Sample Evaporation in Splitless Injection : a problem ?

by Dr. Konrad Grob

My last "Korner" expressed doubts about GC techniques being as well optimized as one would think. This is because nobody feels responsible and no institution is willing to pay employees to solve problems for the approximately 200,000 other users of capillary GC. Many of the existing designs and working rules emerged from specific circumstances and interests rather than thorough investigations. This "Korner" questions such a rule.

Have you ever been puzzled by the fact that most standard methods recommend the use of a packed injector liner for split injection and an empty one for splitless injection? Usually an explanation is given: the residence time in the injector is much shorter for a split injection than for a splitless injection. Is this a satisfactory answer for you? It is not for me.

Quality assurance requires a lot of time to be invested into checking the accuracy of the equipment. Sources of error, which are more demanding to understand and check, are frequently neglected, even though these errors are often the source of more severe errors than, for example, the balance, pipette, or oven temperature. Sample evaporation in splitless injection belongs to them.

Origin of the Rule

The rule that liners for splitless injection should be empty was introduced by my father in the early seventies. He wanted to avoid the retention of solutes on a packing material, which can hinder the transfer of higher boiling and adsorptive components into the column. In fact, during the splitless period, the gas phase of the vaporizing chamber is exchanged at the most twice and minimal retention results in loss. The material reaches the column only when the split outlet is opened and is largely vented through that exit. My father's experience was with manual injections. Furthermore, high accuracy was not his first concern. His rule survived until today without ever having been seriously questioned. There are, however, reasons to have another look at it. I would like to present the problem to experienced users, hoping for responses, which I would like to publish in a future

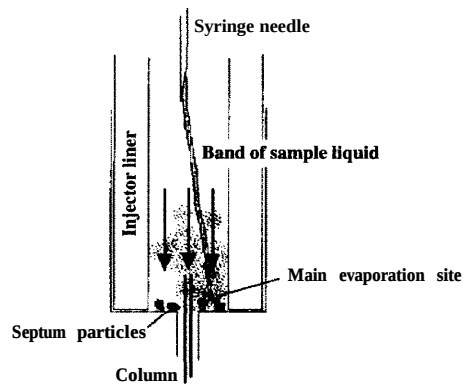
The problem of sample liquid 'shot" to the bottom of the injector chamber

Minimization of retention power in the injector is an important aspect, but not the only one to be considered. A previous "Korner" described the problem of sample evaporation inside a hot injector: if the sample liquid leaves the syringe needle as a narrow band, as water leaves a tap without a hose, it moves at the velocity of a fast car and arrives at the bottom of an empty liner in about a millisecond-far less than required to receive the heat for evaporation. As the sample liquid hits the bottom of the chamber, it may be rejected toward the center, but it is more likely to stay, possibly to be sucked up by septum particles accumulated there. Usually the column entrance is positioned slightly above this "waste bin" of the injector (see Fig. 1) and receives little of the material "shot" to the bottom since the carrier gas comes from the top.

The evaporating solvent produces a volume of vapor that easily expands towards the center of the chamber. Since temperature at the evaporation site remains near the solvent boiling point, solutes hardly have a chance to follow. They are vaporized afterward. However, their vapor volume is so small that it is unlikely that it will reach the column entrance: 10ng of solute produce less than 1nl of vapor. Hence, the vapors remain at the bottom of the chamber until the split outlet is opened and they are vented. Also in splitless injection, the sample must be vaporized above the column entrance.

Splitless injection was conceived for sample evaporation in the gas phase between the needle exit and the column entrance, which, as we know today, presupposes nebulization at the needle exit. Nebulization presupposes partial evaporation inside the needle: the liquid explodes and small droplets are rapidly slowed down by the carrier gas. Evaporation in the gas phase largely avoids adsorption on surfaces and, hence, allows

Figure Incomplete sample evaporation above the entrance results in loss of solute material.



even high-boiling and other difficult compounds to reach the column unhindered. So far, my father's rule is accurate.

Problems arise when samples are not properly nebulized, as is expected, if (1) the sample is dissolved in a high-boiling solvent or (2) one of high surface tension, (3) if it contains an elevated concentration of non-evaporating by-products, and (4) if a fast autosampler is used, suppressing evaporation inside the needle.

"Dirty" samples

Many samples injected by the splitless method are "dirty." We often notice that the same concentration of a component produces a smaller peak in a "dirty" sample than in a mixture of standards. One percent of non-evaporating material was found to result in approximately a 15% loss for the C10-alkane and a 40% loss for C22; losses for C30 sometimes exceeded 90% (J. Chromatogr. 294 (1984) 65). Hence, peaks in "dirty" samples were too small, and the higher-boiling components discriminated more than the volatiles. If a clean mixture of standards is used for calibration, the analysis of a "dirty" sample is correspondingly inaccurate. Glass wool between the needle exit and the column entrance eliminated this matrix effect *Chromatographia* 18 (*1984)* 517). We assume that droplets of non-evaporating by-products carry the sample material to the bottom of the injector.

Fast autosamplers

Fast autosamplers do not reproduce the conditions of manual injection for which the empty liner was designed. Injection is performed in such a short time that evaporation inside the syringe is avoided. The sample leaves the needle as a band of liquid, and, since nebulization is suppressed, it is "shot" to the bottom of the injector (J. Qian et al., J. *Chromatogr.* 609 (1992) 269). Solute degradation on the metal surfaces at the bottom of the injector results not from the chemical activity of these surfaces, but from how the sample material gets there.

Tests on completeness of evaporation

Have you observed the problem described above? If so, how large are the resulting deviations? The following testing procedures may help:

On-column Injection

The most comprehensive control of results obtained by splitless injection compares with on-column injection. One of the samples analyzed is injected a second time by the on-column technique. If no on-column injector is available on the instrument, the column is dismantled from the vaporizing injector. After waiting 20-60s (decompression of the gas in the column will cause backflow), l-2 ul of sample is injected into the column inlet. Use either an on-column syringe with a thin needle or a short piece of 0.53mm i.d. precolumn to enable injection with a standard syringe.

Conditions ensuring nebulizatiun

You may want to test whether conditions for nebulizing the sample would improve your results. Remember what supports nebulization:

- Partial vaporization inside the needle (i.e. use "hot needle" injection), no fast autosampler.
- Use a low-boiling solvent of low surface tension, such as pentane or ether (i.e. substitute at least 90% of a more difficult solvent).
- Use a high injector temperature (above about 240°C).
- Inject a modest volume of sample (e.g.1ul reading on the barrel).

Clean sample

Both tests, mentioned above, are not suitable for checking the effect of non-evaporating sample by-products. Very "dirty" samples cannot be injected on-column and may not be nebulized even when dissolved in pentane. Compare absolute and relative peak areas in a clean mixture of standards and the "dirty" sample with a number of components covering the chromatogram of interest. If peaks are smaller in the sample than in the calibration mixture and if the later eluted components suffer more, this fits the mechanism described above.

Packed inlet

Position a small amount of glass or fused silica wool just above the column entrance in order to stop sample liquid. If the wool increases peak areas for the "dirty" sample, or for a sample injected in a difficult solvent, or for one that is introduced by a fast autosampler, you have "caught the worm."

Conclusions

Unfortunately, interpretation of the test results is complicated by interfering mechanisms. Peak areas of a 1 ul splitless injection might be nearly twice those of a 1ul ll on-column injection because the needle is empty. Losses inside the needle will, on the other hand, reduce the peak areas, discriminating against the high boiling solutes. Packing material may adsorb solutes. Polar by-products may deactivate them again, increasing the areas for the

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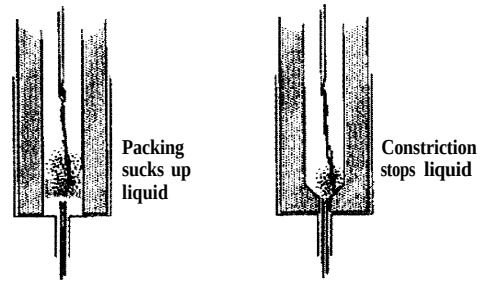
Figure 2. Two arrangements that prevent non-evaporating sample material from dropping below the column entrance: a packing of deactivated glass wool and a liner with a constriction.



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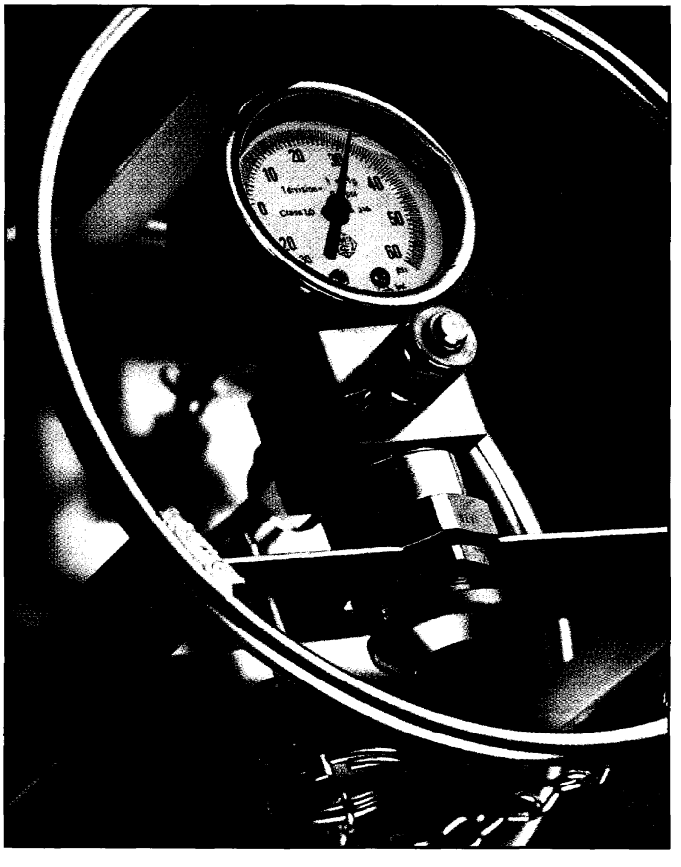

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"dirty" samples. Hence conclusions must be drawn with some care.

Sample evaporation could be forced to occur above the column entrance by the means shown in Fig. 2 (on page 11): A short plug of deactivated glass or fused silica wool is positioned just above the column entrance in order to prevent non-evaporated sample from dropping to the bottom of the chamber. Alternatively, a liner is equipped with a constriction at the bottom, and the column is installed in the orifice. However, these solutions also have drawbacks: Wool is adsorptive and particularly problematic for trace analyses commonly performed with splitless injection. Second, septum particles and other non-evaporating materials now accumulate above the column entrance and may retain the sample components. With the classical arrangement, they were not in the way.