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.