Application and Limitation of using Adsorbents as Stationary Phases in Gas Chromatography for the Separation of Volatile Compounds

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Adsorbents have unique separation characteristics. The adsorption process allows very volatile components to be retained at higher temperatures that create easier conditions to quantify very volatile compounds. Several adsorbents have found wide application in industry. Molecular sieves are used for the separation of inert gases and porous polymers based on styrene divinylbenzene are used for the separation of the more polar compounds. These adsorption materials have also been made available in capillary columns where the retention is generated by a layer of adsorbent particles on the inside wall of a capillary. Such capillaries are called PLOT (Porous Layer Open Tubular) columns and are highly efficient. They produce high theoretical plate numbers and have high operation temperatures.

The challenge of PLOT columns is to stabilize the layer as particles can be dislodged from the layer and form restrictions. Such restrictions can be measured and the values can be used to control PLOT quality. It was also possible to apply the PLOT technology in metal columns (MXT), allowing the process type of applications to take full advantage of these developments. See reference [1] for an historical review.

Challenges in PLOT Column Chemistry

PLOT columns allow separations combining adsorption chromatography with high-resolution capillary columns. The adsorbent is coated as a layer of particles on the inside wall of the capillary. The challenge is to make that layer stable. The layer consists usually of particles which are 0.5–2 microns in diameter. The stability of such a layer depends on the particle size and its physical characteristics.

If the layer is not stable, particles can leave their position and can 'elute' from a PLOT column. Figure 1 shows an example of a PLOT column where the coating is not stable. This will result in different challenges:

- Retention times can change as restrictions are built up;
- Higher pressures are required for the same flow setting;
- Columns need different pressures to operate optimally, depending on restriction.
- Particles hitting the detector, causing contamination

Stabilization of adsorption layers is, therefore, very important.

Measurement of Restriction

PLOT columns will always have a higher restriction simply because the column has less permeability due to the adsorption layer. Figure 2 shows a way to measure the restriction of
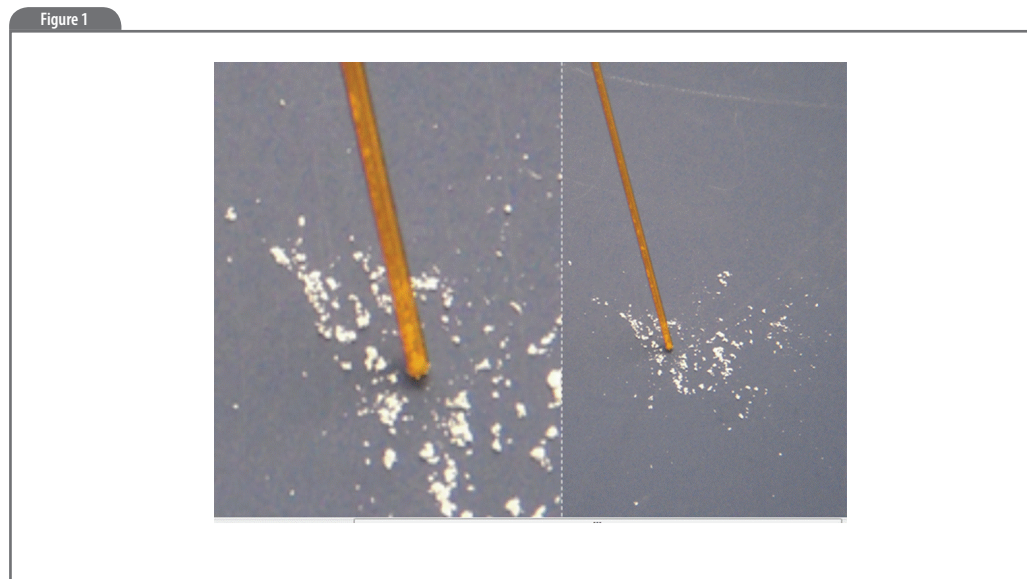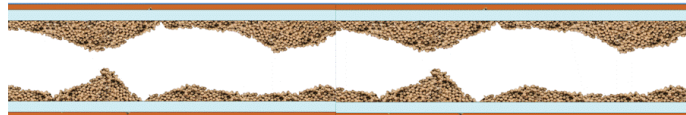

Figure 1: Example of solid particles eluting from a non-stable PLOT column.

Ideal "open" path: Flow-restriction factor = 1.0

PLOT column with Flow-Restrictions: Flow restriction factor "F" = 0.2-0.8

$$F = \frac{t_{r1} \text{ of unretained component [on uncoated tubing]}}{t_{r2} \text{ of unretained component [on column to test]}}$$

Definition of Flow resistance Factor

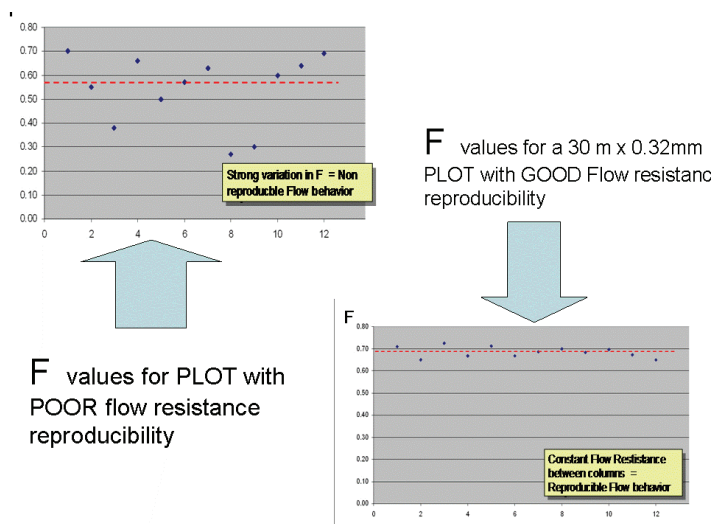**Figure 2: Measuring the flow resistance factor allows a way to measure PLOT column restriction.**

Strong variation in F = Non reproducible Flow behavior

F values for a 30 m x 0.32mm PLOT with GOOD Flow resistance reproducibility

F values for PLOT with POOR flow resistance reproducibility

Constant Flow Restistance between columns = Reproducible Flow behavior

Figure 3: Example of a PLOT column series with good and poor particle stability: variation of the F factor is shown immediately.

HIGHER concentrations:

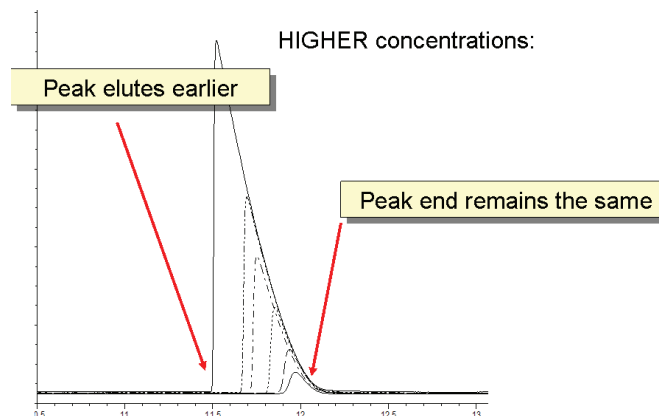Peak elutes earlier

Peak end remains the same

Figure 4: Impact of component concentration on peak shape using PLOT columns. Peak starts to tail and elutes earlier.

PLOT columns, using a flow-restriction factor. This factor is defined using fixed capillary dimensions and measuring the impact of a non retained component on retention time. Ideally in an open tube this factor is 1.0. If a layer is present the ID of the PLOT column will change, and also any irregularity of the layer will contribute to retention. This can be added to the QA procedures of PLOT columns increasing their reliability [2,3].

As a result it was possible to measure reproducibility of flow restriction between different columns. Figure 3 shows some data obtained from commercial columns coated with porous polymers. There are large deviations in the flow restriction factor but it can be controlled by using optimized coating and stabilization techniques.

Manufacture of PLOT Columns

The manufacture of PLOT columns is quite different from liquid-phase coated columns. It requires specialized technology and very few people can make these columns. While liquid phase columns are mainly dealing with dissolving a polymer in a suitable solvent and deposition on the capillary wall, the adsorbent needs a stable suspension or requires complete different coating techniques to build the necessary thick layers. That's probably why PLOT columns are also more expensive. It is possible to increase the stability of PLOTs and as
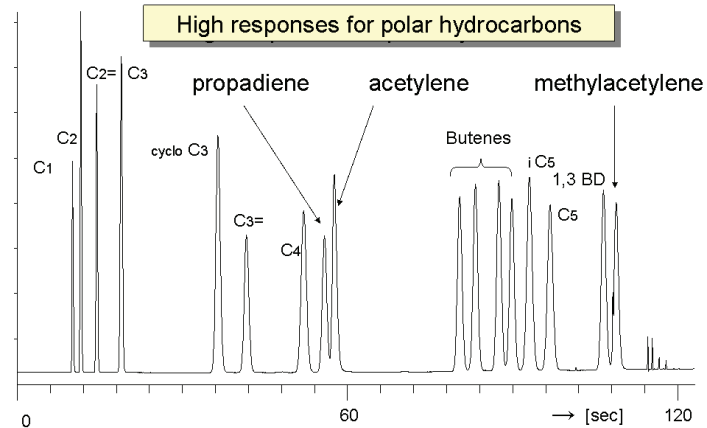
Figure 5: Fast analysis of C1–C5 using Al₂O₃ with special MAPD deactivation. Note high response for methylacelylene, acetylene and propadiene. Column: 15 m x 0.53 mm Alumina BOND/MAPD; carrier He, 100 kPa; Oven: 60 ˚C, 0.5 min => 150 ˚C, 60 ºC/min; Injection: split.
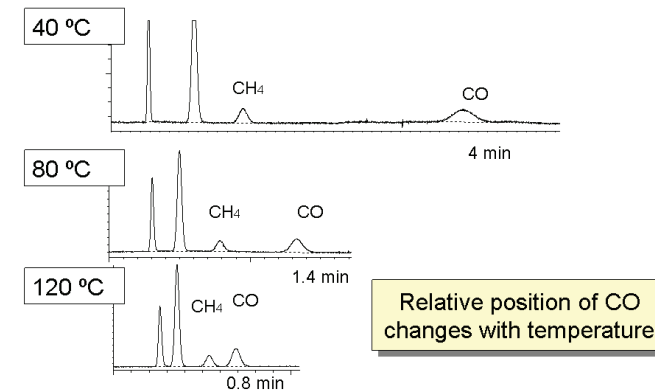

Figure 6: Impact of temperature on molsieve 5A separation: the molsieve 5A adsorbent behaves less polar with higher temperatures, resulting in a faster elution of CO relative to methane.

	Non polar	Polar
Alumina	Al₂O₃/KCl	Al₂O₃/Na₂SO₄, Al₂O₃/MAPD
Porous polymers	Rt-Q-BOND Rt-QS-BOND	Rt-S-BOND Rt-U-BOND

Table 1: Different polarity adsorption columns.

we have now a way to measure this, we can test accordingly.

Behaviour of Adsorbents

Liquid stationary phases are mostly used in GC. Their characteristics are well known. That makes the use of adsorbents quite challenging as they behave quite differently. When adsorbents are overloaded (high component concentration), the resulting peak is deformed. Instead of a 'leading' peak, we get a 'tailing' peak. The more we inject, the bigger the tail becomes. Figure 4 shows an example of what happens if increasing levels are injected on an adsorption PLOT column. Another important phenomena is that the overloaded peak also elutes earlier. That means that any components that elute in front of this peak, will start to co-elute. For several PLOT column types different selectivities are available (see Table 1), which allows a choice of selectivity to maximize the resolution for a highly overloaded peak.

Alumina

Alumina has a unique selectivity for light hydrocarbons. This allows C1–C5 hydrocarbons, including all unsaturated isomers, to be resolved with the highest possible resolution. Selectivity of alumina can be tuned using organic salts, like KCl or Na₂SO₄. Such columns are already in use but still have limitations response factor on compounds such as propadiene, acetylene and also temperature stability is limited. New generation alumina provides very high response factors and can be used up to 250 ˚C. Because of the selectivity the new alumina columns can also be used for very fast analysis (see Figure 5). Such columns not only allow accurate trace analysis of hydrocarbon impurities but can also elute higher hydrocarbons faster and with good peak shape. It also allows a second column to be used at higher temperatures if an alumina column is used.

Alumina surfaces behave more polar if the column is used at lower temperatures. That means , if one wants more retention for polar analytes, the alumina columns must be used running at lower temperatures. This can be done by decreasing the
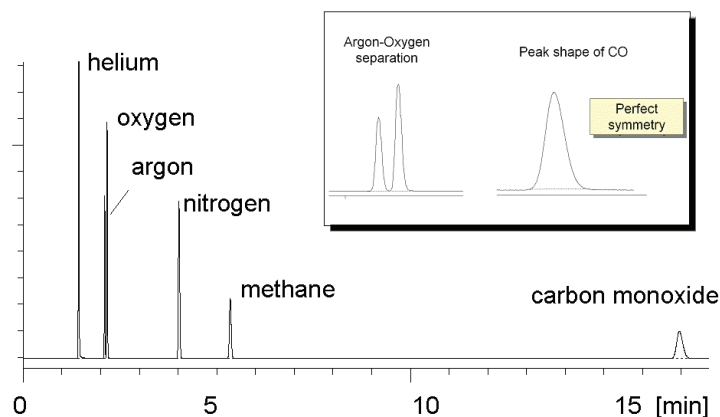
Figure 7: Separation of permanent gases on MXT-Metal 0.53mm molsieve 5A capillary, 30m at 30 C; Detection: u-TCD; Injection: split.

Figure 8: Polar volatiles on porous polymer Rt-U BOND, 30 m x 0.53 mm; Oven: 100 ˚C, Injection: split; Detecction: u-TCD.

starting temperature, using a longer iso time at the starting temperature, using a higher gas flow or using a slower temperature programme. All actions will make the alumina behave less polar and as a result, separations will change. Polar hydrocarbons (acetylenes, popadiene, for example, will move relative to the back of the chromatogram compared with *n*-alkanes. For impact details see reference [4].

Molecular Sieves
To achieve separation of even more volatile compounds a higher surface area is needed. Molecular sieves (zeolites) have very high surface area because of their structures. The zeolite consists of a well defined porous structure that generates retention even for the most volatile gas at temperatures at moderate temperatures. It will separate all the noble gases including carbon monoxide at temperatures above 20 ˚C. When reducing temperature even hydrogen isotopes, including their spin isomers, can be separated.

The selectivity of molsieve is the same as alumina (i.e., strongly temperature dependent). Figure 6 shows the impact of oven temperature on CO elution on a molsieve 5A adsorbent. The position of CO changes drastically when analysis is done at 40, 60 or 80 ˚C. At low temperature the highest retention is obtained (most polar behaviour).
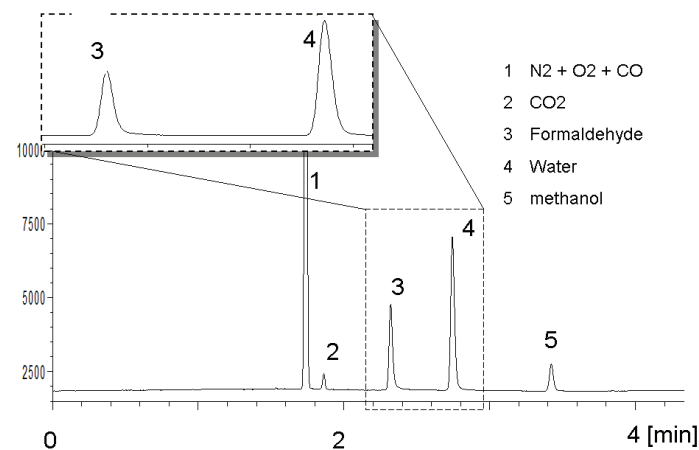
The capillary molsieve columns have high efficiency, also allowing a base line separation of argon oxygen (see Figure 7). Note that this application shows the separation using a MXT-metal molsieve 5A PLOT column. Such columns can be used in miniaturized systems (small diameter coiling) as well as process type equipment where they are to be used under highly stressed conditions [5].

Porous Polymers
Both molsieve and alumina type materials still have a strong physical interaction with polar analytes, such as alcohols, aldehydes, ethers and water. The porous polymer, consisting of a skeleton of divinylbenzene, has the characteristic that it elutes all types of components; polar and non-polar. It is also not sensitive for water. For these reasons porous polymers are a very nice addition to the adsorption columns. Selectivity for hydrocarbons is, however, by far not as good as obtained with alumina, and the retention is not high enough to separate the inert gases. Most applications dealing with gases, use a combination of a porous polymer and a molsieve or an alumina column. Figures 8 and 9 show some typical applications of how porous polymers behave: Peak shape of polar volatiles on a U-BOND porous polymer is very good — note that these are highly polar analytes.

Figure 9 shows another interesting application: elution of trace sulphur gases from the same column: there is no interference of sulphur compounds
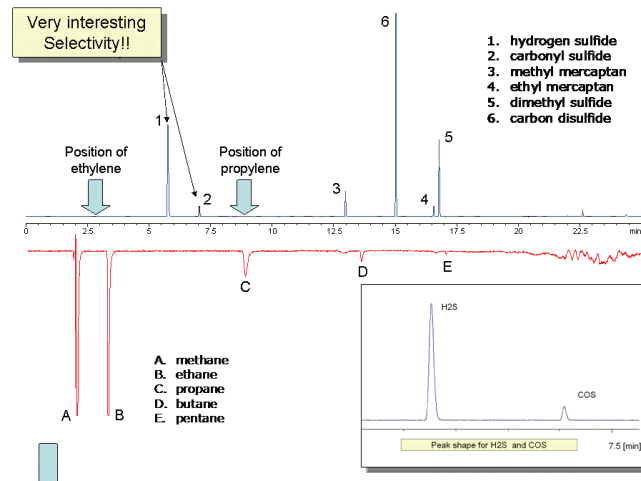
Figure 9: Sulphurs at 1 ppm in natural gas on Rt-U-Bond; column: 30 m x 0.32 mm; Detection: PFPD.

Figure 10: A Q-type PLOT column coated on one side of the fused silica still offers very interesting chromatography.

with hydrocarbons making a trace analysis of low sulphur in C_2/C_3 streams also a very interesting application. The porous polymer technology was also applied to metal columns where we saw similar separation behaviour as with fused silica column.

Other Developments
Porous polymers can also be made in a different way. Figure 10 shows an example of a Q-type PLOT column that was prepared differently. Gravity has caused the layer to be built up on one side of the column. Interestingly, columns like this show high efficiency despite the non-concentric deposition. This is probably caused by the fast kinetics of adsorption. This type of coating may become interesting for coating rectangular channels as the

liquid phases seem to struggle here.

Conclusion
Adsorption materials deposited in PLOT columns show high retention and efficiency allowing fast separation of gases and volatiles. Development of flow restriction specifications made PLOT column more predictable in separation behaviour, which is especially appreciated using flow switching systems. Alumina PLOT column application has been extended because of higher temperature limits and better response factors for polar hydrocarbons. Also porous polymers elute polar compounds including water as good chromatographic peaks. PLOT technologies such as molsieve, alumina and porous polymers have also been applied with metal type capillary
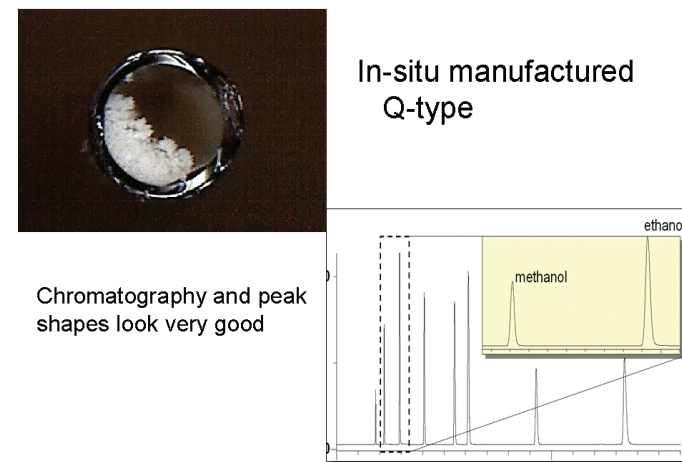
columns allowing high resolution separations to be combined with the robustness of metal capillary tubing.

References
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2. Jaap De Zeeuw, Bill Bromps, Tom Vezza, Rick Morehead, and Gary Stidsen, *American Lab*, 42(5), 38, (2010).
3. Jaap de Zeeuw, Bill Bromps, Tom Vezza, Rick Morehead, Jan Pijpelink, and Gary Stidsenand, PIN, *Analytical Instrumentation*, Feb/March 2010
4. Jaap de Zeeuw, Rick Morehead, Tom Vezza and Bill Bromps, *American Lab.*, Oct 2011.
5. Jaap de Zeeuw, Rick Morehead, Tom Vezza, and Gary Stidsen, PIN, June/July 2011.