The Role of Column Deactivation in today’s High Temperature GC Phases.

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In gas chromatography there is a development making GC column besides low-bleed also as inert as possible. Several new technologies have been introduced to make columns more neutral. One of the technologies Restek started with 5 years ago, was known as “Rxi-deactivation technology”. This technology resulted in a new platform of columns that were far superior in bleed and inertness, compared with state of the art (like the DB-5ms) type technology. Phases like the Rxi-5Sil MS, Rxi-XLB and Rxi-1ms became very popular, and were followed by the polar Rxi-35Sil MS, Rxi-17Sil MS and lately the Rxi-624Sil MS. Recently the Rxi technology was also tested for High Temperature phases, which worked very well, and the Rxi-5HT was a reality, applicable up to 400°C.

For high temperature stable phases inertness is an extra challenge, as often high temperature separations are performed on columns with thin films to make the components elute at lower temperature. As film thickness decreases, the actual deactivation becomes very important and differences become visible. A comparison was done between 4 suppliers that claim High temperature phases. Only new columns were compared, all treated in a similar way, using similar hardware. Evaluation was done using a polarity test mixture with challenging compounds like hexane-diol and decylamine. In this poster the data wil be presented. It was no surprise that columns looked reasonable when 10 ng was analyzed. Differences became dramatic when the amount on-column was reduced, showing clear superiority of the Rxi deactivation technology.

Why is Inertness important?
Components that elute as symmetrical peaks will have higher response and can also be measured at lower levels. The benefits are numerous:

• The components will elute as sharper peaks: Response and peak area's will be higher and more reproducible. Also retention times are more constant as adsorption effects are minimized;

• Allows polar compounds to be measured at increasing lower levels..

• Components elute at FIXED positions, independent of concentration..

• Derivatization often not necessary

• More analysis without maintenance
**Rxi-Technology for better inertness and temperature stability**

Low bleed stationary phases have been commercially available for some time. By using silphenylene type stabilizing groups, the mobility of siloxanes could be reduced significantly which resulted in more stable polymers. As a result the breakdown reaction that is the basis of stationary phase degradation, see figure 1, is more difficult to occur.

![Figure 1: Siloxane degradation mechanism](image)

Restek was the first company that took column technology into its next platform by using Rxi-technology summarized in figure 2. This technology resulted in GC stationary phase program, where a combination of low-bleed, Inertness and reproducibility was realized, see figure 3. Recently also the Rxi-17Sil MS and the
Rxi-624Sil MS were added to the program. For the Rxi-624Sil MS we even managed a max temperature higher then 320ºC.

Rxi polymers are stabilized using stabilizing (Sil-phenylene) groups, that makes the polymer chain more rigid. Additional end-capping of the reactive silanol groups present in the polymer and on the fused silica surface takes place. Incorporation of systematical cross bonds made it possible to link the siloxane chains up to thicker films, while maintain flexibility without cleavage at higher temperature.

Additionally in the Rxi-process, a surface deactivation was developed that allowed surface bonding of all Rxi-polymers. The surface bonding makes the Rxi-polymers extremely stable for mechanical attack of liquids in f.i. splitless injections. This typically translates in longer life times. This deactivation has an important function in shielding any residual activity on the surface, creating a highly inert column.

When using thinner films this effect becomes very visible as will be shown later.

For making very stable high temperature phases, one has to increase the number of cross links and surface bonds, as was implemented with the Rxi-1HT and the Rxi-5HT. Such columns could be used to temperatures of 380 ºC isothermally with low background,. Typical values of 2pA were found. The phase itself can even be used above 400ºC. This is not recommended as the polyimide outside coating becomes brittle which puts the column at higher risk. We ran columns up to 430 ºC without seeing any loss of efficiency or inertness. Bleed values are shown in figure 4.

![Figure 3: Phases stabilized using Rxi technology](image)

![Figure 4: bleed for a 30m x 0.32mm Rxi-5HT at 380, 400 and 430ºC; carrier gas ; Hydrogen](image)
Inertness testing
Historically column inertness has been tested using test mixtures containing components of different functionality. For column quality, the “grob” test mixture has been used for a long time. For differentiation of column inertness, these mixtures are not good enough, as most columns look comparable. To test more critical, one need to take more critical compounds. Also a more critical test was developed for testing the quality of columns in a production environment. Typical changes that were implemented:

State of the art: New Generation Rxi-Inert columns

- Primary alcohol (octanol) → Di-alcohol (2,6-hexane diol)
- Aromatic dimethyl aniline → Primary amine (decylamine)
- Dimethyl phenol → 2,6 – dinitrophenol

The diol functionality reveals the interactions with residual silanols, while the primary amine and nitrophenol are excellent probes for neutrality. Such critical test probes are essential to test and demonstrate the quality of the new Rxi-platform capillary columns.

Temperature / Time stability. Rxi-5HT After 81hrs at 400°C

Figure 5: Time temperature test Rxi-5HT
Column: 30m x 0.32mm 0.1 um Rxi-5HT

Rxi-5HT remains inert after long term exposure at 400°C
**Stability in time at high temperature**

Capillary columns need to keep their performance also if used for longer time at high temperatures. Several suppliers of capillary columns do not intensively condition their columns. This is because the deactivation technique used is not temperature stable and columns develop activity in time. It can be recognized easily by the “color” of the outside coating. If a column is “yellow” it has not seen adequate conditioning time. Rxi columns are always conditioned overnight at their maximum isothermal temperature. This will give each Rxi column a little “brown” color. This is assurance for the customer that the column is clean and that it does not change performance under conditioning or running at high temperature conditions.

To test long-term stability at higher temperatures, a Rxi-5HT column was conditioned for 81 hrs at 400°C. After this exposure the column was tested with the polarity test mixture. Column performed as before wit full degree of inertness, proving that the Rxi-deactivation is also stable up to high temperatures as well as in time., see fig 5.

**Thin-film inert columns**

When going to thinner films the quality of deactivation will show itself for 2 reasons. Thin films have limited “shielding” effects. Stationary phase polymers does not cover active sites, meaning residual activity of deactivation, will be exposed. Thinner films will also elute components faster and at lower temperature. At lower temperature adsorption effects increase exponentially which will impact peak shape.

A comparison was done between 4 High temperature columns all of similar dimensions. New columns were used of respectively DB-5HT, VF-5HT, ZB-5HT and an Rxi-5HT column. All columns were treated the same using the same GC, operator and operating conditions. Samples were introduced using the splitted injection technique. Amounts of 7ng and 2 nanograms of a polarity mixture were injected onto the column and the chromatograms were recorded. The peak height of 2,6-hexanediol and decylamine was related to the response for 4-chlorophenol and methyl nonaoate, peaks that elute next to these target analytes.

At 7 ng levels, the response of most columns for the diol was still acceptable, but when going to 2 ng adsorption effects became visible for the DB-5HT and the VF-5HT columns. The decylamine showed to be even more challenging as this component was completely adsorbed by the VF columns and reduced by a factor 2 on the ZB-5HT and the DB-5HT columns, see figs 6a and 6b.

This data confirmed what was already observed with other Rxi phases. Inertness of the Rxi deactivation is superior to other commercial brands.
Figure 6a: comparison of chromatography of 7 and 2 nanogram injections of polar analytes on DB-5HT and VF-5HT columns. All columns tested in same GC after exactly similar conditioning exposure.

Figure 6b: same as 6a, but done on ZB-5HT and Rxi-5HT
Application.
The Rxi-5HT columns can be used for applications where late eluting compounds are to be expected. For instance in mineral oil analysis. Here heavy hydrocarbons like motor oils, elute at high temperatures. The Rxi-5HT phase has perfect selectivity to separate also the pristane/phytane form neighboring hydrocarbons; Figure 9 shows a medium crude where we virtually do not see any bleed even at temperatures > 380°C. The inertness of the Rxi-deactivation allows the thin-film high temperature phases also to be used for more challenging analytes, like pesticides. Fig 10 shows 50 pico grams of chlorinated pesticides. No sign of decomposition for pesticides like endrin, p,p'-DDT or methoxychlor.

High resolution separation of mineral / motor oil mix on Rxi-5HT

Figure 7: Analysis of mineral and motor oil mixture
Column: 30m/0.32mm Rxi-5HT, df = 0.1 um with 2m x 0.53mm retention gap
Injection: Cold-On-Column; Detection: FID @ 330 C; Oven: 50°C => 300 @ 10/min > hold > 20 min;
Carrier gas: H2 @ 40cm/sec; Sample: C10 – C40, 500 ppm total;
Sample size : 1μl
Figure 8: separation of pristane and phytane; conditions: see fig. 7

Figure 9: Analysis of medium crude; conditions see Fig. 7
Summary

New inert high temperature phases have been successfully developed, using Rxi deactivation technology. Columns remain efficient and inert after prolonged use at temperatures up to 400°C. Practically the user can benefit from having better peak shapes for broad trace analytes, lower background and faster stabilization. High temperature phase stabilization was successfully achieved with the Rxi-5HT and the Rxi-1HT.
Our new line of fused silica capillary GC columns - Rxi® columns - is now available! We have designed these new columns specifically to be the best columns available, for exceptional inertness, ultra-low bleed, and reproducible retention and selectivity. In addition to outstanding performance, this combination of column characteristics assures Rxi® columns will have long lifetimes. The Restek chemists also have developed a stable, reproducible manufacturing process, so that Rxi® columns will meet your needs every time you install a new column.

What do Rxi® columns mean to you? Three things:

- Ultra-low bleed.
- Exceptional inertness.
- Reproducible performance, column after column.

- 40% longer lifetime from specially designed fused silica tubing.
- Columns processed for high temperature applications.
- Temperature range: -60 to 400°C*.

(low polarity phase; 5% diphenyl/95% dimethylpolysiloxane)

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*Column is capable of going to 430°C, but column lifetime will be reduced.*

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