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 advantage.

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...
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 concen-
tration of non-evaporating by-
products, and (4) if a fast
autosampler is used, sup-
pressing 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.
Hence, peaks in “dirty”
samples were too small, and
the higher-boiling com-
ponents discriminated more
than the volatiles. If a clean
mixture of standards is used
for calibration, the analysis
of a “dirty” sample is corre-
spendingly 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.
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), 1-2 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
nebulization
You may want to test whether
conditions for nebuling 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. substi-
tute at least 90% of a more
difficult solvent).
• Use a high injector tempera-
ture (above about 240°C).
• Inject a modest volume of
sample (e.g. 1 ul 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 compli-
cated by interfering mecha-
nisms. Peak areas of a 1 ul
splitless injection might be
nearly twice those of a 1 ul
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

cont. on page 13

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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