mm i.d. (with an internal volume of 0.06-0.25 ml) for another decade. Few seemed to ask where the sample vapors would go. Nobody seemed to know or care to prove if a 2 mm i.d. liner provided enough sample vaporization space. Quantitative work performed with splitless injection during those years was often embarrassingly poor. Some authors concluded that "the splitless injector acts like a non-linear splitting device and delivers unpredictable and irreproducible quantities of individual components on to a WCOT column." Other authors published papers where more than 3u1 of methanol (which has a vapor cloud of 2.5ml) had been injected into a 2mm id. liner with an internal volume of 0.25ml. Letters to the editor reacting to such elementary shortcomings made instrument manufacturers aware of the importance of the size of the vaporizing chamber.

Injection Rate

My father and I are also responsible for an error introduced in 1978. In order to enable injection of larger samples, we recommended introduction at a rate adjusted to the transfer of the vapors into the column, i.e. 1u1 in approximately 10 seconds. As published in 1979, we soon became aware that slow injections result in extremely large losses of higher boiling components inside the syringe (sample evaporation takes place in the syringe needle). However, there are still auto samplers slowly injecting into hot injectors.

Length of Syringe Needle

The syringe needle must be long enough (70-80mm) to bring the center of the vapor cloud just above the column entrance. The vapors must expand backward to make the best use of the liner volume available and ensure that the carrier gas plug between the sample vapors and the column entrance transfers into the column before the sample vapors.

Carrier Gas Flow Rate

In the early days, splitless injection was used with hydrogen carrier gas flow rates of 24 ml/min. As shown in 1981, 2 ml/min. is the lower limit ensuring complete transfer from 4 mm id. liners into the column, i.e. accurate splitless work. Many analysts continue to ignore this fact. For instance, GC-MS units have become popular with analysts with carrier gas flow rates limited to less than lml per minute due to their limited vacuum pump capacity. These MS units are primarily used for trace analysis with splitless injection, but nobody shows concerns about the effect low injector flow rates have on splitless quantitative results.

Injection Design

There are more design characteristics known to be critical but neglected in many of the instruments presently used. The split outlet line should have a small internal volume to prevent the sample from being pushed into it by the pressure wave initiated by sample evaporation. In order to prevent loss of vapors, no flow should pass over the top of the vaporizing chamber during the splitless period. The use of an empty, straight injector liner, as recommended by my father, made sense as long as sample evaporation inside a hot syringe needle supported nebulization of the sample at the needle exit. However, with the introduction of fast auto samplers, conditions have changed and sample evaporation must be reconsidered. This will be the subject in one of my next "Korners."

Conclusions

There has never been a comprehensive, professional investigation resulting in a convincing design of the splitless injector. In contrast to most other products marketed, such as cars or airplanes, the supplier carries no responsibility. Analytical chemistry relies on the knowledge of the analyst. He is responsible for choosing the right instruments and using analytical techniques correctly. Unfortunately, reality is often different, as demonstrated by unoptimized splitless injector designs and improper operating parameters.

I do not have a simple solution to offer, but some consequences seem obvious:

1. Users must realize that many injectors and splitless method parameters have never really been optimized and are prone to error.
2. It would take a lot of money and a concerted effort by all instrument manufacturers and analysts to perfect the splitless injection technique.
3. Maybe combined forces will be more successful. Analysts should publish their observations as well their ideas on what can be improved. If thousands struggle alone in their laboratory, frustration accumulates while problems remain unsolved.
4. Instrument manufacturers wil optimize injector design if customers make it a priority.
5. Quality management puts tough requirements on the accuracy of oven temperature (which has little effect on reliability of quantitative results), but accepts injectors that disregard elementary requirements.
6. Certified methods commonly describe in detail how a sample is prepared, but do not specify how to perform splitless injection properly.

Capillary GC is immature because numerous technical aspects have not been adequately investigated. If this work is not done in the near future, poor quantitative results will invalidate the technique of capillary GC.

E-mail comments/suggestions/questions for Konrad Grob to koni@restekcorp.com