Optimise Ethylene and Propylene Testing with Stable Flow Rt®-Alumina BOND PLOT Columns

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The petrochemical industry depends on alumina PLOT columns for purity testing of ethylene and propylene, products that represent billions of dollars to the industry annually. The value of alumina is that it is one of the most selective adsorbents for light hydrocarbons available, allowing all the unsaturated C1-C5 isomers to be separated with the highest degree of resolution. Selectivity is influenced by deactivation and different deactivation salts are used to optimize separations for polar and nonpolar compounds. Although alumina PLOT columns are not new to the petro market, flow retention reproducibility has always been difficult to achieve and most commercially available columns show large variation in flow and retention, as well as poor loadability. This can cause significant problems with integration, calibration, and, ultimately, quantification. New PLOT column technology from Restek increases flow reproducibility, which results in highly predictable column-to-column retention times. By using new Rt®-Alumina BOND PLOT columns, accurate purity values can be obtained quickly and reliably, allowing better process stream management.

Precision Coating Ensures Consistent Flow and Predictable Retention Times

With traditional PLOT column technology, it is difficult to control stationary phase particle deposition, resulting in variable coating thicknesses along the length of the column. The positions in which the layer is thicker act as a flow restriction for the whole column (Figure 1). Since the number and intensity of these flow restrictions will vary column-to-column, highly variable flow rates are observed. In contrast, the process used to produce Rt®-Alumina BOND PLOT columns results in extremely consistent coatings, which, in turn, provide uniform flow characteristics and predictable retentions times. The data in Table I clearly demonstrate that both phase thickness, as measured by capacity factor (K), and coating efficiency (plates-per-meter) are extremely reproducible.

To demonstrate the effect of coating uniformity on column flow behavior, flow resistance (F) can be calculated using the retention time of an unretained compound (Equation 1). When F values are calculated for a set of columns of the same phase and configuration, tested under the same conditions, variation in flow, as indicated by F, can be used to assess column coating uniformity. As shown in Figure 2, Rt®-Alumina columns have extremely consistent flow characteristics, which ensures that highly predicable retention times are achieved.

(Equation 1)

$$F = \frac{\text{retention time of unretained compound in uncoated tubing}}{\text{retention time of unretained compound in coated column}}$$

Reliable Impurities Analyses Result from Optimised Deactivations

The highly predictable retention times that result from uniformly coated Rt®-Alumina BOND columns can benefit petro labs by reducing the amount of time spent on review and manual integration. Manual processes can also be reduced by the highly selective deactivations, which provide sharp, fully-resolved peaks that can be accurately quantified. The analysis of impurities in propylene and ethylene are an excellent demonstration of column selectivity and how it differs based on the type of deactivation. Restek columns are available with Na_2SO_4 or KCl deactivations, and both have been optimised to provide complete separation of hydrocarbon impurities.

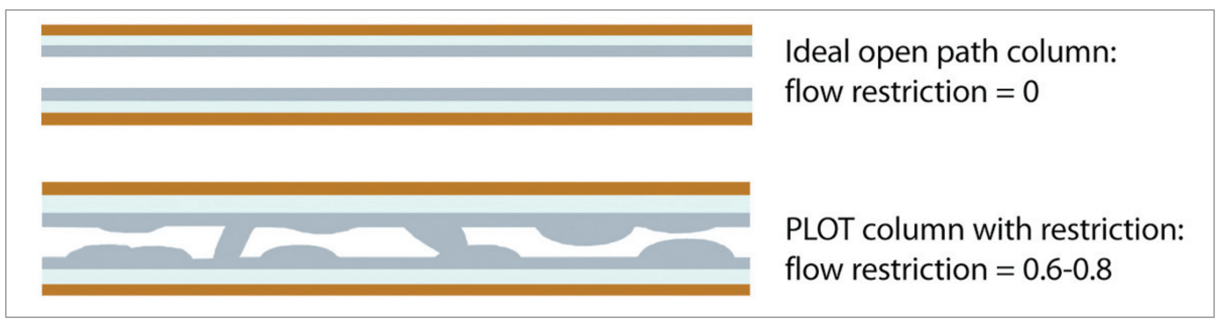

Figure 1: Inconsistent coating thicknesses result in restrictions that cause significant variation in flow.

	Partition Ratio, K (Mean±Std. Dev.)	Efficiency, Plates-per-meter (Mean±Std. Dev.)
Rt®-Alumina BOND (Na_2SO_4) n = 85	2.557 (0.332)	1,542 (59.6)
Rt®-Alumina BOND (KCl) n = 40	4.600 (0.441)	1,206 (113)
Results shown for 1,3-butadiene; Column dimensions: 50 m x 0.53 mm x 10 µm; Sample: refinery gas test mix, 1.0% in nitrogen; Inj.: 5-10 µL test mix; Split flow: 80 mL/min.; Tested isothermally at 130 °C (Na_2SO_4) or 100 °C (KCl); Detector: FID.		

Table I: Tight manufacturing controls result in highly consistent column coatings.

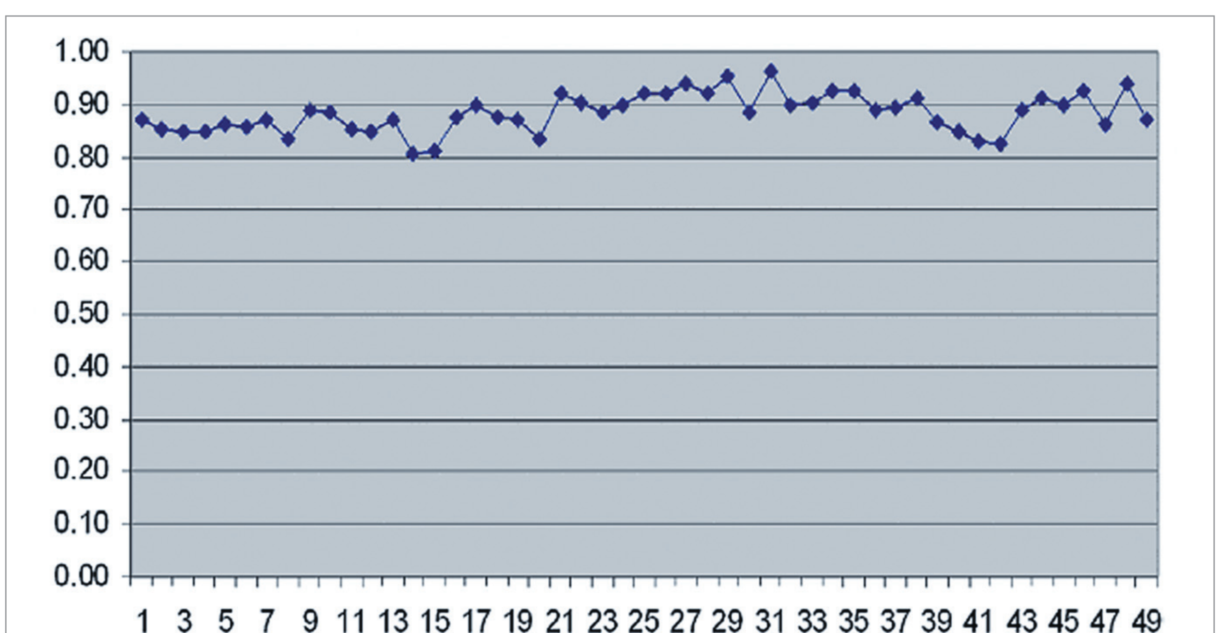

Figure 2: Highly consistent column-to-column flow characteristics (F) of Rt®-Alumina BOND PLOT columns result in predictable retention times and less manual integration.

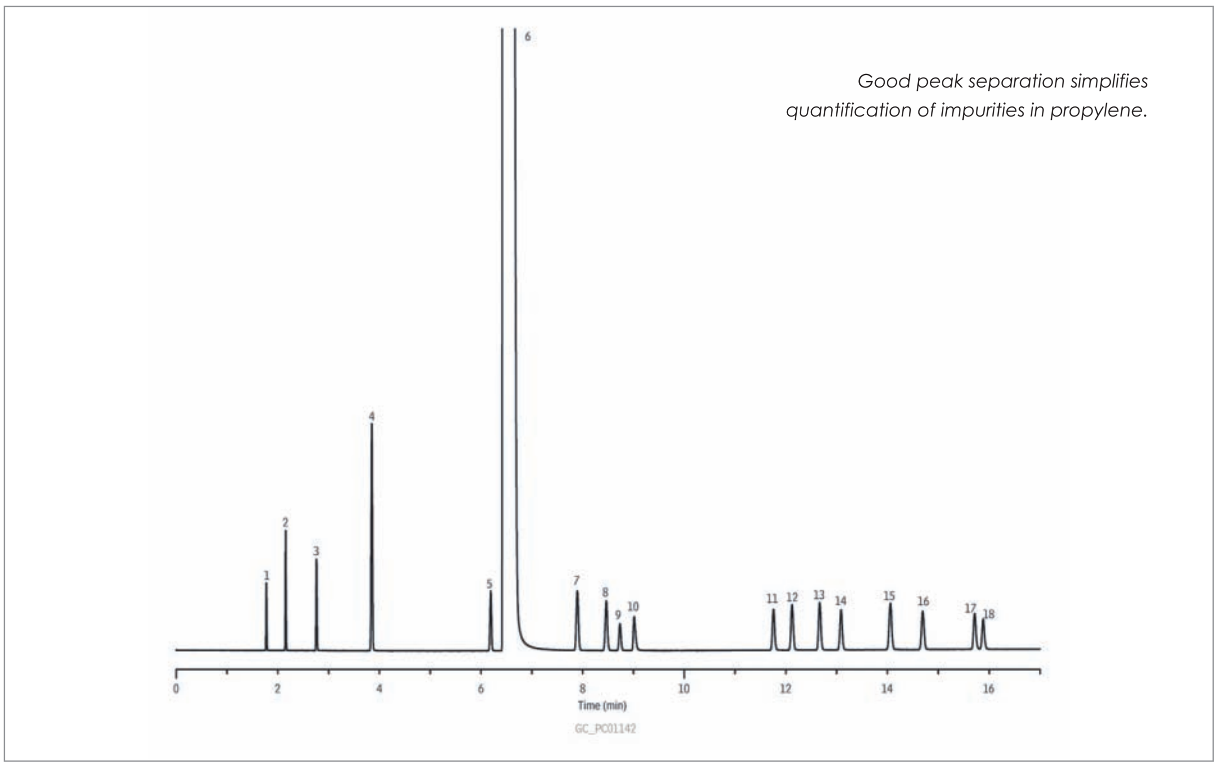

Figure 3: Rt®-Alumina BOND/Na_2SO_4 columns exhibit high loadability and ensure reliable separation of impurities in propylene.

Column: Rt®-Alumina BOND/Na_2SO_4 (50 m x 0.53 mm x 10.0 µm); Sample: propylene and C1-C5 hydrocarbons; Inj.: 10 µm split, 35 mL/min. split vent flow rate; Inj. temp.: 200 °C; Carrier gas: He, 68.9 kPa; Linear velocity: 47 cm/sec. @ 50 °C; Oven: 50 °C to 150 °C at 6 °C/min.; Det.: FID @ 200 °C; Peaks: 1) methane, 2) ethane, 3) ethylene, 4) propane, 5) cyclopropane, 6) propylene, 7) isobutane, 8) n-butane, 9) propadiene, 10) acetylene, 11) trans-2-butene, 12) 1-butene, 13) isobutylene, 14) cis-2-butene, 15) isopentane, 16) n-pentane, 17) 1,3-butadiene, 18) methyl acetylene.

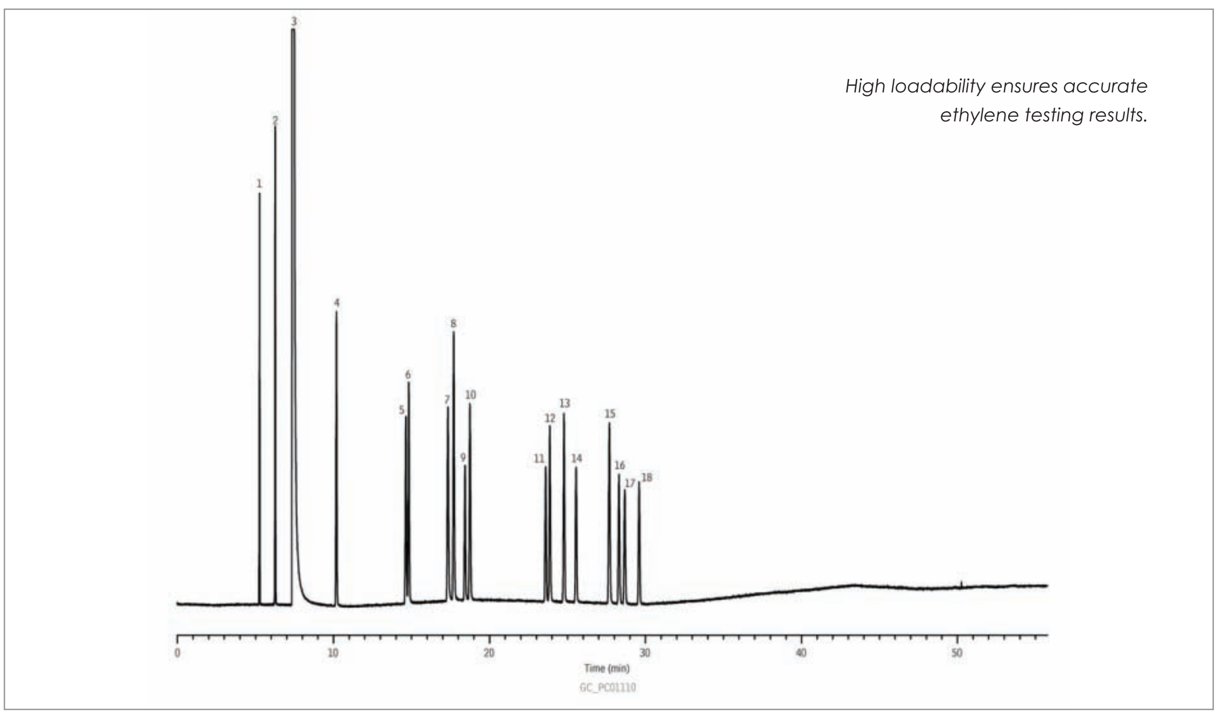

Figure 4: Excellent peak symmetry for ethylene and related impurities is obtained on Rt®-Alumina BOND/KCl columns, resulting in stable retention times and high loadability.

Column: Rt(r)-Alumina BOND/KCl (50 m x 0.53 mm x 10.0 µm) in series with Rtx(r)-1 (30 m x 0.53 mm x 5.0 µm); Sample: ethylene and C1-C5 hydrocarbons; Inj.: 1 µm split, 60 mL/min. split vent flow rate; Inj. temp.: 200 °C; Carrier gas: He, 55.2 kPa; Linear velocity: 25.4 cm/sec. @ 35 °C; Oven: 35 °C (hold 2 min.) to 190 °C at 4 °C/min. (hold 15 min.); Det.: FID @ 200 °C; Peaks: 1) methane, 2) ethane, 3) ethylene, 4) propane, 5) cyclopropane, 6) propylene, 7) acetylene, 8) isobutane, 9) propadiene, 10) n-butane, 11) trans-2-butene, 12) 1-butene, 13) isobutylene, 14) cis-2-butene,15) isopentane, 16) methyl acetylene, 17) n-pentane, 18) 1,3-butadiene.

The analysis of impurities in propylene on an Rt®-Alumina BOND (Na_2SO_4) column is shown in Figure 3. Sharp, symmetric peaks are obtained for all compounds, allowing challenging separations, such as trace levels of cyclopropane from propylene, to be achieved. These columns have high loadability, as demonstrated by the minimal tailing of the propylene peak. Good separation of propadiene and acetylene from n-butane is also observed and can be further increased by lowering elution temperatures. Excellent peak shape is also obtained when using an Rt®-Alumina BOND (KCl) column for the analysis of impurities in ethylene, as shown in Figure 4. Here, the column is coupled to an Rtx®-1 column, as prescribed in ASTM Method D6159, to ensure complete resolution of all compounds. Once again, excellent peak symmetry is obtained, illustrating the high loadability of the column and predictability of retention times. The excellent peak shape and separation seen in both applications illustrates the quality of the deactivations; since column reactivity is minimised, responses for polar unsaturates, such as dienes, are optimised.

Conclusion

Poor reproducibility for flow and retention is a widely-recognised problem with alumina PLOT columns, as inconsistent flow characteristics cause retention times to vary significantly between columns. Restek's new PLOT column manufacturing process provides tight control of the column coating process and, as a result, highly reproducible column flows are achieved. Ultimately, the superior technology used to produce Rt®-Alumina BOND PLOT columns offers petrochemical labs the opportunity to obtain more reliable results in less time for major products such as ethylene and propylene.

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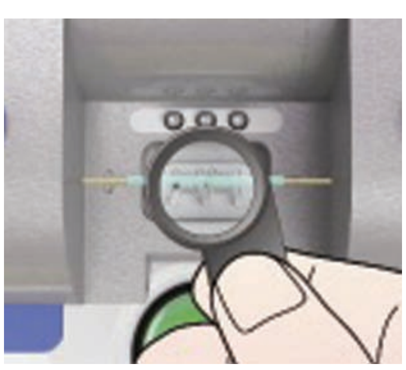

Since the launch of the Meltfit One in January 2008, **Nlisis Chromatography** (The Netherlands) has collected valuable feedback from users throughout the world. Based on these data, Nlisis has announced a new release of the award-winning connection device for capillary columns in GC. The new Meltfit One has an improved performance and usability. Among other things, the new release of the Meltfit One has a battery on board which enables users to make up to 40 connections without having to recharge. In addition, the Meltfit One has become completely portable, since an integral air source has been incorporated in the device, negating the need to have an external air supply nearby. Finally, an new version of the software has been developed, offering more useful functions. Having made these changes NLISIS can fully guarantee that connections made with the proprietary Meltfit glass tubes are always leak tight.

The petrochemical industry is an important market for Nlisis. Shell and ExxonMobil were among the first companies to take advantage of this innovative connection technology. Marketing manager Paul Heere comments: "In the petrochemical industry in particular time equals money. Time spent preparing samples and carrying out sample analysis is wasted if a bad column connection ruins the results. This is particularly true when you take into consideration the wide use of GC/MS and GC x GC in this industry. The Meltfit One removes the worry associated with leaking connections and therefore saves valuable time and money as well as improving the chromatography."

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