

Advances Porous Layer Tubular Columns: Stabilization of particle layers makes PLOT columns more robust and reproducible in retention and flow behavior

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The application of Porous Layer Open Tubular columns (PLOT) has been very beneficial for solving application problems especially for the analysis of volatile compounds. Due to the high selectivity, analysis time can be optimized which is important for laboratory efficiency.

Adsorbents based on molecular sieves, alumina, porous polymers have been available for some time and have been implemented. Although the separation characteristics are well recognized, the PLOT type column is traditionally built by deposition of small particles. Such particles can be kept in place using different techniques like bonding, gluing or in-situ preparation of adsorbent layers. As a result the column reproducibility on retention times, peak elution order and especially permeability is not comparable with the WCOT coated columns.

Restek has developed procedures to manufacture PLOT columns with different stabilized, concentric adsorption layers. Compared with state-of-the-art- type PLOT columns, the new generation PLOT columns show a constant flow behavior (permeability) and have significantly improved mechanical stability, resulting in easier operation, better chromatography, reproducible retention times and longer life time. Data of merit for Molecular Sieves and Porous polymer materials will be presented.

Spiking

One of the biggest problems with PLOT columns is that the layer is built by particles. Any change of gas velocity, pressure, surface stress or vibration can result in a release of particles or even complete segments of the adsorption layer. Such particles are swapped by the carrier gas to the detector or via a back-flush to the injection/valve system. When a particle hits the detector, the detector will produce a “spike”, see figure 1.

If many particles are released, it will result in serious restriction of the column and also contamination of the detection system.

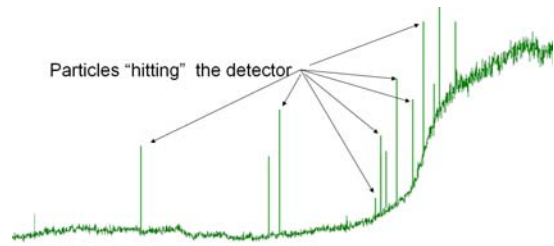


Fig. 1 “Spikes” caused by particle elution produced by an unstable PLOT column

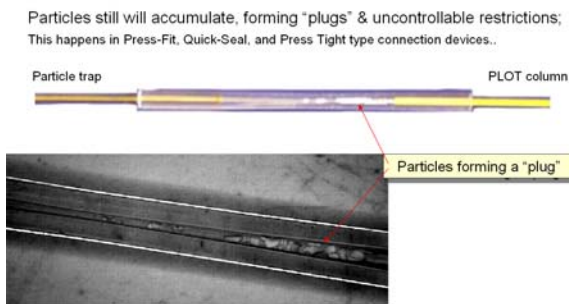


Fig. 2 Particles forming a restriction in a PressTight / PressFit type connection

immobilizes the adsorption particle. If many particles are emitted, a restriction can be built up in the trap. Sometimes this also happens inside the connector, see fig.2.

Flow Resistance

When preparing PLOT columns, the stationary phase consists of particles which are deposited with layers up to 50 micrometer in thickness. Such thick layers are difficult to deposit as a “homogeneous” layer. Typically there will be areas where the layer will be thicker / thinner, see figure 3. As a

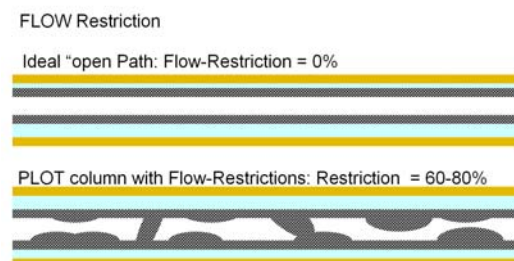


Fig. 3 Side visual of structure of porous layer inside a PLOT column

result, the positions where the layer is thicker, will act as a restriction for the whole column. Depending on the number and intensity of these restrictions, PLOT columns will show more variation on flow-resistance than WCOT coated capillary columns.

Practically, PLOT columns with the same dimensions can differ in flow by a factor 4-6, while operated at the same nominal pressure.

For applications where flow is important, like Deans switching, the non-reproducible flow behavior of most commercially available PLOT columns is a problem.

Flow resistance Factor F

In order to have a value for reproducibility of flow resistance, a new factor is introduced, called the "Flow Resistance factor" F. This factor is calculated according to the formula in fig. 4. The retention time of an unretained component is used as

$$F = \frac{\text{tr1 of unretained component [on uncoated tubing]}}{\text{tr2 of unretained component [on column to test]}}$$

Fig. 4 definition of the flow restriction factor "F"

$$\% \text{ restriction} = (1 - F) \times 100\%$$

Fig. 5 Definition of % restriction

a measurement. For a fixed column dimension and stationary phase coating, the ratio of retention time relative to the uncoated tubing is a measure of the flow resistance. From this one can calculate the % restriction, according to Fig. 5.

The values will always be < 1 as the coated column always has more restriction than the uncoated column. For instance, with Molsieves in a 0.32mm capillary, the internal diameter is reduced by 60 micrometers, just because of the 30 micron Molsieve layer.

What is of importance is how reproducible this value can be in the standard production environment

Molecular Sieve PLOT columns, Rt-MSieve

Rt-MSieve columns are unique because using a new optimized deposition process, the Rt-MSieve columns have high mechanical stability and show superior separation and response characteristics.

corrected pressure for to = 1.08	Flow restriction F	% restriction
4.43	0.41	59
4.37	0.41	59
4.24	0.42	58
4.64	0.39	61
5.18	0.35	65
4.40	0.41	59
4.50	0.40	60
4.15	0.43	57
5.35	0.34	66
4.47	0.40	60
4.36	0.41	59
4.52	0.40	60
4.38	0.41	59
4.54	0.40	60
4.43	0.41	59
	0.40	60

Fig. 6 Typical values of inlet pressure, Flow restriction and % restriction for a 30m x 0.53mm fused silica Rt-MSieve 5A with layer of 50 μ m

Figure 6 - 8 shows a listing and graphs of values measured for Flow resistance and flow restriction. The results are impressive. Absolute variation on flow restriction is within +/- 5% making these columns very reproducible and predictable on flow characteristics. In practice this means the Rt-MSieve columns have predictable reproducibility on flow and can be used in Deans as well as valve switching systems with minimal chance of particle elution.

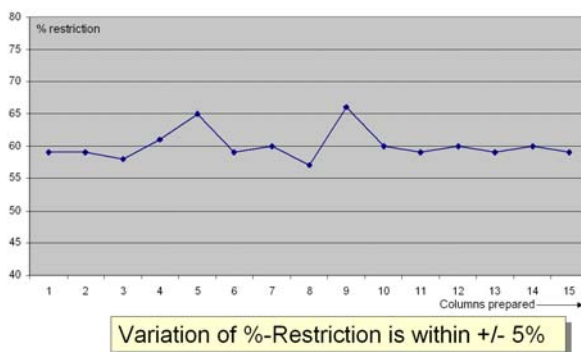


Fig. 7 Variation of Restriction factor F for 30m x 0.53mm Rt-MSieve 5A df = 50 μ

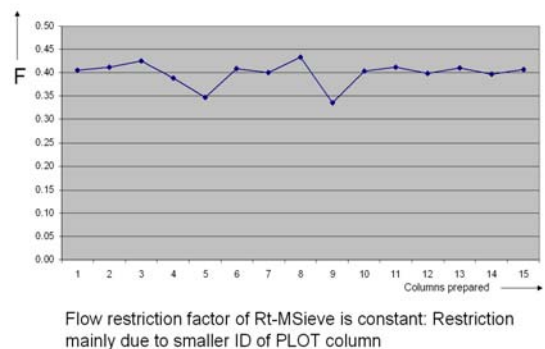


Fig. 8 Variation of % Restriction for 30m x 0.53mm Rt-MSieve 5A, df = 50 μ m

The separation characteristics are also unique, argon-oxygen is resolved with high Resolution, see fig.9 and10, and also the CO peak, fig.11, elutes as a sharp, symmetrical peak, also at very low levels. Figure 12 shows elution of CO at 50 ppm level using PDD detection.

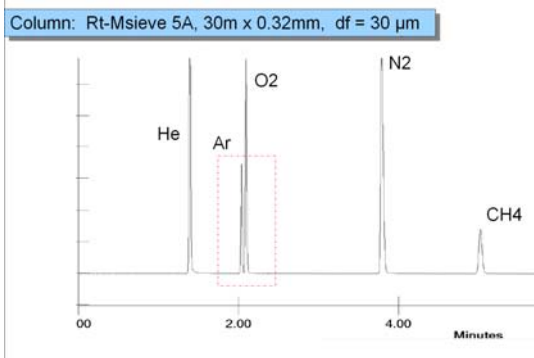


Fig. 9 Permanent gases on 30m x 0.53mm Rt-MSieve 5A, df = 30 μ m; Oven: 30 °C

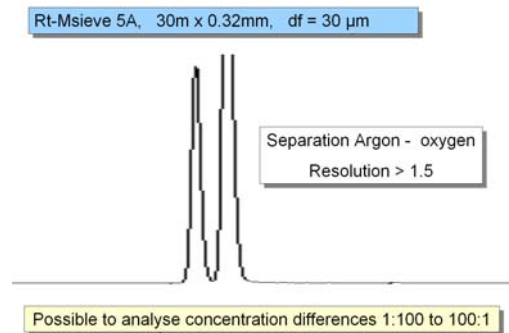


Fig. 10 Separation of Argon / Oxygen on 30m x 0.32mm Rt-MSieve 5A, df = 30 μ m; Oven: 30 °C

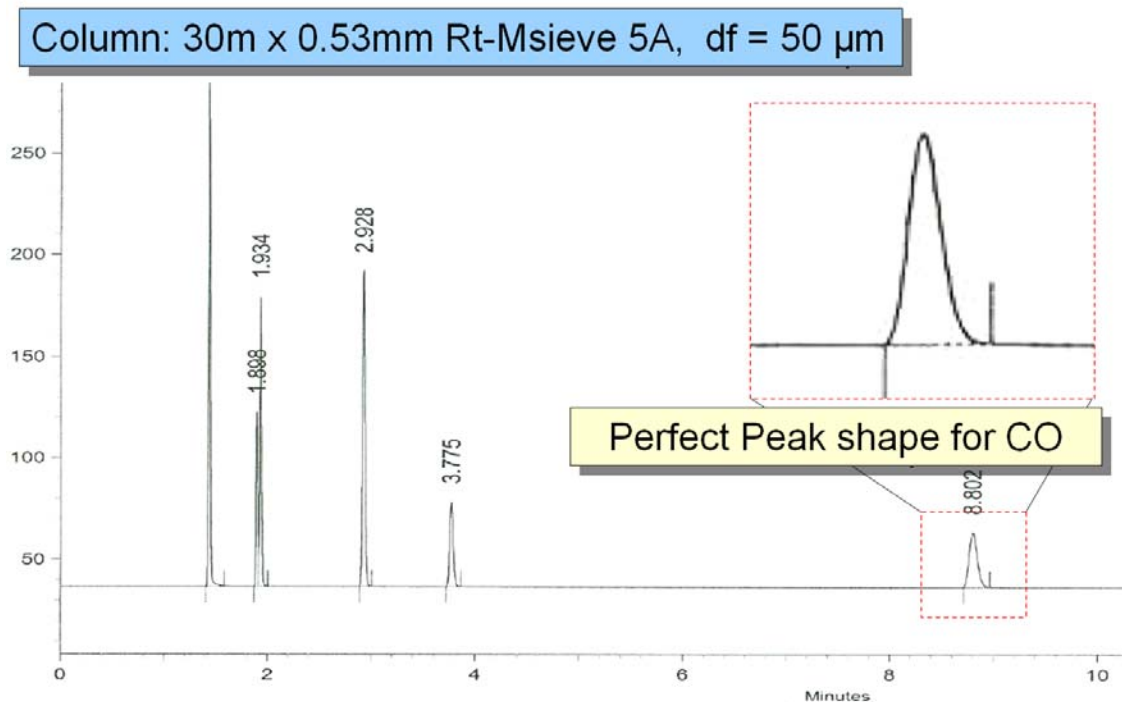


Fig. 11 Elution of permanent gases and CO; Oven: 50 °C; Detection: TCD

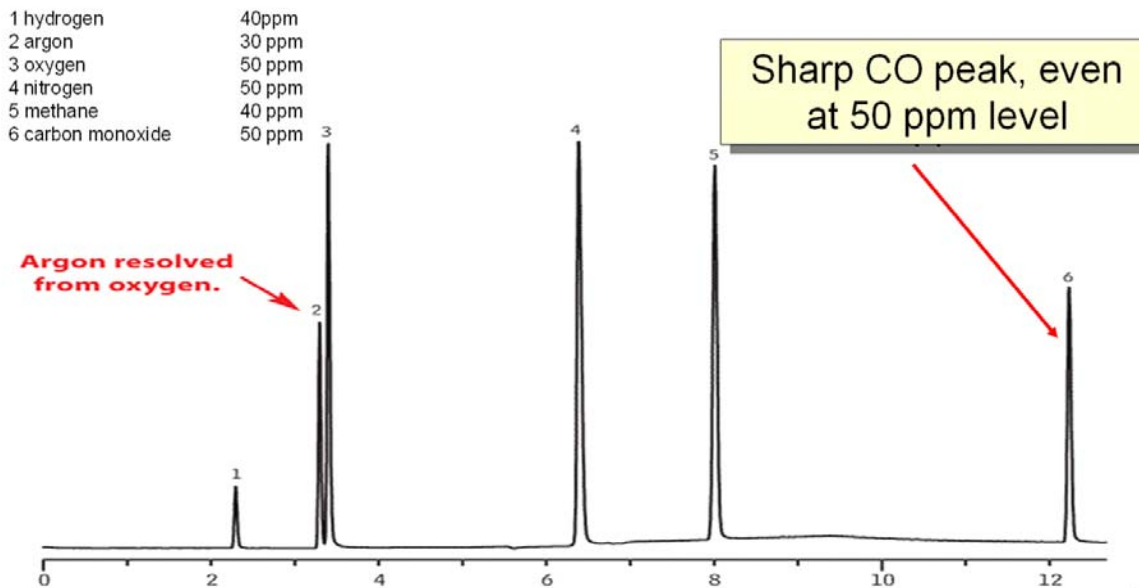


Fig. 12 Separation of Argon / Oxygen and CO; Column: Rt-Msieve™ 5A PLOT 30m x 0.53mm ID, 50µm
 Injection: 5µL sample loop, 6-port Valco valve; Inj. temp.: 200°C; Carrier gas : He, constant flow, 5mL/min.; Oven temp : 27°C (hold 5 min.) to 100°C @ 10°C/min. (hold 5 min.); Detection: Valco helium ionization detector @ 150°C

Porous polymers

Porous polymers are known to be even more challenging. As the material is subject to developing static load, the stabilization of small porous polymer particles is essential.

Recently a new technology was developed for stabilizing porous polymer type PLOT columns. This technology was used for making the Rt-QS-PLOT column. This column has a selectivity similar to the “GS-Q” column but due to the new technology the efficiency, inertness and stability has been greatly improved.

Fig 13 shows the difference between the commercially available porous polymer and the new Rt-QS-PLOT. Efficiency and peak asymmetry are well controlled.

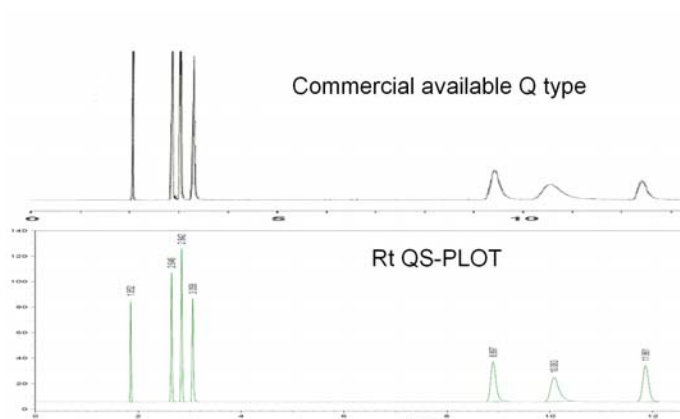


Fig. 13 C1-C3 hydrocarbons on commercial and new Rt-QS-PLOT

Figure 14 shows some data on a series of 22 columns. The reproducibility on retention factor is VERY high. Typically the retention factor deviates in order of +/- 20% for PLOT columns. The process used for Rt-QS-PLOT results in typical deviation of +/-5 %.

		K	N/m	RI ₁	RI ₂	u
866266	081407CSC0102	5.21	1506	186.7	289.7	31.9
866267	081407CSC0102	5.15	1498	188.7	290.0	32.4
866268	081407CSC0102	5.19	1494	186.3	289.5	32.0
866269	081407CSC0102	5.19	1528	186.6	289.6	32.4
866270	081407CSC0102	5.12	1470	188.5	290.0	30.8
866270	081407CSC0102	5.18	1498	186.3	289.5	30.3
866272	120407CSC0108PW	5.52	1513	186.7	289.6	32.5
866273	120407CSC0108PW	5.47	1484	186.5	289.6	30.8
866274	120407CSC0108PW	5.54	1440	187.1	289.8	31.5
866276	120407CSC0108PW	5.46	1516	186.6	289.6	31.5
867418	081407CSC0102	5.53	1479	185.7	289.6	31.3
867419	081407CSC0102	5.23	1438	185.9	289.4	31.9
867420	081407CSC0102	5.21	1509	185.9	289.4	31.3
867421	081407CSC0102	5.30	1453	186.0	289.5	31.3
867422	081407CSC0102	5.59	1499	185.7	289.6	31.9
867423	081407CSC0102	5.25	1371	187.7	289.8	30.8
867424	120407CSC0108PW	5.46	1436	187.6	290.0	31.4
867425	120407CSC0108PW	5.14	1381	188.2	290.0	31.9
867426	120407CSC0108PW	5.27	1408	186.4	289.5	32.5
867427	120407CSC0108PW	5.58	1434	185.6	289.6	31.9
867428	120407CSC0108PW	5.58	1438	185.6	289.5	31.3
867429	120407CSC0108PW	5.58	1452	185.7	289.6	31.3
Average		5.35	1466	186.6	289.7	31.6
Std. Dev.		0.17	43	0.93	0.19	0.59

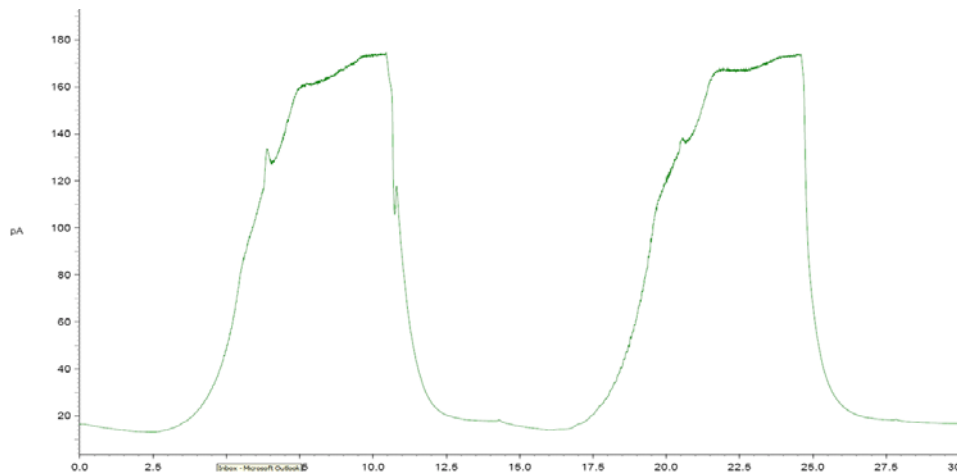
Retention factor K	: 5.35	0.17 (n=22)	< 4%
RI Acetylene	: 186.6	0.9	
N/m	: 1466	43	

Fig. 14 Reproducibility of Rt-QS-PLOT column manufacture, values for 30 m x 0.53mm Rt-QS-PLOT, df = 20 µm

Stability test / Flow restriction / Inertness

To test stability, a PLOT column is operated at a flow rate which was 3 times higher than the normal optimal flow. Under this high flow rate, the column is temperature programmed with 35 °C/min and cooled down with the fastest possible temperature program. During this process, the forces of expanding and shrinking will take place, which normally cause PLOT columns to release particles. Particles or adsorption segments which are not well bonded / stabilized will start to move through the column and can hit the detector, generating a “spike”, like shown in figure 1.

Figure 15 shows the flow stability test obtained with a 30m x 0.53mm Rt-QS-PLOT. There is no sign of particle or conglomerate-elution, indicating a very high stability.

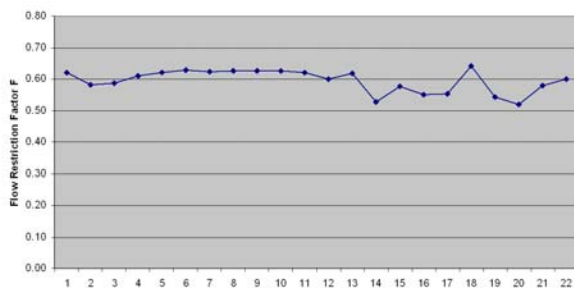


Rt-QS-PLOT Porous polymers are Well bonded resulting in MINIMAL particle elution..

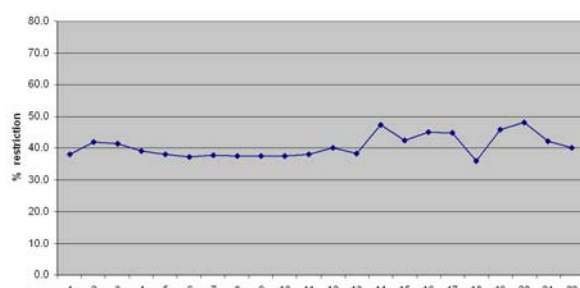
Fig. 15 Stability test using the 30 m x 0.53mm Rt-QS-PLOT, df = 20 μ m;
 Oven 50°C ? 250°C, 35°C/min., 5 min., -70°C/min cool-down; Carrier gas: H₂,
 10.5 Psi;

The stability of the Rt-QS-PLOT layer is also illustrated by the reproducibility of the flow restriction factor and % restriction, see fig. 16. If the flow restriction and % restriction for the Rt-QS-PLOT is calculated and plotted, we see very little deviation in flow characteristics, indicating a stable layer.

The Rt-QS PLOT has high inertness which allows components of different classes to be analyzed. Figure 18 shows the separation on some solvents at nano gram level.



Flow Restriction factor F is between 0.53 and 0.64



% restriction of 0.53mm Rt-QS-PLOT is within +/- 6%

Fig. 16 & 17 Variation of Flow restriction factor "F" and % restriction on a series of 30m x 0.53mm Rt-QS-PLOT, df = 20 μ m

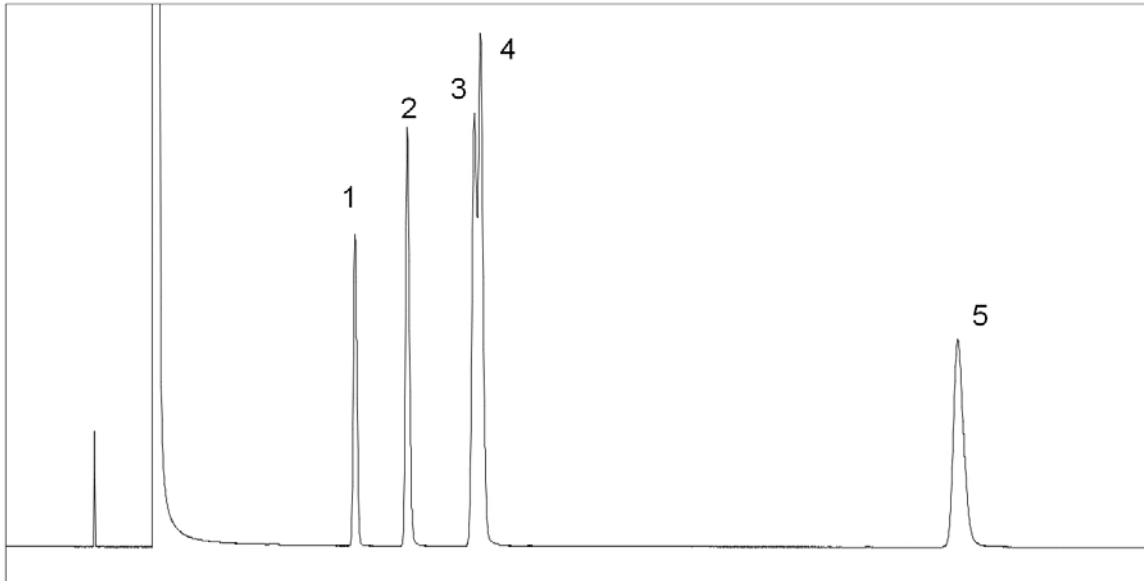


Fig. 18 Solvent analysis on a 30m x 0.53mm Rt-QS-PLOT @ 140C; 1: methylene chloride; 2: Methyl acetate; 3: Pentane; 4: Tr-1,2-dichloroethylene; 5: Ethyl acetate

Benefits of Stable PLOT columns

The benefits of a more stable PLOT column are clear:

- Minimal need for coupling with particle traps, no issues with coupling and maintenance of particle traps;
- Columns have constant flow restriction: Not only from column-to-column, but also when the new generation PLOT columns are operated, the flow and thus the retention times, will remain similar.
- Use with valve injection/ valve switching technologies: as the columns are more robust, they can handle pressure switches much better.
- The new generation PLOT columns have tight specifications on efficiency, capacity, retention and selectivity, which approach those experienced with liquid-phase coated capillary columns

Conclusion

With the availability of a PLOT technology that allows better control of flow restriction, a major new step has been made to make the PLOT columns more robust. This will increase the versatility of PLOT columns, especially for challenging applications where particle elution needs to be minimized and where reproducibility of column flow from column to column AND during application, is important. The technology is initially applied in the Rt-MSieve 5A and the Rt-QS-PLOT columns, but will be adapted for use with other adsorbents.