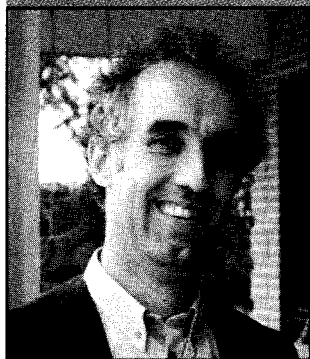




Are GC techniques really optimized?

Splitless injection as an example

by Dr. Konrad Grob



Users tend to think that basic GC techniques have been investigated in all details and sanctioned by a competent committee. In fact, why should one think about the design of an injector liner, after splitless injection has been used for more than 25 years? Modern companies invest 5–10% of their profits into research and development. Hence, bigger instrument manufacturers must have many labs with numerous people optimizing techniques. As splitless injection is probably the most widely used method of sample introduction in capillary GC, manufacturers must have tested their injector with all types of samples before releasing a new instrument. True or not? It would be difficult to find out. I have not seen behind the walls of all the instrument manufacturers, but I have

witnessed most of the development of splitless injection. I have come to the conclusion that the above views are awfully naive. There wasn't the idealist who invested many years to perfect splitless injection, nor an employer financing such a project. No instrument manufacturer had a single person working even just one year in extracting the knowledge from the literature available and checking all possible uses.

Splitless injection was shaped through a number of incidents and particular circumstances with only a few people involved. There were misunderstandings and errors; conditions were changed (such as carrier gas flow rates lowered or the injection process accelerated) without properly taking notice of the consequences. Some assumptions survived over decades without ever having been questioned. No one person took the responsibility for

providing the analyst with an optimized technique.

"Invention by Accident"

Splitless injection was introduced by my father in 1968. He did not "invent" it by developing a concept in his mind and putting it into practice. He simply forgot one morning to open the split vent before performing what should have been a split injection. Peaks turned out to be very large (since all sample material entered the column). More surprisingly, all peaks were perfectly sharp. Everybody at that time was convinced that something like splitless injection would be impossible because the slow transfer of the components into the column created broad initial bands. Under other conditions, peaks were as broad as expected, and it took him about four years to determine the parameters required to produce sharp peaks, i.e. to understand the concepts of solvent effects and cold trapping.

Working in his spare time in the cellar of the school house (he was a teacher), my father had no means to modify the injector. Circumstances thus dictated that the new technique worked with the split injector available. It primarily had to solve his problems in trace analysis and was not developed with the interest of today's maybe 200,000 chromatographers in mind. For instance, he was not interested in highly accurate

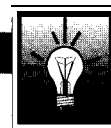
quantitative data. His work was supported by a cigarette company to find out why smoke is harmful, not to develop an injection technique.

Size of the vaporizing chamber

Because my father realized that a larger vaporizing chamber would be needed for storage of the sample vapors between their formation and transfer into the column, he had an injector made by a local mechanical shop. The design of this injector was described in *J. High Resolut. Chromatogr.* 1 (1978) 57. Since 1 µl of liquid transforms into 100–400 µl of vapor (further enlarged by mixing with carrier gas), an 80 x 4 mm i.d. chamber was selected with an internal volume of about 1 ml. There were long discussions concerning the geometry of the liner. A longer, more narrow chamber was preferable because it reduced mixing with the carrier gas and improved the transfer of the vapors into the column because of the higher gas velocity. However, this would require a very long syringe needle to allow the release of the sample near the bottom of the chamber. Because of its length, the syringe needle would be awkward and difficult to use.

This injector almost immediately became the standard for Carlo-Erba instruments. The other manufacturers continued to introduce injectors with chambers of merely 1-2

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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 3 µl of methanol (which has a vapor cloud of 2.5ml) had been injected into a 2 mm i.d. 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. 1 µl 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 (70-80 mm) 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 2-4 ml/min. As shown in 1981, 2 ml/min. is the lower limit ensuring complete transfer from 4 mm i.d. 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 1ml 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.

Injector Designs

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 "Komers."

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 will 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.

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