Ghost Peaks in Gas Chromatography Part 5:

Impact of Injection and Oven Parameters During Injection

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In gas chromatography 80% of the trouble is caused by the injection system. Also here we have seen that by degradation of sample components, O-rings, back flash and septa, extra peaks can be generated. Besides this, the conditions used for injecting the sample can also produce serious extra peaks.

Extra Peaks Formed by Phase Mismatch During the Injection

In capillary GC the sample needs to be introduced as a narrow band. When measuring in 10 ppm or higher, the split technique works well. For lower levels there are different injection techniques that allow the injection of larger volumes. Techniques like splitless and on-column allow injection of several microlitres of sample into the column. As sample volume is big, a focusing mechanism is essential to form a narrow injection band.

In splitless injection, such a focusing mechanism is realized by starting at an oven temperature set at 20 °C below the boiling point of the solvent. The condensing solvent (solvent effect) in the first cm of column will trap the analytes, creating a narrow band. This is where problems can develop if the polarity of solvent and surface are different. This is called solvent mismatch.

Figure 1 shows the problem that can develop if a polar solvent is injected on a non-polar surface. Here acetonitrile was injected splitless on a Rxi-5Sil MS column (non-polar). Instead of one dichlorobenil peak there are many more peaks, which are all ms-identified as dichlorobenil.

This is a good example of ghost peaks formed by a "multiple injection" (1). To enhance the effect, an oven temperature of 40 °C was used to accelerate the condensation and droplet-formation of acetonitrile.

Figure 1

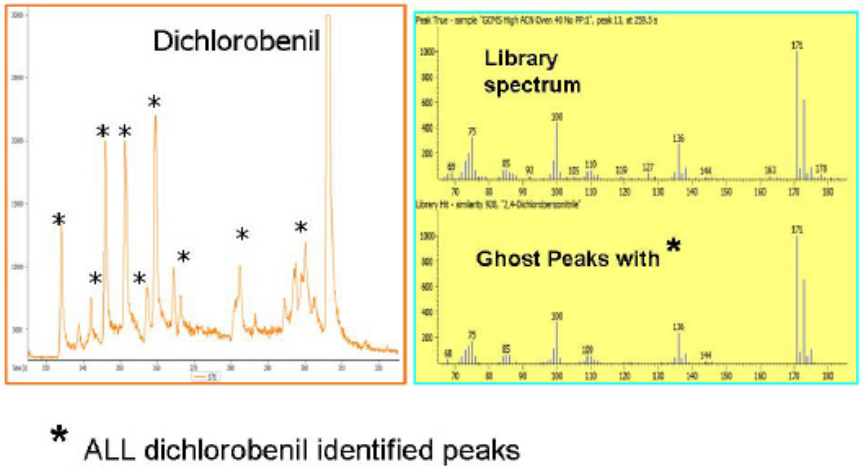


Figure 1: Multiple peaks for dichlorobenil are observed. Solvent: acetonitrile; Oven initial temperature: 40°C during splitless injection; Phase: Rxi-5Sil MS.

Figure 2

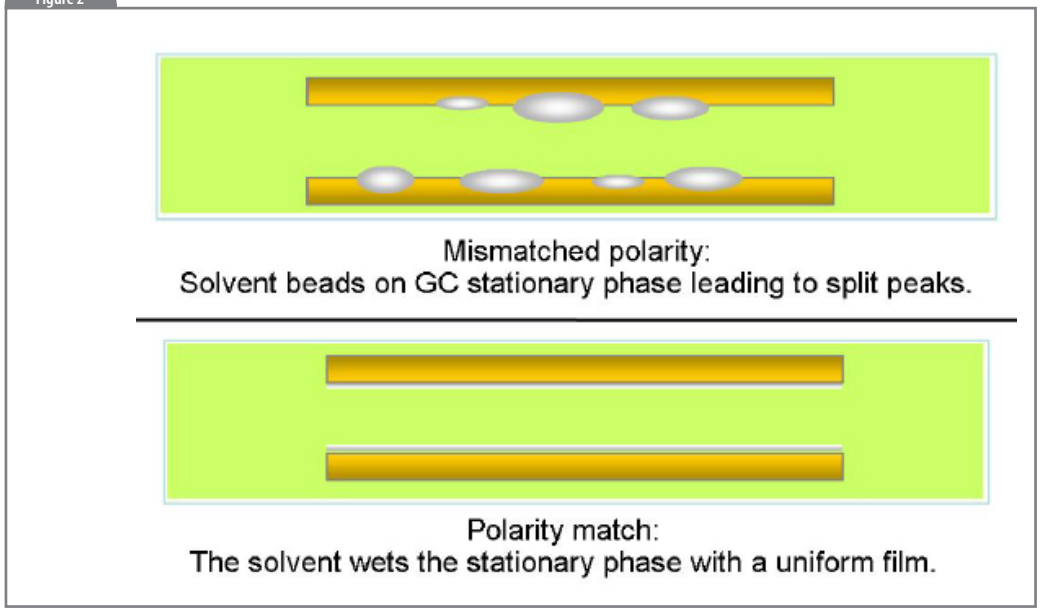


Figure 2: Schematics of the droplet formation when injecting a polar solvent on a non-polar surface and visa-versa.

Figure 3

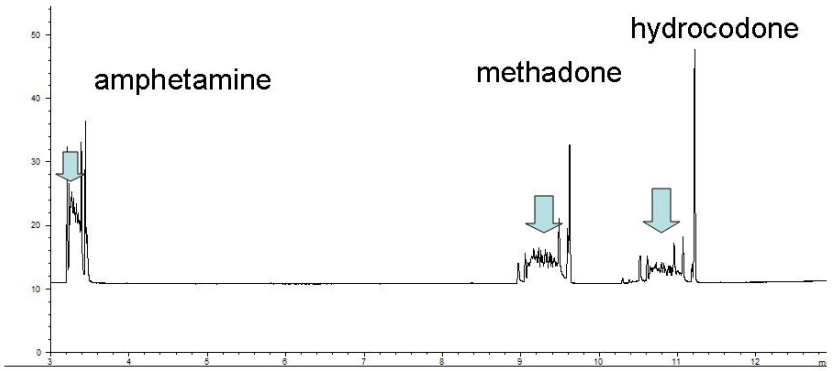


Figure 3: Pulsed 2 µL splitless injection of acetonitrile on a non-polar column. A lot of ghost peaks elute in front of the main peak due to solvent/phase incompatibility.

Figure 2 shows a schematic that explains the effect that causes the formation of these ghost peaks. If a polar solvent is condensing on a non-polar surface, droplets will be formed. Such droplets will be pushed downstream in the column, creating multiple injection bands.

This effect will happen with polar solvents on non-polar surfaces as well as non-polar solvents on polar surfaces. (hexane on a Rtx-Wax).

For polar solvents such as acetonitrile, the impact can be reduced by:

1. Use a retention gap. A non-polar retention gap should be long enough to sufficiently retain the droplets. A polar retention gap can be shorter.
2. Using a higher oven temperature that provide less condensation during injection. This temperature cannot be too high as some condensation is required to get correct focusing (see next paragraph.)
3. Change the matrix of the solvent. Good results are obtained by adding a 25% amount of toluene to the acetonitrile (2).

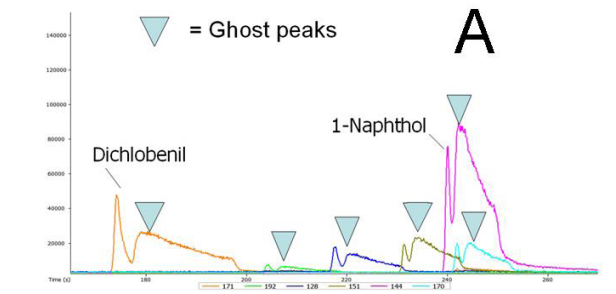
The injection error that is made due to the incompatibility of solvent and surface polarity can also cause ghost peaks for later eluting compounds (see Figure 3). A forest of ghost peaks appear just before the main peak. Note that here a pulsed splitless injection was used that forced the condensed droplets even further into the column enhancing the effect.

Ghost Peaks Formed by Incorrect Focusing During Splitless Injection

In GC it is important to have a narrow injection band. Only then the full efficiency of the column can be utilized. Such a narrow band is easy to obtain using a split injection. This works well for measuring concentrations from approximately 10 ppm to % levels. To detect lower levels, more sample has to be injected onto the column. Several techniques are available for this, for example, the splitless and on-column injection. Here we zoom in the splitless technique, which can show ghost peaks if not done correctly. During splitless injection, the oven is kept at a temperature of 20 °C below the boiling point of the solvent. By doing this, the solvent will form a condensation layer in the inlet of the column. As the whole liner volume needs to be injected, it takes between 30-90 seconds depending on the column flow. During this "injection time", the analytes will be trapped (focused) in this condensed solvent film and a narrow injection band is realized. This is also often referred to as "the solvent effect" in splitless injection.

If the solvent effect cannot happen strange chromatograms are obtained.

Figure 4



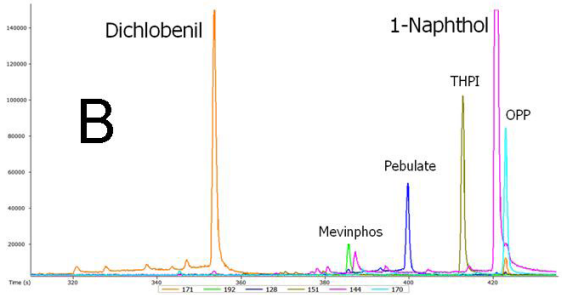
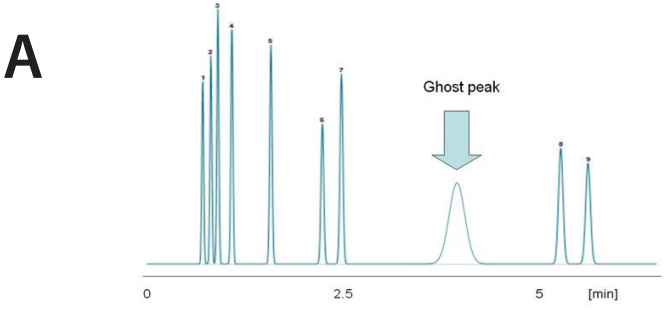


Figure 4: Impact of oven temperature on focusing during splitless injection. Splitless injection of pesticide mixture in acetonitrile.
A: Oven at 120 °C, resulting in deformed peak shapes.
B: Oven at 60 °C, results in acceptable peak shapes.

Figure 5



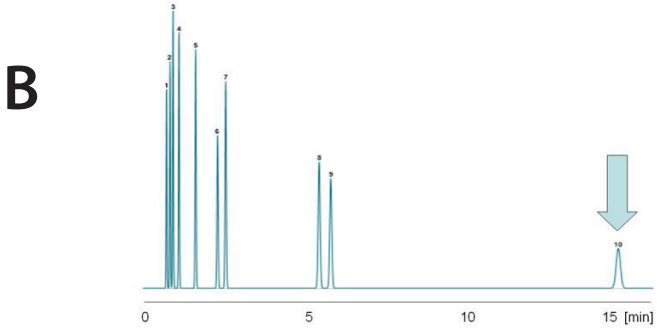


Figure 5: A: Late eluting peaks from the previous run will show up in the chromatogram as a broad peak. Analysis was done isothermal at 60 °C. B: If isothermal time is extended to 15 min also the "ghost" peak (= late eluting compound), will elute.

An example is shown in Figure 4. In Figure 4A, the oven was kept at 120 °C. The solvent used was acetonitrile with a boiling point of 82 °C. As can be seen, there is very poor focusing as the components already start to "move" from the moment the injection started, showing "ghost" peaks. Using the correct splitless temperature, being 20 °C below the boiling point of the solvent, the pesticides are well focused and peak shape is good (Figure 4B).

This effect is best observed on most early eluting compounds. If heavy compounds are present, they will be sufficiently focused by the retention of the stationary phase, to start the separation with a narrow band.

Late Eluting Components

If there is a component in the sample or system, that has a high retention and the cycle time of the analysis does not allow this component to elute, it will elute eventually as a broad peak. Usually these peaks show up in different positions of the chromatogram,

An example is shown in Figure 5A where an isothermal analysis at 60 °C was used to separate. Here a broad "ghost" peak appears between the narrow peaks of the sample. Figure 5B shows the same analysis but now the run time was extended to 15 minutes to make sure that this peak also elutes (see Figure 5B).

If there are even more retaining peaks, they will also show up. The result is a very unstable baseline. There are different ways to prevent this:

- use a temperature programmed analysis and elute later peaks
- use a flow program at the end of the analysis to elute the later peaks
- use a back-flush and elute all the heavy compounds by reversed flow
- a combination of the above.

References

1. Jack Cochran, http://blog.restek.com/?p=556
2. Jack Cochran, http://blog.restek.com/?p=638

Jaap de Zeeuw studied six years of chemistry and graduated in 1979. Jaap has 34 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.