



Ghost Peaks in Gas Chromatography Part 2:

The Injection Port

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In the last issue we discussed possible sources for ghost peaks related to the carrier gas and the gas lines. Here we move into the injection port itself as this is a big source for “trouble”. The injection of the sample is responsible for > 80% of the “troubles” that are experienced in gas chromatography. In the process of rapid evaporation of the sample, several things can go wrong.

In last article we discussed the problem of “flash back”, which is a serious source for creating ghost peaks or “carryover”. It is important not to exceed the liner volume when the sample is introduced.

Injection Port Contamination

When samples are introduced the injection port will always get contaminated. It depends on the cleanliness of the samples but there are a lot of applications where samples with a “strong” matrix are

injected and quantification is done for the volatile parts. Sometimes the sample will leave a memory in the injection port after a few injections. Figure 1 provides an example, which shows a liner after a few analyses. You can see not only the septum particles but also the residues of the sample matrix. Using such contaminated liners will be a perfect source for ghost peaks. It’s very important to replace or clean the liners systematically. Of course, practically you would only do that when the

data does not line up. This is scary as you never tackle the problem BEFORE it shows up. Application of preventive maintenance is a golden rule in routine analysis labs.

Septa

The septum is a big problem in gas chromatography. The septum is used to seal the injection port and it is an interface for injecting the sample. The challenge is that septa are made of polydimethylsiloxane, which is a similar polymer to that used for stationary

phases. When heated, such siloxane polymers will form degradation products that will show up in the GC analysis. Such products are often seen as “ghost peaks”. Figure 2 shows an example of a bleeding septum where a linear series of siloxanes are detected.

There is an option in most gas chromatographs that is called “septum purge” or “septum flush”. This option allows a flow of 3–4 mL/min carrier gas to be set along the septum (the top of the split/splitless injection port), and this flow will take away

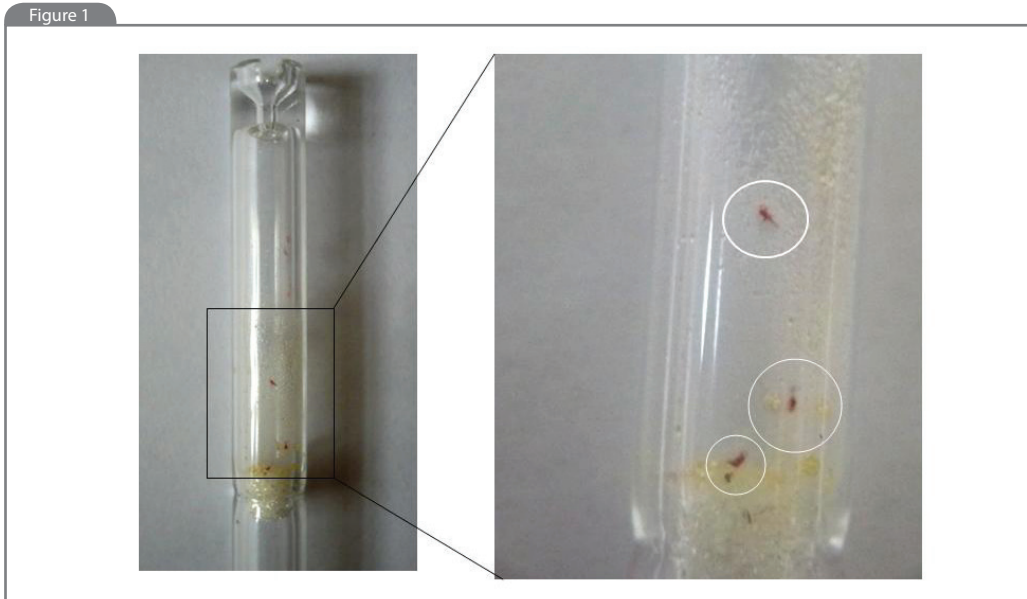


Figure 1: Contaminated liner with residue of sample matrix and septa particles that are ripped-off and are deposited in the liner.

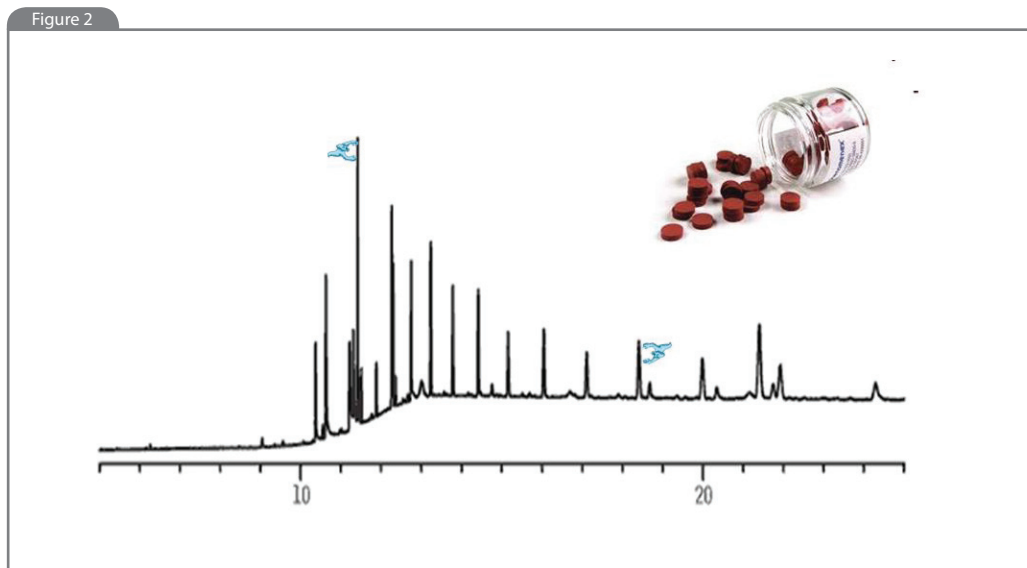


Figure 2: Ghost peaks of bleed products generated by a bleeding septum; Injection port at 300 °C; No injection; septum purge off; Oven at 40 °C for 60 minutes;

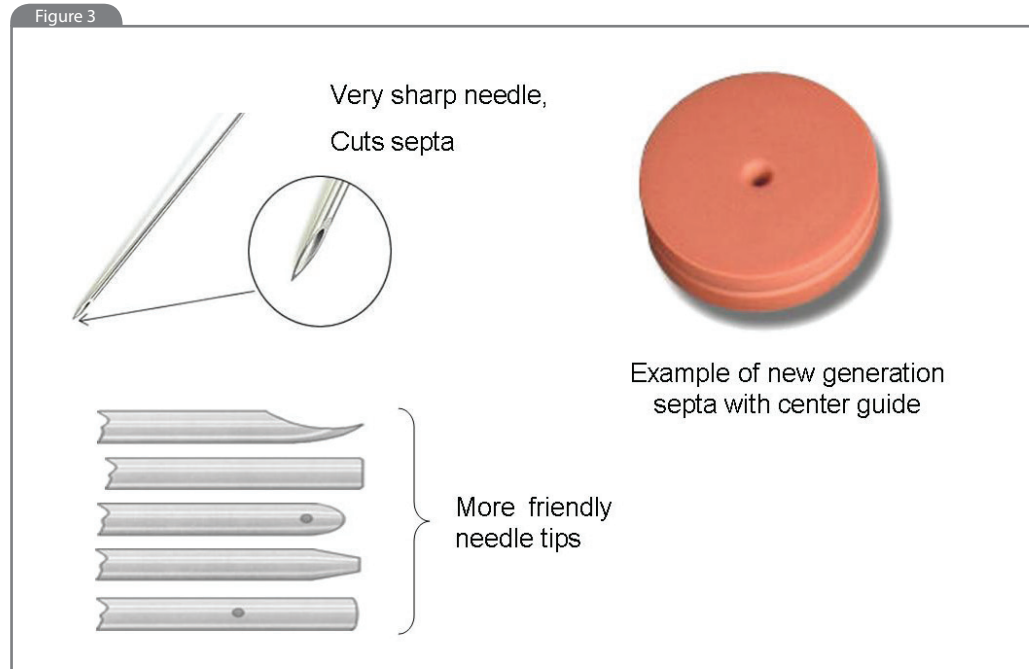


Figure 3: New generation septa with a centre guide to reduce septum particle rip-off. Best used with “friendly” needles without a sharp tip. More reading:

the majority of the septum bleeding products.

When using split or splitless injection it is highly recommended to use this option. There should be no loss of sample analytes, as this flow is only passing along the top of the liner.

Sometimes septa particles are ripped off and are deposited in the liner (Figure 1). Such particles will cause not only siloxane “ghost-peaks”, they will also cause discrimination during injection.

As the injector is hot, these septa particles will start to decompose, generating siloxane bleed, which will show up a series of ghost-peaks

(as in Figure 2). A secondary effect is, that the injection will be delayed as the components introduced, will also dissolve in these septum particles (it is the same type polymer that is used as a stationary phase). This will broaden the injection band and results in broader peaks and reduced sensitivity. This is especially a challenge when doing split injections.

Such septum particles may be avoided using new generation septa and using less sharp needle tips (Figure 3). There are septa available with a “centre-guide”, which can help [5]. Note that this centre guide can also create a problem when operating at higher pressures as the septum can leak

Figure 4



Split-line of after 300 splitted injections soil extract

A



After cleaning with syringe with methylene chloride

B

Figure 4: The split-line is a potential source for ghost peaks and memory effects. A: Split line after 300 split injections. Liner is near blocked; B: after

Figure 5

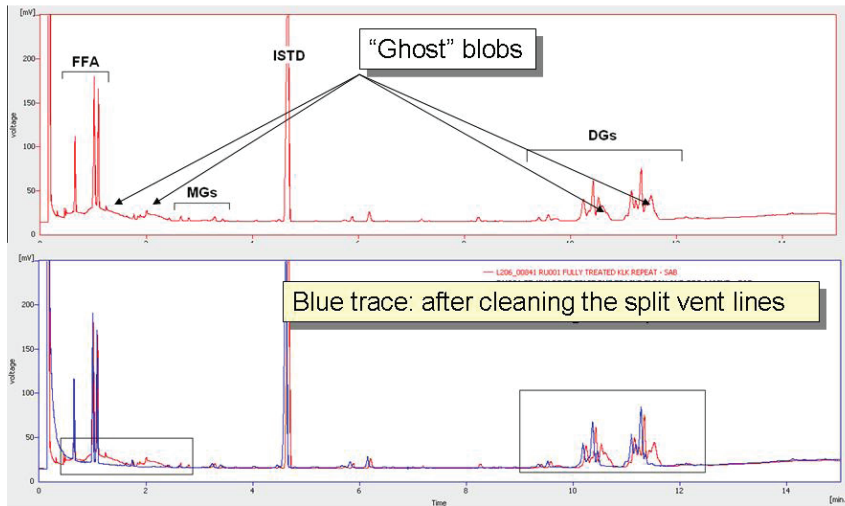


Figure 5: Customer experience of contamination of split line; Thanks to Stephen Botfield from Britannia food ingredients for sharing. Details see ref.

and part of the sample may flush away.

Contamination of The Split Line

While an injection port is usually hot, and the sample is often injected in a split mode, it is expected that all the "waste" sample is removed via the split line. This is a frequent mistake that causes a lot of trouble. When a split injection is used, the split sample will leave via the split-line of the

injection port. The split-line is not heated so a challenge develops here. Figure 4a shows the inside of a split line that was used after a 300 split analysis of an extract. The split line almost completely blocked the split line. In such cases you may wonder how correct are your readings on your digital displays? Figure 4b shows the same line after cleaning with methylene chloride.

Figure 6

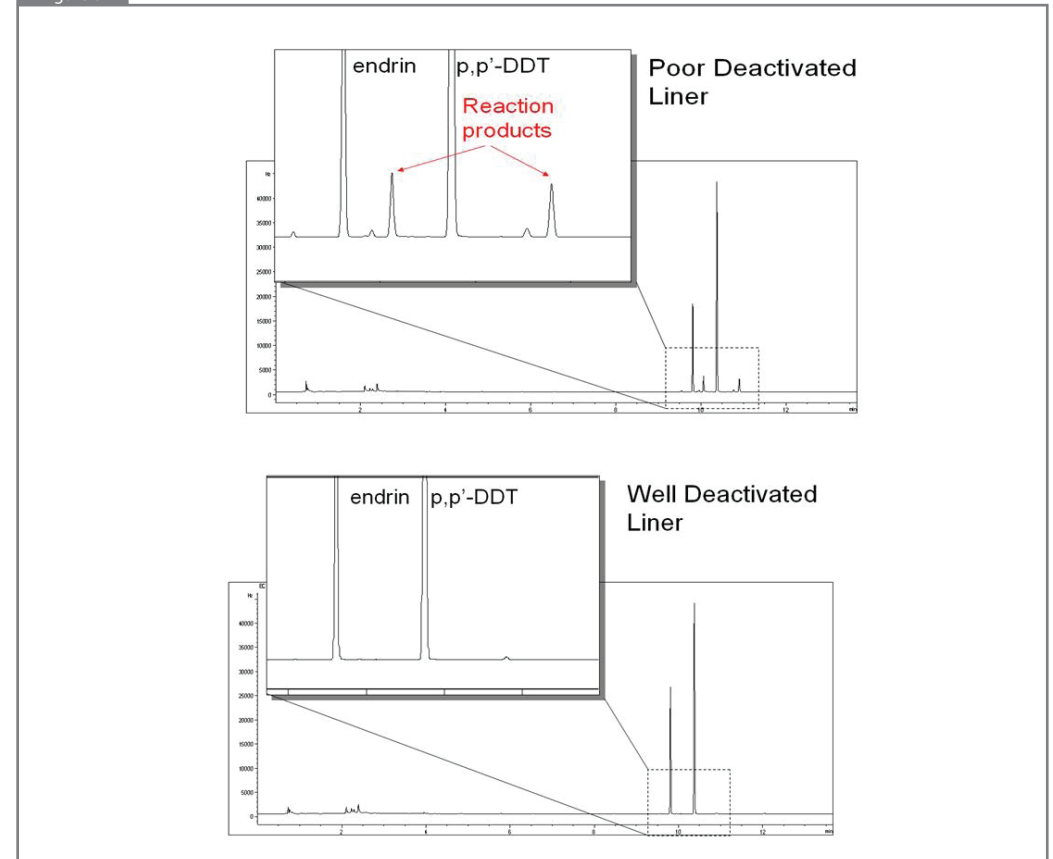


Figure 6: Ghost peaks formed by degradation of components in hot injection ports. Endrin and DDT are known to decompose depending on the activity of liner and seals. Chromatogram courtesy: Scott Grossman, Restek Corporation.

Figure 7

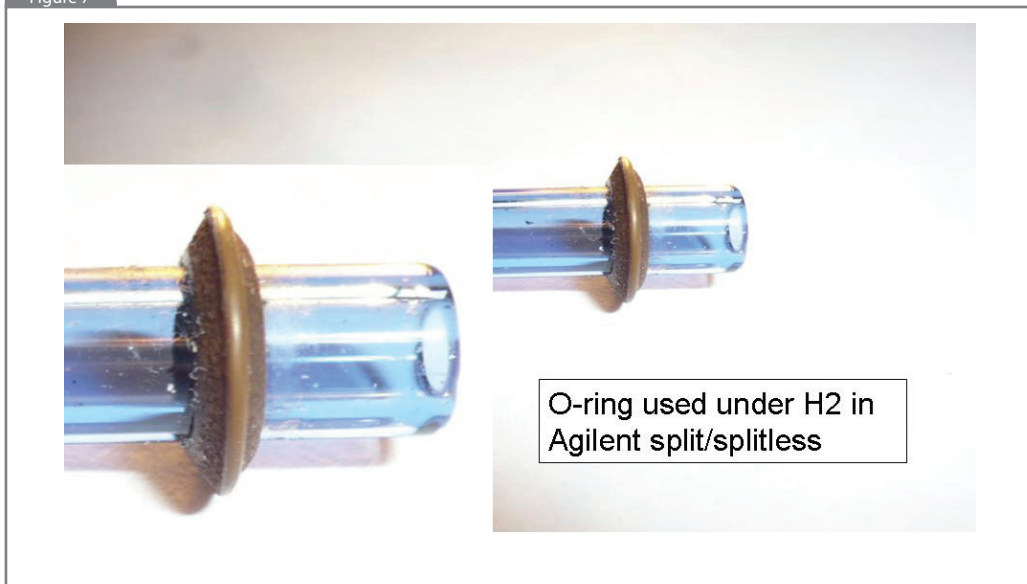


Figure 7: Deformation of “O”-ring when used with hydrogen as the carrier gas. Helium did not show this effect.

Figure 8

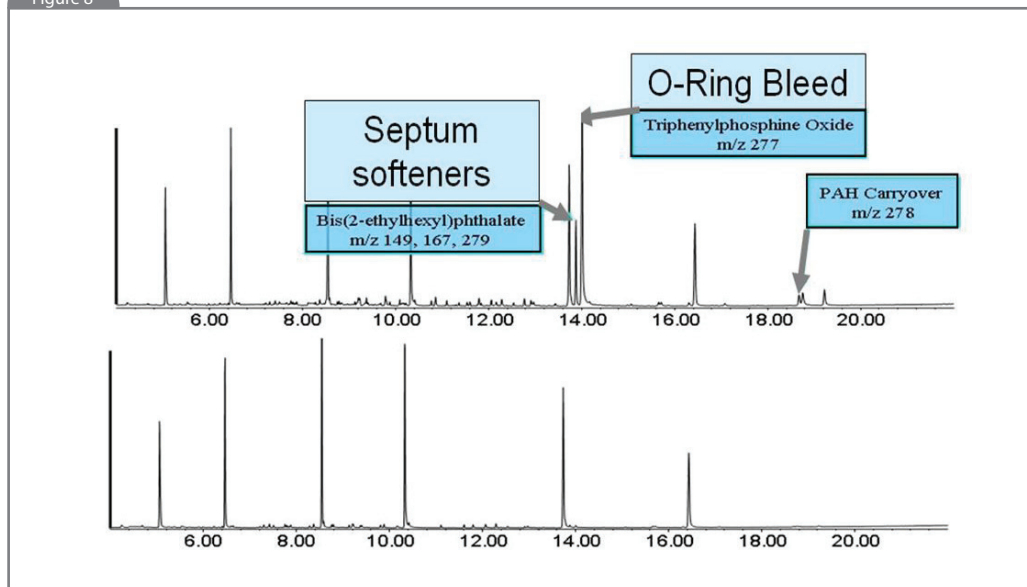


Figure 8: Ghost peaks produced by a dirty injection port. Showing peaks for triphenyl phosphine oxide (m/z 279), phthalates (m/z 149, 167 and 277) and PAH (m/z 278). Full story, see ref. [4].

This is a big source for ghost peaks. Although the sample may deposit in the split (exit) of the injection port, during the injection some residue can always evaporate and enter the column. This can be assigned as “carry over” or “memory effect”, but it is contamination of the injection port. Figure 5 shows a typical challenge of a customer that had this problem. The “ghost peaks” appeared as a broad ghost peak/base line rise. After cleaning the split line, these ghost peaks disappeared.

Note that the sample that is split off is usually trapped in a short column filled with a carbon type adsorbent. That trapping-column needs to be periodically replaced as it will become saturated and all the split products will end up in the laboratory.

Reactivity of The Inlet

This will only happen when analysing “sensitive” compounds. Some components may react in the injection port and form another component. Some methods are even based on this reactivity but it’s quite challenging for quantitative analysis. If a component decomposes in the injection port, the GC analysis will often show multiple peaks: the original and the degradation products.

We use the thermal degradation of some pesticides, to measure deactivation efficiency of deactivated injection ports. For example, pesticides like DDT and endrin are sensitive for activity in the inlet

and when introduced at pg levels, the deactivation quality can be measured. If activity is present the DDT and endrin are converted in their degradation products, which will appear as peaks (see Figure 6). This reactivity is used in our labs and quality control is put in place to test the inertness of Sky-liners. Besides pesticides, other compound classes that are sensitive for injection port decomposition are carbamates [6], explosives and brominated flame retardants.

Often the degradation in the injection port is catalysed by the presence of glass wool. Even deactivated wool does not always eliminate the problem. Often a better solution is to use a liner without wool such as the double gooseneck or the cyclo-splitter.

Other factors that will reduce the injection port decomposition are to reduce injection port temperature and use the shortest transfer time using high flow and pressure pulse. Sometimes using a 0.32 mm column can help as flows can be much higher than used in the 0.25 mm.

“O” – Ring Contamination

Using an Agilent gas chromatograph, the injection port also contains a “O”-ring. This ring prevents the sample from re-entering the liner after injection. The “O” ring is a challenge as it is continuously at high temperature and it is a polymeric material that has to make a good seal. We received customer input that shared issues

with deformed rings in split/splitless injection systems (see Figure 7) which caused injection issues. In this case the “O”-ring deformed and hardened using hydrogen as the carrier gas. It did not happen when helium was used.

The “O”-ring itself can also produce ghost peaks. Figure 8 shows a peak that typically shows up as a “ghost-peak” generated by the “O”-ring. The component, triphenyl phosphine oxide, will accumulate on the column when it’s set at low temperature. It has a *m/z* of 266. The same chromatogram also shows phthalate peaks that are used as septum-softeners.

It is important to make sure that “O”-rings are used with sufficient thermal stability. There are many brands of “O”-rings and problems can result — not only from the formation of ghost peaks but also from the challenge sometimes of getting liners out of injection systems, when maintenance is due.

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.