How To Get More Analysis Out of Your GC System?

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A common question we get asked by our customers is how they can get a longer column lifetime. This can be from a cost perspective (column price) or from a maintenance perspective (downtime, labour, calibration).

Of course, the investment in a new column is large, around $500, but one thing that we should keep in mind is that we have to spread this investment over the total number of analyses. With typically 2000-5000 analysis per column the cost of the column per analyses is 10-25 cents. This must be put in contrast to downtime and sample preparation time.

Column lifetime is defined by several factors:

Contamination brought onto the column

Contamination can cause peak broadening, peak tailing, phase degradation, ghost peaks and high background. If the column is contaminated it will always happen at the inlet side. Therefore, the biggest challenge is to minimize this by injecting the "cleanest possible sample", injecting the "smallest possible amount" or using a different liner/injection systems.

Injection of cleanest possible sample: Samples can be clean and well defined, but they can also be extracts from soil, water, plasma or biological origin such as plants, animal tissue and vegetables. In sample clean up the goal is to eliminate the matrix and keep the target analytes. This is where it become challenging as sample preparation is time consuming and can become very costly. Practically, the lab must find a balance between what is "acceptable" in terms of sample preparation, time and column life-time/maintenance activity. The question on column lifetime usually rises when a method is in place and a longer lifetime is requested. Changing sample preparation methods is however, not commonly on the agenda.

Injection of smallest possible amount: Contamination is proportional to the absolute injected amount. If the injected amount can be reduced contamination will be less. Contamination takes place in both the liner and the column.

- Liner contamination can be reduced by injecting less sample. If we have enough sensitivity we could inject 50% or less using the same injection conditions. One can also dilute sample and inject a larger ammount (a.g.,1 µL. Because we have diluted, there will be less matrix impact. If sensitivity is critical we can also inject less sample and adjust the split ratio, so the same absolute amount enters the column. Instead of 1 µL with a split of 1:60, we can inject 0.5 µL with a split of 1:30, or even 0.3 µL with a split of 1:18. In this way it will take much longer for liners to contaminate while we maintain the injected amount.

Figure 1

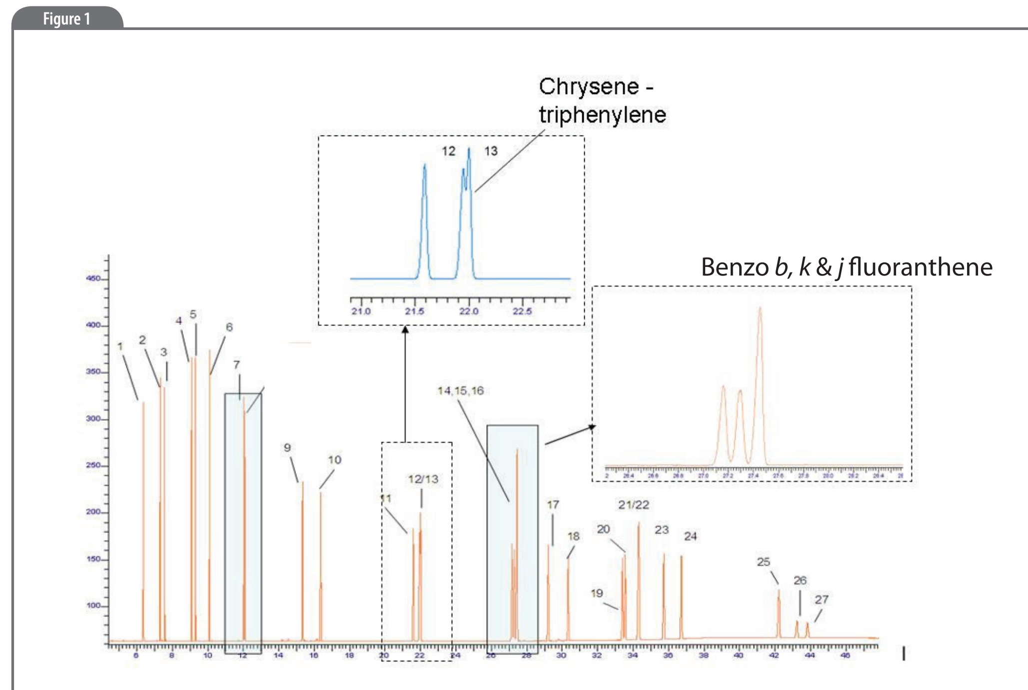

Figure 1: Example of a high temperature separation of PAH using a Rxi-17Sil MS column. Note the baseline resolution of benzo *b, k* and *j* fluoranthene isomer.

Figure 2

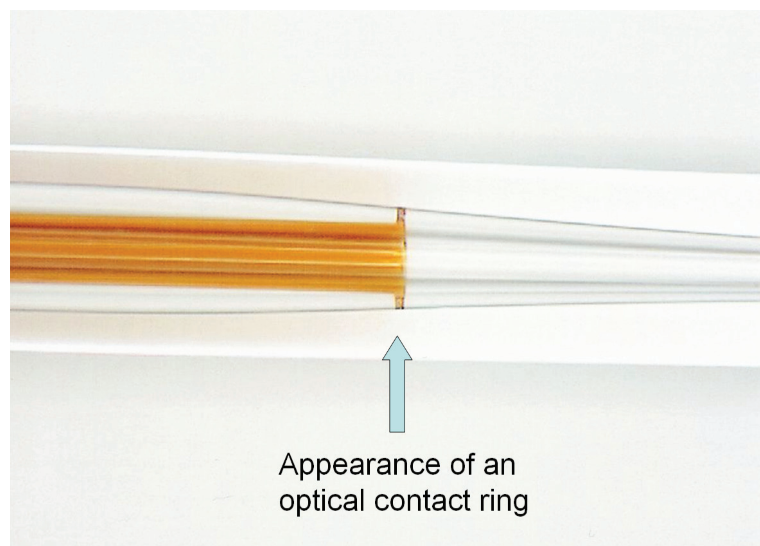

Figure 2: Zoom of press-fit connection.

- Column contamination will be reduced if less sample is allowed onto the column. This can only be done if sensitivity is maintained, which depends on the method. In splitted injection, smaller sample amount is realized by using a larger split ratio, or injection of a smaller volume. Not every autosampler is able to inject less then 1 µL. This is, however, an important consideration for choosing samplers. If good quantification is obtained injecting 1.0 µL, injection of only 0.5 µL, contamination will only be 50% and maintenance will decrease accordingly.
  In splitless injection we cannot change split ratio to inject less, but we still can consider sample dilution or injection of a smaller amount to reduce liner and column contamination.

Using different liner / injection configurations: Most of the contamination will happen in the liner as liners will act as a primary 'filter' before the GC column. It's the "first line defense". Very common is to use some deactivated glass wool in the liner. This material will trap part of the matrix and will reduce column contamination. Lifetime of liners is depends strongly on the type of application, temperature, design etc., and is often chosen on personal preference, based on experience.

Some injection systems, such as PTV type systems, can also be used in a back-flush mode. The carrier gas flow is reversed from bottom-to-top and the liner can be flushed "clean" by high temperature conditioning. One must be careful with such settings as sometimes high temperatures can cause activity (pyrolysis) of contamination or septa residues, causing even bigger injection problems.

Carrier gas purity

Carrier gas sometimes contains small amounts of oxygen and water. This can be introduced via the source (gas purity), via small leaks in the gas distribution system, or via a connection in the GC (column to injector, septum or column to column). At low temperature there will be no issue as most liquid phases will survive that. The only things we have to watch here are the parts of the column that are positioned in the (hot) injector and (very hot) detector. As local temperature is high, reactivity will enhance and activity can be generated. In a later article we will look more closely at detector activity.

When columns are operated at high temperature, lifetime usually increases when oxygen/water is absent.

To reduce risks, gas filtration as well as leak checking is highly recommended, especially when analyses are performed at temperatures above 200 °C.

High column temperatures

Most GC columns can be used at high temperatures. Temperature limits of 360 °C are common exception, even for polar phases. Figure 1 shows a PAH analysis on a selective polar phase that allows baseline separation of critical PAHs such as the fluoranthenes.

Oxidation / Hydrolization: Reactivity of siloxanes with water and oxygen increases exponentially with temperature. Besides clean carrier gas, it is also beneficial to use the lowest possible final oven temperature. If the option of flow programming is available, it is better to elute high boilers by increasing the flow then programming to highest possible temperatures.

As a general guideline: every 15 °C, the retention increases by a factor of 2. This means that by increasing the flow by a factor 2 at the end of the run it is possible to decrease the final temperature by 15 °C. With a fourfold increase in flow it is possible to reduce the final temperature by 30 °C. Increasing flow can only be achieved with non-MS systems as in MS, also the flow must be pumped to maintain vacuum.

Loss of stationary phase and column breakage: If retention times systematically decrease from analysis to analysis, often in combination with a high background signal, it means that the stationary phase is decomposing and eluting as "bleed" products. Make sure to use columns compatible with high temperatures and that are also preconditioned

at such temperatures. The new generation phase technologies known as "ms" or "low-bleed" are very useable for higher temperature work. Higher temperatures can also attack the outside coating. Fused silica is coated with polyimide, which is a temperature stable polymer. However, when heated above 360 °C, the polyimide will slowly pyrolise as columns become brown, dark-brown, or black and the coating will disappear, leaving bare fused silica tubing. This is very tricky as columns can suddenly break into a thousand pieces. When operating fused-silica columns higher then 360 °C, one must keep in mind that the outside coating may be the life-determining factor. For extra security one can also consider the use of metal columns. Metal type columns are also commercially available in many phases and dimensions and show very low bleed because the surface has a stabilizing effect on the coating. Also such columns do not "break" spontaneously.

Protection of analytical columns: guard columns/pre-columns

If all the injection parameters have been aptimized and more analysis from the column is required "guard' columns should be considered.

Such guard columns can be 1-10 m lengths of deactivated fused silica that are coupled with the analytical column. After X analyses a fixed length is cut from the inlet side and the analysis performance is usually restored.

Coupling can be acheived with the press-fit type connectors, see Figure 2. The same connector is used for coupling 0.10mm ID up to 0.53mm ID fused silica tubing. To make the coupling, the column must be cut using a ceramic wafer or another cutting device that can make a sharp cut. The column is cleaned and wetted on the end with some methanol or acetone and pushed inside the tapered press-fit connector. By applying a little force, a dark ring will appear, which is the actual seal that is made on the inside of the press-fit.

Column coupling can be eliminated using integrated guard columns. By leaving the first 5-10 m without stationary phase, an integrated guard column can be created (Figure 3). This concept was developed about 20 years ago and it has been used widely, especially in routine test laboratories.

The disadvantage of such guard columns is that every time a piece is cut from the inlet, the retention times changing (i.e., the column gets shorter).

Using coated guard columns

Another way to extend column lifetime is to use a coated guard column. In this case a guard column with the same phase and film as the analytical column is chosen. A 2 m section is coupled in front of the analytical column and this part will be used as a garbage collector.

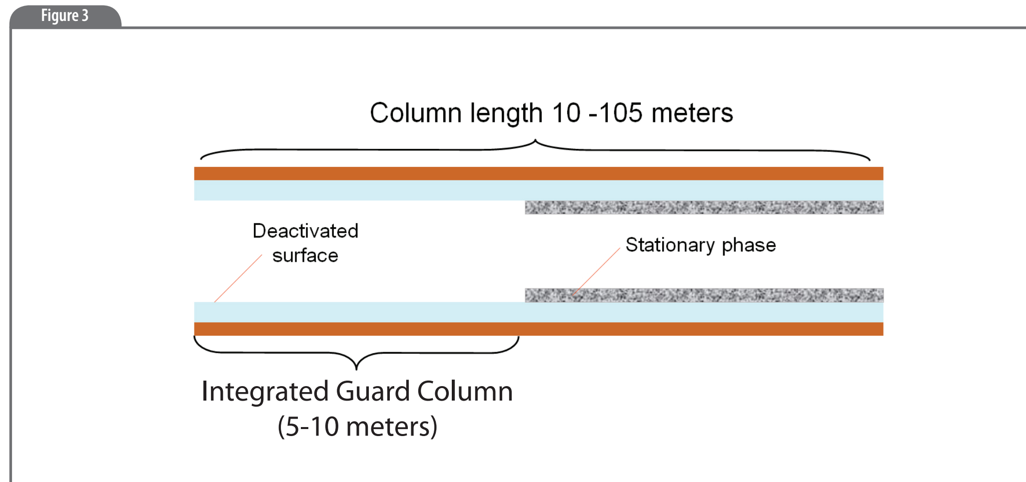

Figure 3: Example of an integrated Guard column. This is possible for a lot of stationary phases and eliminates the use of column coupling. Because columns get shorter, retention time calibration is necessary, which can be avoided by connecting a fixed length guard or coated guard column.

After a number of analyses, when the chromatography or calibration is off, the 2 m section is taken off and replaced with a new 2 m section. There are several interesting features:

- we always have the same column length, so peaks will always elute at the same retention time
- The coated guard column has the same selectivity as the analytical column, so peaks will elute at predictable positions
- We can cut 2 m sections from a second column which has the identical part as the one used for the analysis. From a 30 m column we get 15 coated guard columns... not a bad deal.

The most important advantage is that because this guard columns is coated, it has more capacity to deal with contamination/activity. The coated guard column requires a higher elution temperature, meaning that adsorption, by definition, will always be less.

This type of guard column can used for any type of method. Some users even use less sample preparation as column protection is very predictable and easy to implement.

This article was written by Jaap de Zeeuw. Jaap is a GC specialist working for Restek.