New PLOT Column Technology Stabilises Flow and Improves Analysis of Light Hydrocarbons, Solvents and Permanent Gases

Jaap de Zeeuw, Restek Corporation, Weerhaan 9, Middelburg, The Netherlands
Bill Bromps, Tom Vezza, Rick Morehead, Jan Pijpelink, and Gary Stidsen, Restek Corporation, 110 Benner Circle, Bellefonte, PA, USA.

PLOT columns are widely used in petroleum and other industries because their retention and selectivity characteristics allow gases and volatiles to be separated with high resolution at above ambient temperatures. However, the utility of PLOT columns, particularly of the porous polymer columns, is significantly limited by the mechanical instability of the particle layers. One of the biggest challenges with conventional PLOT columns is that vibrations or any change in gas velocity, pressure, or surface stress can result in a release of particles - or even complete segments - from the adsorption layer. This creates restrictions in the column, which result in highly variable flow behaviours over time and between columns. In practice, conventional PLOT columns of the same dimensions can differ in flow by a factor of 4-6, when operated at the same nominal pressure. This makes them extremely difficult to use reliably in applications where consistent flow and predictable retention times are important, such as when flow or valve switching is utilised.

In addition to creating unpredictable flow behaviour and retention times, particles released from unstable layers can clog valves or cause spiking in the baseline. One way to prevent this is to use particle traps; however, it is much more advantageous to use stabilised PLOT columns that minimise particle generation, as this better protects equipment and extends the lifetime of the column. Restek has developed a bonding process that sets a new standard in PLOT column stabilisation. This innovative process reduces particle release and column blockage, resulting in highly stable flows and retention times, both run-to-run and column-to-column. By replacing conventional PLOT columns with PLOT columns manufactured using this new technology, labs can increase the accuracy of impurities analysis and make better process decisions.

New Technology Results in Consistent Flow and Predictable Retention Times

Restek's new PLOT columns are stabilised through a proprietary process that is based on concentric adsorption layers and improved particle bonding. The resulting columns are far more stable than conventional PLOT columns, as measured by the reproducibility of flow behaviour (permeability). To assess variation in permeability, Restek has intro-

duced a new parameter: flow restriction factor (F), which is the retention time ratio of an unretained compound in uncoated tubing versus in a coated column. As shown in Figure 1, flow resistance varies considerably across a series of conventional Q-type PLOT columns because of differences in column blockage caused by unstable particle layers. In contrast, Restek Rt®-Q-BOND columns are remarkably consistent in flow behaviour column-to-column, indicating a higher degree of mechanical stability. Improved performance is also observed run-to-run; retention times on the Rt®-Q-BOND column remain virtually unchanged even after a series of 500 pressure cycles (Figure 2). This stability is particularly valuable for flow and valve switching applications and allows these procedures to be run with greater confidence. Currently, this innovative stabilisation technology has been applied to porous polymer (4 selectivities), alumina (KCl and Na_2SO_4 deactivations), and molecular sieve PLOT columns, and provides benefits across a wide range of applications.

Porous Polymers

Porous polymers historically are very interesting materials due to their ability to elute both polar and nonpolar compounds. They are highly inert and have been used successfully with a wide variety of challenging sample matrices. Of the various porous polymer chemistries, pure divinylbenzene is the most nonpolar and is used in Rt®-Q-BOND column. The retention characteristics of this column are comparable to packed porous polymer materials like Porapak Q, but some improvements will be observed due to differences in the phase ratio. Using the new stabilising process, Rt®-Q-BOND columns are built with thicker layers, which reduces the phase ratio, resulting in higher retention and improved separation. An example of this using carbon dioxide is shown in Figure 3. Carbon dioxide elutes very quickly on typical Q-type PLOT columns. In contrast, the Rt®-Q-BOND column has nearly twice the retention of the conventional column, providing much better separation and allowing more time for switching to occur between the methane and carbon dioxide peaks. The thicker, more stable porous layer in Rt®-Q-BOND columns also results in higher capacity, meaning that there is more flexibility with loadability.

Figure 3: Higher retention on the new Rt®-Q-BOND column improves the separation of carbon dioxide, which is difficult to retain and detect on conventional Q-type PLOT columns.

Rt®-Q-BOND columns also perform exceptionally well for solvent analysis because of increased retention, inertness, and loadability. As shown in Figure 4, a wide range of solvents can be analysed accurately at high temperatures. Peak shape for all solvent classes is excellent, even for ethanol and acetonitrile. Better peak shape simplifies integration and leads to more accurate quantification. Similar benefits are seen for other PLOT column selectivities. Chromatography for applications on Rt®-Q-BOND, Rt®-QS-BOND, Rt®-S-BOND, and Rt®-U-BOND columns are available at www.restek.com/petro.

Flow restriction factor (F) = (tR in uncoated tubing)/ (tR in coated column), where tR = retention time of an unretained compound
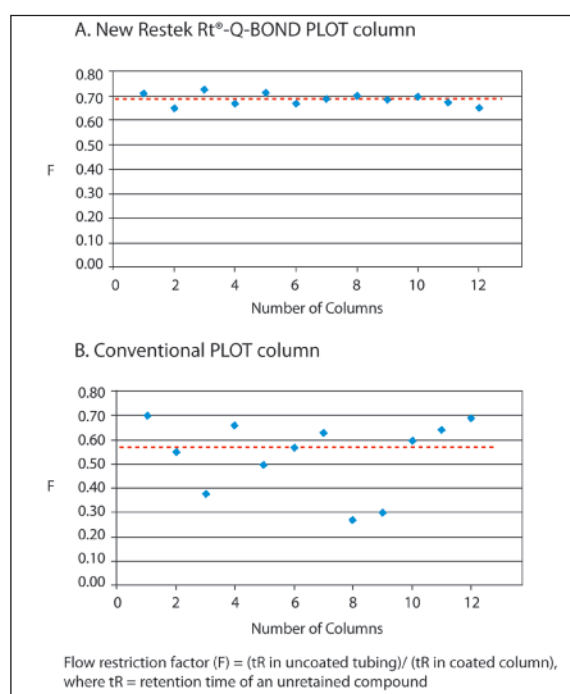
Figure 1: New, stabilised PLOT columns from Restek reduce particle generation and provide more consistent column-to-column flow than typical PLOT columns.
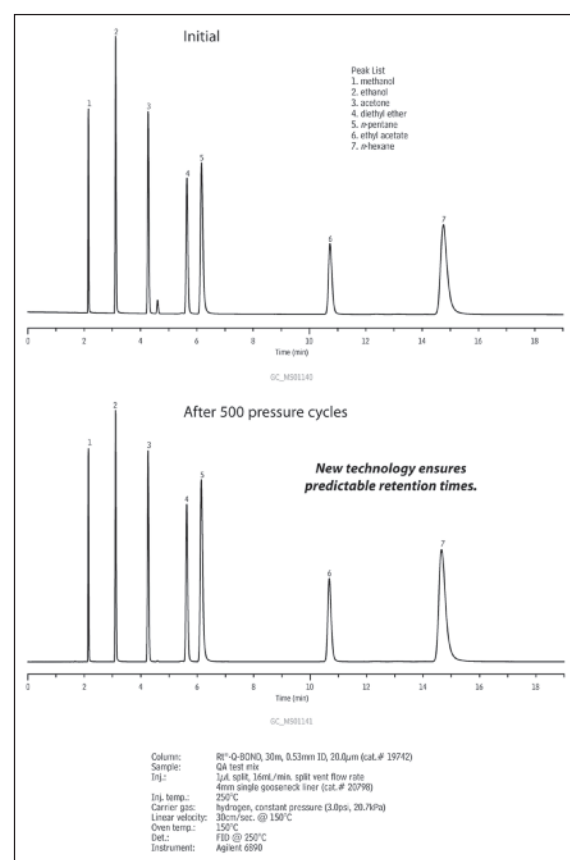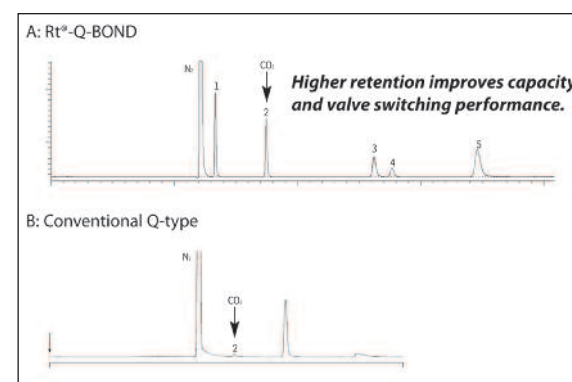

Figure 2: New PLOT column technology assures stable retention times run-to-run, even after 500 pressure cycles (Rt®-Q-BOND PLOT column).
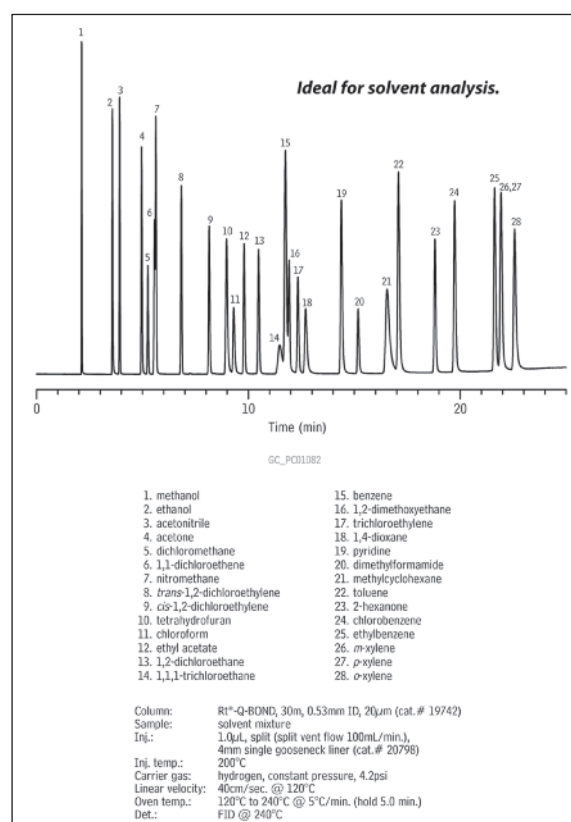
Figure 4: New Rt®-Q-BOND columns are highly inert, providing exellent peak symmetry and predictable retention times, which result in improved quantification for a wide range of solvent classes.

Alumina Columns

Alumina is one of the most selective adsorbents for light hydrocarbons, allowing all C1-C5 isomers to be separated with the highest degree of resolution. Selectivity can be changed using different deactivation salts; columns deactivated with Na_2SO_4 exhibit a relatively polar surface, whereas those produced using KCl deactivation have a relatively nonpolar surface. The polar hydrocarbons acetylene, methyl acetylene, and propadiene are strongly influenced by surface polarity and can be challenging to analyse. Although selectivity can be controlled, most commercially available alumina columns show large variation in retention and poor loadability, which cause significant problems with integration and calibration.

Columns produced by Restek using the new bonding process are highly stable and reproducible. Both deactivations are available and produce excellent peak shape and good separation of impurities in common applications, such as propylene and ethylene analysis. Figure 5 illustrates the analysis of impurities in propylene on an Rt®-Alumina BOND (Na_2SO_4) column. 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 (slower temperature programming, longer hold time at starting temperature, etc.). Performance of the KCl deactivation column is illustrated by the analysis of impurities in ethylene according to D6159 (Figure 6). As prescribed in the method, an Rt®-Alumina BOND (KCl) column is coupled to an Rtx®-1 column 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.
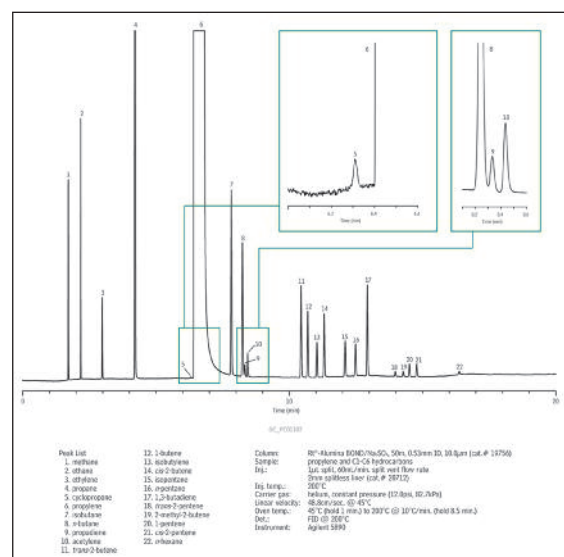

Figure 5: Rt®-Alumina BOND (Na_2SO_4) columns exhibit high loadability, allowing reliable separation of difficult impurities in propylene.

Molecular Sieves

Molecular sieve columns show high retention for permanent gases, but do not always give good peak shape. Carbon monoxide, for example, elutes as a strongly tailing peak on most commercially available molecular sieve columns. In contrast, carbon monoxide elutes as a sharp, symmetric peak on an Rt®-Msieve 5A PLOT column, simplifying integration and improving accuracy (Figure 7). Using an Rt®-Msieve 5A column, accurate measurement of carbon monoxide below part-per-million levels is possible. Rt®-Msieve 5A columns also produce outstanding results for other permanent gases. Argon and oxygen are baseline resolved and can be accurately measured in ratios of 1:100. Like other stabilised Restek PLOT columns, Rt®-Msieve 5A columns have very reproducible flow behaviour, meaning that the retention times for different columns at a constant inlet pressure will be comparable. In practice, this means that Rt®-Msieve 5A columns can be used reliably with valve switching systems.
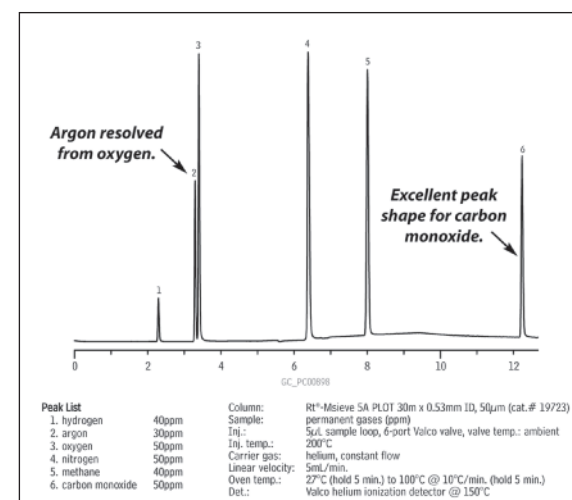

Figure 6: Excellent peak symmetry for ethylene and related impurities is obtained on Rt®-Alumina BOND (KCl) columns, resulting in stable retention times and high loadability.

Figure 7: Sharp, symmetric peaks ensure reliable separation of permanent gases on new Rt®-Msieve 5A columns.

Conclusion

Restek's new series of stabilised PLOT columns sets a new standard in PLOT column technology. These new columns offer significantly reduced particle generation which protects instruments, allows better control of flow switching, and helps petrochemical labs produce more accurate and reliable data. This robust new technology is currently applied to porous polymer, alumina, and molecular sieve PLOT columns and soon will be adapted for use with other adsorbents.