


Figure 2: *Higher capacity results in a wide linear range and accurate quantification, even at levels that can produce tailing and incomplete separations on other MAPD columns.*
(yellow = methyl acetylene, pink = acetylene, blue = propadiene)

High Temp. Stability Problem Solved with New Metal Columns

Analysis of Total Glycerides in Biodiesel Oils by ASTM D-6584 Using New MXT®-Biodiesel TG Capillary Columns

Barry L. Burger, Petroleum Chemist, and Jaap de Zeeuw, International GC Consumables Specialist. This content was previously published in *Petro Industry News*, June, 2007.

One of the biggest challenges in biodiesel fuel analysis is the accurate determination of residual triglyceride content. Triglycerides are present at low levels and elute at high chromatographic temperatures. Any suitable column must be operated at temperatures up to 380°C, which considerably strains conventional capillary tubing and stationary phases. Restek has developed new 0.32mm ID and 0.53mm ID MXT® stainless steel capillary columns—the MXT®-Biodiesel TG line—specifically for high temperature biodiesel analysis. Here we demonstrate the analytical advantages of full metal columns: unsurpassed stability at high temperatures, excellent peak symmetry for triglycerides, highly reproducible retention times, and unsurpassed column lifetimes.

Introduction

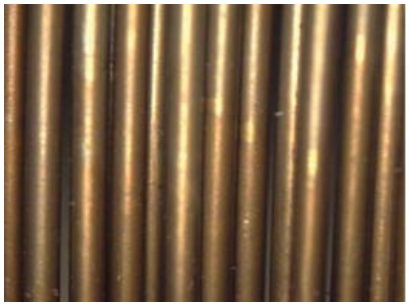
"Biodiesel", "B100", "B20", "B10", and "transesterification" are fast becoming everyday terminology. Biodiesel oil is biodegradable, nontoxic, does not contain aromatics, and the absence of sulfur from B100 precludes sulfur dioxide emissions. The "B" number designates the percentage of biodiesel in a biodiesel/petroleum diesel blend (e.g., B20 is 20% biodiesel / 80% petroleum diesel). Biodiesel is recognized as a desirable alternative energy source to petroleum-based products. However, excessive amounts of glycerides in biodiesel oil products can foul engine injectors and form deposits on valves, pistons, and injector nozzles. Also, separation of the glycerin during storage or in vehicle fuel tanks can reduce the shelf-life of the product. Clearly, accurate, efficient methods for quantifying glycerin and glycerides are critical to the biodiesel industry.

The American Society for Testing and Materials (ASTM) and the European method Deutsches Institut fur Normung (DIN) describe several physical and chemical testing methods for biodiesel oil. Gas chromatography (GC) is ideal for measuring important parameters such as total glycerin, fatty acid methyl esters (FAMEs) and methanol levels in biodiesel fuel. Methods like ASTM D-6584 and EN14105 set the industry standards for testing total glycerin and glycerides in biodiesel oil. The gas chromatographic column recommended for the analysis is a 10m x 0.32mm ID column with a 0.1µm film of 5% diphenyl/95% dimethyl polysiloxane, connected to a 0.53mm retention gap. The high temperatures required by these methods to elute triglycerides are a significant challenge to column stability and restrict column material choice to fused silica or metal.

Full Metal Advantage

Typically the fused silica column is the first choice for GC analysis, however at higher oven temperatures (>380°C) the polyamide coating on the fused silica tubing deteriorates, reducing column lifetimes (Figure 1). Even fused silica columns designed for high temperature applications (HT equivalents) become unpredictable and break down relatively quickly. In response, Restek has developed the MXT®- Biodiesel TG column line, a line of metal columns designed with stainless steel tubing and our patented Siltek® deactivation technology, ensuring maximum heat tolerance. The metal MXT® tubing does not degrade, even under temperatures up to 430°C, which allows analysts to "bake out" any residue eluting out after the triglycerides without damaging the column. This "bake out" process keeps the analytical system clean so subsequent injections do not have carry-over from previous samples.

Figure 1a & 1b MXT®-Biodiesel TG columns (Figure 1a) are undamaged by high temperature heat cycles compared to the HT fused silica columns (Figure 1b) which break down under the same conditions (100 temperature cycles to 430°C totaling 500 minutes at maximum temperature.) Note extensive pitting on the fused silica column.



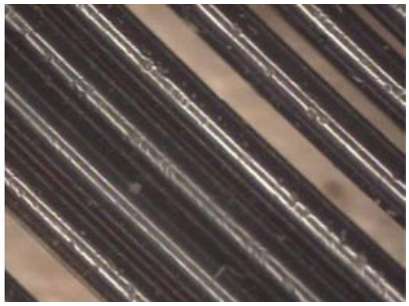


Figure 1a MXT®-Biodiesel TG column

Figure 1b ZB-5HT Inferno column

Stability Solutions

The MXT® Biodiesel TG columns are deactivated using Siltek® technology, which creates a unique intermediate layer that stabilizes the stationary phase and provides unsurpassed inertness. Due to Siltek® deactivation, the stationary phase is extremely stable, exhibiting virtually no bleed even at temperatures as high as 430°C. Column inertness is demonstrated by evaluating peak shape and retention time stability.

Peak shape can be affected by active sites in the analytical column; higher asymmetry values indicate greater exposure to active sites, meaning the column is less inert. Peak symmetry of butanetriol on a commercial HT equivalent fused silica column deteriorates after just 20 injections, compared to the excellent symmetry that is maintained on the MXT®-Biodiesel column (Figure 2). While the HT equivalent fused silica column was specified to be stable up to 430°C the metal MXT®-Biodiesel TG column shows no sign of activity and is clearly more stable and inert.

In addition to peak shape, consistent analyte retention times can be used to demonstrate column stability. The data in Figure 3 show the retention time of tricaprin over 100 injections for the HT equivalent fused silica and the MXT®-Biodiesel TG columns. The decrease in retention time of tricaprin on the HT equivalent fused silica column indicates liquid phase is being lost from the column. In contrast, the retention time for tricaprin on the MXT®-Biodiesel TG column stays consistent, indicating no phase loss due to cycling the column at high temperature. Practically, this translates into reliable performance and longer column lifetimes.

Figure 2 Metal MXT®-Biodiesel TG columns are more stable and inert than the commercially available HT equivalent fused silica columns as evidenced by symmetric and consistent peak shape for the internal standard butanetriol.

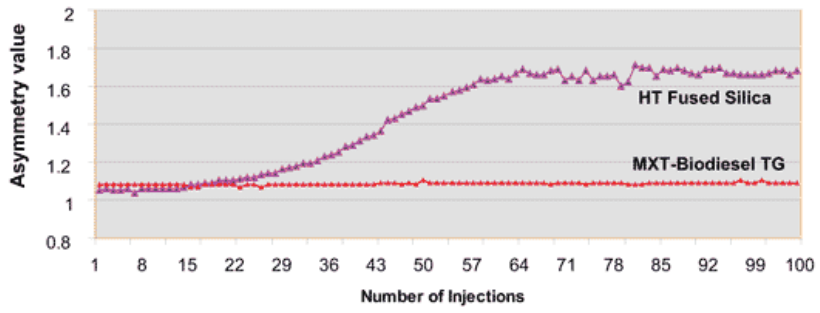
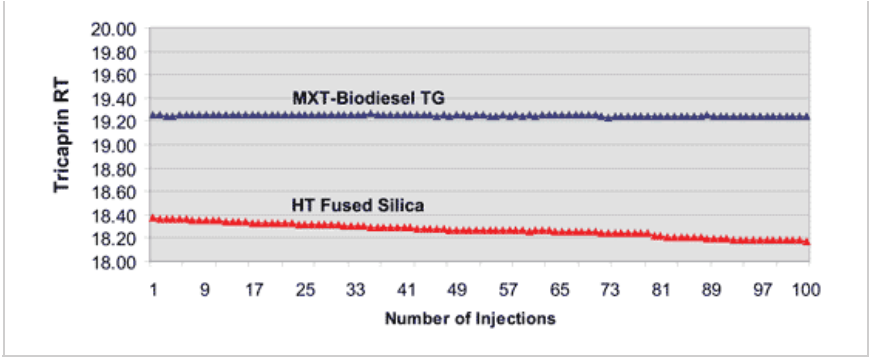


Figure 3 Retention time is stable on metal MXT®-Biodiesel TG columns, even under high temperature cycling.



Unique Solutions that Simplify Practical Operation

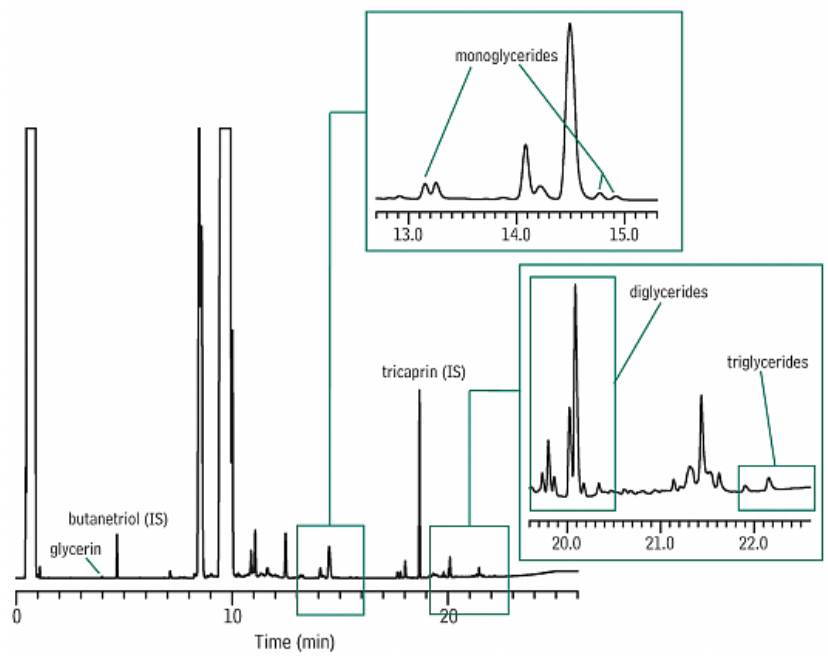
Factory connected 0.32mm MXT®-Biodiesel TG columns & 0.53mm retention gaps

For accurate analysis of heavy triglycerides, on-column or PTV injection is required. Analytical methods ASTM D-6584 and EN-14105 describe the use of a 0.32mm analytical column coupled with a 0.53mm retention gap. The 0.53mm ID retention gap allows the on-column technique to be used, but care must be taken to minimize dead volume and to establish a leak-tight connection. Restek's 0.32mm MXT®-Biodiesel TG columns are factory-coupled to a 0.53mm MXT® retention gap with an Alumaseal™ connector, ensuring a leak-tight connection. Target analytes resolve well and the solvent and triglyceride peaks show excellent symmetry (Figure 4).

0.53mm MXT®-Biodiesel TG columns with Integra-Gap™ technology

The 0.53mm MXT®-Biodiesel TG columns are a simpler alternative to using a 0.32mm column coupled to a 0.53mm retention gap. Restek applied Integra-Gap™ technology to the 0.53mm MXT® Biodiesel TG columns, eliminating the column coupling. These 100% leak-proof columns feature a built-in retention gap, reducing the risk of peak broadening and tailing, and guaranteeing the user many analyses without downtime. Chromatography from the 0.53mm MXT®-Biodiesel TG with Integra-Gap™ technology (Figure 5) is excellent and comparable to that obtained on the 0.32mm ID column in Figure 4.

Figure 4 Glycerin and glycerides in derivatized B100 samples resolve well and show excellent peak symmetry on the 0.32mm MXT®-Biodiesel TG column, which is factory-coupled to a 0.53mm MXT® retention gap.

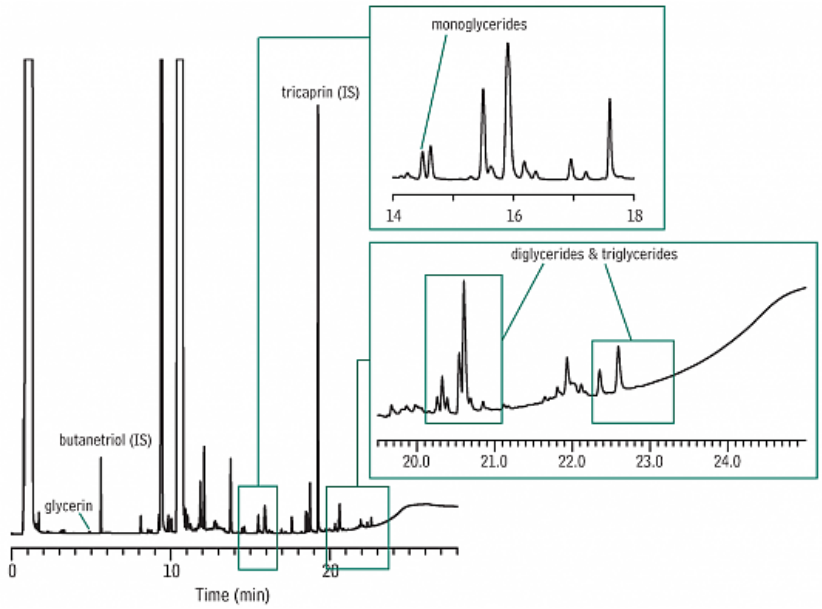


GC_PC00935

Column	MXT®-Biodiesel TG w/2 m x 0.53 mm retention gap, 10 m, 0.32 mm ID, 0.10 µm (cat.# 70290)
Sample	B100 + IS butanetriol & tricaprin derivatized with MSTFA as per ASTM D6584
Injection	

Oven	
Oven Temp.:	50 °C (hold 1 min) to 180 °C at 15 °C/min to 230 °C at 7 °C/min to 430 °C at 30 °C/min (hold 5 min)
Carrier Gas	H_2, constant flow
Flow Rate:	4 mL/min
Detector	FID @ 430 °C

Figure 5 Equivalent chromatographic quality can be obtained on the 0.53mm MXT®-Biodiesel TG analytical column. The built-in retention gap eliminates the need for a connector, thus preventing peak tailing from dead volume.



GC_PC00934

Column	MXT®-Biodiesel TG 13m, 0.53mm ID, 0.16µm with built-in 2m Integra-Gap™ (total column length 15 m)
Sample	B100 + IS Butanetriol & Tricaprin derivatized with MSTFA as per ASTM D-6584
Injection	
Inj. Vol.:	1.0 µL cold on-column
Temp. Program:	oven track
Oven	
Oven Temp.:	50 °C (hold 1 min) to 180 °C at 15 °C/min to 230 °C at 7 °C/min to 430 °C at 30 °C/min (hold 5 min)
Carrier Gas	H_2, constant flow
Flow Rate:	4 mL/min
Detector	FID @ 430 °C
Instrument	Shimadzu 2010 GC
Notes	(Data acquired on prototype column, similar column to cat# 70290)

Conclusion

As demonstrated, for high-temperature GC analysis, the metal MXT®-Biodiesel TG columns are rugged and withstand the harsh temperatures required for total residual glycerin analysis. The columns have the resolution needed for accurate, reliable results and are more stable at high temperatures than competitive fused silica columns. This high temperature stability leads to longer column lifetimes and less downtime for maintenance and/or column change outs.

For additional information about the MXT®-Biodiesel TG capillary column line or other analytical needs for biodiesel analysis contact your nearest Restek Sales Representative or Distributor.

RELATED SEARCHES

biodiesel, *astm d6584*, *6584*, *glycerides*, *total Glycerides*, *triglycerides*, *en14105*, *residual triglyceride*, *b100*

RESTEK
Pure Chromatography

Petrochemical Applications

MXT®-1HT Sim Dist

A High-Temperature Polydimethylsiloxane-Phase Column for ASTM D-6352-98 Simulated Distillation Analyses

Simulated distillation per ASTM D-6352-98 is used for determining the boiling point range distribution of petroleum distillate fractions with initial boiling points (BP) > 174°C and final boiling points < 700°C at atmospheric pressure. High temperature Sim Dist presents many challenges. The stationary phase must meet rigid resolution and retention time requirements, yet be stable at high temperatures. Further, the polyimide protective coating on the outer surface of most capillary columns has a maximum working temperature of about 380°C. Above this temperature the polyimide rapidly deteriorates. When repeatedly programmed to temperatures above 400°C, or allowed to cool below 50°C, the aluminum sheath on most aluminum-clad fused silica columns separates from the underlying fused silica surface. The tubing becomes extremely brittle, and column lifetime is significantly shortened.

To conform to the critical criteria set forth by ASTM, Restek chemists developed the MXT®-1HT Sim Dist simulated distillation column. The MXT®-1HT polymer is a 100% polydimethylsiloxane (PDMS) material that is thermally stable to 430°C, requires minimal conditioning, and is 100% crosslinked. The MXT®-1HT phase is coated onto highly deactivated stainless steel tubing that has the inertness of fused silica without the temperature limitations. The MXT®-1HT Sim Dist column has a lifetime of at least 400 injections under typical Sim Dist conditions.

To demonstrate the robustness of MXT®-1HT Sim Dist columns, we made a series of 400 injections of Polywax® 1000 (cold on-column, CS_2 solvent, 1µL each) onto a randomly chosen column, and monitored critical performance characteristics over the course of these injections: resolution, retention times, stationary phase bleed. Figure 1 illustrates the Polywax® 1000 analysis after 400 injections. The hydrocarbon components still are well resolved and are easily quantified. Figure 2 plots the reproducibility of C50/C52 resolution and Figure 3 shows retention time reproducibility. After 400 injections, both of these critical characteristics still meet simulated distillation specifications. Figure 4 plots the consistently low bleed at 430°C over the series of 400 injections.

Figure 1 Polywax® 1000 hydrocarbons well resolved on an MXT®-1HT Sim Dist column after 400 injections.

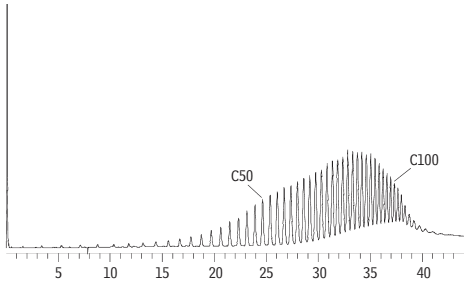


Figure 2 C50/C52 resolution is stable over a series of 400 injections on an MXT®-1HT Sim Dist column.

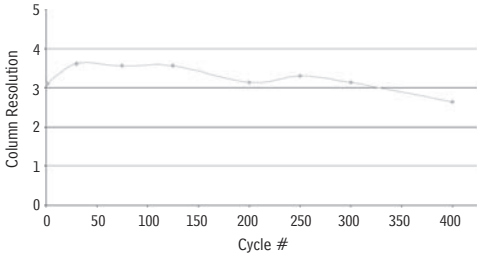
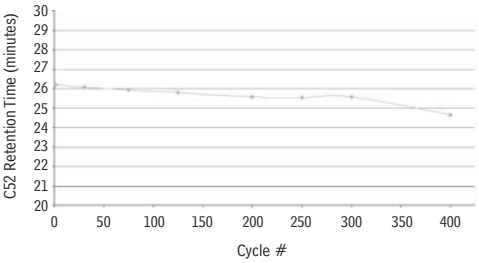


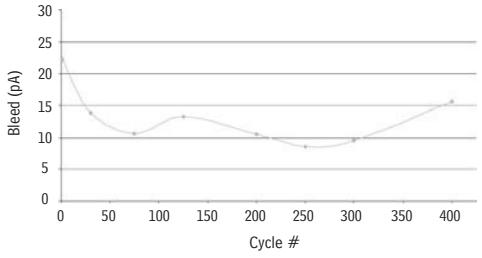
Figure 3 C52 retention shows little change after 400 injections on an MXT®-1HT Sim Dist column.



The stainless steel tubing used to make MXT®-1HT Sim Dist columns incorporates state-of-the-art Siltek® deactivation*. The deactivation layer is incorporated into the framework of atoms on the tubing surface, and will not fracture or flake off, even if the column is flexed or bent. MXT®-1HT Sim Dist columns do not exhibit higher selectivity toward aromatics than toward normal hydrocarbons, thus they provide true boiling point values.

These excellent performance characteristics make MXT®-1HT Sim Dist columns the columns of choice for ASTM D-6352-98 Sim Dist analyses. Note that the demanding temperature conditions of simulated distillation analyses make GC system integrity a prime concern. It is imperative that the GC system be oxygen-free, to prevent phase degradation and maintain the highest level of chromatographic performance. We strongly recommend using oxygen-free carrier gas and routinely leak-testing your system with an electronic leak detection device, such as our Electronic Leak Detector (cat.# 22451), to ensure protection from oxygen.

Figure 4 An MXT®-1HT column produces less than 20pA bleed over a series of 400 injections.



MXT®-1HT Sim Dist Column

(Siltek® treated stainless steel)

- Stable to 430ºC.
- Low bleed.
- Long lifetime at high temperatures.
- Symmetrical hydrocarbon peaks.
- Consistent resolution and retention times.
- Boiling point elution of hydrocarbons.
- Polarity equivalent to existing liquid phases.

ID	df (μm)	temp. limits	length	cat. #
0.53mm	0.10	-60 to 430°C	5-Meter	70100

Polywax® Standards

These high molecular weight hydrocarbon waxes are useful for simulated distillation and other high-temperature GC work.

Compound	qty.	cat.# (ea.)
Polywax® 500	1g	36224
Polywax® 655	1g	36225
Polywax® 850	1g	36226
Polywax® 1000	1g	36227

No data pack available.

Restek Electronic Leak Detector

Small, compact unit—easy to hold and operate.

- Reliable thermal conductivity leak detector.
- Responds to leaks in less than 2 seconds.
- Audible alarm plus LED readout.
- Auto zeros with the touch of a button.
- Built-in rechargeable 9 volt battery.

Leak Detector Facts	
Detectable gases:	helium, nitrogen, argon, carbon dioxide
Battery:	Rechargeable Ni-MH, 9 volt
Operating Temperature Range:	32°-120°F (0°-48°C)
Humidity Range:	0-97%
CE Approved:	Yes

Description	qty.	cat.#
Leak Detector with 110Volt Battery Charger	ea.	22451
Leak Detector with 220Volt European Battery Charger	ea.	22451-EUR
Leak Detector with 220Volt UK Battery Charger	ea.	22451-UK

Caution: The Restek Electronic Leak Detector is NOT designed for determining leaks of combustible gases. A combustible gas detector should be used for determining combustible gas leaks under any condition. The Restek Electronic Leak Detector may be used for determining trace amounts of hydrogen in a GC environment only.

*Siltek® treatment is a proprietary surface treatment for passivating steel, high nickel alloys of steel, glass, and other surfaces. U.S. Patent 6,444,326.

Lit. Cat.# 59479A

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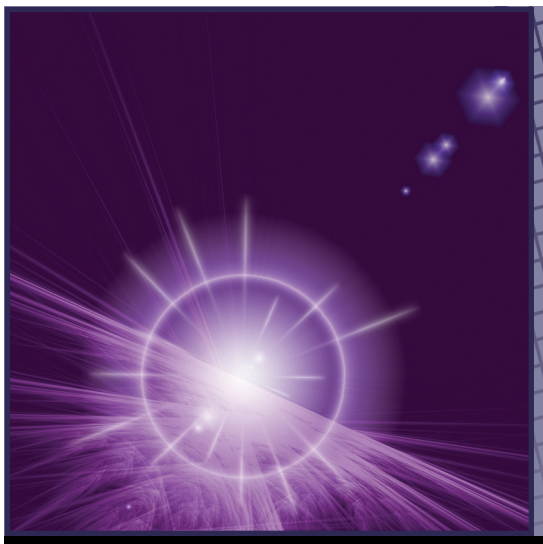

GCxGC Analysis of Complex Petroleum Hydrocarbons: Sulphur Speciation in Diesel

Jack Cochran and Jan Pijpelink, Restek Corporation
110 Benner Circle, Bellefonte, PA, US

Comprehensive 2D GC, also known as GCxGC, is a powerful technique with a great deal of potential for improving separations of complex petroleum and petrochemical samples that contain hundreds—or even thousands—of components. While GCxGC is still considered emerging technology and is used primarily in research and development labs, it has undergone significant growth in the past few years.

As evidenced by recent literature, industrial applications for GCxGC are growing in a number of areas; however, its ability to increase peak capacity and advance separations in complex matrices makes it particularly useful in the petro industries. GCxGC can be used to analyse hydrocarbons ranging in volatility from C4 (butane) to C40 (tetracontane), although with automatic flow programming of the cold jet in the thermal modulator analyses up to C48 have been reported [1]. Other notable recent advances include a full characterisation of middle distillates using supercritical fluid chromatography [2], a high temperature analysis of vacuum gas oils up to nC60 [3], and a partial characterisation of military fog oil [4]. Military fog oil is an extremely complex middle distillate product containing mainly aliphatic compounds. Using GCxGC-TOFMS, Kohl et al. were able to identify a wide range of low concentration aromatics from what would typically be an unresolved complex mixture. Compounds reported included alkanes, cyclohexanes, hexahydroindanes, decalins, adamantanes, bicyclohexanes, alkylbenzenes, indanes, tetrahydronaphthalenes, partially hydrogenated polycyclic aromatic hydrocarbons, biphenyls, dibenzofurans, and dibenzothiophenes. In these and other examples, the analytical power of comprehensive 2D GC is used to achieve a more advanced separation of complex matrices than is possible with 1D GC.

Technical Overview of GCxGC

In comprehensive 2D GC, two independent separations are applied to a single sample injection. A summary of the technique is given here; however, recent review papers provide a more complete description, focusing on recent advances and industrial applications [5,6]. In GCxGC, the first separation is usually based on boiling point and uses a standard nonpolar phase. Next, a thermal or valve modulator is used to focus the effluent from the first column onto the second column, which is a short (1-2 m) column and typically is a polar phase. Inverse polarity column set-ups are also sometimes employed, but with either approach the key to maximising use of the separation space is to choose orthogonal columns that differ significantly in selectivity. Separation results are displayed as a contour plot, which is a three dimensional representation of intensity (z) across the retention times of both column 1 (x) and column 2 (y). The result is a technique with increased peak capacity that can be used to separate compounds which coelute in the first dimension. Ultimately, the increased peak capacity obtainable with GCxGC allows better characterisation of complex petro fractions such as naphtha, gasoline, and diesel.

Sulphur Speciation in Diesel

The analysis of sulphurs, such as dibenzothiophenes, in diesel offers a timely example of the benefits of GCxGC for complex hydrocarbon samples. In recent years, new vehicle emissions standards have been adopted across the globe; these requirements have driven the development of ultra low sulphur diesel that is compatible with new emission control technology. In many countries, specifications for total sulphur in diesel have been reduced from 50 ppm to 10-15 ppm, making the analysis of various sulphur components even more crucial for the refinery industry. Using the analysis of dibenzothiophenes as an example, it is clear that 1D GC is insufficient to distinguish sulphur compounds due to coelutions with other components in the diesel matrix (Figure 1). An MS detector was used for this work because it offers the potential to identify a broad range of analytes from a single injection, compared to the limited information that can be obtained using a sulphur-specific detector. However, even with the power of the MS, the diesel sample was too complex to yield usable results. The spectrum taken at the retention time for dibenzothiophene confirms that the separation of components is not sufficient and the sulphur compounds cannot be identified (Figure 2).

In contrast, when GCxGC is used for the analysis of sulphurs in diesel, individual dibenzothiophenes are resolved both from the interferences that obscured them in the one-dimensional analysis and also from each other. The structured chromatogram (contour plot) that

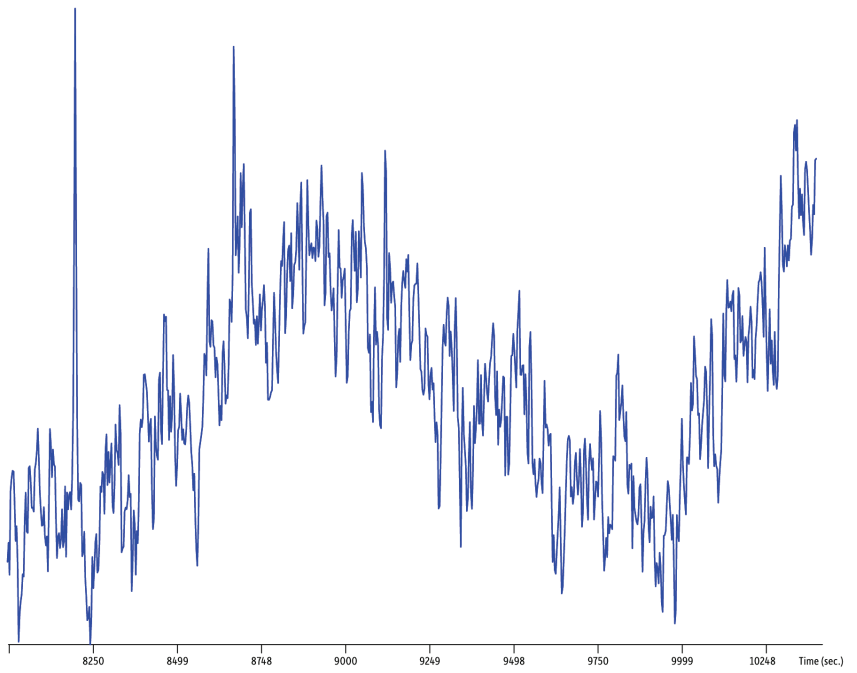

Figure 1: Elution area of dibenzothiophenes in a one-dimensional GC analysis of diesel. The sample is so complex that no distinct chromatographic peaks can be seen.

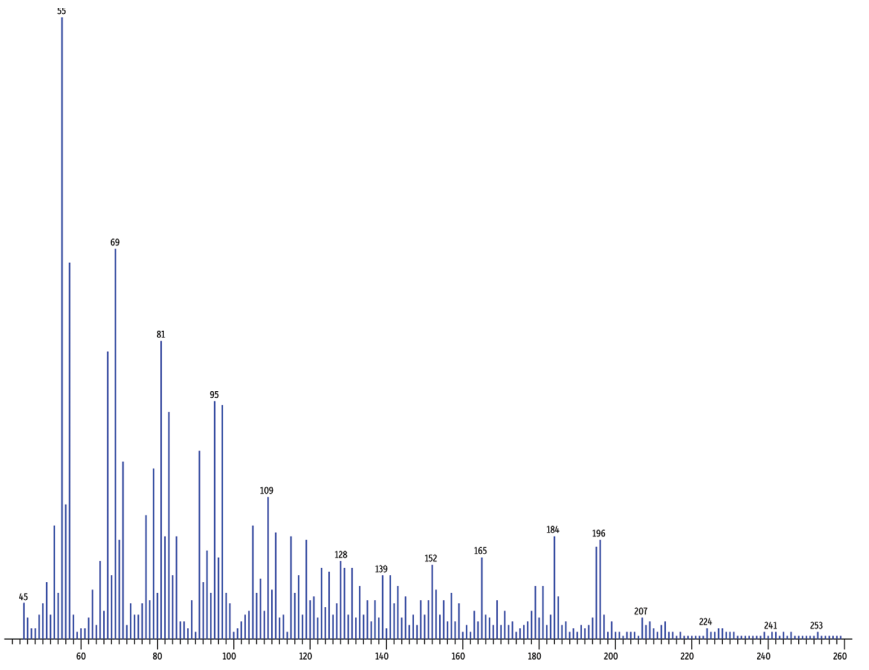

Figure 2: Mass spectrum taken at dibenzothiophene retention time for one-dimensional GC of diesel. The mass spectrum is not representative of dibenzothiophene at all due to sample complexity.

is obtained offers good separation of major groups and even resolves multiple positional isomers within each carbon substituent group (Figures 3-5). Comparison of the sample mass spectrum at the retention time for dibenzothiophene to a reference spectrum reveals a clear match and confirms compound identification (Figure 6). As shown in this example, good use of the separation space is made by optimising parameters for both columns. Often, in order to optimise separations on the second column, the first dimension separation is intentionally slowed in order to produce broader peaks that will accommodate 3-5 modulations per peak. With careful attention to flows, temperatures, and modulator settings, good column efficiencies can be obtained in both dimensions. By employing GCxGC and optimising use of the separation space, peak capacity is significantly increased. This approach, in combination with the use of a powerful MS detector, allows speciation of sulphur compounds in diesel and provides a level of sample characterisation that cannot be obtained using one-dimensional GC.

Analysis of sulphurs in diesel provides a good demonstration of the power of GCxGC for complex matrices. Increased peak capacity allows identification of relevant constituents that cannot be differentiated by GC alone. As this technology is increasingly adopted by the petroleum and petrochemical industries, better materials characterisation and process optimisation can be achieved.

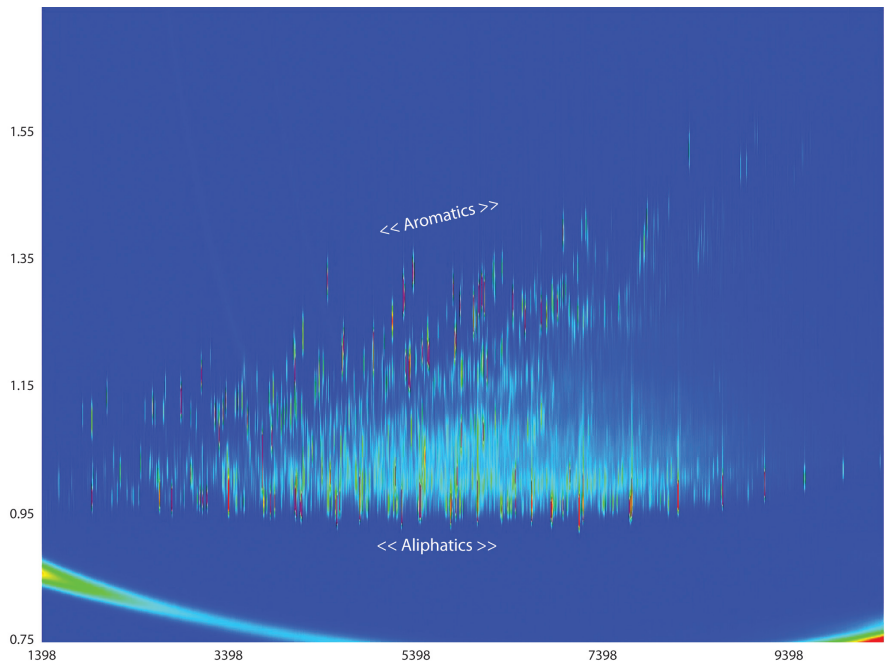

Figure 3: GCxGC-TOFMS chromatogram (contour plot) of diesel analysed with orthogonal Rxi®-1ms and Rtx®-FLD columns showing structured separation of aliphatics and aromatics.

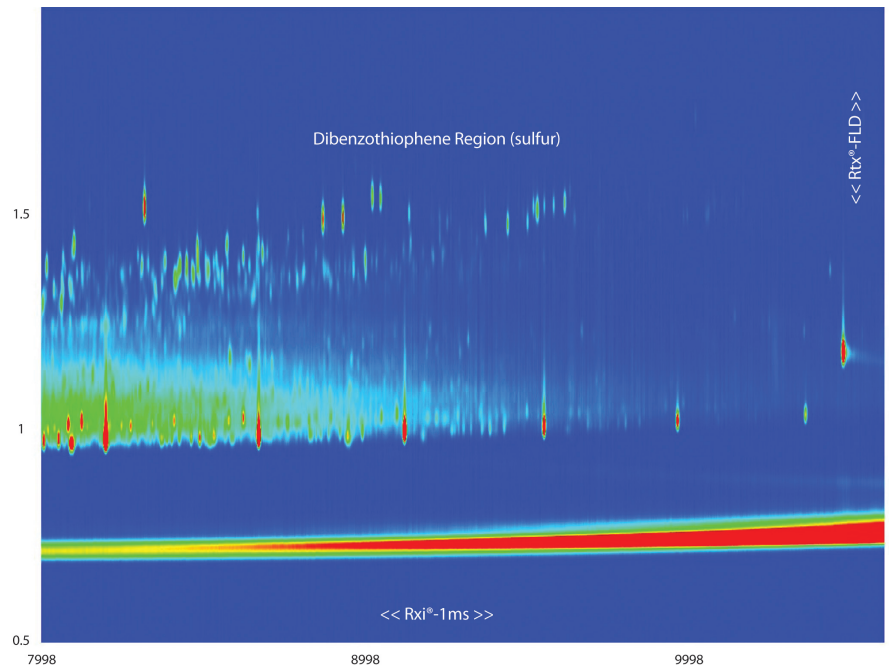

Figure 4: GCxGC-TOFMS contour plot (TIC) of the dibenzothiophene elution region for a diesel sample. The dibenzothiophenes are more retained by the Rtx®-FLD column, which means they are higher on the y-axis of the contour plot than most other components.

Experimental

A Pegasus 4D GCxGC-TOFMS (LECO, St. Joseph, MI,USA) was used with electron ionisation at 70 eV and an MS source temperature of 250°C. The acquired mass range was 45-450 u at 200 spectra/sec. The primary GC column consisted of 2 Rxi®-1ms columns (each 60 m x 0.25 mm x 0.25 µm) press-fitted together. The secondary column, a 1.5 m x 0.25 mm x 0.10 µm Rtx®-FLD column (an experimental phase column), was connected by a press-fit to the end of the primary column. The secondary column was installed in its own oven and terminated in the source of the TOFMS. This column combination was operated with helium carrier at a corrected constant flow of 2.0 mL/min. One microliter 50:1 split injections of a diesel fuel composite were performed into a Sky™ 4.0 mm Precision® inlet liner with wool at 275°C. The primary oven program was: 40°C (hold 1 min.) to 320°C at 1.3°C /min. (hold 1 min.) The secondary oven program was a positive 5°C offset from the primary oven. For GCxGC a quad-jet, dual-stage thermal modulator was used with a temperature offset of 20°C and a modulation time of 3 sec. The hot pulse time was 1 sec. For one-dimensional GC runs, the modulation time was set to zero, and the MS data collection rate was 2 spectra/sec. LECO ChromaTOF software was used for GCxGC-TOFMS data processing and display.

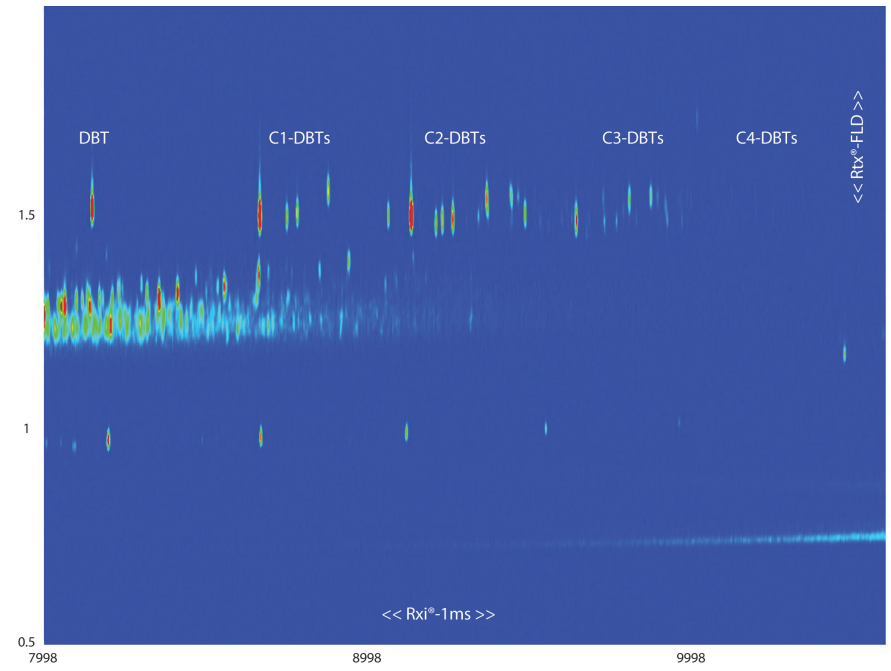

Figure 5: GCxGC-TOFMS extracted ion contour plot of the dibenzothiophene elution area for a diesel sample. Plotting m/z ions 184, 198, 212, 226, and 240 enhances visualisation of the separation of the dibenzothiophenes (including the alkyl substituted isomers).

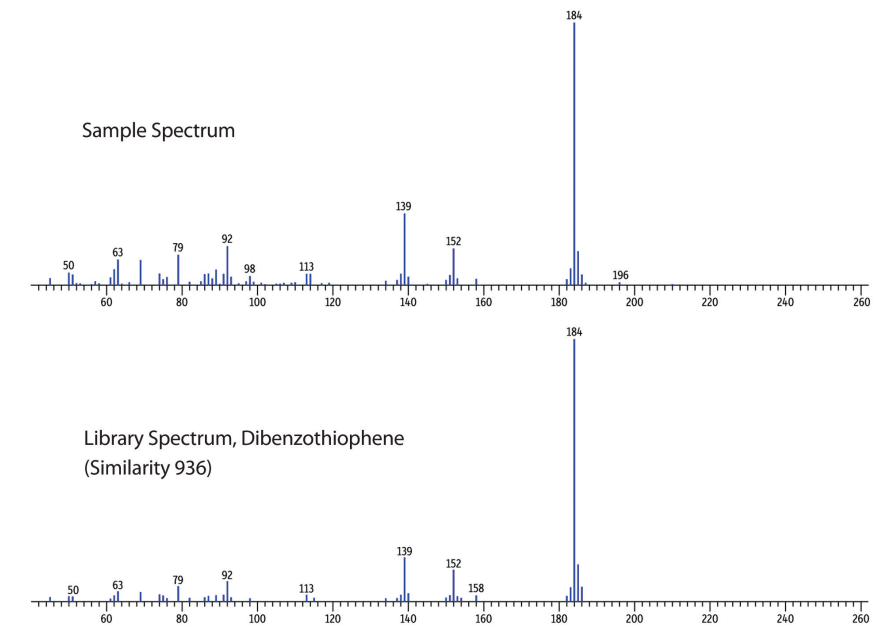

Figure 6: Mass spectrum of dibenzothiophene for comprehensive two-dimensional GC of diesel. The sample mass spectrum (top) is an excellent match with the NIST library mass spectrum (bottom).

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GC Analysis of Total Reduced Sulfurs at ppbv Levels

Using an Rxi®-1ms Column and Sulfur Chemiluminescence Detection

by Silvia Martinez, Innovations Chemist

- Reliable results for ppbv concentrations of highly active sulfur compounds.
- Inert, low bleed column resolves all analytes.
- Column compatible with SCD and other sulfur-specific detectors.

Through the Clean Air Act, the United States Environmental Protection Agency (US EPA) regulates and limits the emission of toxic air pollutants. The determination of total reduced sulfurs, as required by CFR Title 40, requires the use of methods and equipment capable of providing full resolution as well as high sensitivity. Methods TO-15, TO-16 and TO-16A describe GC procedures that apply to the determination of reduced sulfurs from stationary sources, such as recovery furnaces, lime kilns, smelt dissolving tanks, fuel gas combustion devices, tail gas control units, and others. Method TO-16 specifies detectable concentrations of ppbv levels for dimethyl disulfide, dimethyl sulfide, hydrogen sulfide, and methyl mercaptan. While these methods do not specify the analytical GC column to use, they do state that the column must resolve the sulfur compounds.

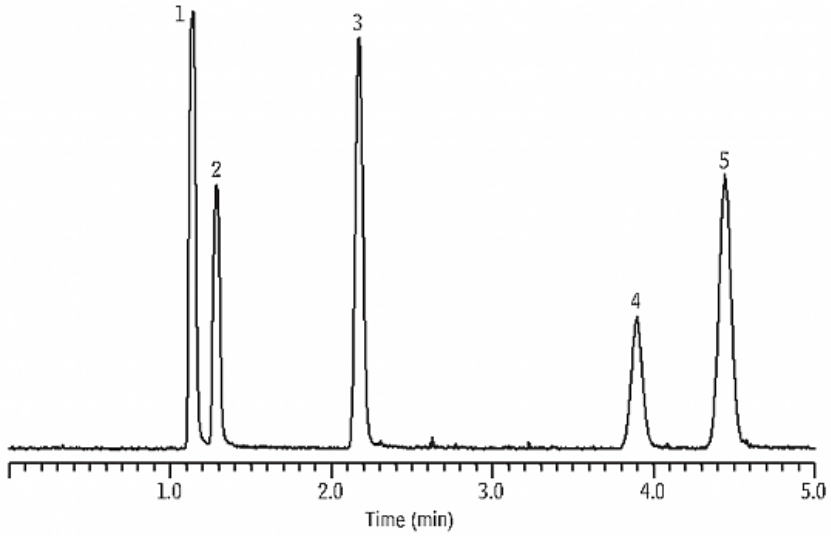
Our new 100% dimethylpolysiloxane column, the Rxi™-1ms column, provides the ultra-low bleed required for low level detection and quantification of sulfur compounds. Its exceptional inertness allows complete separation of these very reactive compounds, with excellent peak shape, at ppbv levels. When this column is coupled with a sulfur chemiluminescence detector (SCD), the analysis is fast and simple.

For our example analysis, we collected a 20mL sample of a gaseous mixture of hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, and dimethyl sulfide in helium, using a Sulfinert®-treated stainless steel sample loop. We transferred the sample to a SilcoCan™ air monitoring canister and pressurized the can to 30psig with dry nitrogen. The Sulfinert® passivation treatment on both the sample loop and canister prevented adsorption losses of the highly active sulfur compounds. We introduced a 1mL aliquot of the diluted gaseous mixture into the Rxi™-1ms column via a second Sulfinert®-treated stainless-steel sample loop, using helium as a carrier, and analyzed the sample isothermally at 30°C.

Figure 1 shows the chromatography for the reduced sulfur compounds, demonstrating full resolution in less than 5 minutes. For collecting, storing, and analyzing active sulfur compounds at levels as low as single parts per billion, the performances of Sulfinert® passivated containers and transfer systems, and inert Rxi™-1ms columns, simply can't be equaled.

Figure 1 Total resolution of reduced sulfur compounds, in less than 5 minutes, using an Rxi™-1ms column.

Peaks
1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Dimethyl sulfide



GC_AR00861

Column	Rxi®-1ms, 30 m, 0.32 mm ID, 4.00 µm (cat.# 13396)
Sample	Hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide
Diluent:	Helium
Conc.:	100 ppbv
Injection	splitless
Inj. Temp.:	30 °C
Oven	
Oven Temp.:	30 °C
Carrier Gas	He, constant pressure
Linear Velocity:	48 cm/sec @ 30 °C
Detector	SCD @ 800 °C
Notes	Injection: sample loop (30°C), 1 mL splitless direct Sample Storage and Tansfer: SilcoCan® air monitoring canister with Siltek®-treated 1/4" valve (cat.# 24182-650); Sulfinert®-treated gas sample loop, 1 cc (cat.# 22848); Sulfinert®-treated gas sample loop, 10 cc (custom order)

RELATED SEARCHES

chemiluminescence, *dimethyl sulfide*, *mercaptans*, *sulfur*, *inertness*, *hydrogen sulfide*, *carbonyl sulfide*, *sulfinert*

Fast, Accurate FAMEs Analyses of Biodiesel Fuel

Using a Stabilwax® Capillary GC Column

By Barry L. Burger, Innovations Chemist

- Stable baselines, excellent peak symmetry, baseline resolution of all compounds.
- Analysis complete in less than 11 minutes.
- All RSD% values less than 1%.

A Stabilwax® fused silica GC column affords excellent peak symmetry, resolution, and reproducibility for determining the fatty acid methyl ester (FAME) and linolenic acid methyl ester content in B100 biodiesel fuel, using European standard method EN 14103. The chromatograms and quantified data shown here were generated from four different sources of biodiesel fuel, and meet or exceed the method criteria.

As biodiesel fuel continues to stimulate interest worldwide as an energy source, several gas chromatographic methods have been developed to determine the quality of B100 fuel. European standard method EN 14103 is used for determining the FAME and linolenic acid methyl ester content, European standard method EN 14105 and ASTM standard method D-6584-00e1 are used for determining free and total glycerin, and European standard method EN 14110 is used for determining residual methanol. Method EN 14103 permits the analyst to assure the B100 product is greater than 90% fatty acid methyl esters (m/m) and the linolenic acid content is between 1% and 15% (m/m). The analysis is appropriate for FAME compositions between C14:0 and C24:1.

In evaluating the suitability of the Stabilwax® column for quantifying FAMEs and linolenic acid methyl ester by method EN 14103, we prepared reference standards from each of the four B100 fuel sources — soy, tallow, rapeseed, and yellow grease (Table 1) — by weighing 250mg of the source material into a 10mL vial, then adding 5mL of a 10mg/mL solution of internal standard methyl heptadecanoate. (Avoid allowing the samples to stand longer than 12 hours, or quantification will be inaccurate.) We installed the 30m x 0.32mm ID x 0.25µm Stabilwax® column (cat.# 10624) in an Agilent 6890 instrument equipped with a split/splitless injector, a flame ionization detector, and ChemStation software. To obtain the fastest analysis, without sacrificing resolution, we selected hydrogen as the carrier gas, supplied from a Parker Balston hydrogen generator.

Figure 1 shows, for each source material, the analysis to FAME C24:1 is completed in less than 11 minutes. Particularly notable are the stability of the baselines, the excellent peak symmetry, and baseline resolution of all compounds of interest. Table 2 summarizes the RSD% values for the FAMEs measurements, all of which are less than 1%.

A 30m x 0.32mm ID x 0.25µm Stabilwax® column, used with hydrogen carrier gas, permits high speed analysis and ensures precise data acquisition for accurate quantification of C14:0-C24:1 FAMEs and linolenic acid methyl ester.

Table I Sources of FAMEs in B100 biodiesel fuel (% m/m).

		Soy	Tallow	Rapeseed	Yellow Grease
Myristic acid	C14:0	0.21	1.7	0.11	0.68
Palmitic acid	C16:0	11.24	25.5	4.1	16.35
Palmitoleic acid	C16:1	0.2	3.27	0.27	1.23
Stearic acid	C18:0	4.04	14.41	1.8	9.32
Oleic acid	C18:1	21.93	40.34	58.57	47.8
Linoleic acid	C18:2	53.84	12.02	22.2	20.01
Linolenic acid	C18:3	7.29	0.99	13.26	2.93
Arachidic acid	C20:0	0.36	0.4	0.79	0.46
Gadoleic acid	C20:1	0.26	1.03	1.79	0.39
Behenic acid	C22:0	0.45		0.57	0.44
Erucic acid	C22:1			0.13	0.23
Lignoceric acid	C24:0	0.16	0.34	0.3	0.24

Nervonic acid	C24:1		0.17	0.54	

Table 2 Relative standard deviations for FAMEs do not exceed 1% in analyses on a Stabilwax® column (n = 3).

		Soy	Tallow	Rapeseed	Yellow Grease
Myristic acid	C14:0	0.33	0.42	0.24	0.36
Palmitic acid	C16:0	0.04	0.06	0.02	0.04
Palmitoleic acid	C16:1	0.23	0.17	0.19	0.09
Stearic acid	C18:0	0.05	0.02	0.13	0.19
Oleic acid	C18:1	0.02	0.3	0.2	0.25
Linoleic acid	C18:2	0.25	0.41	0.11	0.22
Linolenic acid	C18:3	0.13	0.16	0.07	0.14
Arachidic acid	C20:0	0.3	0.37	0.23	0.31
Gadoleic acid	C20:1	0.33	0.28	0.37	0.41
Behenic acid	C22:0	0.28		0.29	0.17
Erucic acid	C22:1			0.21	0.26
Lignoceric acid	C24:0	0.53	0.14	0.1	0.33
Nervonic acid	C24:1		0.55	0.83	

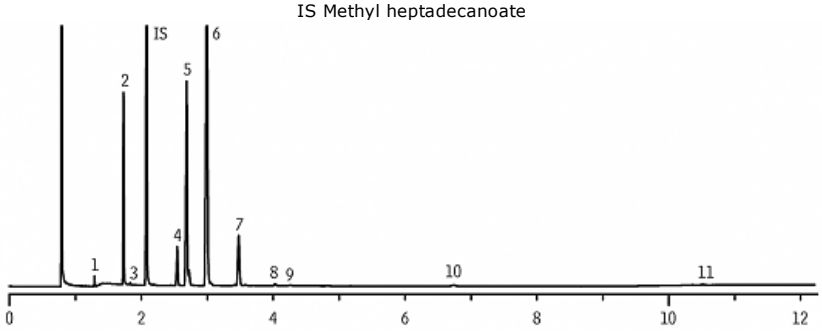
Figure 1 Stable baselines, excellent peak symmetry, and rapid, baseline resolution of all compounds characterize FAMEs analyses on a Stabilwax® column.

Soy

Peaks

1. Myristic acid C14:0
2. Palmitic acid C16:0
3. Palmitoleic acid C16:1
4. Stearic acid C18:0
5. Oleic acid C18:1
6. Linoleic acid C18:2
7. Linolenic acid C18:3
8. Arachidic acid C20:0
9. Gadoleic acid C20:1
10. Behenic acid C22:0
11. Lignoceric acid C24:0

IS Methyl heptadecanoate



GC_PC00915

Column Stabilwax®, 30 m, 0.32 mm ID, 0.25 µm (cat.# 10624)
Sample Soy source of biodiesel (B100), prepared according to European Method EN 14103
Injection
Inj. Vol.: 1.0 µL split (split ratio 100:1)
Liner: Cyclosplitter® (cat.# 20706)
Inj. Temp.: 250 °C
Oven
Oven Temp.: 210 °C (hold 5 min) to 230 °C at 20 °C/min (hold 5 min)
Carrier Gas H_2, constant flow
Flow Rate: 3 mL/min
Linear Velocity: 60 cm/sec
Detector FID @ 250 °C

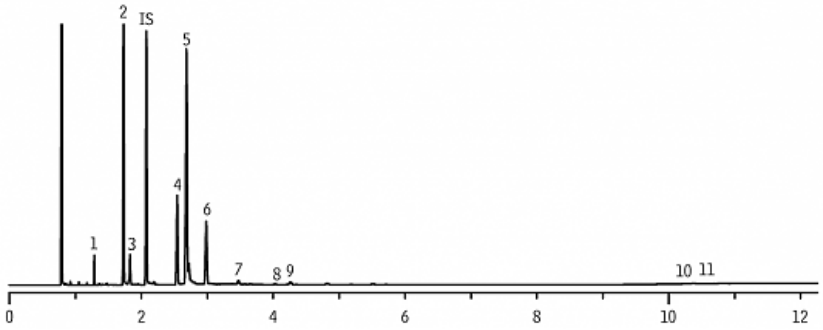
Tallow

Peaks

1. Myristic acid C14:0
2. Palmitic acid C16:0
3. Palmitoleic acid C16:1

7. Linolenic acid	C18:3
8. Arachidic acid	C20:0
9. Gadoleic acid	C20:1
10. Lignoceric acid	C24:0
11. Nervonic acid	C24:1

IS Methyl heptadecanoate



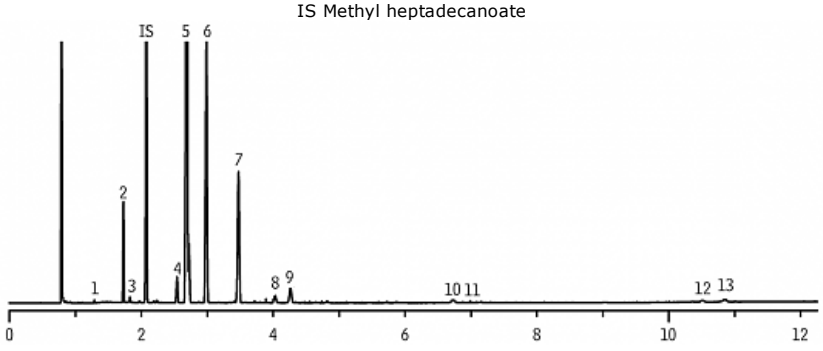
GC_PC00916

Column	Stabilwax®, 30 m, 0.32 mm ID, 0.25 µm (cat.# 10624)
Sample	Tallow source of biodiesel (B100), prepared according to European Method EN 14103
Injection	
Inj. Vol.:	1.0 µL split (split ratio 100:1)
Liner:	Cyclosplitter® (cat.# 20706)
Inj. Temp.:	250 °C
Oven	
Oven Temp.:	210 °C (hold 5 min) to 230 °C at 20 °C/min (hold 5 min)
Carrier Gas	H_2, constant flow
Flow Rate:	3 mL/min
Linear Velocity:	60 cm/sec
Detector	FID @ 250 °C

Rapeseed

Peaks	
1. Myristic acid	C14:0
2. Palmitic acid	C16:0
3. Palmitoleic acid	C16:1
4. Stearic acid	C18:0
5. Oleic acid	C18:1
6. Linoleic acid	C18:2
7. Linolenic acid	C18:3
8. Arachidic acid	C20:0
9. Gadoleic acid	C20:1
10. Behenic acid	C22:0
11. Erucic acid	C22:1
12. Lignoceric acid	C24:0
13. Nervonic acid	C24:1

IS Methyl heptadecanoate



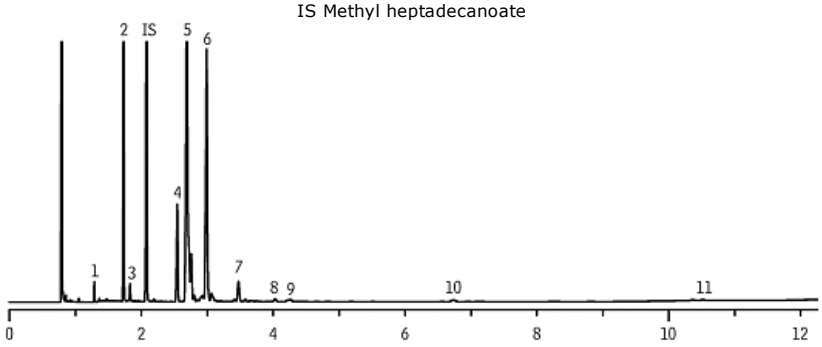
GC_PC00917

Column	Stabilwax®, 30 m, 0.32 mm ID, 0.25 µm (cat.# 10624)
Sample	Rapeseed source of biodiesel (B100), prepared according to European Method EN 14103
Injection	
Inj. Vol.:	1.0 µL split (split ratio 100:1)
Liner:	Cyclosplitter® (cat.# 20706)
Inj. Temp.:	250 °C
Oven	
Oven Temp.:	210 °C (hold 5 min) to 230 °C at 20 °C/min (hold 5 min)
Carrier Gas	H_2, constant flow
Flow Rate:	3 mL/min
Linear Velocity:	60 cm/sec
Detector	FID @ 250 °C

Peaks

1. Myristic acid	C14:0
2. Palmitic acid	C16:0
3. Palmitoleic acid	C16:1
4. Stearic acid	C18:0
5. Oleic acid	C18:1
6. Linoleic acid	C18:2
7. Linolenic acid	C18:3
8. Arachidic acid	C20:0
9. Gadoleic acid	C20:1
10. Behenic acid	C22:0
11. Erucic acid	C22:1
12. Lignoceric acid	C24:0

IS Methyl heptadecanoate



GC_PC00918

Column	Stabilwax®, 30 m, 0.32 mm ID, 0.25 µm (cat.# 10624)
Sample	Yellow grease source of biodiesel (B100), prepared according to European Method EN 14103
Injection	
Inj. Vol.:	1.0 µL split (split ratio 100:1)
Liner:	Cyclosplitter® (cat.# 20706)
Inj. Temp.:	250 °C
Oven	
Oven Temp.:	210 °C (hold 5 min) to 230 °C at 20 °C/min (hold 5 min)
Carrier Gas	H_2, constant flow
Flow Rate:	3 mL/min
Linear Velocity:	60 cm/sec
Detector	FID @ 250 °C

RELATED SEARCHES

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Restek Corporation, U.S., 110 Benner Circle, Bellefonte, PA 16823

Eliminate Column Breakage in High Temperature Biodiesel Analysis

By Barry Burger, Petroleum Innovations Chemist, Gary Stidsen, Product Marketing Manager, and Jaap de Zeeuw, International GC Specialist

Beat high temperature column breakage with Restek MXT®-Biodiesel TG columns. More stable than fused silica, for accurate, reliable performance and longer column lifetime. Available with either factory-coupled or fully-integrated retention gaps.

Restek has raised the bar with a new high-temperature MXT®-Biodiesel TG column line to complement our fused silica column line for biodiesel analysis. These new MXT®-Biodiesel TG columns are stable to 430°C and offer unique retention gap options that minimize dead volume and leaks. Choose either a 0.32mm column factory-coupled to a 0.53mm retention gap, or select a single unit 0.53mm column featuring Integra-Gap™, a built-in retention gap that eliminates the need for a connector. Both designs are extremely stable at high temperatures and produce fast elution times and sharp peaks for high molecular weight glycerides.

Unsurpassed Stability

The high temperature programs required for analysis of biodiesel oils (B100) by either ASTM D-6584 or EN-14105 methodology present a significant challenge to the analytical column. High-temperature fused silica tubing breaks down under these extreme conditions, but the metal MXT® tubing does not degrade, even at temperatures up to 430°C (Figure 1). This allows analysts to bake out any residue eluting after the triglycerides, preventing carryover without damaging the column.

So how well do the MXT®-Biodiesel TG columns perform? We conducted a benchmarking experiment comparing an MXT®-Biodiesel TG column with an Integra-Gap™ retention gap to a high-temperature fused silica column which was coupled to a conventional 0.53mm retention gap. Methodology followed ASTM method D-6584, except the final temperature was modified to 430°C. Both columns were subjected to 100 temperature cycles up to 430°C and then derivatized B100 was injected to check column performance.

This evaluation was performed using a Shimadzu 2010 gas chromatograph equipped with a flame ionization detector, a model AOC 20i + S autosampler with a 10µL SGE syringe and 42mm 26-gauge needle, and a cold on-column programmable injector with a stainless steel injector insert. A Parker hydrogen generator supplied the carrier gas. Peak symmetry and retention time were evaluated as indicators of thermal stability.

Peak symmetry of butanetriol on a commercial high-temperature fused silica column deteriorates after just 20 injections, compared to the excellent symmetry that is maintained on the MXT®-Biodiesel TG column (Figure 2). In addition to peak shape, retention time stability was used to evaluate column performance. The decrease in retention time seen on the high-temperature fused silica column indicates the liquid phase is being lost (Figure 3). In contrast, the consistent retention times obtained on the MXT®-Biodiesel TG column demonstrate its stability. Practically, this translates into reliable performance and longer column lifetimes.

Analytical Alternatives

Factory connected 0.32mm MXT®-Biodiesel TG columns & 0.53mm retention gaps

For accurate analysis of heavy triglycerides, on-column injection is required. ASTM D-6584 describes the use of a 0.32mm analytical column coupled with a 0.53mm retention gap. The 0.53mm ID retention gap allows the cool on-column technique to be used, but care must be taken to minimize dead volume and to establish a leak-tight connection. Restek's 0.32mm MXT®-Biodiesel TG columns are factory-coupled to a 0.53mm MXT® retention gap with an MXT™ low-dead-volume connector, ensuring a leak-tight connection. Target analytes resolve well and the solvent and triglyceride peaks show excellent symmetry (Figure 4).

0.53mm MXT®-Biodiesel TG columns

The 0.53mm MXT®-Biodiesel TG columns are a simpler alternative to using a 0.32mm column coupled to a 0.53mm retention gap. Restek applied Integra-Gap™ technology to the 0.53mm MXT®-Biodiesel TG columns, eliminating the column coupling. These single unit leak-proof columns feature a built-in retention gap, reducing the risk of peak broadening and tailing. Chromatography from the 0.53mm MXT®-Biodiesel TG with Integra-Gap™ technology (Figure 5) is excellent and comparable to that obtained on the 0.32mm

ID column in Figure 4.

Conclusion

As demonstrated, for high temperature GC analysis, the metal MXT®-Biodiesel TG column is a rugged column that withstands the harsh temperatures required for total residual glycerin analysis. The column has the resolution needed for accurate, reliable results and is more stable at high temperatures than competitive fused silica columns, leading to longer column lifetimes. To improve the reliability and robustness of your biodiesel analyses, try a Restek MXT®-Biodiesel TG column.

Figure 1 MXT-Biodiesel TG columns are undamaged by high thermal cycles compared to high-temperature fused silica columns which breakdown under the same conditions.

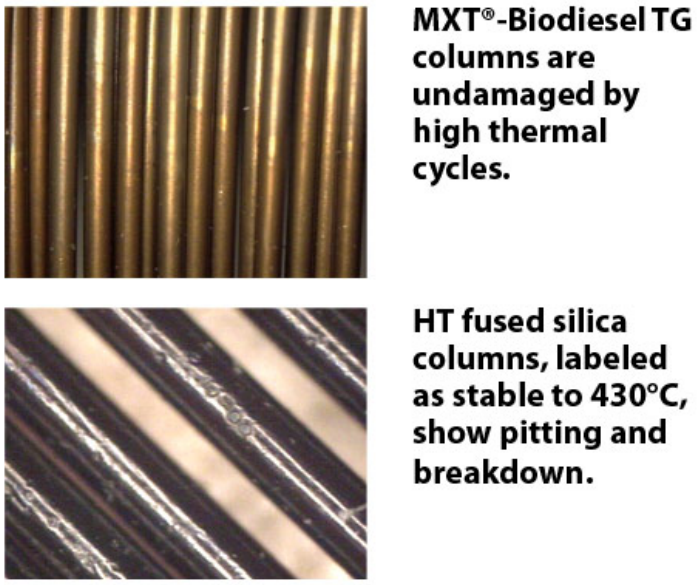


Figure 2 Stable and consistent peak shape for the internal standard butanetriol gives you more accurate quantitation.

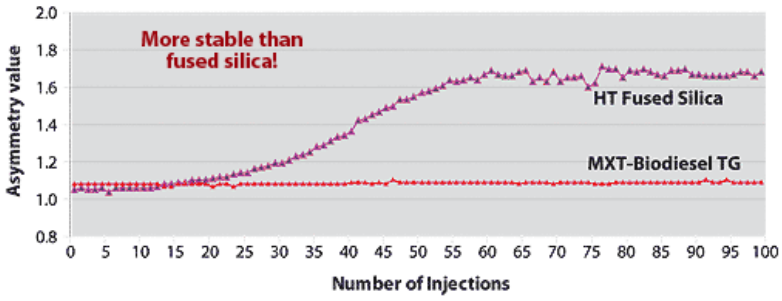


Figure 3 Retention time is stable on a metal MXT®-Biodiesel TG column, even after 100 cycles up to 430°C.

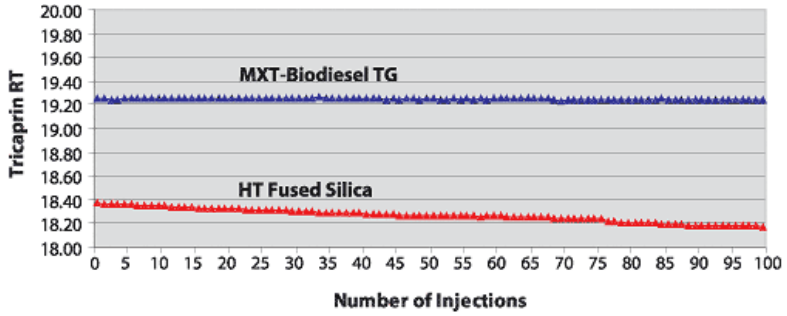
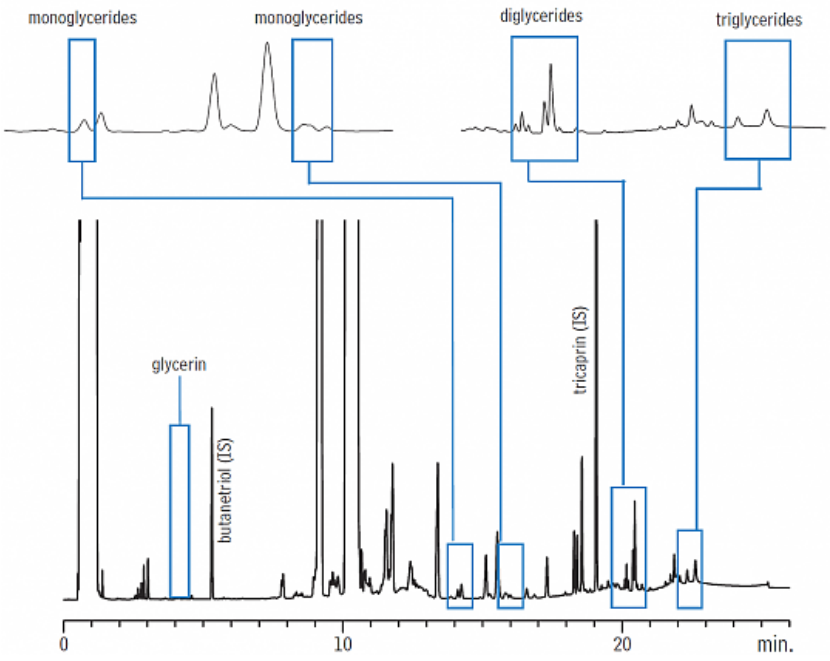


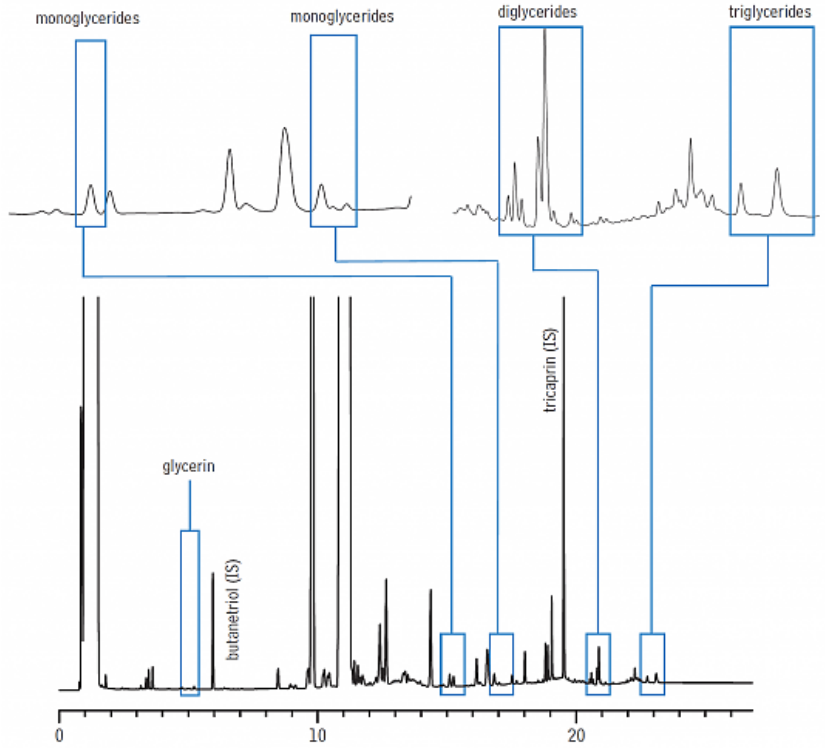
Figure 4 Derivatized B100 samples resolve well on the 15m x 0.32mm MXT®-Biodiesel TG column, which is factory coupled to a 0.53mm retention gap using an MXT™ low-dead-volume connector.



GC_PC00968

Column	MXT®-Biodiesel TG, 15 m, 0.32 mm ID, 0.10 µm (cat.# 70291) with a 2 m x 0.53 mm MXT® retention gap connected with an MXT® low-dead-volume connector (17 m total length)
Sample	Biodiesel (B100), derivatized
Diluent:	Heptane
Injection	
Inj. Vol.:	1 µL cold on-column
Temp. Program:	Oven track
Oven	
Oven Temp.:	50 °C (hold 1 min) to 180 °C at 15 °C/min to 230 °C at 7 °C/min to 380 °C at 30 °C/min (hold 5 min)
Carrier Gas	H_2, constant flow
Flow Rate:	3 mL/min
Detector	FID @ 380 °C

Figure 5 Excellent chromatographic quality and resolution on the 0.53mm MXT®-Biodiesel TG column, with the Integra-Gap™ integrated retention gap.



GC_PC00969

Column	MXT®-Biodiesel TG, 14 m w/2 m Integra-Gap® (16 m total length), 0.53 mm ID, 0.16 µm (cat.# 70289)
Sample	Biodiesel (B100), derivatized
Diluent:	Heptane
Injection	
Inj. Vol.:	1 µL cold on-column
Temp. Program:	Oven track
Oven	
Oven Temp.:	50 °C (hold 1 min) to 180 °C at 15 °C/min to 230 °C at 7 °C/min to 380 °C at 30 °C/min (hold 5 min)
Carrier Gas	H_2, constant flow
Flow Rate:	4 mL/min
Detector	FID @ 380 °C

RELATED SEARCHES

Biodiesel, *mxt-biodiesel*, *b100*, *glycerin*

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See page 5 for details

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Introduction to Biodiesel

Today, as oil prices climb and pollution levels soar, there is significant worldwide interest in alternative fuels. Biodiesel is one of the most popular alternative fuels available today. It may be used in engines, either pure or blended with diesel fuel, to reduce exhaust pollutants. It can be produced easily from sunflowers, soy, rapeseed, tallow, lard, yellow grease, and other sources. Chemically, it is the product obtained when a vegetable oil or animal fat is reacted with an alcohol in the presence of a catalyst, such as sodium or potassium hydroxide, to produce fatty acid methyl esters (FAMEs).

Methods used to test the quality of biodiesel fuels can be categorized into three types based on the target compounds: ASTM D6584 and EN 14105 test for total glycerin, EN 14103 tests for FAMEs, and EN 14110 tests for residual methanol. These methods may be performed using either fused silica or metal columns, but the column chosen must have extremely high temperature tolerance. Restek offers both fused silica and metal columns designed specifically for high temperature biodiesel analysis. These columns, the Rtx®-Biodiesel TG, MXT®-Biodiesel TG, Stabilwax®, and Rtx-1® column lines, offer outstanding performance for biodiesel testing.

Rtx®-Biodiesel TG Columns (fused silica)

- Linearity for all reference compounds exceeds method requirements.
- Low column bleed at high temperatures.
- For glycerin and glycerides analysis, according to ASTM D6584 and EN 14105 methods.

Description	temp. limits	cat.#
10m, 0.32mm ID, 0.10µm	to 330/380°C	10292
10m, 0.32mm ID, 0.10µm with 2m x 0.53mm ID Retention Gap	to 330/380°C	10291
15m, 0.32mm ID, 0.10µm	to 330/380°C	10294
15m, 0.32mm ID, 0.10µm with 2m x 0.53mm ID Retention Gap	to 330/380°C	10293

Biodiesel Calibration Standards

Volume is 1mL/ampul. Concentration is µg/mL in pyridine.

Compound	Conc.	cat.#
(s)-(-)-1,2,4-butanetriol	1,000	33024
(s)-(-)-1,2,4-butanetriol	1,000	33032
diolein (1,3-di[*cis*-octadecenoyl]glycerol)	5,000	33022
glycerin	500	33020
monolein (1-mono[*cis*-9-octadecenoyl]-rac-glycerol)	5,000	33021
monopalmitin	5,000	33026
tricaprin (1,2,3-tricaprinoylglycerol)	8,000	33025
tricaprin (1,2,3-tricaprinoylglycerol)	8,000	33033
triolein (1,2,3-Tri[*cis*-octadecenoyl]glycerol)	5,000	33023

Diesel/Biodiesel 80:20 Blend Standard

The biodiesel component is methyl soyate.

5,000 µg/mL in methylene chloride, 1 mL/ampul	cat.# 31880 (ea.)

Silylation Derivatization Reagents

Compound	CAS #	cat.#
MSTFA (N-methyl-N-trimethylsilytrifluoroacetamide)		
10-pk. (10x1g)	24589-78-4	35600
25g vial	24589-78-4	35601

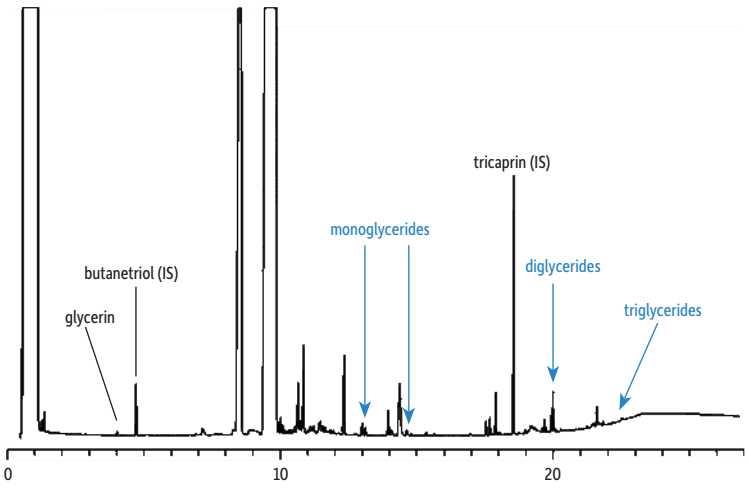
Analyzing Total Glycerin in Biodiesel

Rtx®-Biodiesel TG Fused Silica Columns

Glycerin in biodiesel falls out of solution, causing gumming in fuel systems and malfunctioning of engine parts, which eventually leads to inferior engine performance. Total glycerin presents itself in two forms: free glycerin and bound glycerin in the form of glycerides. Derivatization is required for analysis, and both ASTM D6584 and EN 14105 use N-methyl-N-trimethylsilytrifluoroacetamide derivatization reagent.

A 10 m x 0.32 mm ID Rtx®-Biodiesel TG column with a 2 m x 0.53 mm ID retention gap is ideal for glycerin analysis. The retention gap is factory-coupled using Restek's unique Alumaseal® connector. The data in Figure 1 show the elution of glycerin, monoglycerides, diglycerides, and triglycerides in B100 biodiesel following ASTM Method D6584, utilizing cool on-column injection. The Rtx®-Biodiesel TG column provides good resolution and signal-to-noise ratios for mono-, di-, and triglycerides.

Figure 1 The Rtx®-Biodiesel TG column meets resolution criteria and shows excellent response for determining glycerin in biodiesel.



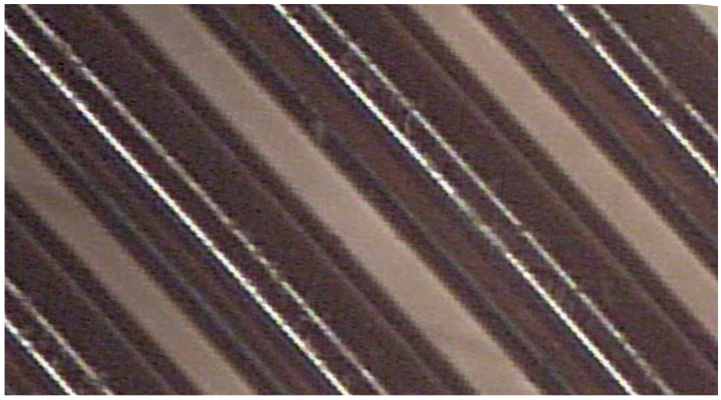
Column	Rtx®-Biodiesel TG, 10 m, 0.32 mm ID, 0.10 µm connected to 2 m x 0.53 mm Hydroguard® tubing using Alumaseal® connector (cat.# 10291)
Sample	biodiesel (B100) plus monoolein, diolein, triolein, glycerin, butanetriol, tricaprin
Injection	1 µL, cool on-column
Inj. temp.:	oven track
Carrier Gas	hydrogen, constant flow
Flow rate:	4 mL/min.
Oven temp.:	50 °C (hold 1 min.) to 180 °C @ 15 °C/min. (hold 7 min.) to 230 °C @ 30°C/min. to 380 °C @ 30 °C/min. (hold 5 min.)
Detector	FID
Det. temp.:	380 °C

Comparing Fused Silica to Metal

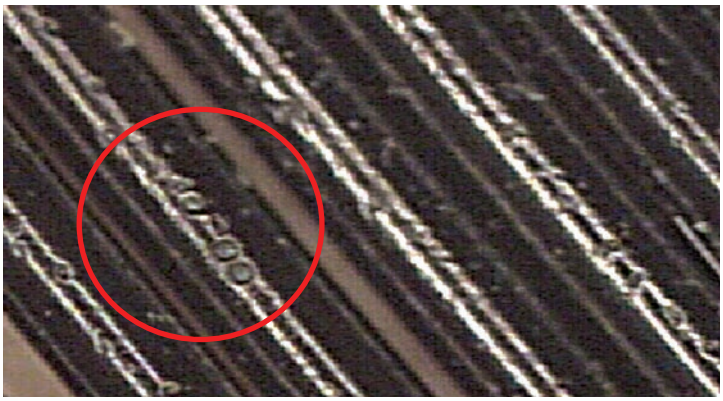
High temperature applications shorten the lifetime of fused silica columns due to deterioration of the polyimide resin used to make the columns. When fused silica columns are exposed to oven temperatures over 400 °C the polyimide coating becomes brittle and the deactivation of the column is compromised. Figure 2 shows the effect of cycling a commercially available fused silica column to 430 °C for 5 minutes 100 times. Although the column was labeled as stable up to 430 °C, the polyimide coating shows damage. The inertness of the column also deteriorates as shown by the loss of peak symmetry for the internal standard butanetriol over multiple injections (Figure 3).

Metal MXT®-Biodiesel TG columns are a better alternative to fused silica columns. As shown in Figure 3, they clearly outperform high temperature fused silica columns under the cycling conditions required for biodiesel analysis. Metal MXT®-Biodiesel TG columns offer greater stability and longer column lifetimes compared to fused silica columns.

Figure 2 Fused silica columns, labeled as stable up to 430 °C, show significant pitting and breakdown.



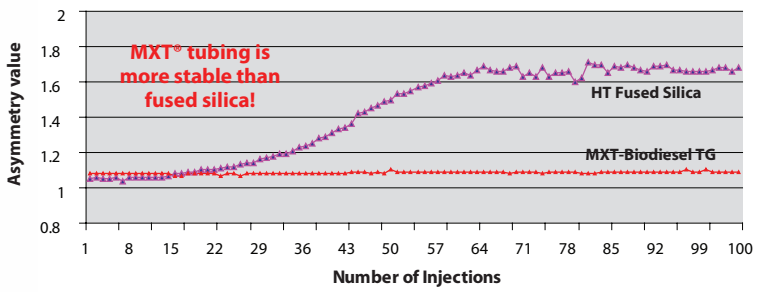
Before



After

100 temperature cycles to 430 °C totaling 500 minutes at maximum temperature.

Figure 3 Stable peak shape for internal standard butanetriol on MXT®-Biodiesel TG columns gives more accurate quantification.



Metal Column Solutions: Two Options for Increased Stability and Performance

- 0.32 mm MXT®-Biodiesel TG column with a 0.53 mm retention gap, factory-coupled with an MXT® low-dead-volume connector
- 0.53 mm MXT®-Biodiesel TG column with a built-in 0.53mm Integra-Gap® integrated retention gap

The primary advantage of using metal MXT® columns is that they are more stable at high temperatures than fused silica columns. This means they will exhibit lower bleed, improving analytical performance, and have longer lifetimes, making them a cost-effective option. They also can be brought to high temperatures (430 °C) allowing nonvolatile material to be heated off of the column, removing carryover contamination and improving cycle times.

Metal MXT®-Biodiesel TG columns are offered in the same column dimensions as their fused silica counterparts. Two different column configurations are available for cool on-column injection: 1) a 10 m (or 15 m) x 0.32 mm ID MXT®-Biodiesel TG column factory-coupled to a 2 m x 0.53 mm retention gap using an MXT® connector, and 2) a 14 m x 0.53 mm ID MXT®-Biodiesel TG column with a built-in 2 m x 0.53 mm ID Integra-Gap® integrated retention gap.

Target analytes resolve well and the solvent and triglyceride peaks show excellent symmetry on both columns (Figures 4 and 5), but the 0.53 mm MXT ®-Biodiesel TG column with the Integra-Gap® integrated retention gap eliminates the need for a connector, making connector-related leaks a thing of the past. Peak shape for butanetriol is very good, demonstrating inertness, and the resolution and responses for the mono-, di- and triglycerides are excellent. The leak-proof 0.53 mm MXT®-Biodiesel TG column with the Integra-Gap® integrated retention gap is the ultimate biodiesel solution (Figure 6).

Figure 4 Derivatized B100 samples resolve well on the 15 m x 0.32 mm MXT®-Biodiesel TG column, which is factory coupled to a 0.53 mm retention gap using an MXT® low-dead-volume connector.

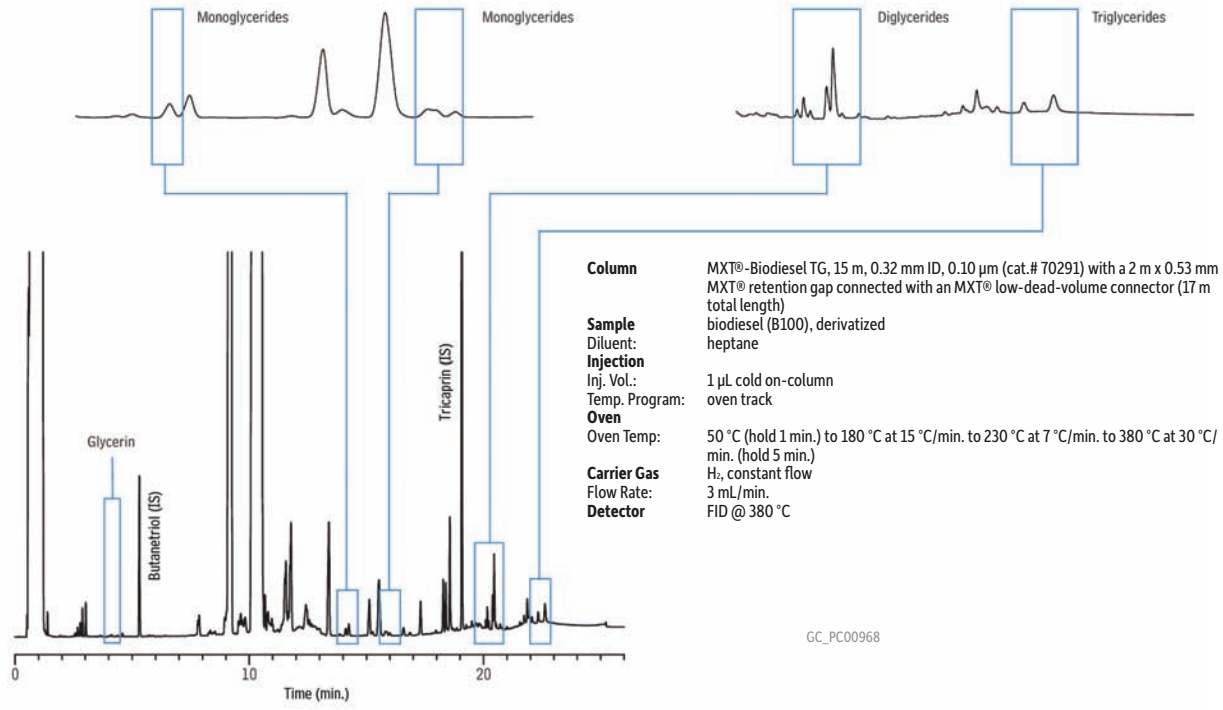
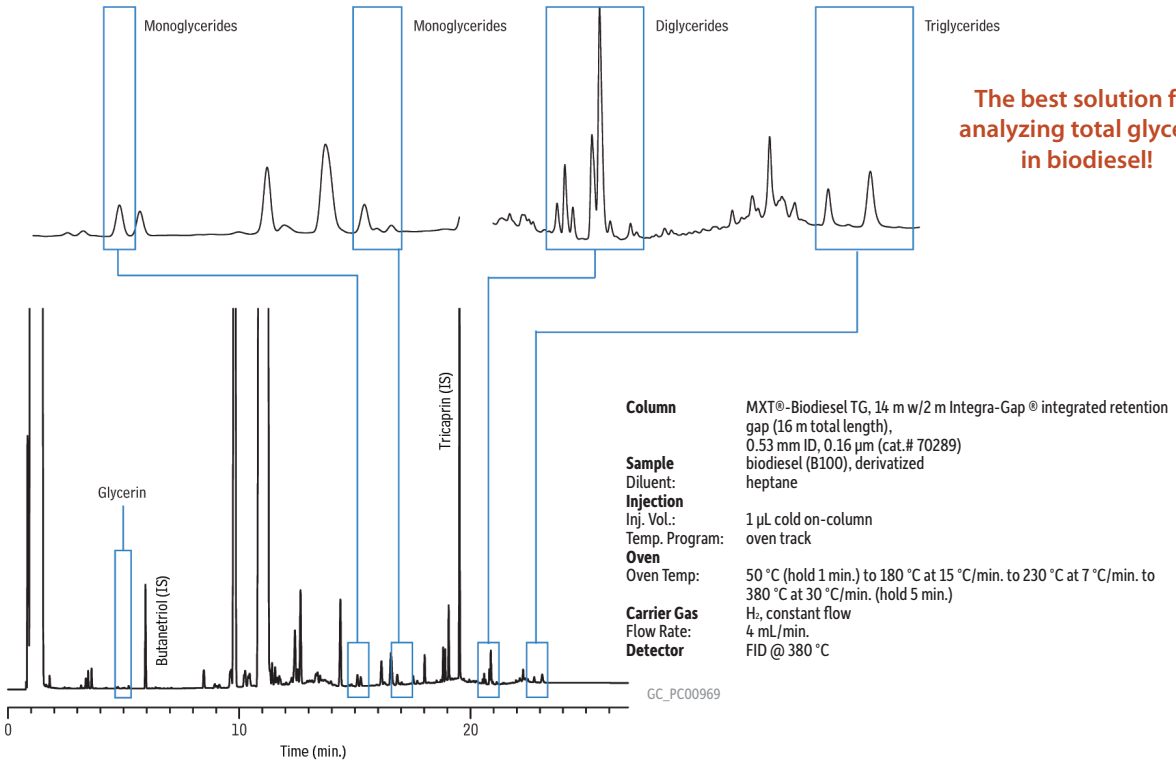


Figure 5 Excellent chromatographic quality and resolution on the 0.53 mm MXT®-Biodiesel TG column with the Integra-Gap® integrated retention gap.

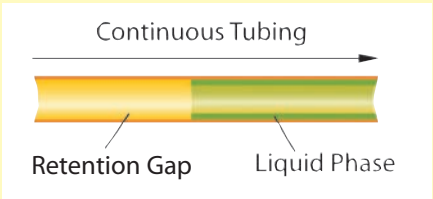


The best solution for analyzing total glycerin in biodiesel!

Column	MXT®-Biodiesel TG, 14 m w/2 m Integra-Gap ® integrated retention gap (16 m total length), 0.53 mm ID, 0.16 µm (cat.# 70289)
Sample	biodiesel (B100), derivatized
Diluent:	heptane
Injection	
Inj. Vol.:	1 µL cold on-column
Temp. Program:	oven track
Oven	
Oven Temp:	50 °C (hold 1 min.) to 180 °C at 15 °C/min. to 230 °C at 7 °C/min. to 380 °C at 30 °C/min. (hold 5 min.)
Carrier Gas	H_2, constant flow
Flow Rate:	4 mL/min.
Detector	FID @ 380 °C

Figure 6 The Ultimate Biodiesel Solution: MXT®-Biodiesel TG column with Integra-Gap® integrated retention gap.

The 0.53 mm MXT®-Biodiesel TG columns are an innovative alternative to using a 0.32 mm column coupled to a 0.53 mm retention gap. Restek applied the Integra-Gap® integrated retention gap technology to the 0.53 mm MXT®-Biodiesel TG columns, eliminating the column coupling. These 100% leak-proof columns feature a built-in retention gap, reducing the risk of peak broadening and tailing, and guaranteeing the user many analyses without downtime.



MXT®-Biodiesel TG Columns (Siltek® treated stainless steel)

- Fast analysis times and sharp mono-, di-, and triglyceride peaks.
- Stable at 430 °C for reliable, consistent performance.
- Integra-Gap® built-in retention gap on 0.53 mm ID column eliminates column coupling completely.

Description	temp. limits	cat.#
14m, 0.53mm ID, 0.16µm with 2m Integra-Gap*	-60 to 380/430°C	70289
10m, 0.32mm ID, 0.10µm	-60 to 380/430°C	70292
10m, 0.32mm ID, 0.10µm with 2m x 0.53mm Retention Gap**	-60 to 380/430°C	70290
15m, 0.32mm ID, 0.10µm	-60 to 380/430°C	70293
15m, 0.32mm ID, 0.10µm with 2m x 0.53mm Retention Gap**	-60 to 380/430°C	70291
2m, 0.53mm ID, Retention Gap	-60 to 380/430°C	70294

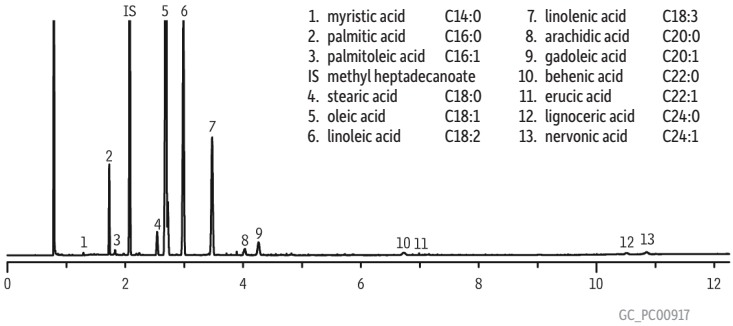
Columns are on a 7" diameter 11-pin cage. To order a 3.5" coil, add suffix -273 to the part number.
*Total column length = 16 meters.
**Connected with low-dead-volume MXT connector.

Analyzing FAMEs in Biodiesel

FAMEs are the desired end product of biodiesel production and they are analyzed to determine the percent of usable fuel in the final product. A Stabilwax® fused silica GC column affords excellent peak symmetry, resolution, and reproducibility for determining the FAMEs and linolenic acid methyl ester content in B100 biodiesel fuel, following European standard method EN 14103.

As shown in Figure 7, C14:0-C24:1 FAMEs and linolenic acid methyl ester can be determined in less than 11 minutes using a 30 m x 0.32 mm ID x 0.25 µm Stabilwax® column. Particularly notable are the stability of the baseline, excellent peak symmetry, and baseline resolution of all compounds of interest. The Stabilwax® column shows excellent peak shape for all FAMEs, even at low concentrations, which is critical for accurate quantification (Table I).

Figure 7 Stable baselines, excellent peak symmetry, and rapid, baseline resolution of all compounds characterize FAMEs analyses on a Stabilwax® column.



1.	myristic acid	C14:0	7.	linolenic acid	C18:3
2.	palmitic acid	C16:0	8.	arachidic acid	C20:0
3.	palmitoleic acid	C16:1	9.	gadoleic acid	C20:1
IS	methyl heptadecanoate		10.	behenic acid	C22:0
4.	stearic acid	C18:0	11.	erucic acid	C22:1
5.	oleic acid	C18:1	12.	lignoceric acid	C24:0
6.	linoleic acid	C18:2	13.	nervonic acid	C24:1

Column:	Stabilwax®, 30 m, 0.32 mm ID, 0.25 µm (cat.# 10624)
Sample:	rapeseed source of biodiesel (B100), prepared according to European Method EN 14103
Inj.:	1.0 µL split (split ratio 100:1), Cyclosplitter® inlet liner (cat.# 20706)
Inj. temp.:	250 °C
Carrier gas:	hydrogen, constant flow, 3 mL/min.
Linear velocity:	60 cm/sec.
Oven temp.:	210 °C (hold 5 min.) to 230 °C @ 20 °C/min. (hold 5 min.)
Det.:	FID
Det. temp.:	250 °C

Table I Sources of FAMEs in B100 biodiesel fuel (% m/m).

		Soy	Tallow	Rapeseed	Yellow Grease
Myristic acid	C14:0	0.21	1.7	0.11	0.68
Palmitic acid	C16:0	11.24	25.5	4.1	16.35
Palmitoleic acid	C16:1	0.2	3.27	0.27	1.23
Stearic acid	C18:0	4.04	14.41	1.8	9.32
Oleic acid	C18:1	21.93	40.34	58.57	47.8
Linoleic acid	C18:2	53.84	12.02	22.2	20.01
Linolenic acid	C18:3	7.29	0.99	13.26	2.93
Arachidic acid	C20:0	0.36	0.4	0.79	0.46
Gadoleic acid	C20:1	0.26	1.03	1.79	0.39
Behenic acid	C22:0	0.45		0.57	0.44
Erucic acid	C22:1			0.13	0.23
Lignoceric acid	C24:0	0.16	0.34	0.3	0.24
Nervonic acid	C24:1		0.17	0.54	

Stabilwax® Columns (fused silica)
(polar phase; Crossbond® Carbowax® polyethylene glycol)

ID	df	temp. limits	length	cat. #
0.32mm	0.25µm	40 to 250/260°C	30-Meter	10624

Analyzing Methanol in Biodiesel

Methanol is commonly used to produce biodiesel by derivatizing the fatty acids to methyl esters. The amount of residual methanol must be determined because engine performance can be negatively affected if the methanol concentration in the final product is too high. Methanol in biodiesel is quantified using a headspace method (e.g. EN 14110). We recommend an Rtx®-1 column (30 m, 0.32 mm ID, 3 µm) for this analysis. The selectivity of the Rtx®-1 column is ideal for resolving methanol from interfering peaks in biodiesel fuels.

Conclusion

Whether testing for glycerin, FAMEs, or methanol, Restek can supply the high quality chromatography products required for biodiesel testing. We offer an array of metal and fused silica GC columns designed for high performance biodiesel analysis, including our innovative MXT®-Biodiesel TG column with an Integra-Gap® integrated retention gap (Table II). Our columns, accessories, and analytical reference materials are designed to improve analytical quality, simplify lab work, and increase productivity. Rely on Restek for innovative solutions to your biodiesel testing needs.

Rtx®-1 Columns (fused silica)
(nonpolar phase; Crossbond® 100% dimethyl polysiloxane)

ID	df	temp. limits*	length	cat. #
0.32mm	3.00µm	-60 to 280/300°C	30-Meter	10184

Table II GC column selection guide for biodiesel fuel methods.

Fused Silica GC Columns	Description	Injection Type	ASTM D6584 Free and Total Glycerin	EN 14103 Ester and Linoleic Acid Methyl Esters	EN 14105 Free and Total Glycerin and Mono, Di, and Triglycerides	EN 14110 Methanol
Rtx-Biodiesel TG (max temp. 380°C)	15 m, 0.32 mm ID, 0.1 µm with 2 m x 0.53 mm ID retention gap	cool on-column	10293	—	10293	—
Rtx-Biodiesel TG (max temp. 380°C)	15 m, 0.32 mm ID, 0.1 µm	PTV**	10294	—	10294	—
Rtx-Biodiesel TG (max temp. 380°C)	10 m, 0.32 mm ID, 0.1 µm with 2 m x 0.53 mm ID retention gap	cool on-column	10291	—	10291	—
Rtx-Biodiesel TG (max temp. 380°C)	10 m, 0.32 mm ID, 0.1 µm	PTV**	10292	—	10292	—
Stabilwax	30 m, 0.32 mm ID, 0.25 µm	split/splitless	—	10624	—	—
Rtx-1	30 m, 0.32 mm ID, 3.0 µm	headspace	—	—	—	10184
Metal (MXT) GC Columns						
*MXT-Biodiesel TG (max temp. 430°C)	14 m, 0.53 mm ID, 0.16 µm with 2 m Integra Gap	cool on-column	70289	—	70289	—
MXT-Biodiesel TG (max temp. 430°C)	15 m, 0.32 mm ID, 0.1 µm with 2 m x 0.53 mm ID retention gap	cool on-column	70291	—	70291	—
MXT-Biodiesel TG (max temp. 430°C)	15 m, 0.32 mm ID, 0.1 µm	PTV**	70293	—	70293	—
MXT-Biodiesel TG (max temp. 430°C)	10 m, 0.32 mm ID, 0.1 µm with 2 m x 0.53 mm ID retention gap	cool on-column	70290	—	70290	—
MXT-Biodiesel TG (max temp. 430°C)	10 m, 0.32 mm ID, 0.1 µm	PTV**	70292	—	70292	—

*Recommended for total glycerin analysis. **PTV=programmed temperature vaporizer.

GC Accessories

BTO® Septa

- Usable to 400 °C inlet temperature.
- Precision molding assures consistent, accurate fit.
- Partial predrilled CenterGuide design.
- Preconditioned and ready to use.
- Do not adhere to hot metal surfaces.
- Packaged in precleaned glass jars.
- Each batch GC/FID tested.
- Bleed and temperature optimized; ideal for demanding GC and GC/MS applications.

Septum Diameter	50-pk.	100-pk.
5mm CenterGuide	27100	27101
6mm (1/4")	27102	27103
9mm CenterGuide	27104	27105
9.5mm (3/8")	27106	27107
10mm	27108	27109
11mm (7/16") CenterGuide	27110	27111
11.5mm CenterGuide	27112	27113
12.7mm (1/2") CenterGuide	27114	27115
17mm CenterGuide*	27116	27117
Shimadzu Plug	27118	27119

Note: Due to the injection port temperatures, Restek recommends using only BTO septa in Thermo Scientific instruments.
*For 17 mm injectors, the maximum temperature is 330 °C.

Parker Balston® PEM Hydrogen Generators

- Proton Exchange Membrane (PEM) cell eliminates the need for liquid electrolytes.
- Reliably generate 99.9995% pure hydrogen—for better chromatography.
- Eliminates high-pressure cylinders—greater convenience and improved lab safety.

Specifications

Purity:	99.9995% pure hydrogen	Outlet Port:	1/8" compression
Delivery Pressure:	10-100 psig ± 1 psig (69-689 kPa ± 7kPa)	Electrical Requirements:	100-230 VAC/50-60 Hz

Description	Model #	Capacity	qty.	cat.#
Hydrogen Generator	H2PEM-100	100cc/min.	ea.	23065
Hydrogen Generator	H2PEM-165	165cc/min.	ea.	23066
Hydrogen Generator	H2PEM-260	260cc/min.	ea.	23067
Hydrogen Generator	H2PEM-510	510cc/min.	ea.	23068
Replacement and Maintenance Components for Hydrogen Generators (for all models listed above)				
Replacement Desiccant Cartridge for H2PEM Generators			ea.	23069
6-Month Maintenance Kit for H2PEM Generators *Includes: 1 deionizer cartridge, 1 water filter, 3 environmental filters*			kit	23070
24-Month Maintenance Kit for H2PEM Generators *Includes: 1 deionizer cartridge, 1 water filter, 3 environmental filters, 1 water level sensor, 1 water pump, and 1 desiccant cartridge*			kit	23071

- Dimensions: 17.12" x 13.46" x 17.95"
- 40 lb. dry weight

Don't let a small leak turn into a costly repair—protect your instrument and analytical column by using a Restek Leak Detector.

Restek Electronic Leak Detector

Features & Benefits include:

- Optimized sample flow path.
- New ergonomic, hand-held design.
- Rugged side grips for added durability.
- Handy probe storage for cleanliness and convenience.
- Longer lasting battery, up to 6 hours of continuous use.
- Automatic shut-off.

Leak Detector Facts

Detectable gases:	helium, nitrogen, argon, carbon dioxide, hydrogen
Battery:	Rechargeable Ni-MH internal battery pack
Operating Temp. Range:	32°-120°F (0°-48°C)
Humidity Range:	0-97%
Warranty:	one year
Certifications:	CE, Ex, Japan
Compliance:	WEEE, RoHS

Description	qty.	cat.#
Leak Detector with Hard-Sided Carrying Case and Universal Charger Set (US, UK, European, Australian)	ea.	22839
Leak Detector Routine Maintenance Review†	ea.	22839-R
Soft-Side Storage Case	ea.	22657
Small Probe Adaptor	ea.	22658

Avoid using liquid leak detectors on a GC! Liquids can be drawn into the system.

*Caution: The Restek Electronic Leak Detector is designed to detect trace amounts of hydrogen in a noncombustible environment. It is NOT designed for determining leaks in a combustible environment. A combustible gas detector should be used for determining combustible gas leaks under any condition. The Restek Electronic Leak Detector may be used for determining trace amounts of hydrogen in a GC environment only.

†Routine maintenance includes inspection of the probe tip, internal/external tubing and a battery replacement.

Also available in money-saving 50-packs!

Capillary Ferrules for 1/16-Inch Compression-Type Fittings

Graphite Ferrules

- Preconditioned to eliminate out-gassing.
- High-purity, high-density graphite.
- Stable to 450 °C.

Vespel®/Graphite Ferrules

- 60%/40% Vespel®/graphite blend, offering the best combination of sealing and ease of workability.
- Stable to 400 °C.

Ferrule ID	Fits Column ID	qty.	Graphite	Vespel/Graphite
0.5mm	0.32mm	10-pk.	20201	20212
0.8mm	0.45/0.53mm	10-pk.	20202	20213

For more ferrule choices visit us at **www.restek.com/biodiesel**

FID Replacement Jets

- Available untreated or Siltek® treated, for maximum inertness.

Capillary Adaptable FID Replacement Jet for Agilent 5890/6890/6850 GCs

Description	Similar to Agilent part #	qty.	cat.#	qty.	cat.#
Standard, 0.011-Inch ID Tip	19244-80560	ea.	20670	3-pk.	20671
High-Performance Siltek Treated, 0.011-Inch ID Tip	19244-80560	ea.	20672	3-pk.	20673

Capillary Dedicated FID Replacement Jet for Agilent 6890/6850/7890 GCs

Description	Similar to Agilent part #	qty.	cat.#	qty.	cat.#
Standard, 0.011-Inch ID Tip	G1531-80560	ea.	21621	3-pk.	21682
High-Performance Siltek Treated, 0.011-Inch ID Tip	G1531-80560	ea.	21620	3-pk.	21683
High-Temperature, 0.018-Inch ID Tip	G1531-80620	ea.	23078	3-pk.	23079

RESTEK

Lit. Cat.# PCFL1409-UNV

www.restek.com

Biodiesel Analysis by European Methodology

Exceptional Peak Symmetry, Using an Rtx®Biodiesel GC Column

By Barry L. Burger, Petroleum Chemist

- Excellent peak shape, even for free glycerin.
- Low column bleed at >350°C.
- Quantify oil components more easily and more reliably.

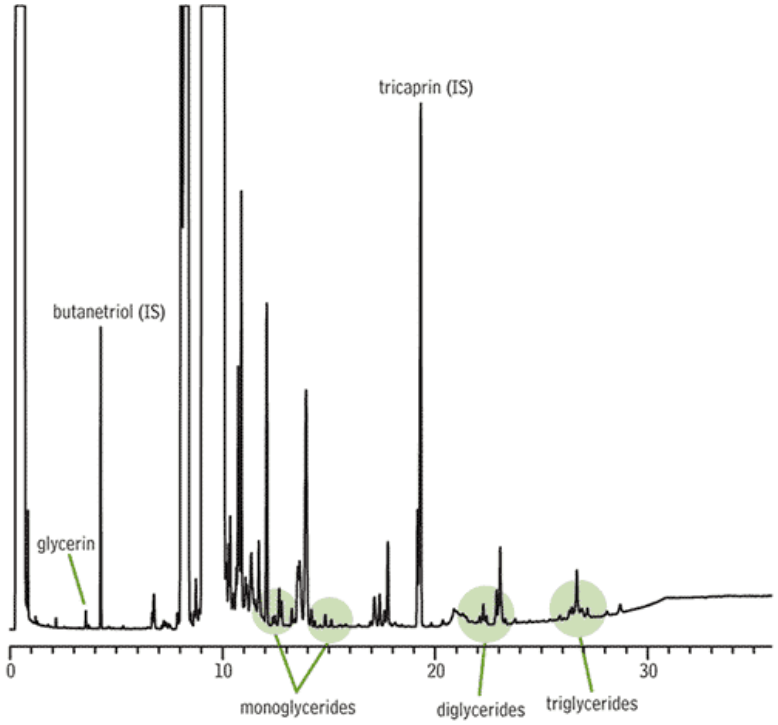
In less than a decade biodiesel oil has become a significant fuel source, especially in European countries, where current usage has soared to 1,800,000 tons annually.[1] Transesterification of the rapeseed oil or other fats from which biodiesel oil is prepared yields two products: methyl esters — biodiesel oil — and glycerin. Glycerin is extremely challenging to analyze by GC, but because excessive amounts in biodiesel products can cause problems during storage or in the engine it is necessary to monitor glycerin levels. In the US, American Society for Testing and Materials (ASTM) Method D6584-00e1 is an accepted GC procedure for biodiesel oil analysis; the standard European method is Deutsches Institut fur Normung (DIN) EN14105. Both methods set limits on free glycerin and glycerides in biodiesel oil product. While these methods differ in GC column specifications and chromatographic conditions, both require a column that can perform reliably at elevated temperatures, with minimal bleed.

Figure 1 shows the chromatography for the DIN analysis, using an Rtx®-Biodiesel column. Peaks for glycerin and the glycerides exhibit minimal tailing, and bleed is low, even at 370°C. Thus, components of the oil can be more easily and more reliably quantified. These results confirm the Rtx®-Biodiesel column is a wise choice for biodiesel oil analysis according to DIN EN14105 conditions. The Rtx®-Biodiesel column also has proven well suited for analyzing biodiesel oil according to the ASTM method.[2]

To obtain Figure 1, we spiked a soybean oil-based sample of B100 biodiesel oil with internal standards butanetriol and tricaprin, silylated the mixture with MSTFA and, using simple on-column injection mode, injected a 1µL aliquot into a low dead volume direct injection liner in a Shimadzu 2010 GC equipped with an on-column injector (OCI). The liner has a 1mm internal diameter and a Press-Tight® constriction one-third of its length from the outlet end. The Rtx®-Biodiesel column forms a seal with the liner at the Press-Tight® constriction; the sample is injected into, and vaporizes in, the top two-thirds of the liner.

Glycerin is a notoriously difficult challenge in GC, particularly at the levels involved in biodiesel oil analysis, yet an Rtx®-Biodiesel column provides a symmetric peak that makes quantification easier and more reliable. Restek chromatographers always are happy to help you with your toughest analytical problems. If you have questions regarding biodiesel oil analysis, please call our technical service team, or contact your Restek distributor, for fast and reliable assistance.

Figure 1 Biodiesel oil analysis using an Rtx®-Biodiesel column and DIN EN14105 conditions: peaks for glycerin and glycerides are symmetric, and bleed is low, even at 370°C.



GC_PC00901

Column:	Rtx®-Biodiesel, 10m, 0.32mm ID, 0.10µm (cat.# 10292)
Sample:	B100 biodiesel oil plus butanetriol and tricaprin, in heptane, derivatized with MSTFA 1µL onto Shimadzu on-column injector (OCI) equipped with low dead volume
Inj.:	Shimadzu direct injection liner
Inj. temp.:	oven track
Carrier gas:	hydrogen, constant flow
Flow rate:	4mL/min.
Oven temp.:	50°C (hold 1 min.) to 180°C @ 15°C/min., to 230°C @ 7°C/min., to 370°C @ 10°C/min. (hold 5 min.)
Det.:	FID
Det. temp.:	390°C

REFERENCES

1. www.ufop.de/publikationen_english.php
2. Restek Advantage 2006.04, pp 3-5 (2006).

RELATED SEARCHES

ASTM Method D6584, *ASTM D6584*, *EN14105*, *biodiesel*, *glycerin*, *glycerides*

Benefits and Considerations of Converting to Hydrogen Carrier Gas

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Many gas chromatography (GC) labs use helium as a carrier gas because it is faster than nitrogen and safer than hydrogen. Unfortunately, helium is a limited natural resource that is becoming much scarcer. The current shortage has severely impacted chromatographers who are finding that helium has become significantly more expensive and is not always available when needed. While helium is abundant in the universe, it is rare on Earth where it is produced by fractional distillation of natural gas.

The United States is a primary producer, but its major reserve, the United States National Helium Reserve (which accounts for approximately 30% of the global supply) is expected to be depleted by 2018 [1]. Other helium supplies are not expected to alleviate the current shortage, so many GC labs are considering moving to hydrogen carrier gas as an alternative. The faster analysis times, lower cost, and unlimited availability of hydrogen make it the best chromatographic choice, but its flammability means implementation must be carefully considered. By using safe, reliable hydrogen generators and understanding how to adapt methods, labs can reap the productivity and cost savings of switching from helium to hydrogen.

Safety Considerations

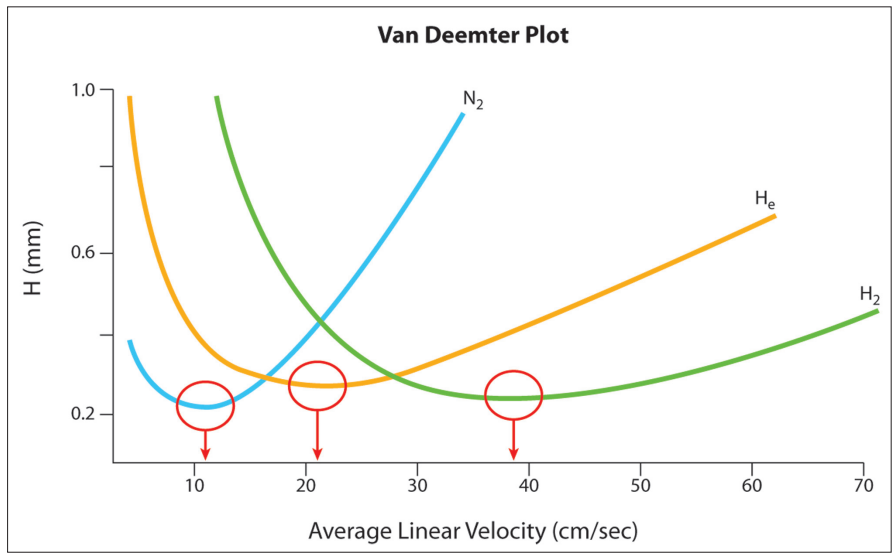
The first concern when switching to hydrogen carrier gas is understanding and managing the safety issues. Fortunately hydrogen generators minimise much of the risk. In contrast to high-pressure gas cylinders, which typically contain 50 L at 200 atm, hydrogen generators generally store only 60 mL at 7 atm or less. This means that although a generator can continually produce hydrogen on demand, the stored quantity is quite small making it a considerably safer choice. In addition, the flow of hydrogen from the generator is controlled and on typical units the maximum flow is approximately 500 mL/min, which is well below the 2 L/min of flow required to reach the lower explosive limit (LEL) for hydrogen in air when released in the oven of an average GC. Generators are also equipped with built-in leak sensors and automatic shut-off features, which turn the unit off if a leak is detected. With soaring helium costs, generators pay for themselves, guarantee a gas supply, and also eliminate the risk posed by keeping high volumes of hydrogen in free-standing, high-pressure gas cylinders.

Another way safety can be improved is by using flow-controlled analysis. In today's GC lab, analysts can choose between pressure and flow controlled analysis. When using hydrogen, flow-controlled operation is the best option as the worst that can happen is the fused silica capillary column breaks at the injection port. With the flow controlled method, only the volume of hydrogen in the inlet and column can be released. This is because the pressure regulator in the injector of an electronic pressure regulation GC will not be able to build pressure, so the system will sense a problem and will automatically enter standby mode. If greater assurances of safety are desired, systems are available that sample the oven air and detect the presence of a different gas (e.g., helium or hydrogen). As a further level of protection, analysts can use metal capillary MXT® columns, which are virtually unbreakable, instead of more fragile fused silica columns. Metal capillary columns are standard for high-temperature applications, such as simulated distillation and biodiesel analysis, but they also perform very well for lower temperature work. While some metal columns may have activity issues, excellent results can be obtained when highly inert, Siltek®-treated columns are used.

Benefits and Application

The biggest advantage to using hydrogen as a carrier gas is that it can significantly decrease analysis time. Realistically, analysis times can be reduced by a factor of 1.5 or 2 with only minor losses in separation, which greatly improves throughput and productivity. A quick review of a van Deemter plot for common carrier gases makes this quite clear (Figure 1). Nitrogen offers the greatest efficiency (shortest height equivalent to a theoretical plate), but its maximum efficiency is only obtained when operating at a very slow rate (~10 cm/sec); when linear velocity is increased, efficiency is lost at a dramatic rate. Helium is somewhat less efficient, but offers more reasonable operating rates (~25 cm/sec is optimal and less efficiency is lost at higher rates). However, the best chromatographic performance is seen using hydrogen. Maximum efficiency is comparable to helium, but good results can be obtained across a much wider operating range. Optimal linear velocity when using hydrogen is

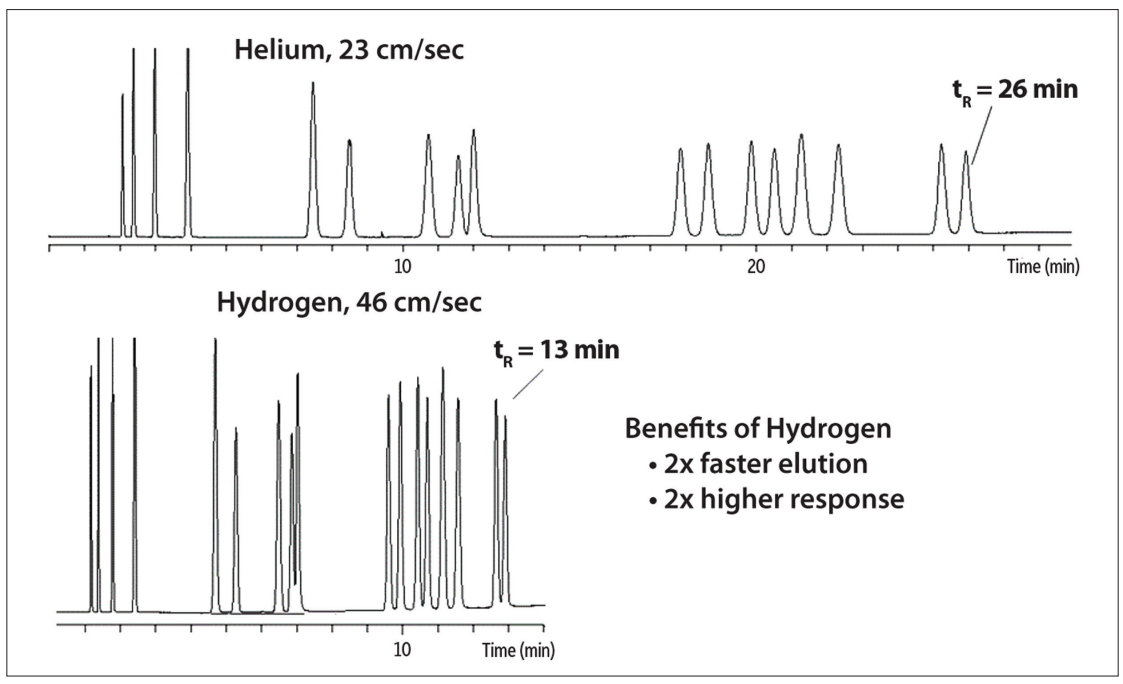
Figure 1: Using hydrogen as the carrier gas allows efficient separations to be obtained in half the time compared to when using helium.



approximately 40-45 cm/sec; this means analysis times are much faster compared to when using helium, and in many cases results can be obtained in half the time.

The theoretical benefits to productivity when using hydrogen are clear, but let's look at a practical example. Figure 2 shows the analysis of a hydrocarbon mixture in the same GC using helium versus hydrogen. When using hydrogen, twice the linear velocity was used and the components eluted twice as fast with minimal negative impact on efficiency. Peak separations were

Figure 2: Hydrocarbons can be separated in half the time using hydrogen as the carrier gas, significantly improving productivity.



n mixture; Injection: Split; Linear velocity: 23 cm/sec (helium), 46

maintained and since peaks are twice as narrow, they are also twice as high. This enhances sensitivity and can lead to lower detection limits, but it also allows the injection of smaller sample volumes. The advantages of using hydrogen are clear, but attention must also be given to method conversion prior to implementation.

Adapting methods to hydrogen carrier gas requires some consideration of elution temperature. Changing from helium to hydrogen is relatively simple for isothermal methods; the linear velocity is increased by roughly a factor of two and 50% of the sample volume is injected using the same split ratio. This results in the same sensitivity (peak height). Injecting less sample has the additional benefit of reducing contamination, which in turn reduces the costs and time required for inlet and column maintenance. However, converting temperature-programmed methods is more complex and requires additional changes. If the same peak elution order is desired when using hydrogen, the oven temperature program rate must also be changed or the components will elute at different times and the elution order may change. In order to ensure that the target analytes elute at the same elution temperatures, a change of oven temperature program rate is needed. Roughly, when twice the linear velocity is used, the isothermal times must be cut in half and temperature programs must be multiplied by a factor of two in order to obtain the same separation in half the time. While one can calculate this, there are freeware programs available on the web that are helpful for more complex methods. Or you can use the helpdesk of companies like Restek (support@restek.com) to assist you in determining the new settings.

Summary

As the cost of helium continues to soar and its availability becomes more and more uncertain, many labs using gas chromatography are considering switching to hydrogen carrier gas. Hydrogen can be reliably produced on demand using hydrogen generators, which are safer and more cost-effective than free-standing, high-pressure gas cylinders. In addition, using hydrogen allows efficient separations to be obtained twice as fast compared to helium, which offers clear benefits to sample throughput and overall lab productivity.

Restek Corporation

Restek is a leading developer and manufacturer of chromatography columns, standards, and accessories. We provide analysts around the world with the innovative products and services they need to monitor the quality of air, water, soil, food, pharmaceutical, chemical, and petroleum products.

www.restek.com

References

[1] T. Newcomb, Time NewsFeed (August 23, 2012). http://newsfeed.time.com/2012/08/23/theres-a-helium-shortage-on-and-its-affecting-more-than-just-balloons/#the-government (accessed November 1, 2012).

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ASTM Petrochemical Method Chromatography Product Guide

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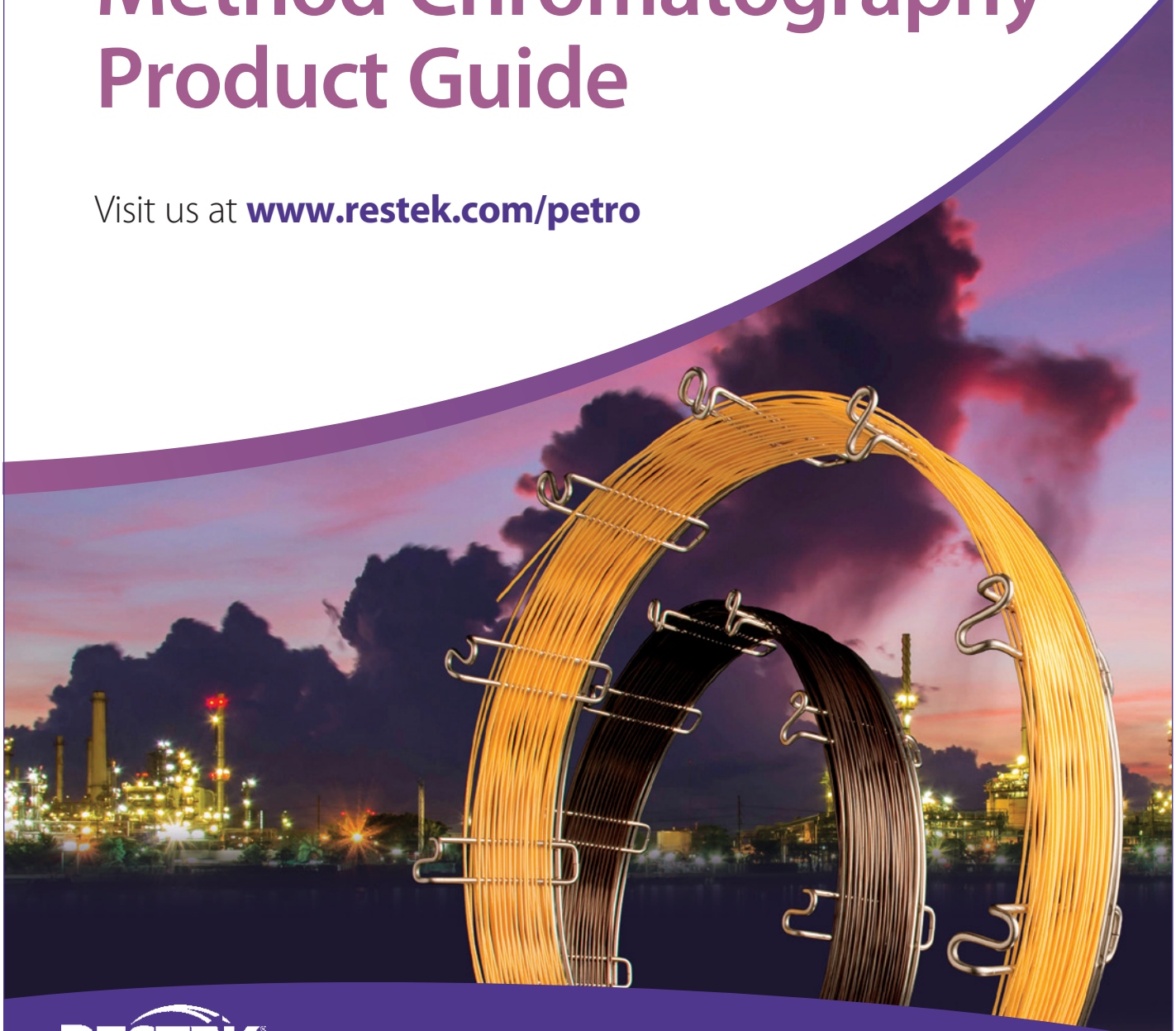

RESTEK Pure Chromatography www.restek.com

ASTM Petrochemical Method Chromatography Product Guide

Restek is your ideal partner for integrated petrochemical solutions, and the following ASTM method product guide will help you quickly pick the right GC columns and reference standards for SimDist, DHA, finished gasoline, and other common petroleum analyses.

If you have any questions or need more information, visit **www.restek.com/petro** for additional resources or to contact one of our in-house petroleum experts for assistance.

Method #	Method Title	Restek® Column(s)	Restek® Reference Standard(s)
(High-Temperature) Simulated Distillation (SimDist)			
D2887	Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography (C5–C44)	MXT®-2887, Siltek®-treated stainless steel, 10 m x 0.53 mm x 2.65 µm - cat.# 70199 *or* MXT®-1HT SimDist, Siltek®-treated stainless steel, 10 m x 0.53 mm x 2.65 µm - cat.# 70132	ASTM D2887-12 Calibration Standards - cat.# 31674 - cat.# 31675 Polywax® Standards - cat.# 36224–36227 D2887 Calibration Mix - cat.# 31222
D7213	Standard Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 to 615 °C by Gas Chromatography (C5–C60)	MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.10 µm - cat.# 70112 *or* MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.20 µm - cat.# 70115 *or* MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.88 µm - cat.# 70131	E-mail standards@restek.com for more information.
D6352	Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range From 174 to 700 °C by Gas Chromatography (C10–C90)	MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.10 µm - cat.# 70112 *or* MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.20 µm - cat.# 70115	Polywax® Standards - cat.# 36224–36227
D7398	Standard Test Method for Boiling Range Distribution of Fatty Acid Methyl Esters (FAME) in the Boiling Range from 100 to 615 °C by Gas Chromatography	MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.88 µm - cat.# 70131	Polywax® Standards - cat.# 36224–36227
D7500	Standard Test Method for Determination of Boiling Range Distribution of Distillates and Lubricating Base Oils in Boiling Range From 100 to 735 °C by Gas Chromatography (C7–C110)	MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.10 µm - cat.# 70112 *or* MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.20 µm - cat.# 70115	Polywax® Standards - cat.# 36224–36227
D7169	Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High-Temperature Gas Chromatography	MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.10 µm - cat.# 70112 *or* MXT®-1HT SimDist, Siltek®-treated stainless steel, 5 m x 0.53 mm x 0.20 µm - cat.# 70115	Polywax® Standards - cat.# 36224–36227
D7096 (replaces D3710)	Standard Test Method for Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography	MXT®-1, Siltek®-treated stainless steel, 15 m x 0.53 mm x 5.00 µm - cat.# 70177 *or* MXT®-1, Siltek®-treated stainless steel, 30 m x 0.53 mm x 5.00 µm - cat.# 70179	E-mail standards@restek.com for more information.
Detailed Hydrocarbon Analysis (DHA)			
D5134	Standard Test Method for Detailed Analysis of Petroleum Naphthas through *n*-Nonane by Capillary Gas Chromatography	Rtx®-DHA-50, 50 m x 0.20 mm x 0.50 µm - cat.# 10147	E-mail **standards@restek.com** for more information.
D6729	Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Meter Capillary High-Resolution Gas Chromatography	Rtx®-DHA-100, 100 m x 0.25 mm x 0.50 µm - cat.# 10148	DHA Standards - cat.# 33034 - cat.# 30725–30731
D6730	Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100–Meter Capillary (with pre-column) High-Resolution Gas Chromatography	Rtx®-DHA-100, 100 m x 0.25 mm x 0.50 µm - cat.# 10148 *and* Rtx®-5 DHA Tuning, 5 m x 0.25 mm x 1.00 µm - cat.# 10165	DHA Standards - cat.# 33034 - cat.# 30725–30731
D6733	Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 50-Meter Capillary High-Resolution Gas Chromatography	Rtx®-DHA-50 , 50 m x 0.20 mm x 0.50 µm - cat.# 10147	DHA Standards - cat.# 33034 - cat.# 30725–30731
D5501	Standard Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography	Rtx®-DHA-150, 150 m x 0.25 mm x 1.00 µm - cat.# 10149	E-mail **standards@restek.com** for more information.

Method #	Method Title	Restek® Column(s)	Restek® Reference Standard(s)
Finished Gasoline			
D3606	Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography	D3606 Application 2-Column Set - cat.# 83606-800 Specified in the D3606 method addendum - includes: - Rtx®-1 , 6' (1.8 m), 1/8" OD, 2.0 mm ID *and* - proprietary packing, 16' (4.9 m), 1/8" OD, 2.0 mm ID	D3606 Standards - cat.# 30647–30674
D4815	Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol, and C1 to C4 Alcohols in Gasoline by Gas Chromatography (Oxygenates)	Micropacked with 20% TCEP on 80/100 Chromosorb PAW 0.56 m x 0.75 mm ID x 1/16" OD - cat.# 19040 *and* Rtx®-1 , 30 m x 0.53 mm x 3.00 µm - cat.# 10185	E-mail standards@restek.com for more information.
D5580	Standard Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C9 and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography	Micropacked with 20% TCEP on 80/100 Chromosorb PAW 0.56 m x 0.75 mm ID x 1/16" OD - cat.# 19040 *and* Rtx®-1, 30 m x 0.53 mm x 5.00 µm - cat.# 10179	E-mail standards@restek.com for more information.
Biodiesel			
D6584	Test Method for Determination of Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography	MXT®-Biodiesel TG, 14 m x 0.53 mm x 0.16 µm with 2 m Integra-Gap® - cat.# 70289 *or* MXT®-Biodiesel TG, Siltek®-treated stainless steel 10 m x 0.32 mm x 0.10 µm with 2 m x 0.53 mm retention gap - cat.# 70290 *or* Rtx®-Biodiesel TG, 10 m x 0.32 mm x 0.10 µm with 2 m x 0.53 mm retention gap - cat.# 10291	Biodiesel Standards - cat.# 31880 - cat.# 33020–33026 - cat.# 33032–33033
Natural Gas			
D1945	Standard Test Method for Analysis of Natural Gas by Gas Chromatography	MXT®-Msieve 5A, Siltek®-treated stainless steel, 30 m x 0.53 mm x 50 µm - cat.# 79723-273 *and* MXT®-Q-BOND, Siltek®-treated stainless steel, 30 m x 0.53 mm x 20 µm - cat.# 79716-273	Natural Gas Standards - cat.# 34438–34440
Refinery Gas			
D2163	Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography	Rt®-Alumina BOND/Na_2SO_4, 50 m x 0.53 mm x 10 µm - cat.# 19756	Refinery Gas Standards - cat.# 34441–34443
D1946 (UOP 539)	Standard Practice for Analysis of Reformed Gas by Gas Chromatography	2abc Refinery Gas Packed Column Set - cat.# 88000-875 *or* MXT®-Msieve 5A, Siltek®-treated stainless steel, 30 m x 0.53 mm x 50 µm - cat.# 79723-273 *and* MXT®-Q-BOND, Siltek®-treated stainless steel, 30 m x 0.53 mm x 20 µm - cat.# 79716	E-mail standards@restek.com for more information.
Impurities			
D2593	Standard Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography	Rt®-Alumina BOND/MAPD, 50 m x 0.53 mm x 10 µm - cat.# 19778	Refinery Gas Standard #5 - cat.# 34443
D2712	Standard Test Method for Hydrocarbon Traces in Propylene Concentrates by Gas Chromatography	Rt®-Alumina BOND/Na_2SO_4, 50 m x 0.53 mm x 10 µm - cat.# 19756	Refinery Gas Standard #5 - cat.# 34443
D6159	Standard Test Method for Determination of Hydrocarbon Impurities in Ethylene by Gas Chromatography	Rt®-Alumina BOND/KCl, 50 m x 0.53 mm x 10 µm - cat.# 19760 *and* Rtx®-1, 30 m x 0.53 mm x 5.00 µm - cat.# 10179	Refinery Gas Standard #5 - cat.# 34443
Sulfur			
D6228	Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection	Rtx®-1, 60 m x 0.53 mm x 7.00 µm - cat.# 10193 *or* MXT-®-1, Siltek®-treated stainless steel, 60 m x 0.53 mm x 7.00 µm - cat.# 70193	E-mail standards@restek.com for more information.
D5623	Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection	Rtx®-1, 30 m x 0.32 mm x 4.00 µm - cat.# 10182	E-mail standards@restek.com for more information.

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- We support the most **ASTM petrochemical methods** in the chromatography industry.
- Our **integrated petroleum solutions** include columns, standards, accessories, method-compliant applications, and resources.
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ISO 9001 · 17025 · Guide 34

Lit. Cat.# PCAR2082A-UNV

Petrochemical Applications

Analyzing Oxygenates in Gasoline

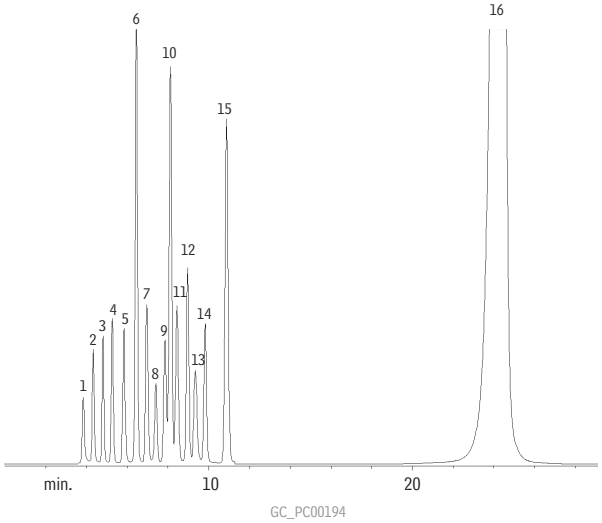
Using TCEP and Rtx®-1/MXT®-1 Columns

Oxygenate additives in gasoline potentially consist of several ethers and/or alcohols with either methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), or ethanol being major constituents. Two GC methods can be used for the measurement of the individual alcohols and ethers in gasoline: the single-column OFID method[1,2] and the dual column ASTM method D4815-93.[3] Restek offers columns and specially deactivated tubing for the analysis of alcohols and ethers in gasoline according to both ASTM and EPA methodology.

ASTM Test Method D4815-93 specifies the use of two columns, a micro-packed pre-column of 1,2,3-tris-2-cyanoethoxy-propane (TCEP), and an analytical capillary column of methyl silicone (Rtx®-1 or MXT®-1). These columns are configured with a 10-port valve to accomplish the heartcutting and back-flushing necessary in order to resolve oxygenates from hydrocarbons present in gasoline. The sample is first directed to the TCEP column. This column has high retention for polar oxygenates, while the more volatile hydrocarbons are vented. The valve is then actuated, backflushing the remaining sample to the Rtx®-1 or MXT®-1 column where separation of oxygenates occurs. After the elution of the last oxygenate (*tert*-amyl methyl ether), the valve is redirected and remaining heavy hydrocarbons are backflushed from the Rtx®-1 column as a single peak. A separation example of all the specified alcohols and ethers appears in Figure 1.

Fused silica lined stainless steel improves peak shapes for alcohols.
In order to achieve optimum peak width in this valve system, small diameter sample transfer tubing is recommended to minimize band broadening and resolution loss. Because alcohols can adsorb on both the stainless steel transfer line tubing and TCEP pre-column stainless steel surface, Restek recommends using Silcosteel® treated* stainless steel for transfer lines and the TCEP pre-column. Silcosteel® treated

Figure 1 TCEP and Rtx®-1 columns, connected in series, resolve C1-C4 alcohols, MTBE, ETBE, and TAME.



1. methanol
2. ethanol
3. isopropanol
4. *tert*-butanol
5. *n*-propanol
6. methyl *tert*-butyl ether
7. *sec*-butanol
8. diisopropyl ether (DIPE)
9. isbutanol
10. ethyl-*tert*-butyl ether (ETBE)
11. *tert*-amyl alcohol
12. dimethoxyethane (DME)
13. *n*-butanol
14. benzene
15. *tert*-amyl methyl ether (TAME)
16. total heavy hydrocarbons

0.56m, 0.75mm ID 20% TCEP on Chromosorb® P A/W (cat.# 19040) and
30m, 0.53mm ID, 3.0µm Rtx®-1 (cat.# 10185) connected in series
0.5µL split injection of oxygenates blend 1–10% wt in surrogate gasoline

Oven temp.:	60°C
Inj. / det. temp.:	200°C / 250°C (FID)
Carrier gas:	helium, 5mL/min. set @ 60°C
Split ratio:	15:1

*Silcosteel® treatment is a proprietary surface treatment for passivating steel and stainless steel. U.S. Patent 6,511,760.

tubing provides the inertness of fused silica tubing, resulting in excellent peak shape for the oxygenates (Figure 1). The Restek TCEP micropacked column is prepared using 0.75mm ID tubing, which gives a more reproducible retention time than columns prepared from smaller ID tubing. This column also produces a slightly longer and more reproducible valve time (i.e., 0.28 minutes), which helps when initially setting this critical parameter. For methods using the oxygen-specific OFID, a 60-meter Rtx®-1 column will resolve the oxygenated compounds.

Summary

To meet the requirements of ASTM Test Method D4815-93, an analyst must consider the sample handling system and choice of columns. By implementing a low volume valve and small ID Silcosteel® treated transfer lines, optimum resolution of oxygenates can be achieved. In addition, by using a Silcosteel® treated 0.75mm ID TCEP pre-column and the Rtx®-1 or MXT®-1 analytical column, optimum resolution can be attained. For the OFID procedures, Restek offers a low-bleed, 60-meter Rtx®-1 or MXT®-1 methyl silicone column.

References

1. 40 CFR Part 30, Federal Register, 59(32): 7716-7878, Feb. 16, 1994.
2. ASTM Test Method D5599-94, *Determination of Oxygenates in Gasoline by Gas Chromatography and Selective Flame Ionization Detection.*
3. ASTM Test Method D4815-93, *Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-amyl Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography.*

References not available from Restek.

For ASTM D4815-93:

Rtx®-1 Column (fused silica)

(Crossbond® 100% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #
0.53mm	3.00	-60 to 270/290°C	30-Meter	10185

MXT®-1 Column

(Silcosteel® treated stainless steel)

(Crossbond® 100% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #
0.53mm	3.00	-60 to 285°C	30-Meter	70185

Micropacked TCEP Column

	ID	OD	Temp. Range	0.56-Meter
20% TCEP on 80/100 Chromosorb® PAW	0.75mm	1/16"	0–120°C	19040

Valve Transfer Line:

Silcosteel® Treated Coiled 304 Grade Stainless Steel Tubing†

ID	OD	cat.#
0.020" (0.51mm)	1/16" (1.59mm)	20593

†Silcosteel® treated and siloxane deactivated. For Silcosteel® treatment only, add-279 to the cat.#.

Minimum order is 5 ft. Price breaks are available at 25 ft., 200 ft., and 400 ft.

For OFID Procedure:

Rtx®-1 Column (fused silica)

(Crossbond® 100% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #
0.25mm	1.00	-60 to 320/340°C	60-Meter	10156

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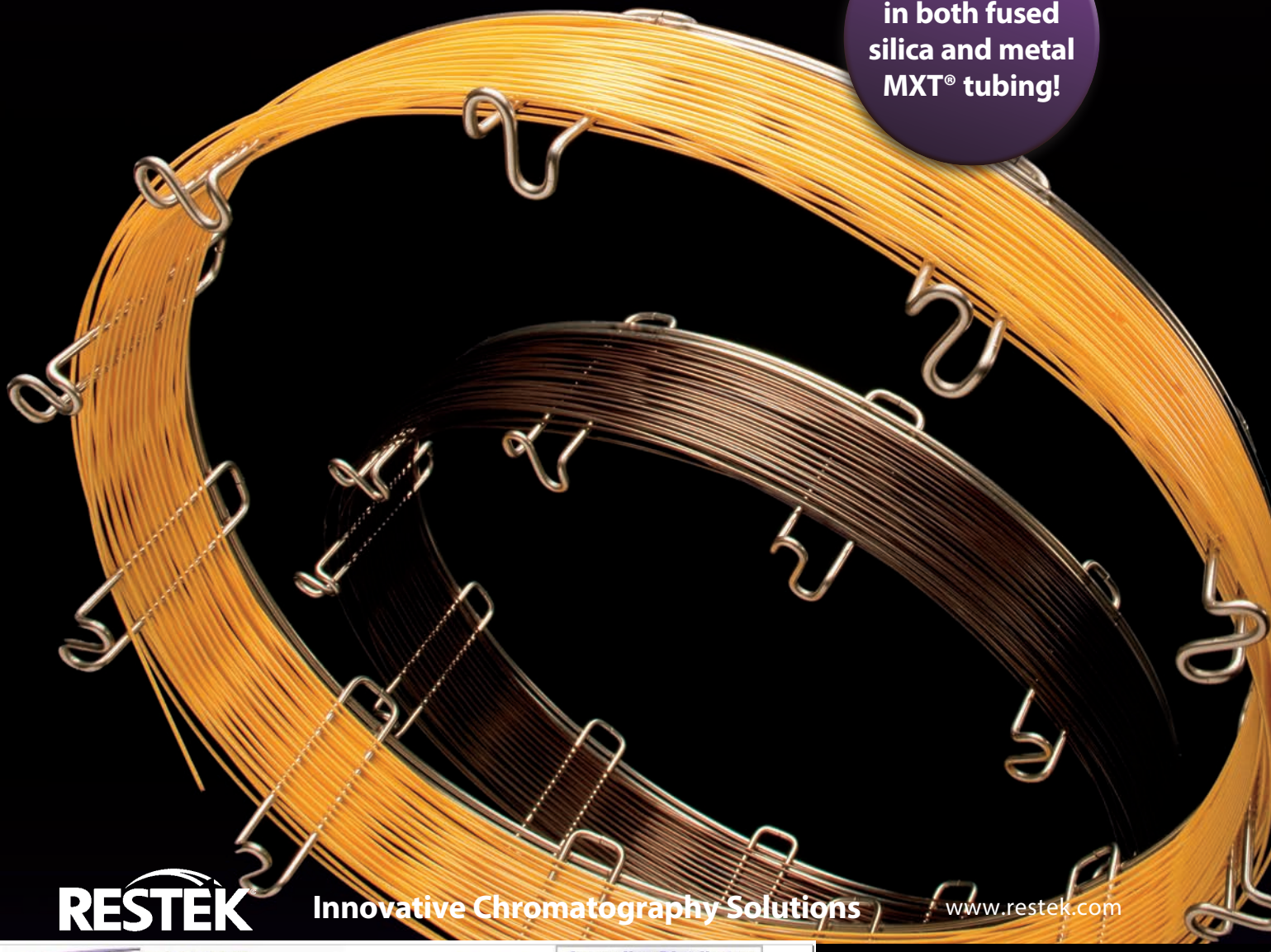
Analyze Trace Polar Hydrocarbons More Accurately and Reliably With **Alumina BOND/MAPD PLOT Columns!**

- Reproducible, predictable responses for reduced calibration frequency.
- Exceptional sample loading capacity, which improves resolution and response.
- Highest temperature stability—application range extended to 250 °C.

Available in both fused silica and metal MXT® tubing!



RESTEK **Innovative Chromatography Solutions** www.restek.com

Restek® MAPD Column Technology Improves Trace Analysis of Polar Hydrocarbons

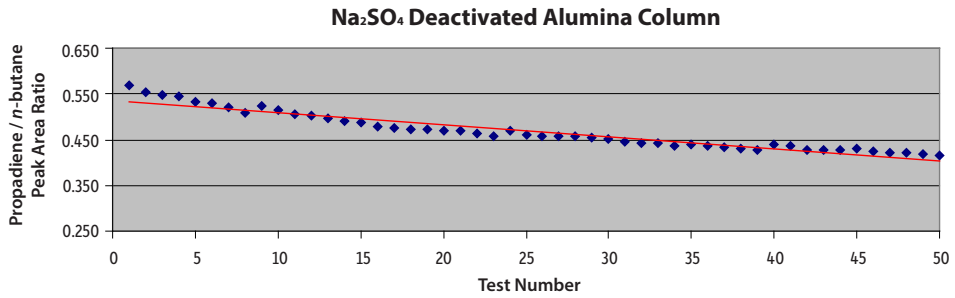
The chromatographic analysis of light hydrocarbons, including unsaturated isomers, is common in the petrochemical industry. Adsorption chromatography using alumina stationary phases has proven to be very effective for the separation of these compounds. However, challenges still exist, particularly for trace analysis of polar hydrocarbons like propadiene, acetylene, and methyl acetylene. Successful analysis of these compounds is highly dependent on the deactivation of the alumina. For example, responses for these analytes are highly variable on sodium sulfate deactivated columns (Figure 1). While some columns, known as MAPD columns (for methyl acetylene and propadiene), have been developed specifically for these compounds, existing MAPD column solutions show limitations in response, reproducibility, capacity, and temperature stability.

Restek has solved these problems by developing a line of MAPD alumina columns with a unique, high-performance deactivation. These columns—the Rt®-Alumina BOND/MAPD (fused silica) and MXT®-Alumina BOND/MAPD (metal) columns—offer several significant improvements over conventional MAPD columns:

- Reproducible, predictable responses for reduced calibration frequency.
- Exceptional sample loading capacity, which improves resolution and response.
- Highest temperature stability—application range extended to 250 °C.

These features are a significant step forward in MAPD column technology and have resulted in improvements in column performance compared to other MAPD columns. New Rt®-Alumina BOND/MAPD and MXT®-Alumina BOND/MAPD columns are not only perfect for analysis of polar hydrocarbons such as acetylene, methyl acetylene, and propadiene, but also perform well for generic light hydrocarbon analysis.

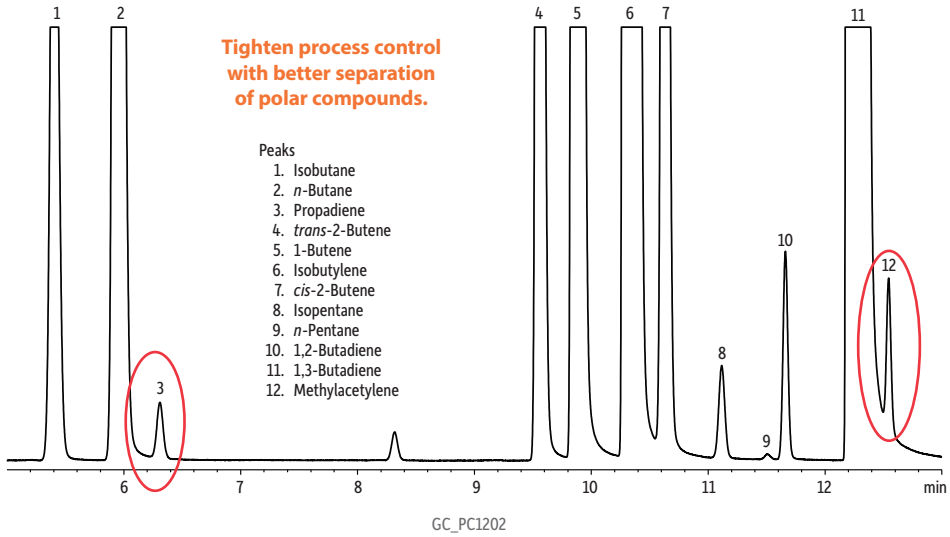
Figure 1: Conventional Na_2SO_4 deactivated columns show poor response stability over time.



Key Application: Separation of Methyl Acetylene (MA) and Propadiene (PD)

Since small amounts of methyl acetylene and propadiene can interfere with the conversion of propylene, ethylene, or 1,3-butadiene into polypropylene, polyethylene, or synthetic butadiene rubber, respectively, separation and quantification of these compounds at trace levels is critical. The new Rt®- and MXT®-Alumina BOND/MAPD columns not only provide excellent separation of these analytes (Figure 2), but also elute them with high peak responses due to the inertness of the column. This makes light hydrocarbon purity methods more sensitive and accurate, allowing much tighter process control.

Figure 2: Excellent separation of methyl acetylene and propadiene from 1,3-butadiene and other hydrocarbons.

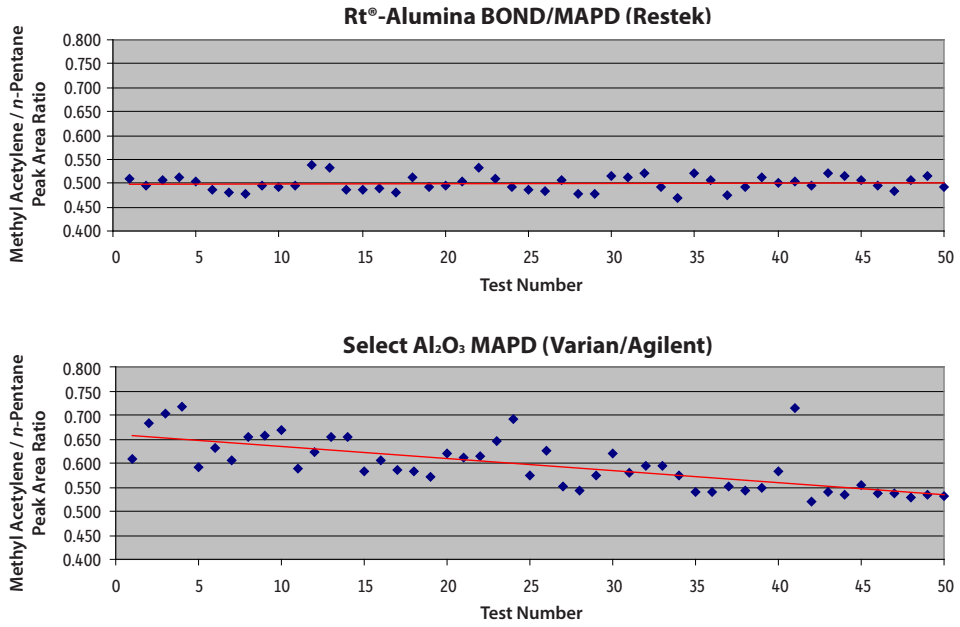


Column: Rt®-Alumina BOND/MAPD, 50 m, 0.53 mm ID, 10 µm (cat.# 19778); **Sample:** crude 1,3-butadiene; Diluent: none; **Injection:** Inj. Vol.: 5 µL split; Liner: 2 mm ID straight inlet liner (cat.# 20712); Inj. Temp.: 200 °C; Split Vent Flow Rate: 45 mL/min; **Oven:** Oven Temp: 70 °C (hold 5 min) to 200 °C at 10 °C/min (hold 10 min); **Carrier Gas:** He, constant pressure (20 psi, 137.9 kPa); Temp.: 70 °C; **Detector:** FID @ 200 °C; Make-up Gas Flow Rate: 30 mL/min; Make-up Gas Type: N_2; Data Rate: 20 Hz; **Instrument:** HP5890 GC

Reproducible Responses Reduce Calibration Frequency

The technology employed in making Restek's new alumina BOND/MAPD columns ensures more consistent, predictable responses for critical compounds like methyl acetylene over many injections. As shown in Figure 3, methyl acetylene response is much more reproducible when using a Restek alumina MAPD column compared to other commercially available MAPD columns. Greater response stability reduces the frequency of recalibration, which is a key benefit for process-type applications.

Figure 3: Restek® Rt®- Alumina BOND/MAPD columns provide more reproducible, reliable results.



Higher Temperature Stability Extends Application Range

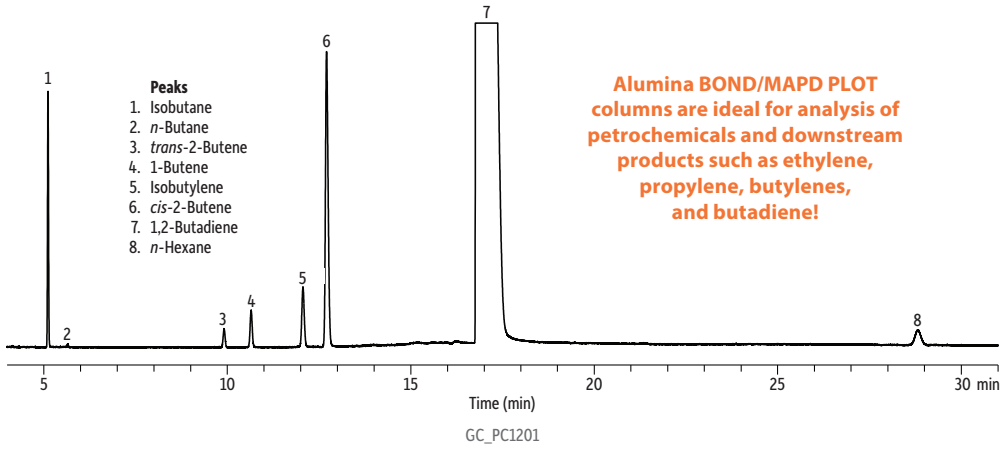
Conventional alumina PLOT columns have a maximum temperature of 200 °C, but Restek® alumina BOND/MAPD PLOT columns are stable up to 250 °C. This higher maximum temperature means higher molecular weight hydrocarbons can be eluted quickly, extending the typical application range of alumina PLOT columns. In addition, the higher temperature tolerance allows faster column regeneration to remove adsorbed water, shorter conditioning times, and the flexibility of operating two columns in one oven up to 250 °C.

Restek Alumina BOND/MAPD Columns— The Best Choice for Polar Hydrocarbon Analysis!

The proprietary deactivation technology used for Rt®-Alumina BOND/MAPD and MXT®-Alumina BOND/MAPD columns results in improved analysis of trace polar hydrocarbons like acetylene, methyl acetylene, and propadiene in typical C1-C5 hydrocarbon streams. Figures 2 and 5 show real-world examples of column performance. The new deactivation produces a highly inert column that offers superior response reproducibility, which allows analysts to maximize the number of samples analyzed before recalibration is required. Significantly higher capacity reduces peak tailing, further improving the separation and response of target compounds.

In addition, only Rt®-Alumina BOND/MAPD and MXT®-Alumina BOND/MAPD columns are stable up to 250 °C, extending the application range beyond what conventional MAPD columns offer. This means higher molecular weight hydrocarbons can be eluted more quickly, and it also reduces regeneration time when the column is exposed to water from samples or carrier gases. Whether you use fused silica columns in a laboratory environment or require stainless steel columns for process GCs or field instruments, Restek® alumina BOND/MAPD columns are the best choice for polar hydrocarbon analysis.

Figure 5: 1,2-butadiene analyzed on an Rt®-Alumina BOND/MAPD column.



Column: Rt®-Alumina BOND/MAPD, 50 m, 0.32 mm ID, 5.0 µm (cat.# 19780); **Sample:** Crude 1,2-butadiene; Diluent: none; **Injection:** Inj. Vol.: 1 µL split; Liner: 2.0 mm ID Straight Inlet Liner (cat.# 20712); Inj. Temp.: 200 °C; Split Vent Flow Rate: 80 mL/min; **Oven:** Oven Temp: 100 °C (hold 31 min); **Carrier Gas:** H_2, constant linear velocity; Linear Velocity: 17.40 psi, 120.0 kPa @ 100 °C; **Detector:** FID @ 200 °C; Make-up Gas Flow Rate: 30 mL/min; Make-up Gas Type: N_2; Data Rate: 20 Hz; **Instrument:** HP5890 GC

tech tip

Traces of water in the carrier gas and sample will affect the retention and selectivity of alumina. If the column is exposed to water, the retention times will shorten. Alumina columns can be regenerated by conditioning for 15-30 minutes at 200-250 °C under normal carrier gas flow. Periodic conditioning ensures excellent run-to-run retention time reproducibility.

The maximum programmable temperature for Rt®- and MXT®-Alumina BOND/MAPD columns is 250 °C. Higher temperatures cause irreversible changes to the porous layer adsorption properties.

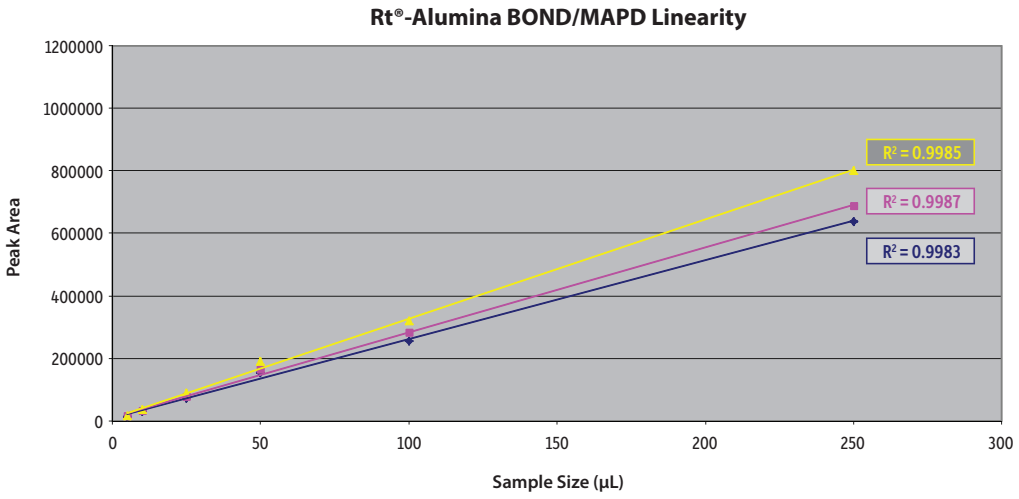
Exceptional Sample Loading Capacity Improves Resolution and Response

In gas-solid chromatography, phase overload produces tailing peaks, an issue that is further complicated by activity on adsorptive surfaces like alumina. This activity, which is defined by the nature of the alumina, contributes to the behavioral differences observed between different brands of alumina columns. The new Rt®-Alumina BOND/MAPD and MXT®-Alumina BOND/MAPD columns are designed to maintain the retention characteristics of a typical alumina column, but with much greater sample loading capacity. As shown in Table I, the Rt®-Alumina BOND/MAPD column shows less tailing (i.e., higher capacity) over a broad range of on-column amounts compared to another commercially available alumina MAPD column. Less tailing results in higher signal-to-noise ratios, which produces better separations and higher responses. In addition, the Restek alumina BOND/MAPD column produces excellent response linearity over a wide range of on-column amounts (Figure 4).

Table I: Peak asymmetry comparison. Poor capacity is evident even at 25 µL on a conventional Al2O3 MAPD column, while the new Rt®-Alumina BOND/MAPD column shows higher capacity over a broad concentration range.

	Rt®-Alumina Bond/MAPD		Select Al_2O_3 MAPD	
Sample Size (µL)	1,3-Butadiene	Methyl Acetylene	1,3-Butadiene	Methyl Acetylene
5	1.02	1.08	1.11	1.13
10	1.06	1.13	1.18	1.23
25	1.16	1.22	1.37	1.52
50	1.29	1.39	1.69	1.90
100	1.48	1.55	2.14	2.53
250	2.15	2.22	3.44	4.11

Figure 4: Not only does the Rt®-Alumina BOND/MAPD column show higher loading capacity, but it also produces excellent linearity for propadiene (blue line), acetylene (pink line), and methyl acetylene (yellow line) over a wide range of on-column amounts.



RESTEK

Restek® ProFLOW 6000 Electronic Flowmeter

Flowmeters that can measure flammable gases are becoming mandatory due to the increased use of hydrogen in chromatography. With its Ex rating, the Restek® ProFLOW 6000 flowmeter is designed specifically with explosive and flammable gases in mind.

The Restek® ProFLOW 6000 is the only flowmeter you need for any type of chromatography gas measurement because of its wide range of capabilities. The ProFLOW 6000 is an electronic device capable of measuring volumetric flow for most gases. Real-time measurements can be made for various types of flow paths, including continually changing gas types. This portable unit is designed for easy handheld use, and the stand adds benchtop convenience.

Description	qty.	cat.#
Restek ProFLOW 6000 Electronic Flowmeter With Hard-Sided Carrying Case	ea.	22656
ProFLOW 6000 Recalibration Service	ea.	22656-R
Soft-Sided Storage Case for Leak Detector or ProFLOW 6000 Flowmeter	ea.	22657

*The flowmeter is designed to measure clean, dry, non-corrosive gases.
Patented.

Restek® Super-Clean Gas Filter Kits and Replacements

- High-purity output ensures 99.9999% pure gas (at max. flow of 2 L/min).
- "Quick connect" fittings for easy, leak-tight filter cartridge changes.
- Glass inside to prevent diffusion; polycarbonate housing outside for safety.
- All traps measure 10 5/8" x 1 3/4" (27 x 4.4 cm).
- Each base plate unit measures 4" x 4" x 1 7/8" (10.2 x 10.2 x 4.8 cm).


22020


22022

Description	qty.	cat.#
Carrier Gas Cleaning Kit Includes: mounting base plate, 1/8" inlet/outlet fittings, and oxygen/moisture/hydrocarbon triple gas filter	kit	22019
Fuel Gas Purification Kit Includes: mounting base plate, 1/8" inlet/outlet fittings, and hydrocarbon/moisture fuel gas filter	kit	22021
Ultra-High Capacity Hydrocarbon Filter	ea.	22030
Ultra-High Capacity Moisture Filter	ea.	22028
Ultra-High Capacity Oxygen Filter	ea.	22029
Replacement Triple Gas Filter (removes oxygen, moisture, and hydrocarbons)	ea.	22020
Replacement Fuel Gas Filter (removes moisture and hydrocarbons)	ea.	22022
Helium-Specific Carrier Gas Cleaning Kit Includes: mounting base plate, 1/8" inlet/outlet fittings, and oxygen/moisture/hydrocarbon helium-specific filter	kit	21983
Replacement Helium-Specific Gas Filter (removes oxygen, moisture, and hydrocarbons)	ea.	21982
Gas Filter Bundle Kit Includes: one triple gas filter (cat.# 22020) and two fuel gas filters (cat.# 22022)	kit	22031

Restek® Filter Base Plates

- End fittings available in brass or stainless steel.
- Base plates fit all stand alone Super-Clean gas filters offered.


22025


22026


22027

	Brass		Stainless Steel	
Description	qty.	cat.#	qty.	cat.#
Filter Base Plate, Single-Position	ea.	22025	ea.	22344
Filter Base Plate, 2-Position	ea.	22026	ea.	22345
Filter Base Plate, 3-Position	ea.	22027	ea.	22346

Sample Cylinders

- All cylinders have 1/4" female NPT threads on both ends.
- TPED compliant cylinders available for EU community.

Swagelok® sample cylinders are made of 304L and 316L stainless steel to resist corrosion and DOT rated to 1,800 and 5,000 psig (TPED cylinders rated to 1,450 and 4,350 psig), which allows sampling at gas wellheads as well as on-site refineries. Each cylinder is hydrostatically tested to at least 5/3 the working pressure.

Sample Cylinders, Ultra-High Pressure

(Stainless Steel & Sulfinert® Treated)

- 316L stainless steel; DOT rating to 5,000 psig (TPED cylinders to 4,350 psig).
- Range of cylinder sizes, 150 cc to 500 cc.

	5,000 psig (34,474 kPa), 316L SS		TPED, 4,350 psig (29,992 kPa), 316L SS	
	Stainless Steel	Sulfinert Treated	Stainless Steel	Sulfinert Treated
Size	cat.#	cat.#	cat.#	cat.#
150 cc	22927	22111	22927-PI	22111-PI
300 cc	22928	22112	22928-PI	22112-PI
500 cc	22929	22113	22929-PI	22113-PI

Sample Cylinders, High Pressure

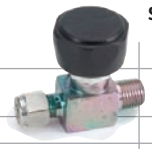
(Stainless Steel & Sulfinert® Treated)

- 304L stainless steel; DOT rating to 1,800 psig (TPED cylinders to 1,450 psig).
- Range of cylinder sizes, 75 cc to 2,250 cc.

	1,800 psig (12,411 kPa), 304L SS		TPED, 1,450 psig (9,997 kPa), 304L SS	
	Stainless Steel	Sulfinert Treated	Stainless Steel	Sulfinert Treated
Size	cat.#	cat.#	cat.#	cat.#
75 cc	22921	24130	22921-PI	24130-PI
150 cc	22922	24131	22922-PI	24131-PI
300 cc	22923	24132	22923-PI	24132-PI
500 cc	22924	24133	22924-PI	24133-PI
1,000 cc	22925	24134	22925-PI	24134-PI
2,250 cc	22926	21394	22926-PI	21394-PI

Sample Valves (Stainless Steel & Sulfinert® Treated)

- Multiple valve configurations, including dip tube and rupture disks.
- Large, durable, Kel-F® seat ensures leak-free operation.
- Temperature range: -40 °C to 120 °C



Description	Stainless Steel cat.#	Sulfinert Treated cat.#
3,500 psig (24,132 kPa) DOT Pressure Rating		
1/4" Male NPT x 1/4" Male NPT	26297	21400
1/4" Male NPT x 1/4" Female NPT	26298	26299
1/4" Male NPT x 1/4" Male Compression	26300	21401
1/4" Male NPT x 1/4" Male NPT w/5.25" Dip Tube*	26301	21402*
1/4" Male NPT x 1/4" Male NPT w/1,800 psi (12,411 kPa) Rupture Disc	26302	26303
1/4" Male NPT x 1/4" Female NPT w/1,800 psi (12,411 kPa) Rupture Disc	26304	26305
Replacement Rupture Disc, 1,800 psig (12,411 kPa)	26320	—
5,000 psig (34,474 kPa) DOT Pressure Rating		
1/4" Male NPT x 1/4" Male NPT	26306	26307
1/4" Male NPT x 1/4" Female NPT	26308	26309
1/4" Male NPT x 1/4" Male Compression	26310	26311
1/4" Male NPT x 1/4" Male NPT w/5.25" Dip Tube*	26312	26313
1/4" Male NPT x 1/4" Male NPT w/2,850 psi (19,650 kPa) Rupture Disc	26314	26315
1/4" Male NPT x 1/4" Female NPT w/2,850 psi (19,650 kPa) Rupture Disc	26316	26317
Replacement Rupture Disc, 2,850 psig (19,650 kPa)	26324	—

*To order a sample cylinder valve with dip tube, please call Customer Service at 1-800-356-1688, ext. 3, or contact your Restek representative. Specify dip tube length or % outage when ordering (maximum length = 5.25"/ 13.3 cm). Note: End of part will not be treated after cutting tube to length.

Sample Cylinder Accessories

Description	Fittings	qty.	cat.#
Sample Cylinder Carrying Handle, 304 SS for 1.9" & 2" OD Cylinders (Includes handle and two attachment rings)		ea.	26373
Sample Cylinder Carrying Handle, 304 SS for 3.5" & 4" OD Cylinders (Includes handle and two attachment rings)		ea.	26374
Sample Cylinder 316 SS End Pipe Plug, Stainless Steel	1/4" Male NPT	ea.	26375
Sample Cylinder 316 SS End Pipe Plug, Sulfinert Treated	1/4" Male NPT	ea.	26376
Sample Cylinder 316 SS Hollow Hex Plug	1/4" Male NPT	ea.	26377
Sample Cylinder SS Pipe Cap w/Lanyard	1/4" Female NPT & 20" Lanyard	ea.	26378
Sample Cylinder SS Pipe Cap, Stainless Steel	1/4" Female NPT	ea.	22969
Sample Cylinder SS Pipe Cap, Sulfinert Treated	1/4" Female NPT	ea.	22970

SS = Stainless Steel

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RESTEK®

Lit. Cat.# PCBR1412A-UNV

Petrochemical Applications

Analyze ppb Level Sulfur Compounds Using an Rt®-XLSulfur Micropacked GC Column or an Rtx®-1 Thick Film Capillary GC Column

Sulfur compounds in petroleum streams can have detrimental effects on the performance and longevity of the catalysts used in hydrocarbon processing. Furthermore, the toxicity and odor associated with sulfur compounds is of significant environmental importance. In short, to protect both processing equipment and the environment, the ability to quantify sulfur compounds to ppb levels is imperative.

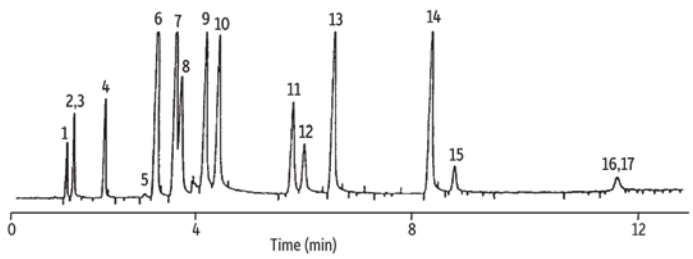
Gas chromatography is the method of choice for analyzing ppb level sulfur compounds in petroleum streams. Both packed and capillary GC columns have been successfully used for analyzing sulfurs and hydrocarbons in petroleum, although this often is a difficult application. With packed columns, the choice of column tubing is critical for accurate determination of sulfur compounds, particularly at low concentrations. Analyses on glass, PTFE, or stainless steel columns all present distinct problems. Glass columns exhibit poor inertness and lack ruggedness for field or process control use, and results are subject to variability because of column-to-column variation in ID. PTFE tubing, although more robust than glass, is plagued by three significant problems: 1) shrinkage as the column cools causes back diffusion of oxygen and water into the packing material which, if not addressed, can cause retention times to vary by as much as 15%; 2) oxygen and water diffuse through the tubing wall, significantly decreasing column longevity and creating reproducibility problems; and 3) a maximum column temperature limit of only 210 °C makes it impossible to quickly elute high molecular weight sulfur compounds. Without specialized surface passivation, stainless steel columns simply do not offer the inertness needed to monitor active sulfur compounds at ppb levels.

One of the proven approaches for analyzing ppb level sulfur compounds by GC is to use a thick film, 100% polydimethylsiloxane Rtx®-1 capillary column. Figure 1 illustrates the analysis of sulfur compounds on a 60 m x 0.53 mm ID x 7 µm Rtx®-1 column. The thick film is needed to resolve the volatile sulfur compounds, but makes for long retention times for higher molecular weight sulfur compounds. Alternatively, a 30 m x 0.32 mm ID x 4 µm Rtx®-1 column can be used to analyze higher molecular weight sulfur compounds, such as thiophenes.

Another excellent approach for analyzing low molecular weight sulfur compounds is the use of micropacked columns. The Rt®-XLSulfur micropacked column contains a specially deactivated divinylbenzene porous polymer in stainless steel tubing, deactivated through the Sulfinert® passivation process. The inertness of both the packing material and the tubing ensure a column that is capable of analyzing active sulfur compounds to 10 ppb. Moreover, the Rt®-XLSulfur micropacked column displays minimal bleed, well within the limits necessary for ppb level sulfur analysis, after a brief conditioning period (<30 minutes). The maximum temperature limit, 310 °C, allows rapid elution of the higher molecular weight analytes. This column achieves the critical separation of hydrogen sulfide (H_2S), carbonyl sulfide (COS), and sulfur dioxide (SO_2), as defined in the International Society of Beverage Technologists (ISBT) Procedure 14.0. Figure 2 shows the highly volatile H_2S and COS separated using a 1 m x 0.75 mm ID Rt®-XLSulfur micropacked column. Additionally, these volatile sulfur compounds are well-retained and well-resolved from the hydrocarbons that could interfere with quantification on some sulfur-specific detectors (Figure 3).

Note that to achieve this high level of sensitivity, every component of the sample pathway must be inert: the porous polymer, the column tubing, the column end fittings, and, additionally, the sample loop and/or inlet liner. Sample pathways in the analyses shown in Figures 1 through 3 were passivated using the Sulfinert® deactivation process. Figure 4 shows a schematic diagram of a system designed to analyze volatile and reactive sulfur compounds. From the Sulfinert®-treated sample cylinder used to collect and store the sample, to the Sulfinert®-treated valve and sample loop used to transfer the sample to the GC system, to either the inert capillary or packed column, Restek offers a complete line of products to ensure consistent and reliable analysis of ppb level sulfur compounds in petroleum streams.

Figure 1: Sulfur compounds on a thick film Rtx®-1 capillary column.

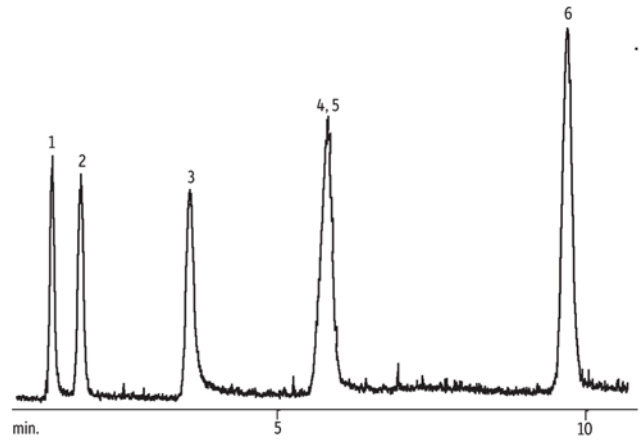


GC_PC1223

Peaks
1. Hydrogen sulfide
2. Sulfur dioxide
3. Carbonyl sulfide
4. Methyl mercaptan
5. Ethyl mercaptan
6. Carbon disulfide
7. Dimethyl sulfide
8. 2-Propyl mercaptan
9. Allyl mercaptan
10. 1-Propyl mercaptan
11. Ethyl sulfide
12. Butyl mercaptan
13. Dimethyl disulfide
14. Allyl sulfide
15. Propyl sulfide
16. Butyl sulfide
17. Allyl disulfide

Column	Rtx®-1, 60 m, 0.53 mm ID, 7.00 µm (cat.# 10193)
Sample	
Conc.:	~10 ppm each
Injection	
Inj. Vol.:	100 µL direct
Inj. Temp.:	50 °C
Oven	
Oven Temp:	50 °C to 200 °C at 15 °C/min.
Carrier Gas	He, constant linear velocity
Linear Velocity:	30 cm/sec. @ 50 °C
Detector	FPD @ 230 °C

Figure 2: An Rt®-XLSulfur micropacked column exhibits excellent inertness for low ppbv levels of sulfur compounds.

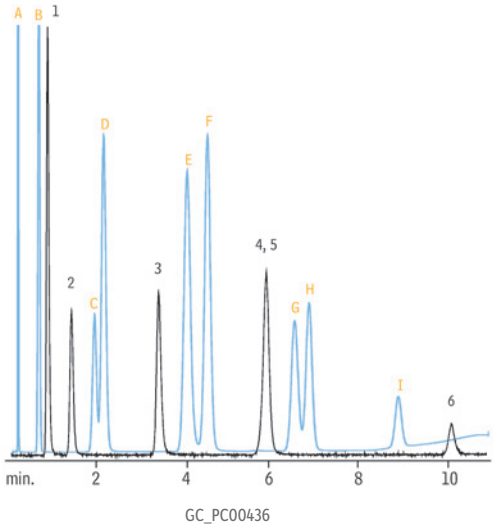


GC_PC1221

Peaks
1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Dimethyl sulfide
6. Dimethyl disulfide

Column	Rt®-XLSulfur, 1 m, 0.75 mm ID (cat.# 19806)
Sample	
Conc.:	1 mL of 50 ppbv each sulfur compound
Injection	sample valve
Oven	
Oven Temp:	60 °C to 230 °C at 15 °C/min.
Carrier Gas	He, constant flow
Flow Rate:	9 mL/min.
Detector	SCD

Figure 3: Sulfur compounds resolved from C1-C6 hydrocarbons, using an Rt®-XLSulfur micropacked column.

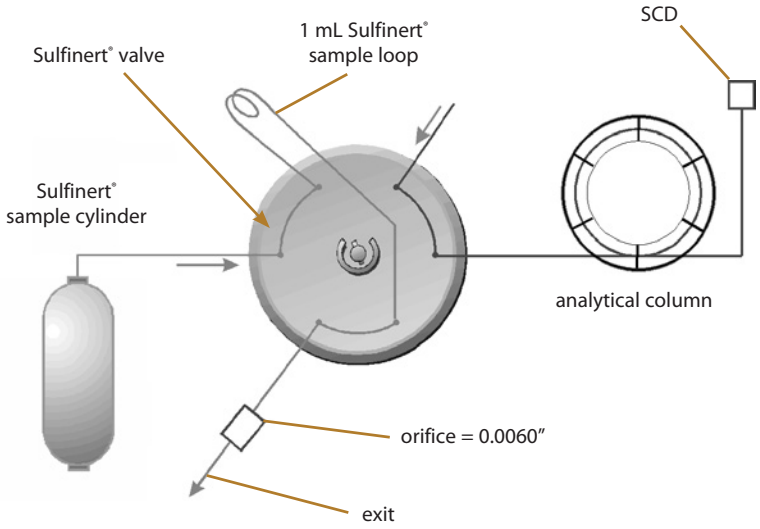


Sulfurs
1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Dimethyl sulfide
6. Dimethyl disulfide

Hydrocarbons
A. Methane
B. Ethane
C. Propylene
D. Propane
E. Isobutane
F. Butane
G. Isopentane
H. Pentane
I. Hexane

Column	Rt®-XLSulfur, 1m, 0.95mm OD, 0.75 mm ID (cat.# 19806)
Sample	
Conc.:	50 ppb each
Injection	packed not on-column
Oven	
Oven Temp:	60 °C to 230 °C at 15 °C/min.
Carrier Gas	He, constant flow
Flow Rate:	9 mL/min.
Detector	SCD/FID
Acknowledgement	Sulfur standards courtesy of DCG Partnership 1 Ltd., Pearland, TX.

Figure 4: Analytical system designed to analyze volatile and reactive sulfur compounds.



Lit. Cat.# PCAN1499-UNV

Analyze Hydrocarbons on OPN/Res-Sil™ C Bonded GC Packing

Superior Replacement for Porasil® Packings

By Barry Burger, Petroleum Chemist

- Unique separations of saturated and unsaturated hydrocarbons.
- Innovative bonding chemistry for batch-to-batch reproducibility, excellent thermal stability, and long life.
- Other bonded phases available.

For years, Porasil® C and Porasil® B, modified with covalently attached liquid phases such as OPN (cyanopropyl) or *n*-octane functional groups, offered important advantages, relative to conventional GC packings, in analyses of C1-C4 hydrocarbons: faster separations, higher thermal stability, shorter conditioning times, and longer lifetimes. Porasil® C / Porasil® B products were discontinued in the 1980s, however, and inventories have been depleted, forcing those that used these packings to search for comparable materials.

Restek chemists solved the problem by developing Res-Sil™ C and Res-Sil™ B bonded packings. These packings afford all of the advantages of the Porasil® C and Porasil® B materials, with the added advantage of consistent batch-to-batch performance - and they are readily available for immediate delivery. Compared to diatomaceous earth media, Res-Sil™ C has a small surface area, good inertness, low friability, and less reactivity.

Unique Selectivity for Process GC and High-Speed Analysis

Speed of analysis is crucial in process GC, and in laboratory gas analyzers in which multiple columns and valve switching are used to separate complex gas mixtures. Res-Sil™ C bonded packings are ideal for resolving the difficult-to-separate saturated and unsaturated C4 hydrocarbons under these demanding conditions. Figure 1 illustrates the unique selectivity of OPN on Res-Sil™ C packing for eluting cis-2-butene before 1,3-butadiene. When used in series with other columns, this unique material provides petroleum and petrochemical method developers with a powerful tool for fast determination of C1-C4 hydrocarbons. (1)

Stringent QA Assures Batch-to-Batch Consistency

Historically, one of the problems with bonded phases on Porasil® media was batch-to-batch variations in the amount of liquid stationary phase incorporated on the silica support. Through our new synthesis pathways, we precisely control the amount of bonded liquid phase on Res-Sil™ C in every batch of packing, assuring reproducible retention times and separations. Each batch of packing is tested with a complex mixture of hydrocarbons, to confirm it meets demanding retention time and retention index specifications. We evaluate column bleed at the recommended maximum temperature, 150°C, to ensure that there are no retention shifts or elevated baselines.

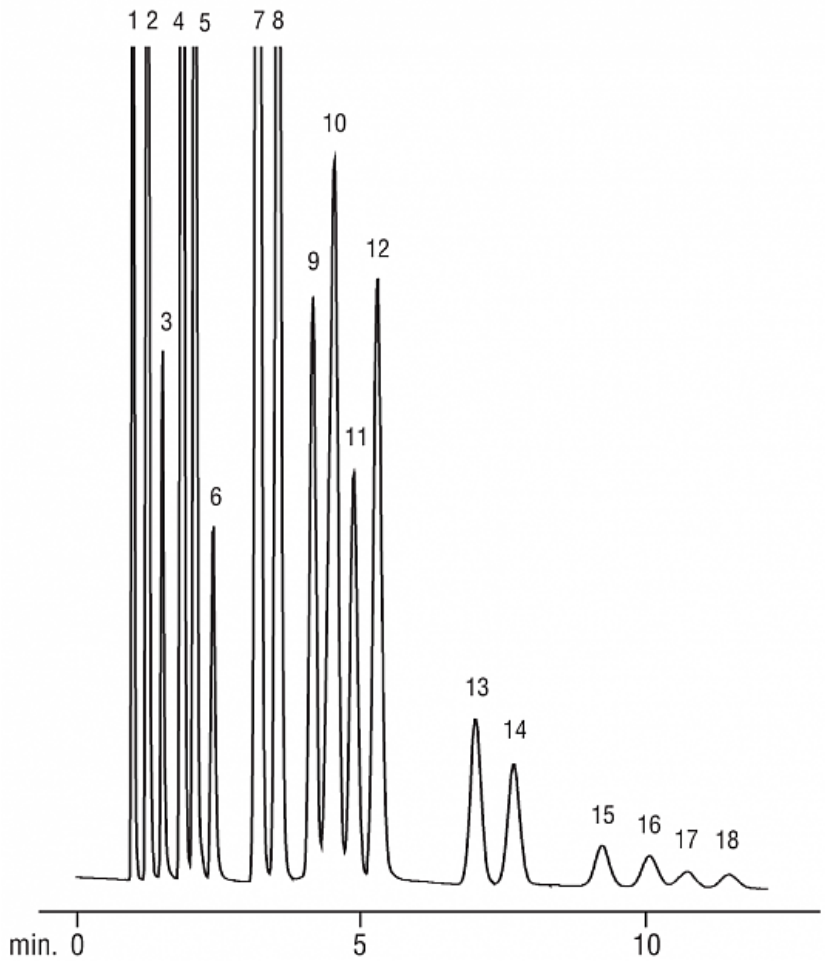
In addition to OPN on Res-Sil™ C packing, we bond *n*-octane and Carbowax® 1540 phases to Res-Sil™ C. Each of these packings offers a conditioning time of less than 30 minutes, low bleed, long lifetime, and consistent batch-to-batch reproducibility. We test every batch of every Restek bonded phase packing for bleed, efficiency, retention index, and retention time reproducibility. In addition, we make a broad range of packed and micropacked columns in specially-deactivated Silcosteel® tubing, for superior inertness and efficiency.

If you have been looking for a replacement for a Porasil® C or Porasil® B packing, we invite you to contact us. Your search should end here.

Figure 1 OPN on Res-Sil™ C packing has unique selectivity for *cis*-2-butene and 1,3-butadiene.

Peaks	Retention Indices	Peaks	Retention Indices

3. Acetylene		260	12. 1,3-Butadiene		454
4. Propane		300	13. Isopentane		488
5. Propylene		321	14. Pentane/3-methyl-1-butene		503
6. Propadiene		345	15. 1-Pentene		522
7. Isobutane		386	16. *trans*-2-Pentene		533
8. Butane		400	17. *cis*-2-Pentene		540
9. 1-Butene		422	18. 2-Methyl-2-butene		549



GC_PC00373

Column	OPN, 80/100 mesh on Res-Sil® C packing, SilcoSmooth® tubing, 12 ft., 1/8 in. OD, 2 mm ID (cat.# 80437-800)
Sample	Refinery gas
Conc.:	0.1-6 absolute mole %
Injection	
Inj. Vol.:	20 µL packed on-column
Inj. Temp.:	200 °C
Oven	
Oven Temp.:	50 °C
Carrier Gas	He, constant flow
Flow Rate:	30 mL/min
Detector	FID @ 200 °C
Acknowledgement	Standard courtesy of AC Analytical Controls

References

1. Saha, N.C., S.K. Jain, and R.K. Dua. *J. Chromatogr. Sci.* 16: 323-328 (1978). *Reference not available from Restek*.

RELATED SEARCHES

packed column, *c4*, *thermal stability*, *res-sil*, *carbowax*

Analyze Biodiesel Oil for Glycerin

Using Restek's Robust Rtx®-Biodiesel Capillary GC Column

By Barry L. Burger, Petroleum Chemist

- Linearity for all reference compounds exceeds method requirements on an Rtx®-Biodiesel Column.
- Alumaseal™ connector provides leak-free connection, guard column extends column life.
- Low column bleed at high temperatures.

"Biodiesel", "B100", "B20", "B10", and "transesterification" are becoming everyday terminology as of late. Biodiesel oil is biodegradable, nontoxic, and contains no aromatics, and the absence of sulfur from B100 precludes sulfur dioxide emissions. The "B" number designates the percentage of biodiesel in a biodiesel/petroleum diesel blend (e.g., B20 is 20% biodiesel / 80% petroleum diesel). In the United States, biodiesel is recognized as an alternative energy source by the Environmental Protection Agency and the Department of Energy, which qualifies the fuel for mandated programs under the Clean Air Act of 1992.

Transesterification of the animal fat or used vegetable oil from which biodiesel oil is prepared yields two products: methyl esters (biodiesel oil) and glycerin. Excessive amounts of free or bound glycerin in biodiesel oil product can foul injectors and form deposits on valves, pistons, and injector nozzles. Separation of the glycerin during storage or in vehicles' fuel tanks can reduce the shelf life of the product. The American Society for Testing and Materials, ASTM, describes several physical and chemical testing methods for biodiesel oil. In this article we focus on gas chromatographic method ASTM D-6584-00, which sets the industry standards for testing B100 biodiesel oil. Through this method, the analyst can quantify free glycerin in the range of 0.005 to 0.05 mass % and total glycerin from 0.05 to 0.5 mass %. The column recommended for the analysis is a 10m x 0.32mm ID fused silica column with a 0.1µm film of 5% diphenyl/95% dimethyl polysiloxane. The stationary phase and the polyimide coating on the tubing must be sufficiently robust to withstand high temperatures, and the column must exhibit low bleed.

We initiated this project to demonstrate the performance of our Rtx®-Biodiesel fused silica column for conformance to the ASTM method. In addition, we used a 5m x 0.53mm intermediate polarity (IP) deactivated fused silica guard column, coupled to the analytical column through an Alumaseal™ connector, to trap high molecular weight sample components and thereby increase the longevity of the analytical column. An Agilent 6890 GC, equipped with a cool on-column injector and FID, was used for analysis. Hydrogen, supplied from a Parker/Balston hydrogen generator, was both the FID fuel gas and, for optimum performance, the carrier gas. ChemStation® software was used as the data collection system.

The column was conditioned at 380°C for an hour prior to analysis. Calibration standards were prepared and silylated per ASTM method D-6584-00. To achieve the highest degree of accuracy we chose, and recommend the use of, a 250µL glass syringe, as opposed to automatic pipette-type dispensers. After adding the N-methyl-N-trimethyltrifluoracetamide (MSTFA) silyating agent, we gently agitated the vial for approximately two minutes, and then allowed it to stand at room temperature for 20 minutes.

GC parameters were as recommended in the method. Figure 1 illustrates the calibration curves for each reference compound. Each plot from the Rtx®-Biodiesel column, including triolein, complies with the established method linearity criteria ($r^2 \geq 0.99$). Triolein, used for triglyceride quantification, historically has been difficult to calibrate. During this study we also evaluated a competitor's column and, while the linearity for other compounds was acceptable, the result for triolein ($r^2 = 0.9698$) on the competitor's column did not conform to the method specification. This low r^2 value could not be corrected by reinstalling the column or optimizing the GC conditions.

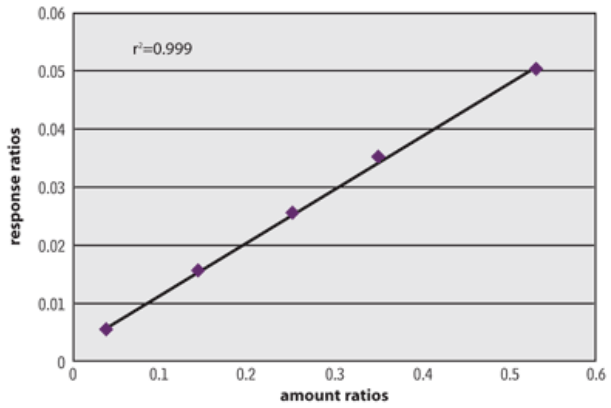
After developing the calibration curves, we spiked a sample of B100 biodiesel oil with the two internal standards, butanetriol and tricaprin, then silylated the mixture with MSTFA. Data from the subsequent analysis are illustrated in Figure 2. Results using the Rtx®-Biodiesel column were 0.05 mass % free glycerin, 0.44 mass % bound glycerin, and 0.49 mass % total glycerin, which are within the target range of the method. Column performance at high temperatures also was strong — bleed was low even at 380°C.

The Rtx®-Biodiesel column, coupled to a guard column through an Alumaseal™ connector, guarantees the performance required to meet the stringent standards for biodiesel analysis. Restek's technical experts are here to offer practical solutions to your toughest analytical problems. If you have questions regarding

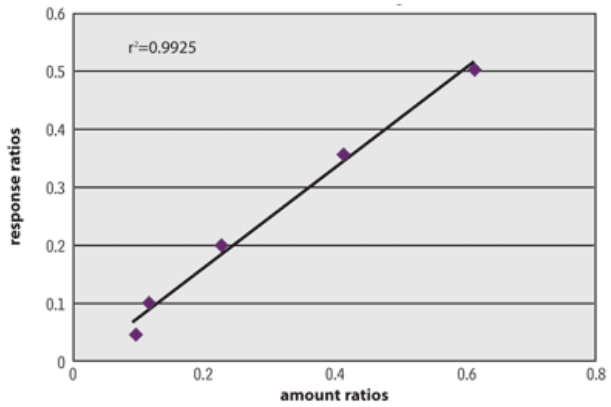
biodiesel analysis, or other challenging applications, please call our technical service team for assistance.

Figure 1 An Rtx®-Biodiesel column meets correlation coefficient specifications for determining glycerin in biodiesel oil.

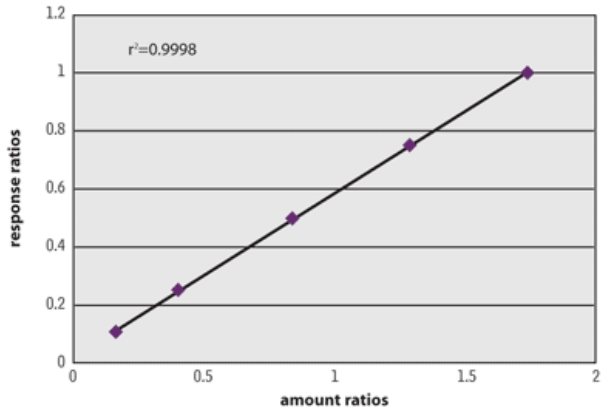
Glycerin (5-50mg)



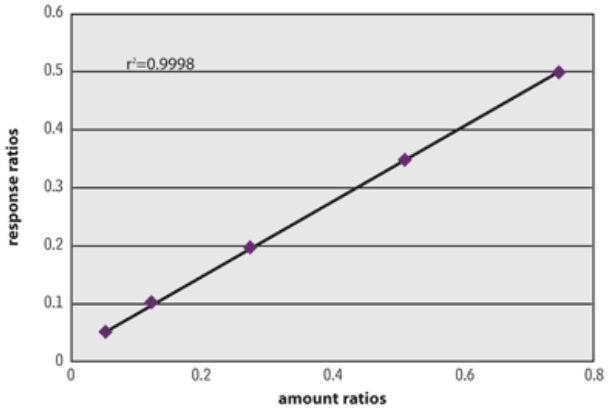
Triolein (50-500mg)



Monolein (100-1000mg)

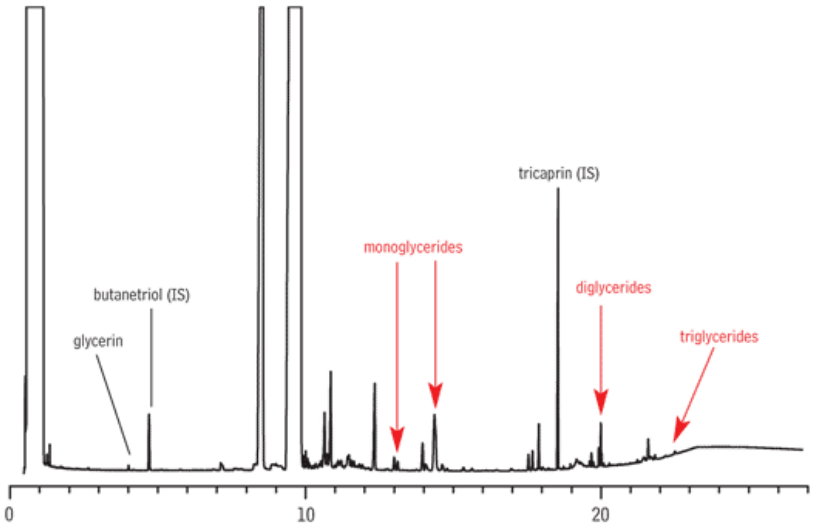


Diolein (50-500mg)



For conditions, see Figure 2.

Figure 2 Resolution of biodiesel oil (B100) and internal standards: the Rtx®-Biodiesel column provides reliable data for mono-, di- & triglycerides.



GC_PC00908

	Rtx®-Biodiesel, 10m, 0.32mm ID, 0.10µm (cat.# 10291)
Column:	2m, 0.53mm ID Hydroguard connected via Alumaseal™ connector
Sample:	biodiesel oil (B100) plus internal standards butanetriol and tricaprin, and derivatized per ASTM Method D 6584
Inj.:	1µL, cool on-column
Inj. temp.:	oven track
Carrier gas:	hydrogen, constant flow
Flow rate:	4mL/min.
	50°C (hold 1 min.) to 180°C @ 15°C/min. (hold 7 min.) to 230°C @ 30°C/min. to 380°C @ 30°C/min.
Oven temp.:	(hold 5 min.)
Det.:	FID
Det. temp.:	380°C

is a petrochemical product, its cost will continue to rise, domestically and internationally. Chromatographers must look for cost effective, ultra-pure gas alternatives to supply their instruments and state-of-the-art analytical columns. Fortunately, we do have options.

Relative to helium as the GC carrier gas, hydrogen from a gas generator reduces gas costs, cuts analysis time by 50%, and reduces temperatures needed for eluting analytes — which increases column lifetime. Parker ChromGas® hydrogen generators are safe, convenient, reliable, and easy to use.

For more information see the article "*Parker PEM Hydrogen Generators*".

*Cost estimate for USA, in US $.

RELATED SEARCHES

rtx-biodiesel, *biodiesel*, *glycerin*, *astm d6584*, *6584*, *b100*

RESTEK Pure Chromatography

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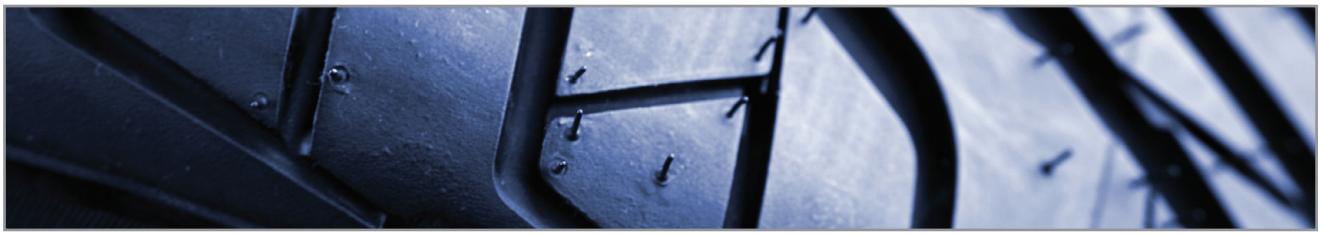


Petroleum & Petrochemical Applications

Analysis of Trace Hydrocarbon Impurities in 1,3-Butadiene

Using Optimized Rt®-Alumina BOND/MAPD PLOT Columns

By Rick Morehead, Jan Pijpelink, Jaap de Zeeuw, Tom Vezza

Abstract

Identifying and quantifying trace impurities in 1,3-butadiene is critical in producing high quality synthetic rubber products. Standard analytical methods employ alumina PLOT columns which yield good resolution for low molecular weight hydrocarbons, but suffer from irreproducibility and poor sensitivity for polar hydrocarbons. In this study, Rt®-Alumina BOND/MAPD PLOT columns were used to separate both common light polar contaminants, including methyl acetylene and propadiene, as well as 4-vinylcyclohexene, which is a high molecular weight impurity that normally requires a second test on an alternative column. By using an extended temperature program that employs the full thermal range of the column, 4-vinylcyclohexene, as well as all of the typical low molecular weight impurities in 1,3-butadiene, can be analyzed in a single test.

Introduction

1,3-butadiene is typically isolated from products of the naphtha steam cracking process. Prior to purification, 1,3-butadiene can be contaminated with significant amounts of isobutene as well as other C4 isomers. In addition to removing these C4 isomeric contaminants during purification, it is also important that 1,3-butadiene be free of propadiene and methyl acetylene, which can interfere with catalytic polymerization. Alumina PLOT columns are the most commonly used GC column for this application, but the determination of polar hydrocarbon impurities at trace levels can be quite challenging and is highly dependent on the deactivation of the alumina surface.

While alumina columns provide highly selective retention for both saturated and unsaturated volatile hydrocarbons, poor response and irreproducibility are often seen for polar compounds such as methyl acetylene and propadiene. Potassium chloride and sodium sulfate deactivations are commonly used to reduce the reactivity of the alumina adsorbent, but methyl acetylene/propadiene (MAPD) deactivations can be more effective for determining trace levels of these analytes. In this work, both crude and refined 1,3-butadiene samples were analyzed on an Rt®-Alumina BOND/MAPD PLOT column in order to evaluate column performance for both low and high molecular weight polar impurities. This column was selected for evaluation because, in addition to the specialized MAPD deactivation, it has a higher maximum operating temperature than other MAPD columns, which extends the application range to higher molecular weight impurities.

Experimental

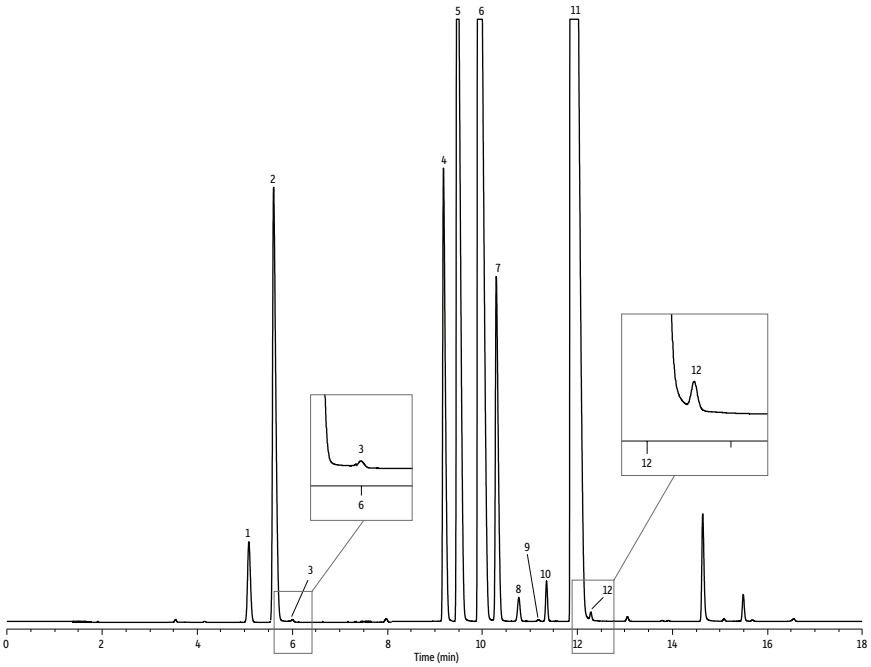
Samples of crude 1,3-butadiene and refined 1,3-butadiene were analyzed using a 50 m x 0.53 mm ID x 10 µm Rt®-Alumina BOND/MAPD PLOT column (cat.# 19778) and an Agilent 5890 GC. 10 µL split injections were made using a 200 °C injector temperature and split flow of 100 mL/min. Helium carrier gas at 20 psi (140 kPa) was used. Different oven programs were used for analyzing crude and refined 1,3-butadiene. For the crude, the oven was held at 70 °C for 5 minutes and then brought up to 200 °C at 10 °C/min. For the refined product, the oven was held at 70 °C for 5 minutes and then brought up to 250 °C at 10 °C/min. and held there for 5 minutes. All samples were analyzed with an FID at 250 °C.

Results and Discussion

The Rt®-Alumina BOND/MAPD column used in this application provided excellent resolution and response for polar hydrocarbons in crude 1,3-butadiene (Figure 1). The column exhibited a high degree of inertness toward polar impurities and provided excellent resolution for all the C4 contaminants, as well as propadiene and methyl acetylene. In addition, another small impurity was resolved from pentane and identified as 1,2-butadiene in this analysis.

Figure 1 Analysis of crude 1,3-butadiene on an Rt®-Alumina MAPD/BOND PLOT column. Effective deactivation of the alumina results in good separation of polar hydrocarbon impurities, such as propadiene and methyl acetylene.

Peaks
1. Isobutane
2. *n*-Butane
3. Propadiene
4. *trans*-2-Butene
5. 1-Butene
6. Isobutene
7. *cis*-2-Butene
8. Isopentane
9. *n*-Pentane
10. 1,2-Butadiene
11. 1,3-Butadiene
12. Methyl acetylene



GC_PC1211

Column	Rt®-Alumina BOND/MAPD, 50 m, 0.53 mm ID, 10.0 µm (cat.# 19778)
Sample	Crude 1,3-butadiene
Injection	
Inj. Vol.:	10 µL split
Liner:	2.0 mm ID straight inlet liner (cat.# 20712)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	100 mL/min.
Oven	
Oven Temp:	70 °C (hold 5 min.) to 200 °C at 10 °C/min. (hold 0 min.)
Carrier Gas	He, constant pressure (20 psi, 137.9 kPa)
Detector	FID @ 250 °C
Make-up Gas Flow Rate:	30 mL/min.
Make-up Gas Type:	N_2
Data Rate:	20 Hz
Instrument	HP5890 GC

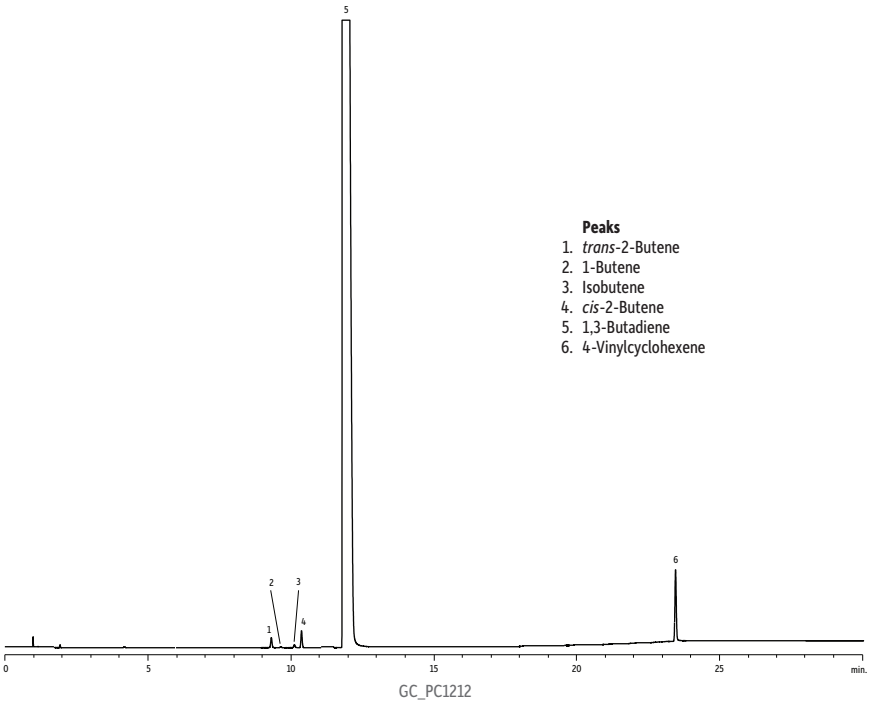
While the column provided good separation of all compounds under the conditions used here, it is important to note that instrument conditions can also affect the elution order and retention times of volatile hydrocarbons [1]. Using higher flows, lower starting temperatures, or longer initial hold times results in elution at lower temperatures which increases the separation of propadiene and acetylene from n-butane. Optimizing instrument parameters, in combination with using an Rt®-Alumina BOND/MAPD column, allows greater control of key separations during impurity analyses.

Since 1,3-butadiene is a reactive chemical and has a limited shelf life, it is typically stored with an inhibitor to prevent polymerization during storage. However, even in the presence of an inhibitor, small amounts of 1,3-butadiene dimer (4-vinylcyclohexene) form during long term storage. Typically, alumina PLOT columns cannot be used to analyze this and other heavier impurities due to limitations in their maximum operating temperature. However, the Rt®-Alumina BOND/MAPD column used here has a maximum operating temperature of 250 °C, which is 50 °C higher than standard alumina PLOT columns. As seen in Figure 2, this extended temperature range allows for the analysis of both trace amounts of the residual C4 impurities as well as higher molecular weight impurities, such as 4-vinylcyclohexene, in refined 1,3-butadiene.

Conclusions

The Rt®-Alumina BOND/MAPD column tested here performed well for the analysis of impurities in 1,3-butadiene. Due to the effectiveness of the column deactivation toward polar impurities, critical components, including propadiene and methyl acetylene, all were resolved and identified in the crude material. Also, the expanded operating temperature range permitted the analysis of 4-vinylcyclohexene, which usually has to be determined on a second column. The ability to analyze both low and high molecular weight contaminants in the same analysis should allow 1,3-butadiene purity testing to be done with greater laboratory efficiency for synthetic rubber production and other applications.

Figure 2 Analysis of refined 1,3-butadiene on an Rt®-Alumina MAPD/BOND PLOT column. Rt®-Alumina MAPD/BOND columns extend the application range of alumina PLOT columns due to their higher temperature stability.



Column Rt®-Alumina BOND/MAPD, 50 m, 0.53 mm ID, 10.0 µm (cat.# 19778)
Sample Refined 1,3-butadiene
Injection
Inj. Vol.: 10 µL split
Liner: 2.0 mm ID straight inlet liner (cat.# 20712)
Inj. Temp.: 200 °C
Split Vent Flow Rate: 100 mL/min.
Oven
Oven Temp: 70 °C (hold 5 min.) to 250 °C at 10 °C/min. (hold 5 min.)
Carrier Gas He, constant pressure (20 psi, 137.9 kPa)
Detector FID @ 250 °C
Make-up Gas Flow Rate: 30 mL/min.
Make-up Gas Type: N_2
Data Rate: 20 Hz
Instrument HP5890 GC

References

1. J. de Zeeuw, R. Morehead, T. Vezza, B. Bromps, *Chromatographic Behavior of Activated Alumina Adsorbents for the Analysis of Hydrocarbons*, American Laboratory (2011).

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Petroleum & Petrochemical

Alternative Carrier Gases for ASTM D7213 Simulated Distillation Analysis

By Katarina Oden, Barry Burger, and Amanda Rigdon

Introduction

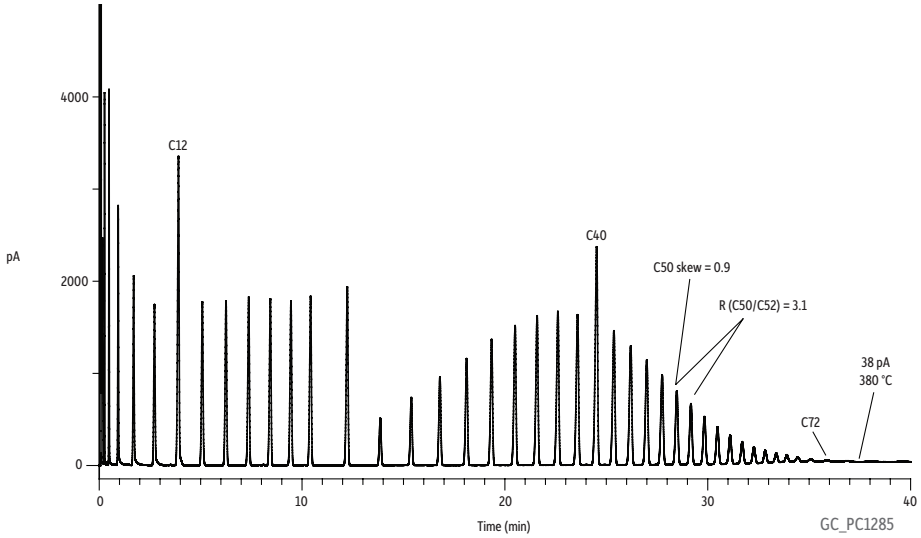
Crude oil consists of thousands of different hydrocarbons that span a very wide volatility range. In order to efficiently produce quality finished products, refineries depend on simulated distillation (SimDist) analyses to characterize the composition of their crude feedstock prior to processing. SimDist is a gas chromatography (GC) technique that allows fast, reproducible, and easily automated determination of boiling point distribution of crude oil samples.

Until recently, helium has been the only accepted gas for ASTM SimDist analysis. The ASTM SimDist committee now has approved the use of alternative carrier gases—nitrogen and hydrogen—for SimDist analyses. This article will explore alternative carrier gas options for SimDist analyses and discuss their various benefits and drawbacks.

Nitrogen or Hydrogen: Both are Sustainable Alternatives

Alternative carrier gases for SimDist analysis are explored in this article in the context of ASTM Method D7213. This method was developed to cover boiling range distribution of petroleum products and fractions such as medium and heavy naphtha, kerosene, jet fuels, and diesel, which have initial boiling points greater than 100 °C and final boiling points less than 615 °C, ranging from C5-C60. ASTM D7213 specifies that in order to successfully conduct the analysis, resolution between C50 and C52 must be greater than 1 and not more than 10. Additionally, peak symmetry or "skewness" must be greater than 0.5 and must not exceed 2. A traditional ASTM D7213 analysis using helium carrier gas is shown in Figure 1.

Figure 1: All ASTM Method D7213 requirements are met using an MXT®-1HT SimDist Column under typical conditions using helium as the carrier gas.



Column	MXT®-1HT SimDist, 5 m, 0.53 mm ID, 0.88 µm (cat.# 70131)
Sample	Retention time standard for D7213 (C5-C72), Separation Systems, Inc.
Diluent:	Carbon disulfide
Conc.:	1 wt%
Injection	
Inj. Vol.:	1 µL PTV on column
Liner:	Sky® 1.7 mm ID on-column inlet liner (cat.# 23430.1)
Inlet Temp. Program:	90 °C to 380 °C at 20 °C/min
Oven	
Oven Temp.:	40 °C to 380 °C at 10 °C/min (hold 10 min)
Carrier Gas	He, constant flow
Flow Rate:	12 mL/min
Detector	FID @ 390 °C
Make-up Gas Flow Rate:	18 mL/min
Make-up Gas Type:	N_2
Hydrogen flow:	43 mL/min
Air flow:	400 mL/min
Instrument	Agilent 7890B GC

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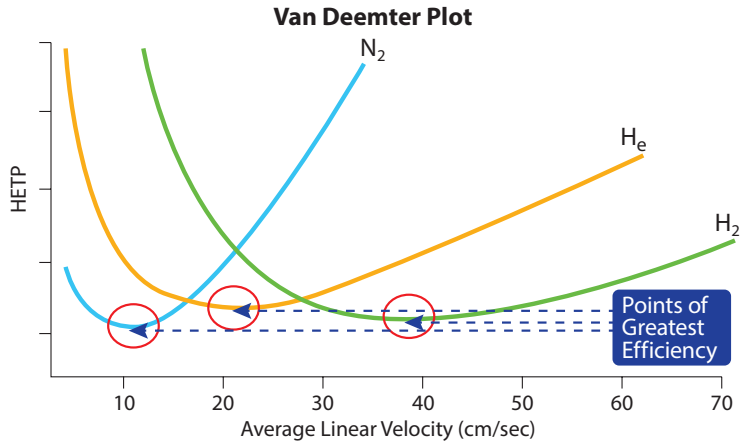
Figure 1 shows that Restek's 5 m x 0.53 mm x 0.88 µm MXT®-1HT SimDist column (cat.# 70131) has excellent sample capacity, ensuring peaks do not exceed the method skewness requirements. Extremely low column bleed results in accurate and reproducible retention times for the later eluting hydrocarbons.

Nitrogen

Nitrogen is a very good alternative carrier gas because it is readily available in cylinders or from nitrogen generators and has no explosive properties. Additionally, nitrogen is the most efficient carrier gas in comparison to helium and hydrogen when operated at their respective optimum velocities.

Figure 2: Van Deemter curves for hydrogen, helium, and nitrogen. Optimum efficiency is obtained at the linear velocity corresponding to the minimum point on each curve.

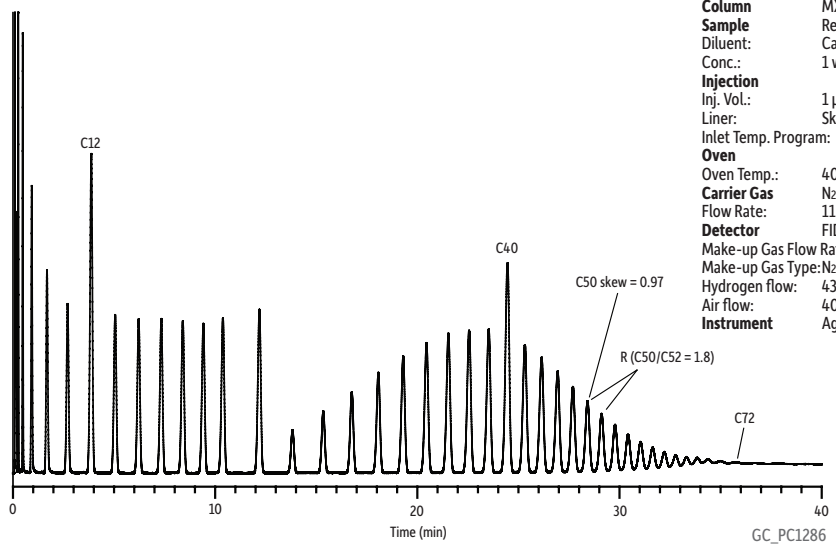


Efficiency directly relates to peak width—more efficient separations will have narrower peaks with higher resolution. Figure 2 shows van Deemter curves for hydrogen, nitrogen, and helium. The y-axis measures "height equivalent to a theoretical plate" (HETP) and higher efficiency occurs at lower HETP values. Therefore, efficiency is maximized at the minimum point of each van Deemter curve. The x-axis measures carrier gas linear velocity, thus, Figure 2 shows that the separation efficiency with each carrier gas differs depending on linear velocity.

Nitrogen has the lowest minimum van Deemter curve value; however, this minimum occurs at a very slow linear velocity. This means that even though very good separations can be achieved using nitrogen carrier gas, the analysis time will be longer compared to using helium or hydrogen when operated at their respective optimum velocities. Increasing the linear velocity in order to decrease the analysis time when using nitrogen will result in a rapid loss of column efficiency.

The MXT®-1HT SimDist column was tested for ASTM D7213 performance using nitrogen carrier gas. If nitrogen were employed at its optimum linear velocity, the resulting method would be much longer than the original method. Instead of translating methods to yield maximum efficiency, many nitrogen users simply replace helium with nitrogen, keeping all other method parameters the same (e.g., carrier gas linear velocity and oven program). Even though some efficiency is lost when employing nitrogen as a carrier gas without flow optimization, Restek's MXT®-1HT SimDist column offers enough efficiency to easily meet ASTM requirements for resolution between C50 and C52. Due to the loss of efficiency, peak heights are lower, meaning some response may be lost, but the low-bleed performance of this column allows for detection of broader peaks at lower levels, and baseline resolution of high molecular weight hydrocarbons is possible (Figure 3).

Figure 3: Even with nitrogen as the carrier gas, MXT®-1HT SimDist columns provide adequate resolution to meet ASTM Method D7213 requirements.



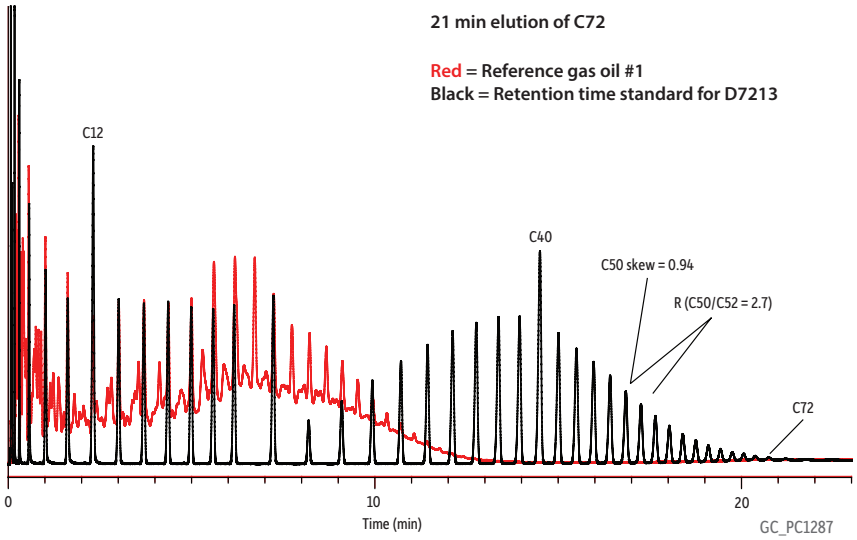
Column MXT®-1HT SimDist, 5 m, 0.53 mm ID, 0.88 µm (cat.# 70131)
Sample Retention time standard for D7213 (C5-C72), Separation Systems, Inc.
Diluent: Carbon disulfide
Conc.: 1 wt%
Injection
Inj. Vol.: 1 µL PTV on column
Liner: Sky® 1.7 mm ID on-column inlet liner (cat.# 23430.1)
Inlet Temp. Program: 90 °C to 380 °C at 20 °C/min
Oven
Oven Temp.: 40 °C to 380 °C at 10 °C/min (hold 10 min)
Carrier Gas N_2, constant flow
Flow Rate: 11.9 mL/min
Detector FID @ 390 °C
Make-up Gas Flow Rate: 18 mL/min
Make-up Gas Type: N_2
Hydrogen flow: 43 mL/min
Air flow: 400 mL/min
Instrument Agilent 7890B GC

Hydrogen

Hydrogen is comparable in price to nitrogen, and it has the additional advantage of being easy to generate. In contrast to nitrogen, hydrogen has a faster optimum linear velocity than helium (Figure 2). This means that with proper translation, methods can be shortened by approximately 25% when switching to hydrogen carrier gas.

Restek's *EZ*GC® method translator (http://www.restek.com/ezgc-mtfc) was used in custom mode to translate ASTM D7213 from helium to hydrogen carrier gas. Since the optimum linear velocity of hydrogen is faster than that of helium, changing the linear velocity to match the optimum for hydrogen will result in a faster analysis. However, the oven ramp rates must be changed proportionally in order to preserve the chromatography of the original method. Figure 4 shows the chromatogram generated using hydrogen carrier gas at 20 mL/min with a translated oven program. Elution time of C72 was shortened by 15 minutes (compared to using helium in Figure 1) while maintaining very good resolution between C50 and C52.

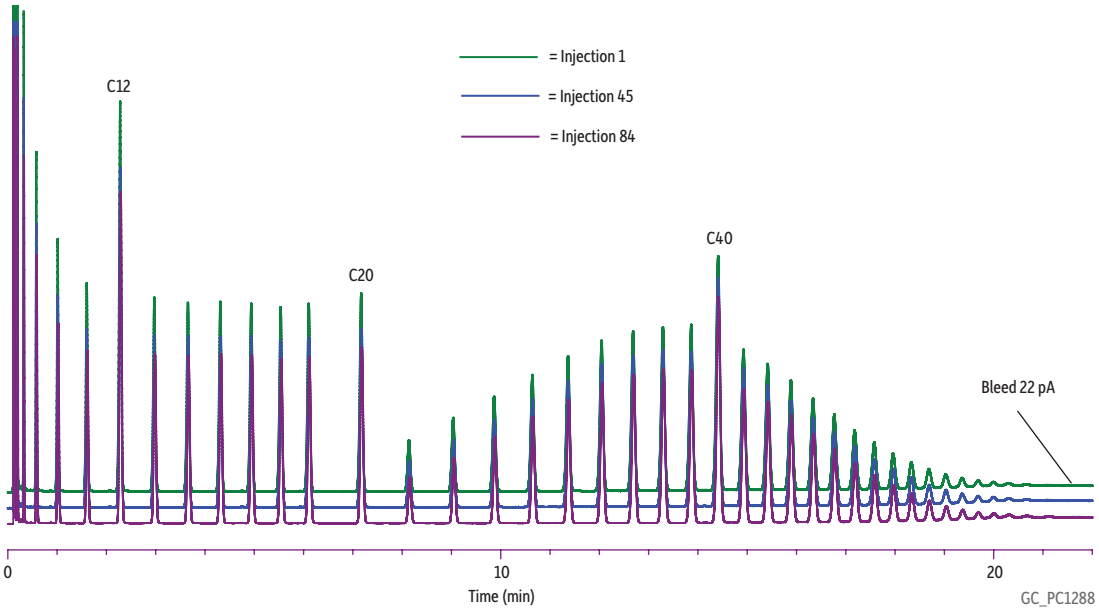
Figure 4: Overlay of chromatograms of a qualitative mixture of normal paraffins (C5-C72) and a reference gas oil comparing their boiling point distributions.



Column MXT®-1HT SimDist, 5 m, 0.53 mm ID, 0.88 µm (cat.# 70131)
Sample Retention time standard for D7213 (C5-C72), Separation Systems, Inc.
Reference gas oil #1
Injection
Inj. Vol.: 1 µL PTV on column
Liner: Sky® 1.7 mm ID on-column inlet liner (cat.# 23430.1)
Inlet Temp. Program: 90 °C to 380 °C at 20 °C/min
Oven
Oven Temp.: 40 °C to 380 °C at 16.9 °C/min (hold 5 min)
Carrier Gas H_2, constant flow
Flow Rate: 20 mL/min
Detector FID @ 390 °C
Make-up Gas Flow Rate: 25 mL/min
Hydrogen flow: 25 mL/min
Air flow: 400 mL/min
Instrument Agilent 7890B GC

Although hydrogen is affordable and allows the opportunity to significantly shorten analysis time, it is an explosive gas, which causes concern for some laboratories. Additionally, hydrogen is a reducing gas, meaning it is reactive whereas nitrogen and helium are nonreactive. In general, concerns regarding the reactivity of hydrogen revolve around higher temperature analysis of active analytes, but poorly coated metal columns also can be prone to reduction reactions from hydrogen at high temperatures. The MXT®-1HT SimDist column shows no decrease in performance over many temperature cycles and CS_2 injections using hydrogen carrier gas, indicating a rugged, high-quality column coating (Figure 5, Table I).

Figure 5: Excellent repeatability for C5-C72 hydrocarbons is obtained using the MXT®-1HT SimDist column, ensuring consistent performance from injection to injection.



Column	MXT®-1HT SimDist, 5 m, 0.53 mm ID, 0.88 µm (cat.# 70131)
Sample	Retention time standard for D7213 (C5-C72), Separation Systems, Inc.
Diluent:	Carbon disulfide
Conc.:	1 wt%
Injection	PTV on column
Liner:	Sky® 1.7 mm ID on-column inlet liner (cat.# 23430.1)
Inlet Temp. Program:	90 °C to 380 °C at 20 °C/min
Oven	
Oven Temp.:	40 °C to 380 °C at 16.9 °C/min (hold 5 min)
Carrier Gas	H_2, constant flow
Flow Rate:	20 mL/min
Detector	FID @ 390 °C
Make-up Gas Flow Rate:	25 mL/min
Make-up Gas Type:	N_2
Hydrogen flow:	25 mL/min
Air flow:	400 mL/min
Instrument	Agilent 7890B GC

Table I: Retention time repeatability for selected carbon numbers taken from the GC chromatograms of the C5 to C72 reference standard analyzed in Figure 5.

Carbon No.	Run 1 (min)	Run 45 (min)	Run 84 (min)	% RSD (n=3)
C8	0.328	0.322	0.322	1.069
C10	1.023	1.013	1.011	0.633
C14	3.668	3.658	3.654	0.197
C20	7.182	7.173	7.168	0.010
C28	10.654	10.646	10.641	0.062
C36	13.303	13.295	13.29	0.049
C40	14.419	14.410	14.411	0.034
C50	16.776	16.772	16.767	0.027
C60	18.696	18.691	18.685	0.030
C66	19.691	19.688	19.684	0.018

Conclusion

Carrier gas changes for SimDist methods, such as ASTM Method D7213, can be easily implemented in your daily process. MXT®-1HT SimDist columns offer excellent efficiency so adequate separations can be achieved even when operating at faster-than-optimal linear velocities. In addition, these columns are robust enough to withstand high temperatures and extreme conditions and still provide the low bleed levels needed for accurate boiling point determination analyses. Using MXT®-1HT SimDist columns and *EZ*GC® method translation software (http://www.restek.com/ezgc-mtfc), helium-based SimDist methods can be easily translated to alternative carrier gases while maintaining ASTM Method D7213 requirements.

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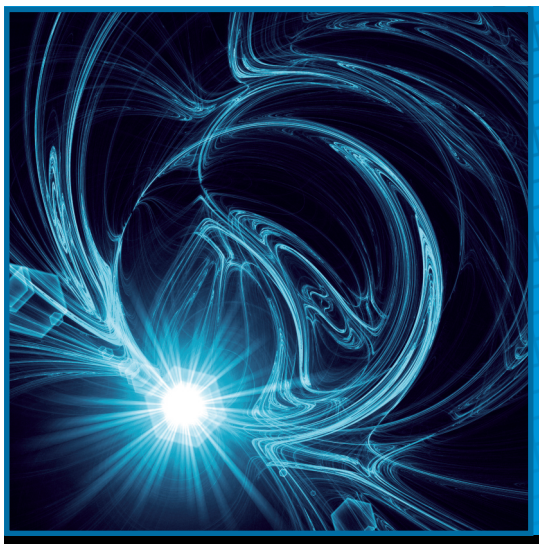

Advanced Capillary Column Technology Improves Analysis of Volatile Amines

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Short-chain volatile amines, such as monomethylamine, diethylamine, and triethylamine, are of great importance in the petrochemical industry and play a critical role inhibiting corrosion. Volatile amines are used as gas-scrubbing agents to remove hydrogen sulphide from refinery and natural gas streams, as well as for removing carbon dioxide during the production of ammonia. While accurate data on volatile amine content is vital for optimising the manufacture of compounds of many different classes, gas chromatographic analysis can be quite challenging due to their basic nature and high polarity. Because of these characteristics, amines will interact with active sites in the analytical column and along the sample pathway, resulting in broad, tailing peaks that are difficult to integrate accurately.

In order to improve chromatography for volatile amines, capillary columns must be highly inert and offer good retention and efficiency at low temperatures. In addition, they must be able to withstand tough matrices, as amines are often analysed in the presence of water, alcohol, or ammonia. Base-modified polyethylene glycol columns are one option, but they suffer from relatively poor stability and a loss of efficiency below 60°C. Siloxane columns are another option, but most commercially available siloxane-based columns for amine applications work well for pure samples, but perform poorly in the presence of tough matrices, such as water (Figure 1).
Until recently, commercially available columns for the analysis of volatile amines suffered from short lifetimes and displayed poor reproducibility in amine response. A new column developed by Restek, the Rtx®-Volatile Amine column, offers improved chromatographic performance and stability.

New Rtx®-Volatile Amine Column Produces Stable, Symmetrical Peaks

In order to assure symmetrical peaks and good reproducibility, both surface deactivation and polymer stability were considered in the development of the Rtx®-Volatile Amine capillary GC column. Proper deactivation reduces surface adsorption of short-chain amines, which improves peak shape significantly. As shown in Figure 2, highly symmetrical peaks are obtained for monomethylamine, diethylamine, and triethylamine, as well as for methanol. In addition, the film thickness was increased in order to maintain efficiency at temperatures as low as 40 °C. The stationary phase was intensively cross-linked in order to improve mechanical stability in the presence of water. The result is a new column chemistry that reliably produces good peak shape and response for volatile amines. As shown in Figure 3, even after 40 injections of amines in water, peak shapes are almost identical.

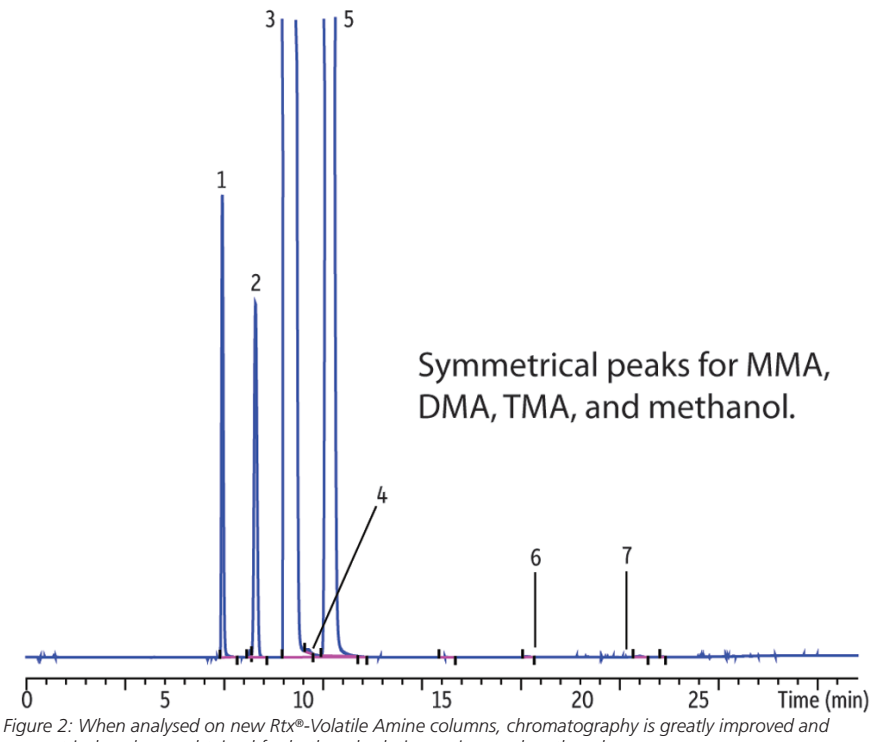


Figure 2: When analysed on new Rtx®-Volatile Amine columns, chromatography is greatly improved and symmetrical peaks are obtained for both early eluting amines and methanol.

Columns: Rtx®-Volatile Amine, 60 m x 0.32 mm ID (cat.# 18078); Sample: short-chain amines in water; Injection: 1 µL (split ratio 15:1), 220 °C; Oven: 40 °C (hold 10 min) to 250 °C at 20 °C/min (hold 10 min); Carrier gas: hydrogen, 2 mL/min, 35 cm/sec; Detector: FID @ 250 °C. Peaks: 1. Monomethylamine (MMA), 2. Methanol, 3. Dimethylamine (DMA), 4. Ethylamine, 5. Trimethylamine (TMA), 6. Dimethylethylamine, 7. Methyldiethylamine. Acknowledgement: Gilbert Baele, Taminco (Antwerp, Belgium).

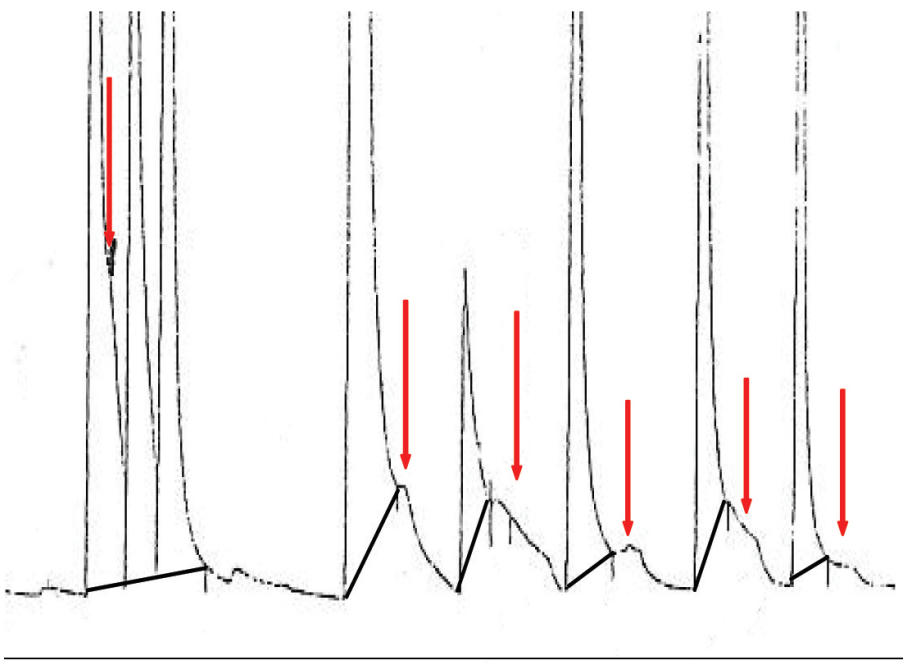
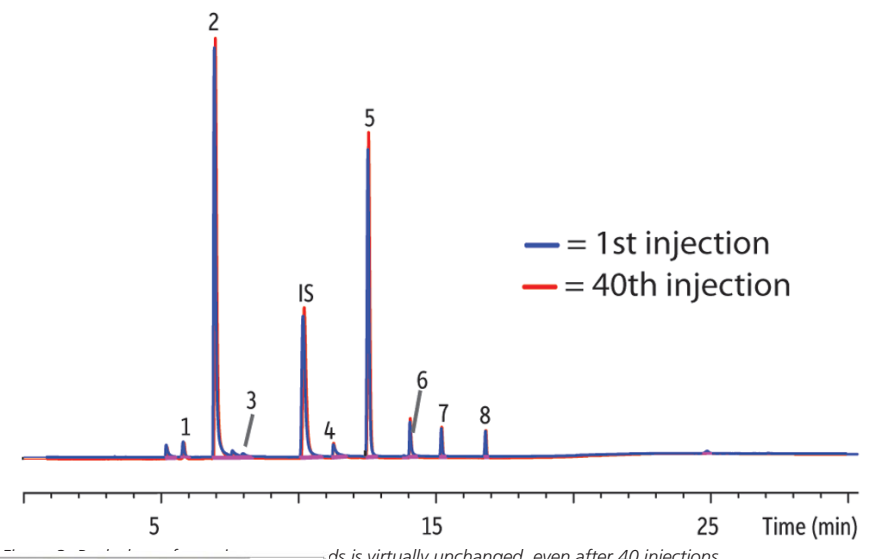


Figure 1: Short-chain volatile amines often exhibit broad, tailing peaks when analysed in water on typical volatile a



ds is virtually unchanged, even after 40 injections.

2 mm ID (cat.# 18078); Sample: short-chain amines in water; Injection: C (hold 10 min) to 250 °C at 20 °C/min (hold 10 min); Carrier gas: : FID @ 250 °C. Peaks: 1. Methanol, 2. Dimethylamine, 3. Dimethylethylamine, 6. Diethylamine, 7. Methyldiethylamine, 8. : Baele, Taminco (Antwerp, Belgium).

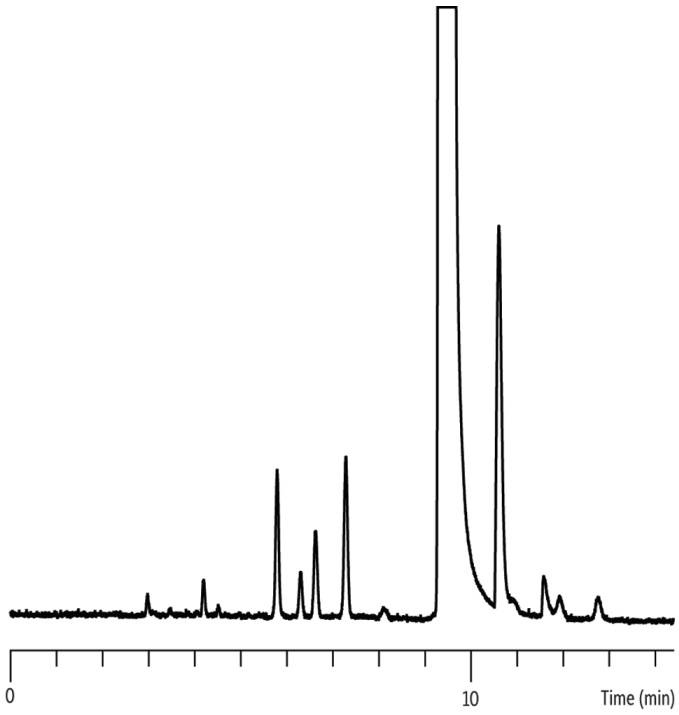


Figure 4: Impurities in pyridine.

Columns: Rtx®-Volatile Amine, 60 m x 0.32 mm ID (cat.# 18078); Sample: pyridine; Injection: 1 µL (split ratio 15:1), 250 °C; Oven: 120 °C, Carrier gas: hydrogen, 2 mL/min; Detector: FID @ 250 °C.

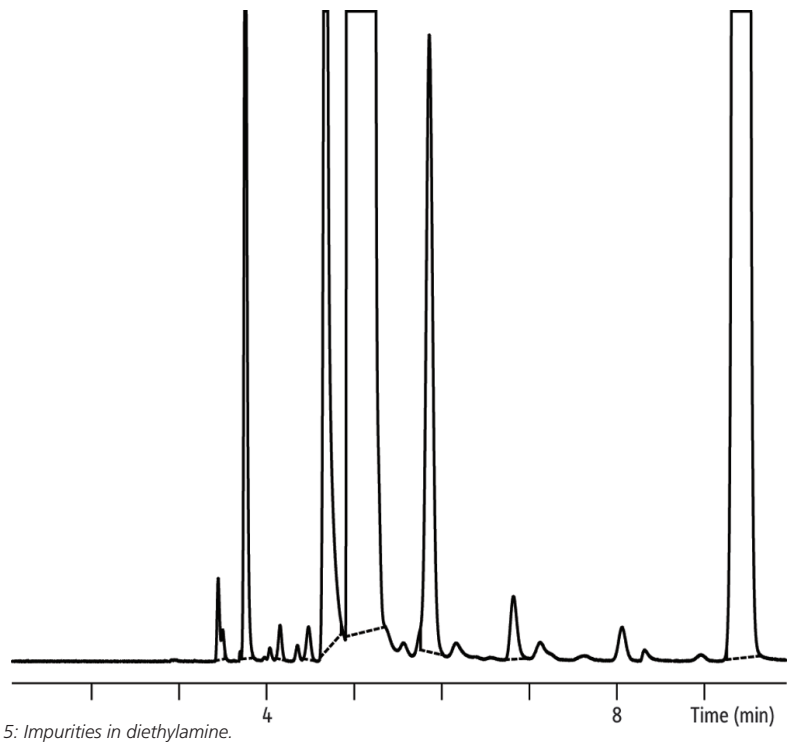


Figure 5: Impurities in diethylamine.

See Figure 4 for conditions.

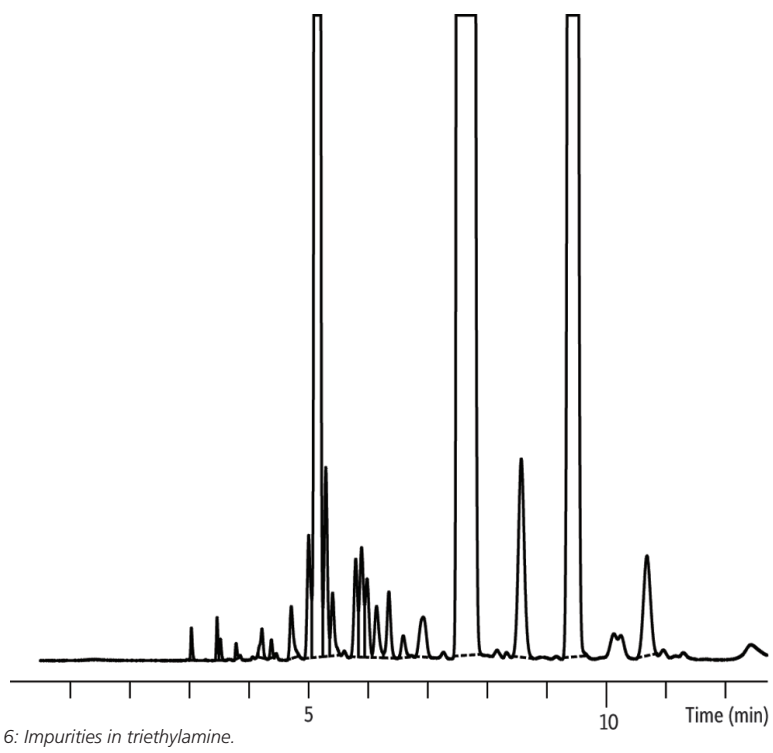


Figure 6: Impurities in triethylamine.

See Figure 4 for conditions.

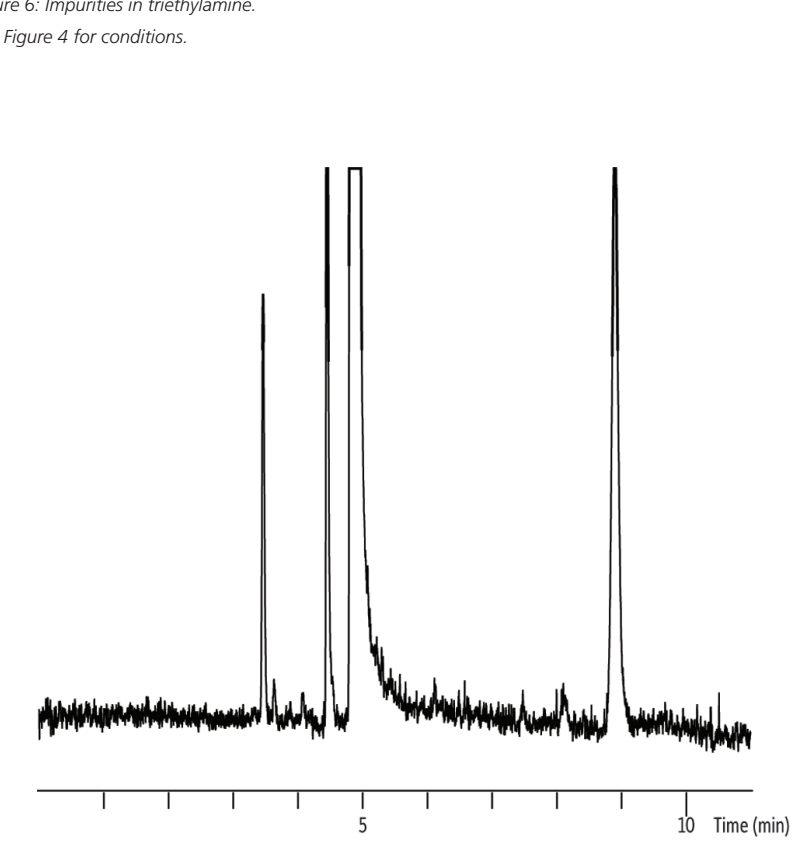


Figure 7: Impurities in isopropylamine.

See Figure 4 for conditions.

Practical Solutions for Analysing Volatile Amines

The strong dipole in the basic amino group is what causes the interactions with the surface silanols that result in nonlinear adsorption effects. In practice, derivatisation can be used to reduce these interactions, but it is time-consuming and can produce secondary matrix effects that alter recoveries. Derivatisation can be avoided by using an Rtx®-Volatile Amine GC column as the robust column chemistry minimises reactivity and elutes the amine compounds in sharp peaks, even in the presence of water. Priming is another technique that is often used in amine analysis. In this approach, several initial injections of a high boiling point amine are performed so that the priming amine compound reacts with any active sites and provides a systemic, but short-lived, deactivation. While, using a properly deactivated analytical column provides a better long-term solution, priming can be useful in that the priming compound can, at least temporarily, deactivate non-column parts of the sample pathway, including the injection and detection port liners.

In addition to its inertness and tolerance of aqueous matrices, the Rtx®-Volatile Amine column also offers high loadability. As shown in Figures 4-7, this column provides excellent chromatographic separations of impurities in pyridine, diethylamine, triethylamine, and isopropylamine. In addition, when analysing ammonia and water, both compounds elute as nearly symmetrical peaks (Figure 8).

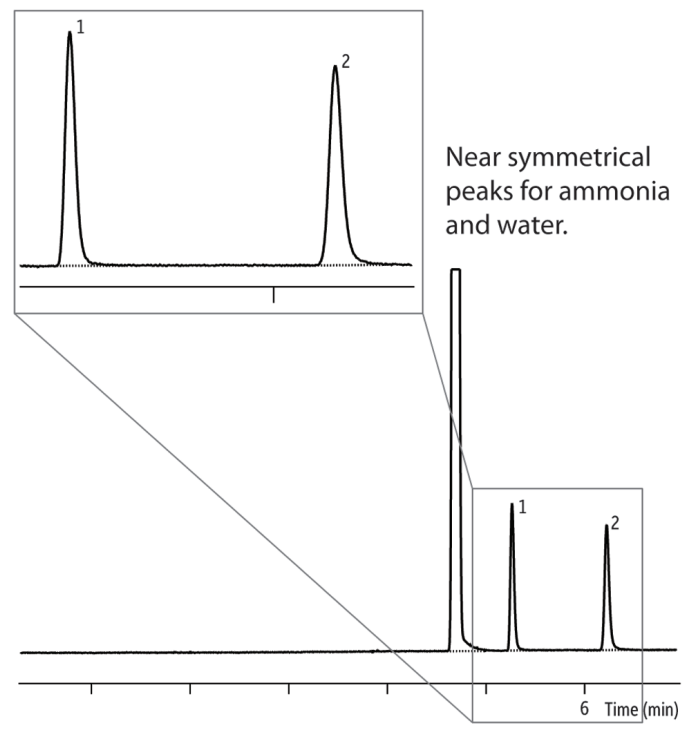


Figure 8: Ammonia and water analysed on an Rtx®-Volatile Amine column.

mm ID (cat.# 18078); Injection: split (10:1); Oven: 45 °C; Carrier gas: Peaks: 1. Ammonia, 2. Water.

Summary

A new stationary phase for short-chain amine applications has been developed using nonpolar stabilised polysiloxane. Rtx®-Volatile Amine columns are extremely inert, assuring accuracy and sensitivity when analysing volatile amines, including free ammonia. In addition, the highly robust phase withstands repeated water injections, resulting in improved column lifetime.

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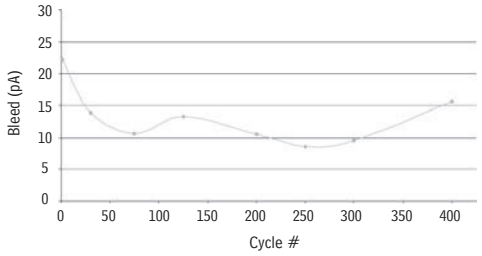
These excellent performance characteristics make MXT®-1HT Sim Dist columns the columns of choice for ASTM D-6352-98 Sim Dist analyses. Note that the demanding temperature conditions of simulated distillation analyses make GC system integrity a prime concern. It is imperative that the GC system be oxygen-free, to prevent phase degradation and maintain the highest level of chromatographic performance. We strongly recommend using oxygen-free carrier gas and routinely leak-testing your system with an electronic leak detection device, such as our Electronic Leak Detector (cat.# 22451), to ensure protection from oxygen.

Figure 4 An MXT®-1HT column produces less than 20pA bleed over a series of 400 injections.



MXT®-1HT Sim Dist Column

(Siltek® treated stainless steel)

- Stable to 430ºC.
- Low bleed.
- Long lifetime at high temperatures.
- Symmetrical hydrocarbon peaks.
- Consistent resolution and retention times.
- Boiling point elution of hydrocarbons.
- Polarity equivalent to existing liquid phases.

ID	df (µm)	temp. limits	length	cat. #
0.53mm	0.10	-60 to 430°C	5-Meter	70100

Polywax® Standards

These high molecular weight hydrocarbon waxes are useful for simulated distillation and other high-temperature GC work.

Compound	qty.	cat.# (ea.)
Polywax® 500	1g	36224
Polywax® 655	1g	36225
Polywax® 850	1g	36226
Polywax® 1000	1g	36227

No data pack available.

Restek Electronic Leak Detector

Small, compact unit—easy to hold and operate.

- Reliable thermal conductivity leak detector.
- Responds to leaks in less than 2 seconds.
- Audible alarm plus LED readout.
- Auto zeros with the touch of a button.
- Built-in rechargeable 9 volt battery.

Leak Detector Facts	
Detectable gases:	helium, nitrogen, argon, carbon dioxide
Battery:	Rechargeable Ni-MH, 9 volt
Operating Temperature Range:	32°-120°F (0°-48°C)
Humidity Range:	0-97%
CE Approved:	Yes

Description	qty.	cat.#
Leak Detector with 110Volt Battery Charger	ea.	22451
Leak Detector with 220Volt European Battery Charger	ea.	22451-EUR
Leak Detector with 220Volt UK Battery Charger	ea.	22451-UK

Caution: The Restek Electronic Leak Detector is NOT designed for determining leaks of combustible gases. A combustible gas detector should be used for determining combustible gas leaks under any condition. The Restek Electronic Leak Detector may be used for determining trace amounts of hydrogen in a GC environment only.

*Siltek® treatment is a proprietary surface treatment for passivating steel, high nickel alloys of steel, glass, and other surfaces. U.S. Patent 6,444,326.

Lit. Cat.# 59479A

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