

Ghost Peaks in Gas Chromatography Part 4:

Reactivity in The Column While Doing Separations

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In the last issues we discussed possible sources for ghost peaks related to the carrier gas, gas lines, injection port and parts, degradation and the column. Here we move onto several other contributions that are not as obvious as the former options.

Activation of Stationary Phase

One of the problems that can happen in GC and what many users do not realize, is that active sites can be formed while keeping the column at low temperature.

This will happen in:

- Injection ports: if the injection port temperature is not reduced when maintenance is done.
- Detection ports: if the detector is "hot", any water/oxygen can immediately create activity;
- Transfer lines: often the transfer line temperature is not reduced when doing maintenance.

Such activated surfaces can also cause reactivity, depending on the analyte.

An example is shown in Figure 1. Here an air sample was injected

on a porous polymer PLOT type column. The detector was a flame ionization detector, meaning that air does not normally produce a signal. Despite this a huge ghost peak was observed in the beginning of the chromatogram, at a retention time where the "air" peak elutes. Knowing that FID does not detect air, this ghost peak was difficult to explain.

After cutting 20 cm from the outlet of the column, the ghost peak was gone. The last 20 cm of column was highly activated and produced the "ghost peak".

This is a classic example of phase oxidation initiated by back diffusion of detector gases.

This column was used in a system, where the carrier gas was turned off and the detector gases remained

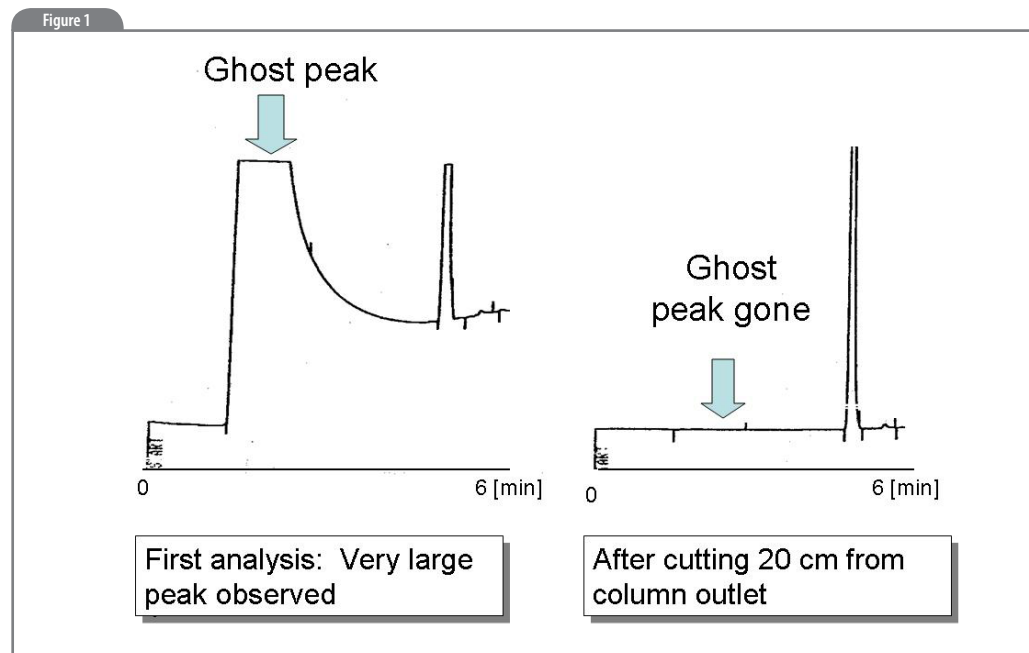


Figure 1: Ghost peak formed by reaction of activated porous polymer PLOT with air at the column outlet. Column performance was restored after removing the last 20 cm of the column.

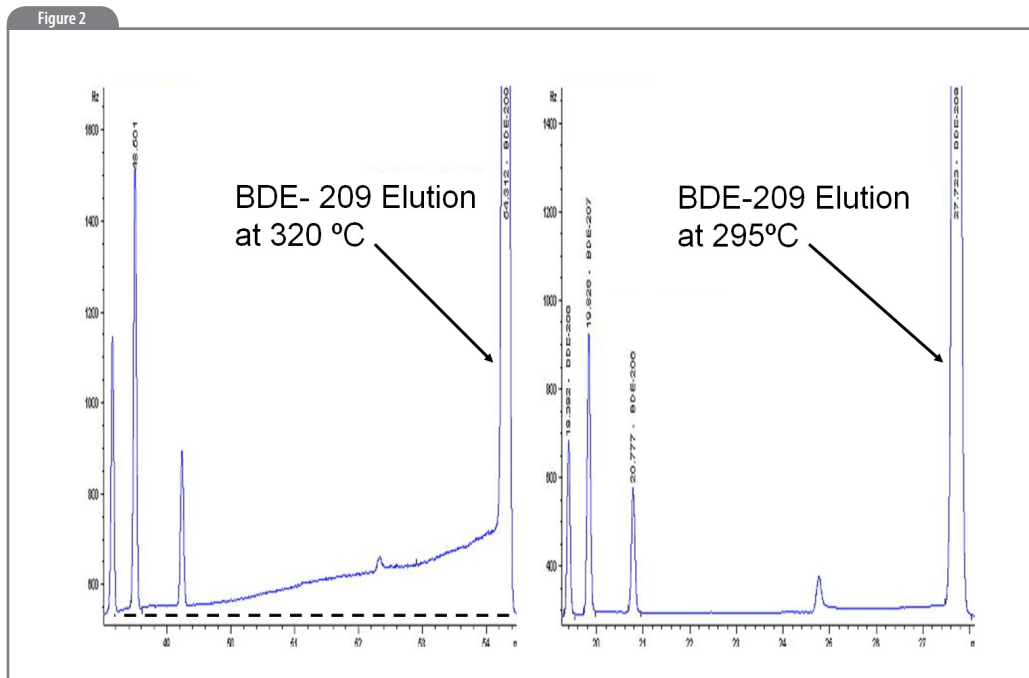


Figure 2: Analysis of flame retardants according to EPA 1614. If the elution temperature is high, there is a lot of degradation. Using GC conditions where the BDE-209 elutes at lower temperature, will decrease decomposition, resulting in better response and better reproducibility. Column: 30 m x 0.25 mm Rtx-1614, $df = 0.10 \mu\text{m}$. See reference 1.

on, while the detector was at a high temperature. As there is always an over pressure in the detector, the H_2/air gas mixture was entering the outlet of the PLOT column. As the detector was hot, the stationary phase was activated.

The result was, that the moment the air peak passed this section of the PLOT column, the stationary phase was decomposing, forming a degradation product, that was measured in the FID.

What was done here was the “indirect measurement of oxygen in a gas mixture via reaction gas

chromatography, using the response of degradation products of in-situ activated porous polymers making FID detection possible”. This may be a nice topic for some future investigation. Our key learning here is that this can also happen with any system in the lab. Always make sure that detector gases and temperature are switched off before stopping the flow through a capillary.

Degradation of Components During Separation

A number of components are known to be difficult to chromatograph

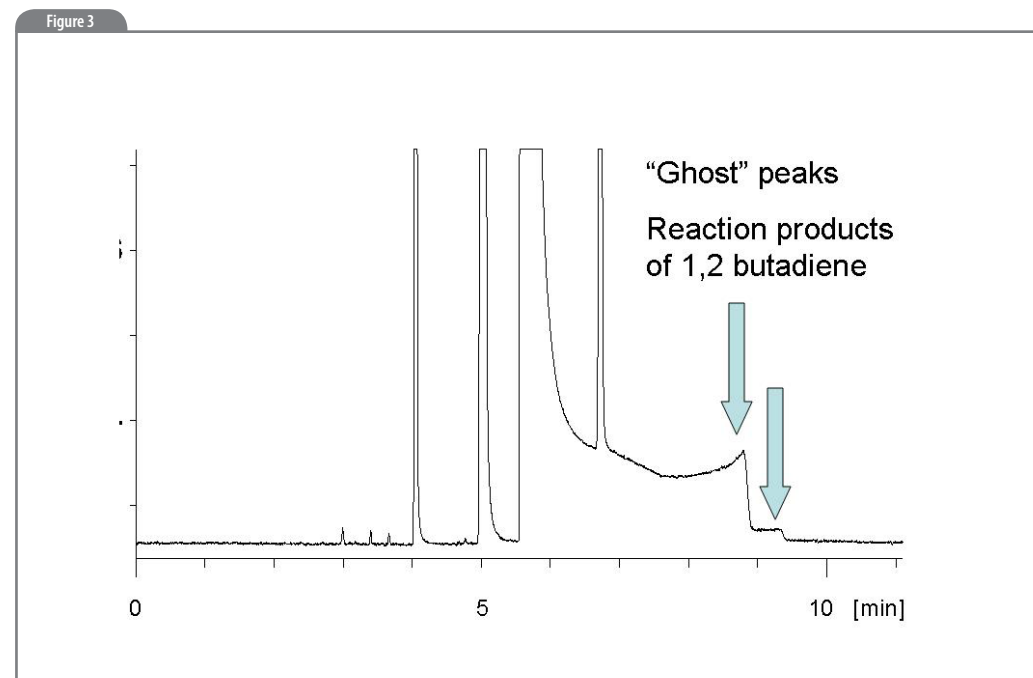


Figure 3: Reactivity of 1,2-butadiene while moving through an alumina capillary column.

correctly. The result is that such components will start to decompose the moment they are entering the column. The injection technique can be optimized to minimize the degradation (by using cold on-column or a PTV). Degradation reactions are temperature dependent and by using a temperature programmed analysis, the degradation will increase as the component travels through the column. The resulting chromatogram will show the decomposition product with an elevated base line that ends in the original component. Some examples follow:

Reactivity: Brominated Flame Retardants

These compounds are flame retardants and are –per definition– not very temperature stable. There is an EPA method developed, (EPA 1614), to measure these compounds. Already in the method the BDE-209, shows a very strange form (see Figure 2). There is strange elevation of the base line which runs into the BDE-209 peak. The fact that there is not a big signal for the decomposition product is because this process starts at higher temperatures when the peak is already “moving” with a

Figure 4

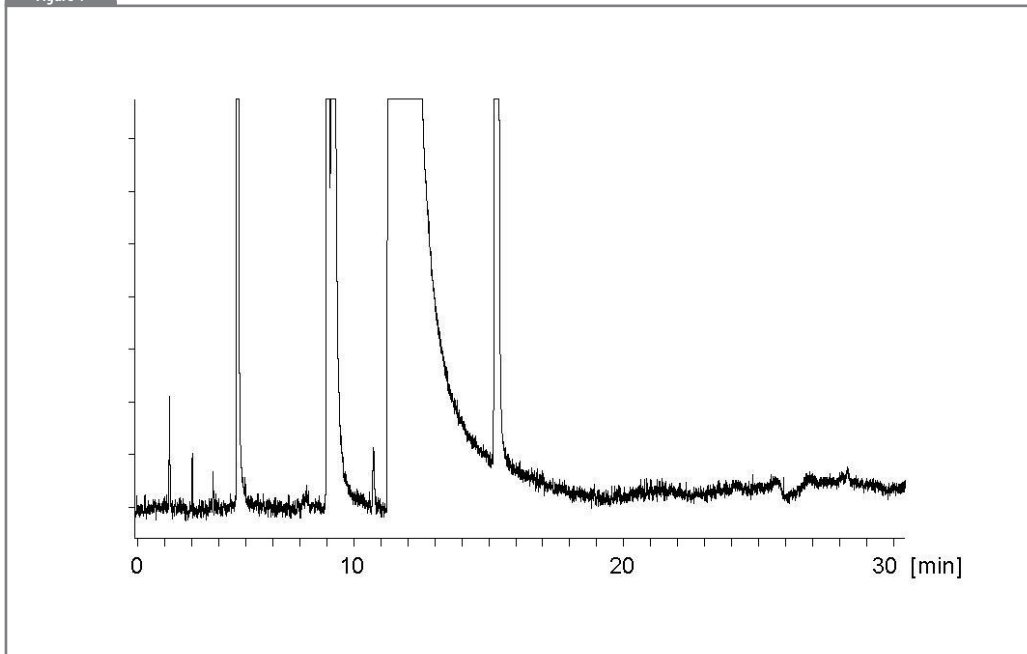


Figure 4: The same 1,2-butadiene sample as in Figure 3, but analysed at 110 °C. Decomposition is significant less. Analysis time is much longer.

certain speed. The BDE-209 elutes here at 320 °C. If the conditions of analysis are changed to make this component elute at lower temperature, the decomposition is much reduced (see reference 1).

There are several ways to change the conditions to realize lower elution temperatures:

Use higher flow-rate, a flow programme or a pressure programme: Already doubling the optimal flow-rate, the elution temperatures will already be reduced by 20–25 °C. This usually is very effective with non-ms detection systems. The higher flow will cause some loss of efficiency, so it may

be considered to start the pressure program after the key separations are obtained.

Use a slower temperature programme: Slower programmes will result in a lower elution temperature

Use hydrogen as the carrier gas instead of helium: Due to the higher optimal flow-rate, we can benefit from lower elution temperatures, while working under optimal conditions. Here safety issues must be dealt with.

Use columns with thinner films: Elution temperature is directly dependent on the amount of stationary phase (film thickness). Use a 0.10 µm film instead of 0.25 µm.

Use a capillary with a larger ID

Figure 5

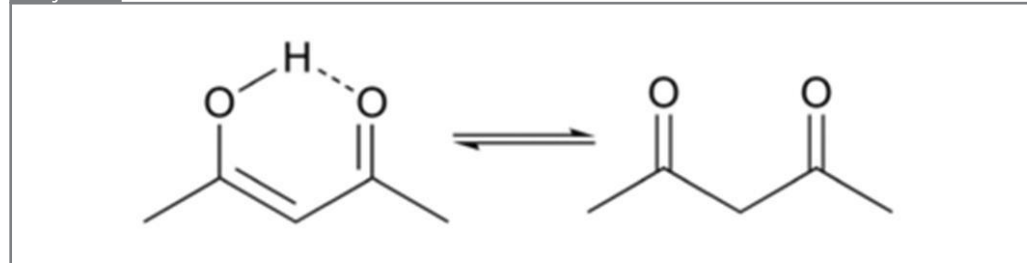


Figure 5: Tautomers of 2,3-pentadione. These components are both present in a “pure” sample of pentadione.

(0.32 mm instead of 0.25 mm): A 0.32 mm capillary with 0.1 µm film will have a higher phase ratio, which results again in a lower elution temperature. The 0.32 mm column, however, will be lower in efficiency, so some separation efficiency may be lost. If the target components elute with sufficient resolution from the neighbours, you can also consider using a pressure or flow programme. This is very effective with 0.32 mm columns.

Reactivity: unsaturated hydrocarbons: 1,2-butadiene:

1,2-butadiene is an unstable component that easily shows reactivity. GC analysis can be done using polydimethyl siloxane phases, like Rtx-1, providing lowest elution temperatures. Selectivity for unsaturated hydrocarbons is much better using alumina. The downside of alumina is, that it offers high retention and the alumina adsorbent can contain impurities that can act as catalysts.

Figure 3 shows how this component

chromatographs on an active alumina column at 150 °C. There are two products formed that may be ethyl acetylene and/or dimethyl acetylene (crotonylene). This is not positively identified but they are the only components we can expect to elute on these positions using an alumina column.

The formation of these components is very temperature dependent. By reducing the elution temperature the degradation reaction can be reduced. Figure 4 shows the same sample, but now at 110 °C isothermally. Decomposition is almost completely prevented. There is a price to pay and that is analysis time. Here a pressure programme may help to reduce the run time. See also reference 2.

Reactivity: Tautomer Formation

Some component structures can convert in another form that has a more favourable energy/entropy level. This is a pure intermolecular process and is called tautomer interconversion. I don't know if it's physical or chemical but it's a rearrangement

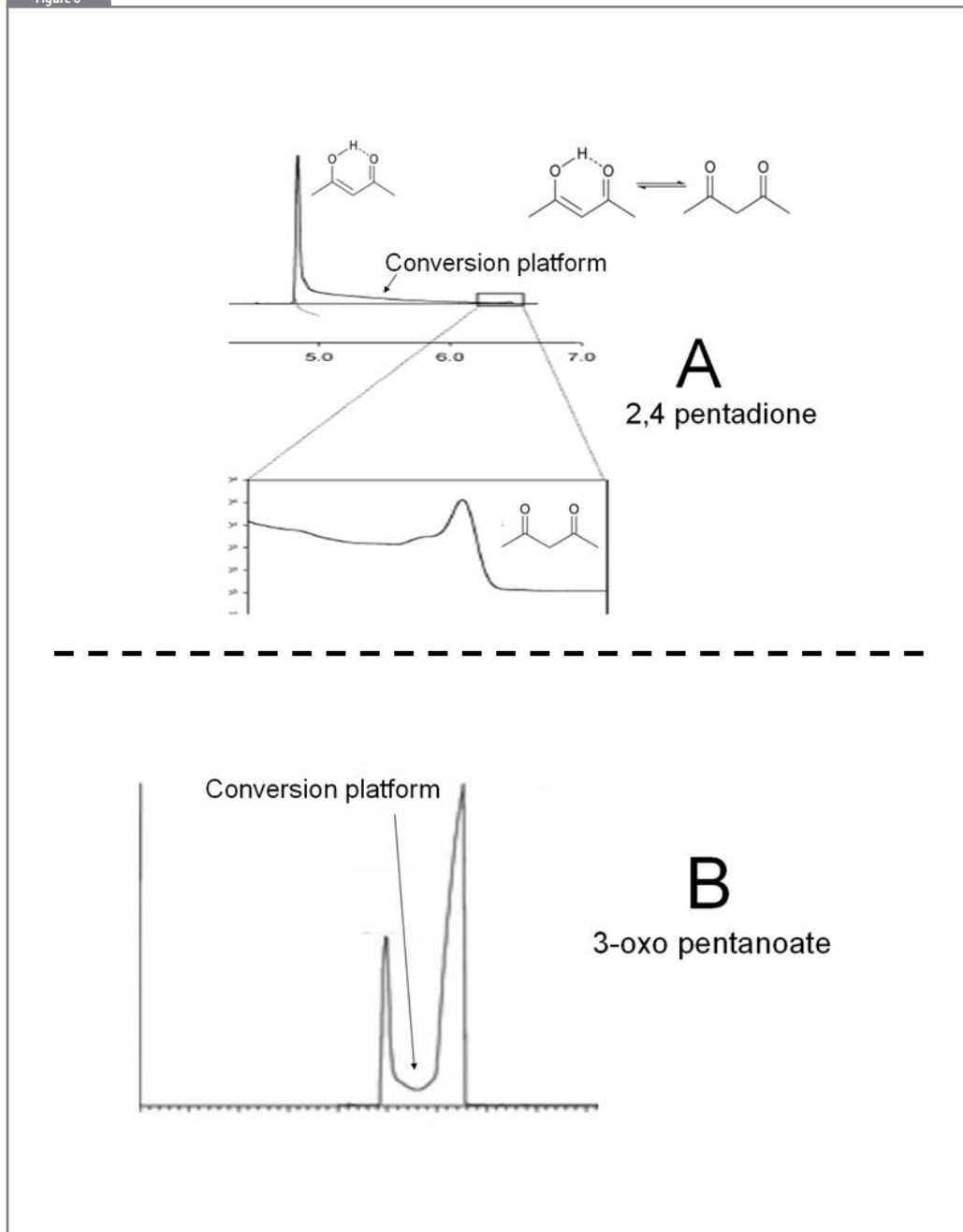


Figure 6: Tautomers of 2,4 pentadione, separated via GC. There is a “conversion” platform between both peaks.

of atoms within a molecule. Enol-keto is one of the most known system. Such components can exist next to each other and will show up in GC analysis as two separate peaks. Depending on the temperature and stationary phase, the equilibrium can change. Figure 5 shows the tautomers of 2,4 pentadione. Analysing such a mixture via GC will result in two peaks, but as these components can easily convert into the other, also a reaction platform will be formed, see Figure 6 [3, 4]. This platform will change when different conditions are applied.

Maximizing Signal/Area and Minimize Breakdown for Thermally Labile Compounds

To maximize the signal or the peak area for thermally labile compounds the following general rules must be considered.

- use the lowest possible injection port temperature
- use the highest possible flow-rate (use 0.32 mm columns)
- use a pressure pulse during injection (only with splitless)
- use inert liners (siltek or siloxane deactivated)
- be careful with glass wool packings as these may initiate decomposition

This way we can minimize thermal stress. An alternate injection technique to consider is the programmed temperature injection or PTV. Here the sample is introduced

in a cold liner and flash evaporated when the injector is heated. It's not as good as the cold-on-column but better than the splitless technique.

References

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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 of 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.