Petrochemical Applications

Virtually Particle-Free Rt®-Silica BOND Columns

Provide Reliable PLOT Column Performance With Less Time Lost for Maintenance

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- 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 forwater-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.

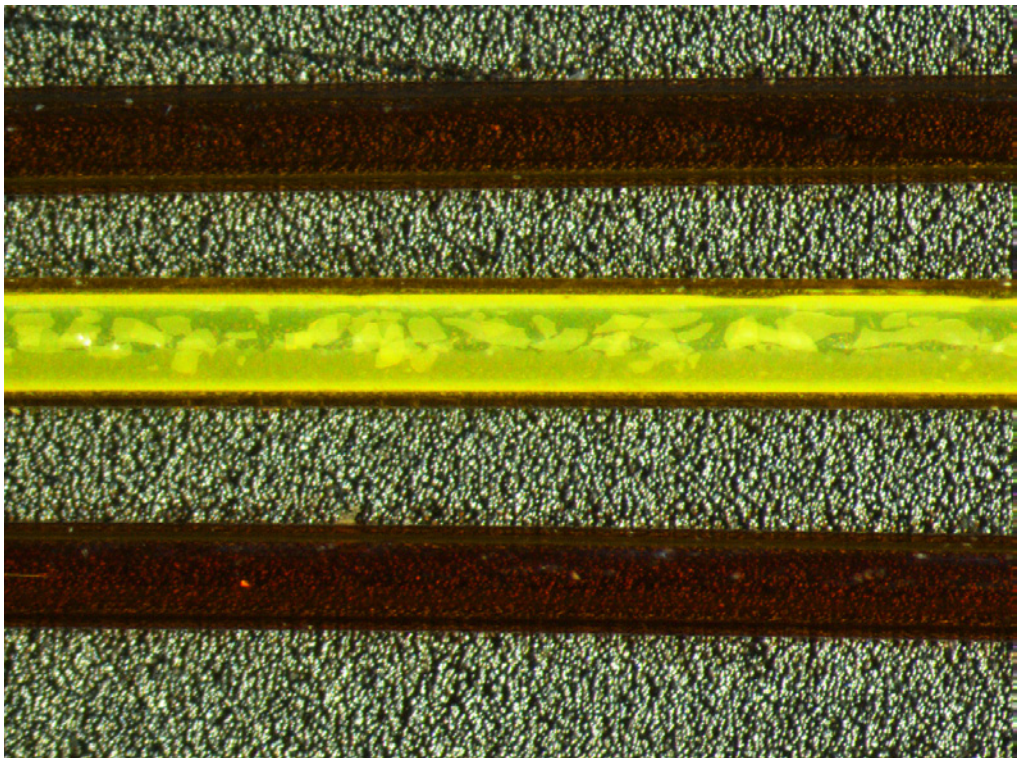
Porous layer open tubular (PLOT) columns are very useful to GC analysts working on a wide variety of applications, and the unique selectivity of PLOT columns makes them particularly good for separating gaseous compounds without cryogenic cooling. However, the overall utility of traditional PLOT columns 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.

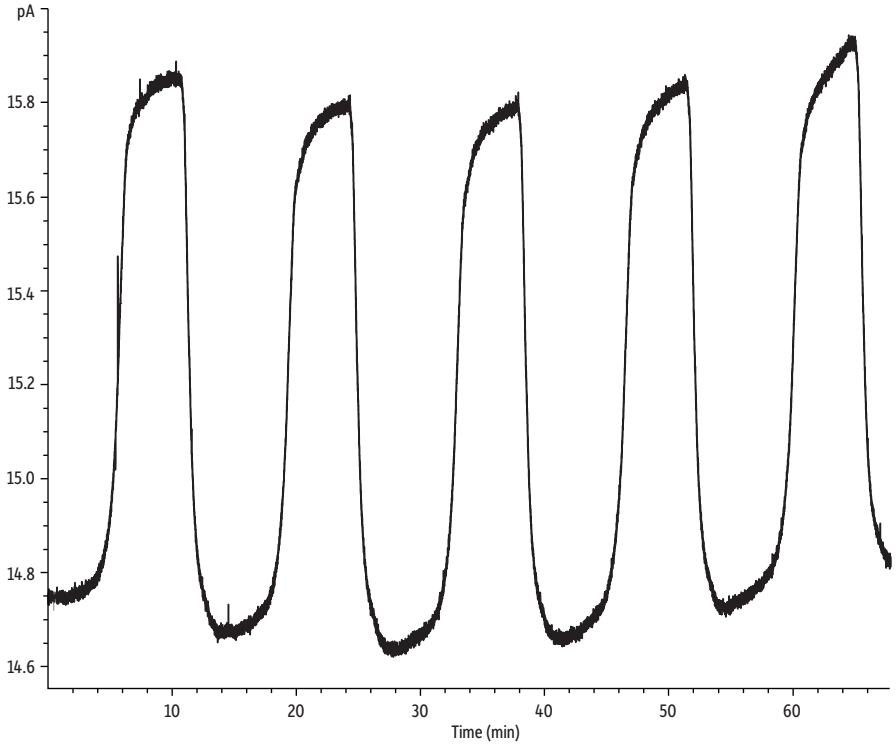
Figure 1 shows a magnified picture of three fused silica columns. The middle column is a traditionally-manufactured PLOT column, the bottom column is a wall-coated open tubular column, and the top column is an Rt®-Silica BOND PLOT column. Note the uneven layer of particles on the middle column, as well 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.

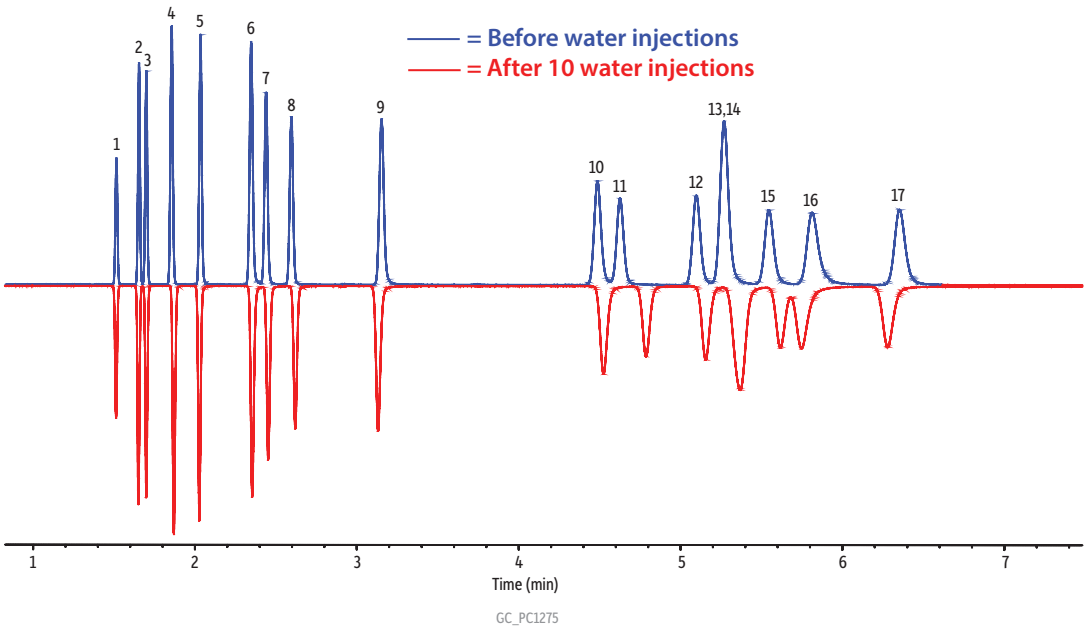


Column	Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785)
Injection	split (split ratio 35:1)
Liner:	Sky® 2.0 mm ID straight inlet liner (cat.# 23313.1)
Inj. Temp.:	250 °C
Oven	
Oven Temp.:	50 °C to 250 °C at 35 °C/min (hold 5 min) to 50 °C at 70 °C/min
Carrier Gas	He, constant flow
Linear Velocity:	114 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.

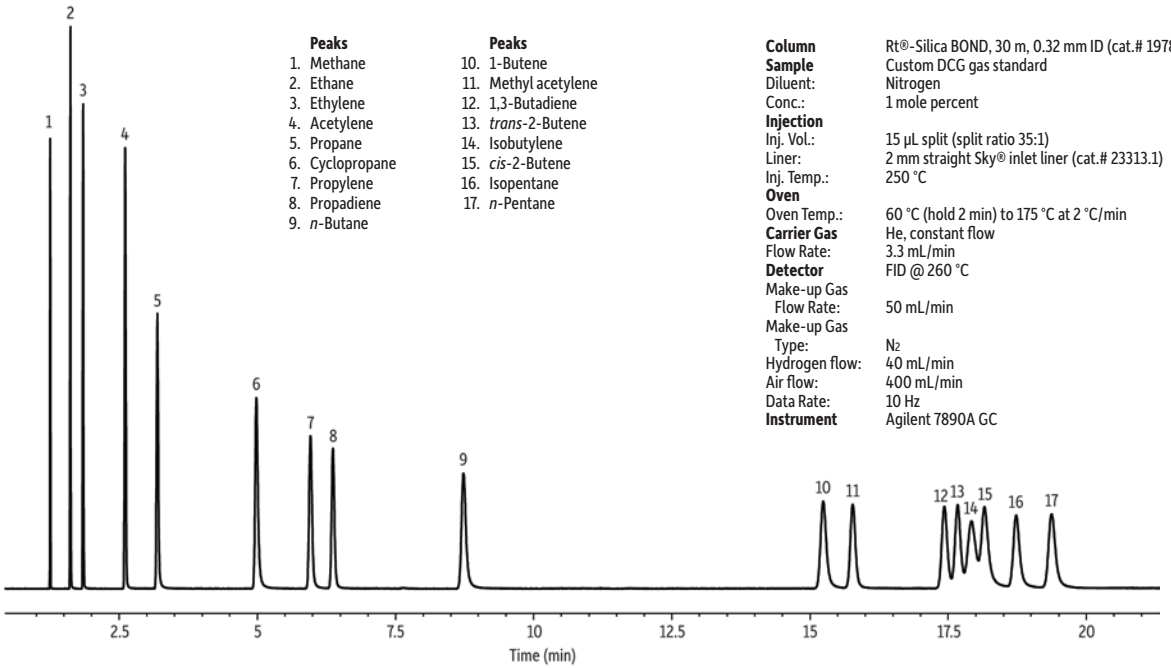


Figure 5: Sulfur Compounds in Propane

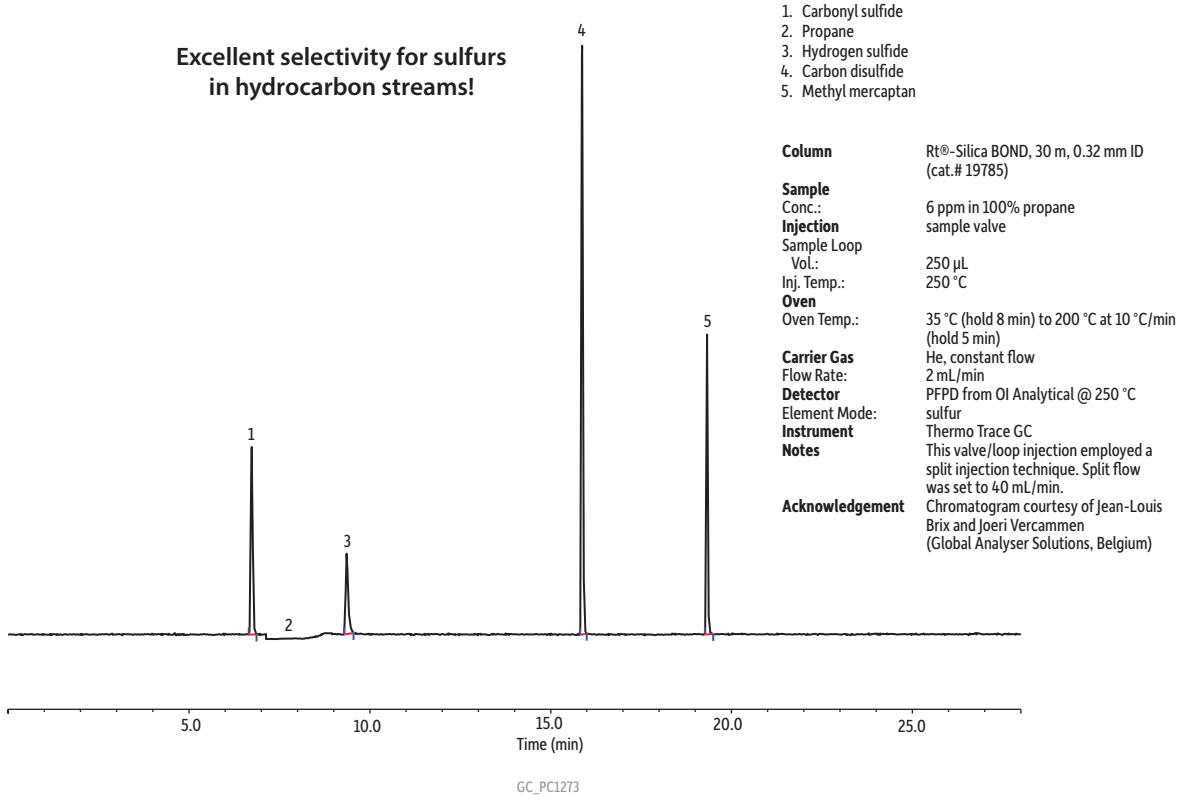
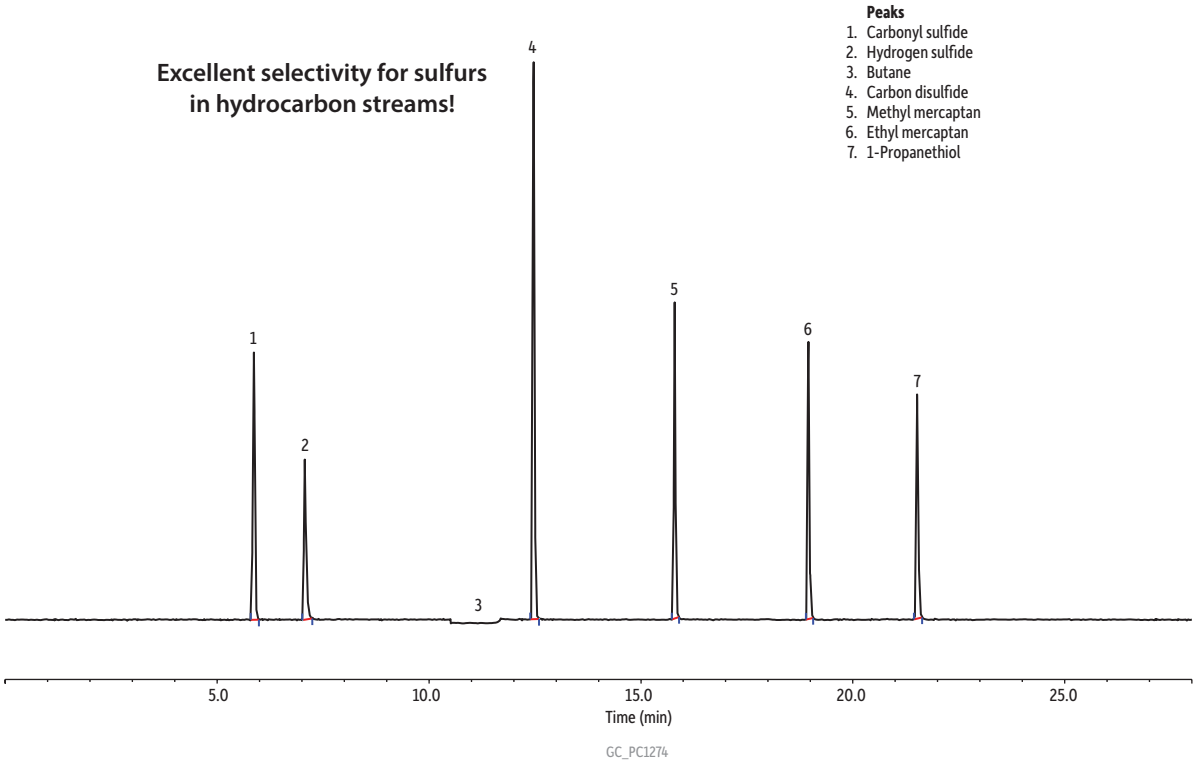


Figure 6: Sulfur Compounds in Butane

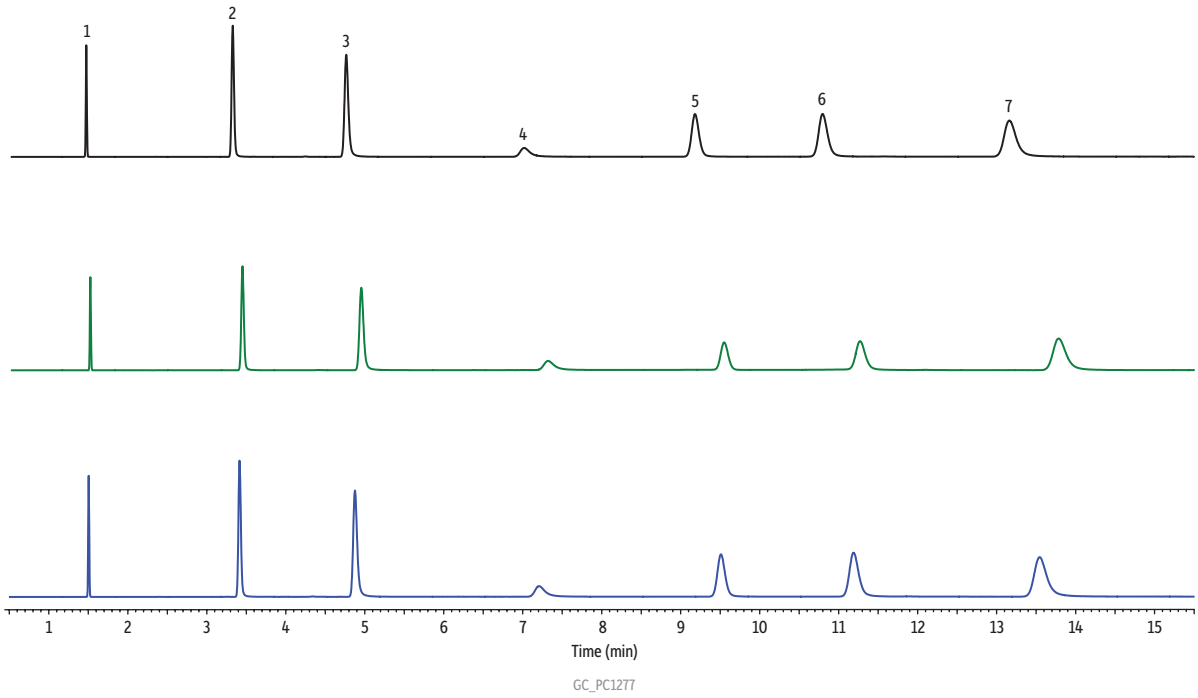


Column	Rt®-Silica BOND, 30 m, 0.32 mm ID (cat.# 19785)	**Carrier Gas**	He, constant flow
Sample		Flow Rate:	2 mL/min
Conc.:	6 ppm in 100% butane	**Detector**	PFPD from OI Analytical @ 250 °C
Injection	sample valve	Element Mode:	sulfur
Sample Loop Vol.:	250 µL	**Instrument**	Thermo Trace GC
Inj. Temp.:	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.

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