



Ghost Peaks in Gas Chromatography Part I:

The Carrier Gas and Carrier Gas Lines

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We get always a number of inquiries from customers that see peaks show up in their chromatogram when they do not inject them. There are several sources for these “ghost peaks” which we will discuss in several articles.

What are Ghost Peaks?

“A ghost peak is a peak that appears at a position where we do not expect a peak”. It is a component that shows up in the system and it may show up everywhere in the chromatogram. Sometimes it is a sharp peak, sometimes it's a broad peak or a “hump” and sometimes it is a rising baseline.

Some of the key origins for ghost peaks are:

- the purity of the carrier gas
- using non-GC grade carrier gas tubing

- memory effects due to back flash
- contamination of injection port
- Injection port reactivity
- Septum, O-rings
- Analytical column bleed
- Column installation
- Sample contamination from syringe, rinse vials, vial-septa or gloves.

In this part we will focus on the carrier gas and the gas lines.

Carrier Gas Purity

The carrier gas must be of high purity. On average attention is paid to the residual oxygen and moisture

content of the carrier gas. Oxygen can oxidize surfaces of liners and columns but this usually happens at higher temperatures. Water initiates hydrolyzation that can also start at lower temperatures and often relates to the stability of the deactivations used. Hydrolyzation of liner and glass wool surfaces will create adsorption sites that interact with polar analytes when doing an injection. The result is lower response, peak broadening and even discrimination and reactivity can be enhanced. Hydrolyzation of the stationary phase is a bigger problem

as terminal silanol groups are formed that will initiate phase degradation (see Figure 1). This reaction is also temperature dependent. Most Rtx/Rxi phases can deal very well with water, if analysed as compound or introduced as the matrix. Water will elute at low oven temperatures. If water is in the carrier gas, it will also be introduced when the column is at high temperature, initiating the hydrolyzation. For the same reason, one must check carefully for leaks at column connections and also the septum.

Figure 1

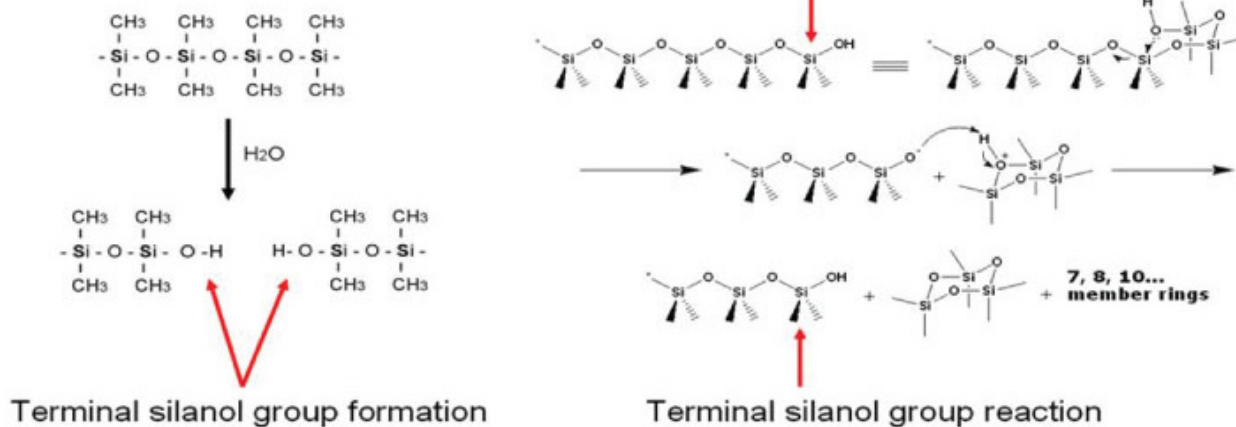


Figure 1: Formation and reactivity of silanol groups.

Figure 2

Figure 2: Carrier gas purification for O_2 , H_2O and hydrocarbon removal. Most popular are the cartridge filters: System remains pressurized; they have indicators and filter exchange is very fast.

Purification of Carrier Gas

One can choose ultrapure carrier gas and assume a perfect sealed gas distribution system. There is practically always a risk that carrier gases get contaminated. Each time a cylinder is changed some air can enter the system. Also there are many fittings/couplings used in gas lines that are sources for leaks. If systems are not used, there is often back diffusion of air into the gas lines. Concentration gradients are very strong drivers for diffusion.

It is highly recommended to use filtration devices to clean carrier gas. There are different systems available varying from in-line filters to cartridge filters, indicating and non-indicating. The cartridge filters have become quite popular as filter exchange is very fast and there is no down time

because the main gas lines remain pressurized. An example system is shown in Figure 2. Such systems are available for filtering carrier gas for oxygen and moisture. Also charcoal filters can be beneficial, especially for filtering FID gases. Charcoal may also be used for carrier gas line purification in case hydrocarbon contamination is suspected. This can be the case when gas lines are used that are not cleaned thoroughly. Although molecular sieve filters have a huge trapping effect for water and linear hydrocarbons, they do not have high retention for branched hydrocarbons. Branched hydrocarbons will only be retained by the outer surface of the molecular sieve 5A particles, which means they will elute very fast (for example: on molecular sieve 5A iso-butane even elutes before nitrogen at $50^\circ C$, while n-butane elutes at $300^\circ C$).

Filters are best placed as close as possible to the instrument. Try always to maintain a positive flow through the filters. Instruments that are "shut-off" sometimes show back-diffusion of air through regulators, contaminating the gas lines. Filter life time is usually about one year. Although filters can be "indicating" via a change of colour, this often is not checked due to the lab's workload. If applicable, it's a good habit to replace all filters during a period when workload is not that big.

Carrier Gas Tubing

Normally gas lines do not contain "hydrocarbons" but that is only true

Figure 3

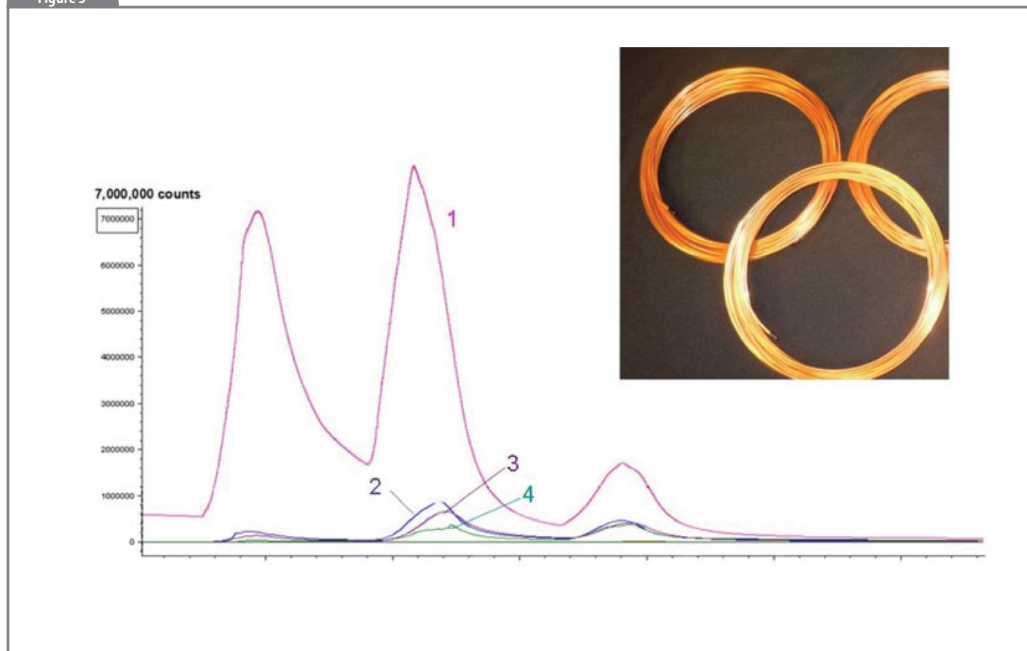


Figure 3: FID bake out of four different batches of copper tubing.

if GC-cleaned tubing is used. In the process of drawing metal tubing, a lot of hydrocarbon-based "greases" are used. As a result metal tubing is strongly contaminated and cleaning is required. Recently a study was done on this as a new source for copper tubing became available. Figure 3 shows a comparison of a "bake out" of similar lengths of copper tubing using FID signal. Note that the scale was 7,000,000 counts. If not removed, these hydrocarbons will accumulate on the columns and cause background and ghost peaks. For new GC lines, make sure that GC-grade tubing is used.

How to Test if a Ghost Peak Comes from Carrier Gas Contamination?

The easiest way to test the carrier gas for hydrocarbon contamination is to trap the components on the GC column and look at the response. In order to do this, the injection port and the GC oven plus the column is cooled down to room temperature. The injector must be cold as this is another big source for ghost peaks, which will be discussed in the next issue. By keeping the injector cold, the contribution will be minimal. When the oven is set at low temperature, the column will act as a "trapping device", meaning that any component that is present or

Figure 4

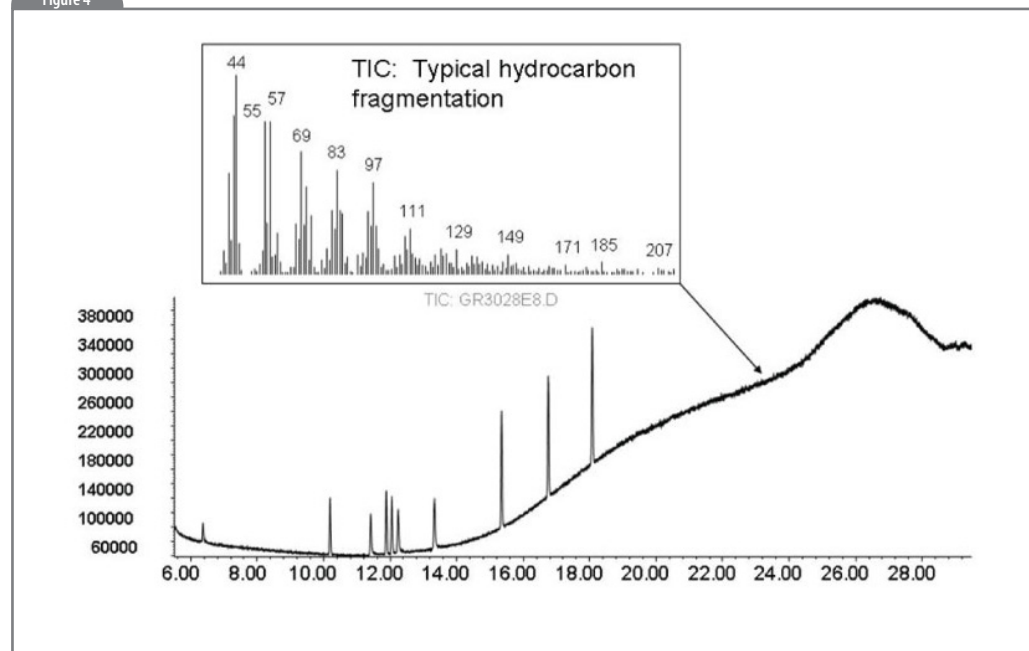


Figure 4: A drift of baseline due to overlapping compounds that are moving to the column caused by back-flash contaminated injection port.

formed in the gas system before the column, will be trapped (and focused) on the GC column. The amount of component will relate to the time and flow that is used during the trapping period. After 10 minutes of "trapping" the oven is programmed to the upper temperature of the application for that GC and the baseline is observed.

After this, the oven is cooled again and the trapping time is repeated but now the oven is kept for a longer time at a low temperature, such as 30 minutes. Again the oven is programmed and the baseline is observed. If there are visible peaks on the baseline and these peaks are 3x higher in the second run,

contaminants are coming from before the injection system.

Filters have to be checked and maybe also the tubing from the filter to the GC inlet.

There may also be another reason for contamination in the carrier gas line: this is called back-flash and here often the full range of (heavier) components show up that are typically analysed on this GC. This is also often called "memory-effect".

Back-flash

Back-flash occurs when the sample injected exceeds the volume of the liner. The excess sample will be pushed out the liner and can get into

Table 1

Solvent	Expansion factor	Maximum Injection Volume 50% liner volume [μL]		
	250 °C, 73 kPa	1 mm liner	2 mm liner	4 mm liner
Isooctane	153	0.2	0.8	3.3
Toluene	237	0.12	0.5	2.0
Methanol	645	0.05	0.20	0.8
Water	1399	0.02	0.09	0.34

Table1: Maximum injection volume.

the carrier gas line.

Because the carrier gas line is outside the heated zone, the sample components will condense and slowly evaporate. This causes “memory-effects” and also impacts quantification for single analytes. If complex samples are analysed, the ghost peaks all merge together and result in an increase of baseline. Figure 4 shows an example where the injection port was contaminated with hydrocarbon oils. Usually when observing such a baseline, the first reaction is that the column bleeds, but in this case the detector was a MS and the TIC signal showed very recognizable spectra for hydrocarbons. This injection port had to be cleaned and for future work, a smaller amount had to be injected.

Depending on the injection port liner, the maximum injected amount should not be exceeded. The vapour volume of the sample depends mainly on the amount and the molecular weight of the solvent used. Table 1 shows a few maximum amounts related to a 2 and a 4 mm

ID liner. The maximum amount is set to 50% of the liner volume of that solvent at given temperature/pressure. The biggest risk for back-flash is with using the splitted injection.

Cleaning a contaminated injection port is best done using the next steps:

- Remove the analytical column and replace it for a short length of fused silica capillary (2–3 m from an old column with the same diameter);
- Set the carrier gas at a high flow-rate for the column and split line. Also make sure the septum purge is open; (If hydrogen is used, the column end is best positioned outside the oven);
- Heat the injector to a high temperature (325–350 °C) and flush the inlet for 30–60 minutes; Indirectly the carrier gas lines will also be warmer and back-flashed residues will evaporate;
- Cool injector and replace seals, liner, O-ring and septum.
- Connect the column again and also condition the column;

- If the ghost peaks still show up, you may extend the flushing time.

Jaap de Zeeuw studied six years of chemistry and graduated in 1979. Jaap has 33 years' experience in GC capillary technology and has developed many PLOT columns as well as bonded-phase columns. He is also the originator for simple concepts for fast GC–MS using a high vacuum inside the capillary column. He has published more than 100 publications in the field of GC on column technology and application. He worked for 27 years for Chrompack/Varian and for the last six years has served as an international specialist on gas chromatography for Restek in The Netherlands.

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