Peak Tailing in GC Trace Analysis

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In chromatography the analysis methods are becoming more and more challenging. Lower detection limits are required especially if quantification is required at trace levels. As soon as activity develops in a GC system, the first component that starts to loose response, will be ones that have polar functionality. This can be hydroxyl, amine, carboxyl groups or combinations. Peaks usually start to tail and even retention times can change.

To optimize a GC system for trace analysis of a challenging compound, one needs to optimize all steps. It starts with finding the correct extraction methodology, to isolate (and concentrate) the target compounds of interest. We need to work very clean and use highly inert labware and clean chemicals. Once the sample is ready for GC analysis we need to minimize the activity in all parts of the GC system. Most critical is the injection port, but also the column and detection connections are important.

The injection port

90% of the challenges in gas chromatography are related with the injection of the sample. If peaks are not symmetrical it means there is adsorption (or retention) process within the injection port.

Figure 1

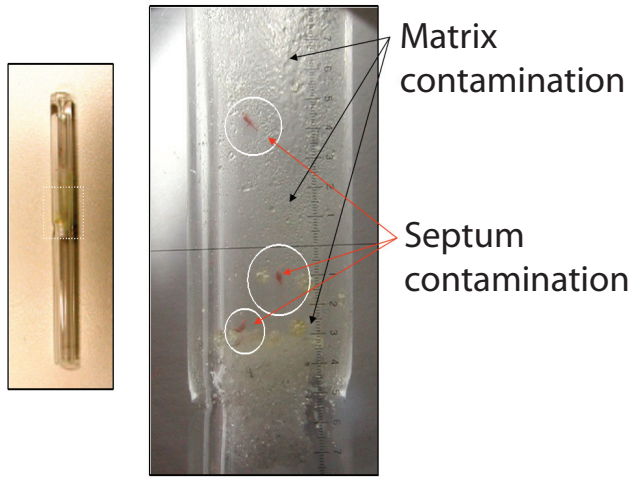


Figure 1: Matrix as well as septum particles are accumulating in the liner. This will cause adsorption/retention and will reduce peak height even before the component is injected onto the column.

Figure 2

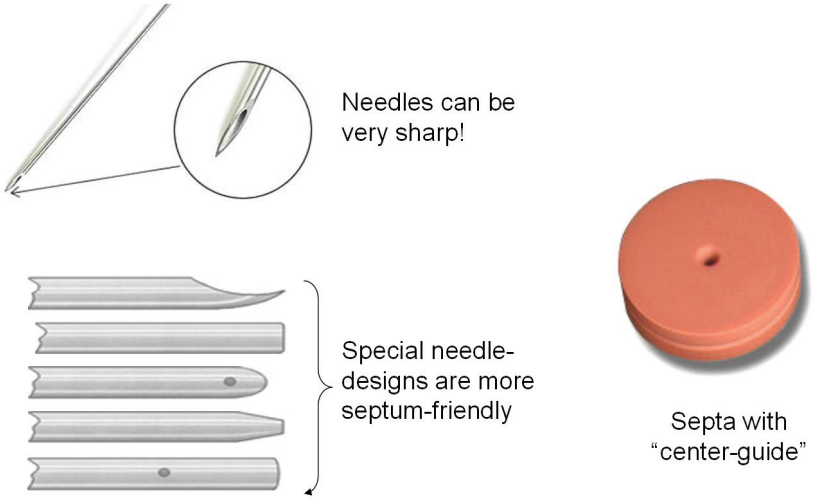


Figure 2: Needles are sharp. Reduce septum ripping by using round-top needles and new generation septa, for instance with center guide.

Adsorption/retention is caused by activity, which can be formed in the liner by:

1. Hydrolysis of the deactivated liner surface

Popular liner deactivations are siloxane or Siltek® based. When moisture is present in the sample or the carrier gas, this will hydrolize the siloxane deactivation, forming silanol groups. As the liner is at high temperature, this process will exponentially increase with temperature. It is important is to use clean carrier gas, preferably filtered for water and oxygen. If samples

contain water, use, lowest possible liner temperatures and inject small absolute sample size

2. Hydrolysis of deactivated glass wool

The same as for the liner, but with an even higher impact is the glass wool. Glass wool is used to increase the surface area and heat capacity of liners, so the evaporation process will be very efficient. Active glass wool is a known problem maker for polar compounds. Also, here activity development can be decreased using small injection, volumes and lower temperatures. A better solution is to use a liner without glass wool, but reproducibility will be more challenging

3. Contamination of the liner

If repeated injections are performed, the liner will become contaminated by the sample matrix (figure 1). This level of contamination will increase after each injection and it can affect the injection quality. If liners have to be replaced to often, one can increase life time by injecting a smaller absolute amount.

For instance, if the method prescribed to inject 1 µL with a split of 1:100, It is better to inject 0.5 µL with a split of 1:50. In this way we inject the same amount onto the column, but we reduced the contamination of the liner by 50%.

Another important contamination factor is the septum. As injections are performed, particles of septa

Figure 3

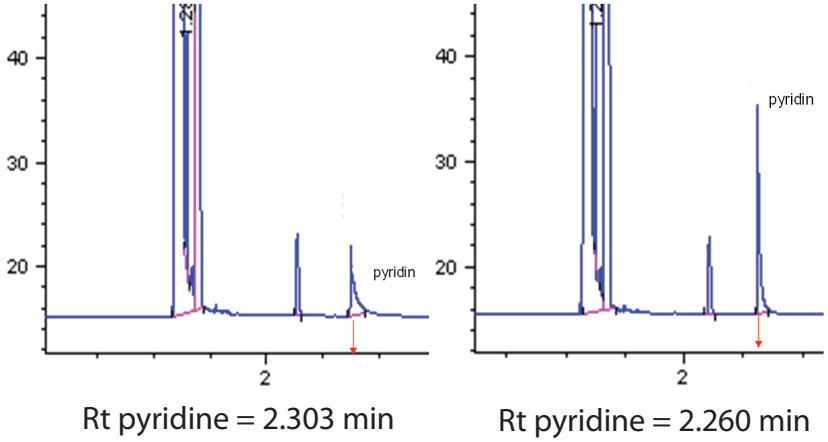
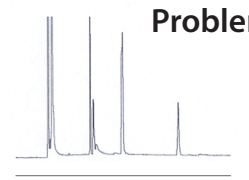


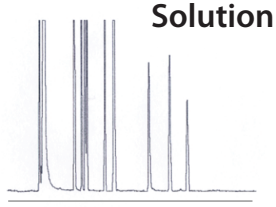
Figure 3: For trace analysis of polar compounds, the column must be well deactivated.

Figure 4



Problem

- Only hydrocarbon peaks elute
- Low response for compounds
- No elution of alcohols, esters, amines, phenols



Solution

Solution: Removal of 60 cm column and replacement of septum and liner

Height of signal completley restored!

Figure 4: Activity development is happening in 95% of the cases at the inlet side. By cutting off this section, the chromatography is fully restored.

may be ripped off, ending up in the liner. Such particles are pure polydimethyl siloxane, which will not only retain the components, but also will generate an on-going stream of septum bleed products, that are injected into the column. This will cause ghost peaks and higher backgrounds. There are solutions available, such as septa with a center guide, which can be used with special design needles, or one can use a special seal like those offered by Merlin or Gerstel.

4. Activation of the column part in the injection port

The column that is installed in the injection port, is also always exposed to the high temperatures. It may very well be possible that this part is oxidized/hydrolized, causing a change of peak shape. For instance, polyethylene glycol phases cannot be used higher then 250 °C as they will decompose. Injection temperature should not exceed those limits.

5. Injection port temperature

If the injection port is not heating correctly, the components will not evaporate slowly. As a result injection will be poor, resulting in discrimination/tailing. The temperature must be checked.

The Analytical Column

For separation of polar analytes, a well deactivated column is required. Commercial columns can vary, especially when polar components are measured at trace levels. Figure 3 shows a pyridine peak on 2

Figure 5

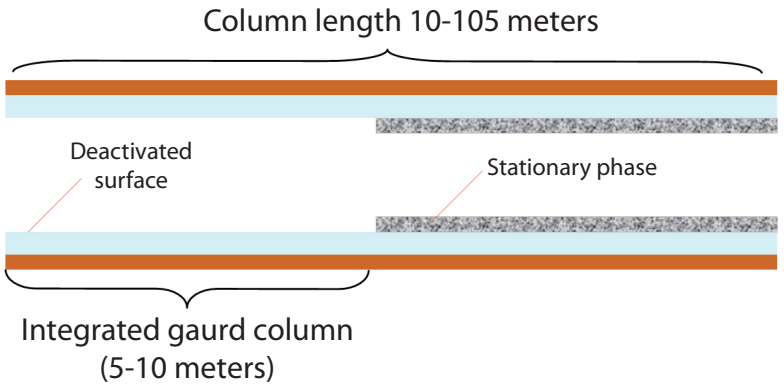


Figure 5: Making the guard column part of the analytical column.

different column types, showing a big difference in peak response. Such activity will reduce sensitivity and can cause identification challenges as peaks will not elute at the correct retention times.

The response for tailing components can be improved by running the application at a higher oven temperature as adsorption effects will be reduced. For the same reason one can choose a column with a thicker film. Additionally, thicker films will have better shielding of active sites, resulting in improved peak symmetry.

When the first analysis shows an acceptable peak shape, but with increased number of samples the peak becomes lower and peak shape deteriorates, it can be the column inlet that is developing activity. Figure 4 shows an example of this where after use, the column developed activity at the inlet section. Only hydrocarbons elute as defined peaks. This is a common issue, but can be resolved simply by cutting of the contaminated section of the analytical column. As can be seen, after cutting 1 coil (60 cm) of the inlet section, the chromatography is completely restored In routine applications, I would recommend you to cut always the same length of the inlet. This can be 20 cm or a full coil (60 cm) off the column. As the column gets a little shorter, the retention times will also change by a few seconds. If the cutting of the column is always the same the retention time change can be easily predicted.

If its is known in an application that the column develops activity, one can also use guard columns and position them in front of the analytical column. This can be done by

- coupling a piece of deactivated fused silica in front of the column using a Press-Tight type connection;
- applying integrated guard columns, (see Figure 5), where the guard column in an integrated part of the whole capillary.

Such guard columns can be chosen with any length; typically 5-10 m sections are used. If very aggressive sample-matrices have to be analysed, which are known to destroy columns, one can also use a coated column as the guard. Instead of one column, you can use two. The second column can be used as "pre-column". As this "pre column" is coated it will have more capacity to deal with the aggressive matrix. By keeping the pre-column the same length, the retention times will also be similar when replacing this section. Additionally, it is economical as one can make 15 pre-columns out of a 30 m analytical column.

Detection Port Liners

The detection port liner can cause big problems as this section is often very active. For instance, in a flame ionization detector, when a column is disconnected, the FID liner is in direct contact with air. Often the air flow stays on, having a small over-pressure, causing the air to enter the liner via the flame tip. The net result is, that FID lines are often very active. Normally this is not a problem if the column is installed correctly. By positioning the capillary just below the detection point eliminates the activity of the liner completely. Therefore, it is important to know the installation distance for each detection port liner.

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