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Note

Checking the capacity of a splitless injector — a simple test

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This paper deals with an old problem that has still not been adequately solved. In conventional splitless injection, sample vapour generated on introduction into the hot injector must be "stored" within the vaporization chamber until transferred into the column[1]. However, a rapid calculation immediately reveals that many vaporizing injectors built into current gas chromatographic (GC) equipment are simply too small to house the sample vapour.

REQUIRED INJECTOR VOLUME

On injecting a sample volume that corresponds to 1 μl read on the barrel of a standard 10-μl syringe, usually about 2 μl of liquid are introduced into the injector, as the needle is likely to be emptied by evaporation of the sample matrix (*e.g.*, if the latter consists of one of the commonly used solvents). If hexane is the sample solvent, these 2 μl of liquid form a vapour about 600 μl in volume, depending on the carrier gas inlet pressure and the temperature of the injector. If methanol is the solvent, the vapour has the large volume of about 1.5 ml. Further, it must be considered that one cannot prevent that sample vapour being diluted with carrier gas. In fact, the vapour clouds are easily 50–100% larger than calculated above. A vaporization chamber of, *e.g.*, 8 cm length and 2 mm I.D. has a volume of 250 μl, thus is far too small to retain the sample vapour in splitless injection, and we should consider what happens to these vapours then. The explosion-like evaporation of the sample increases the pressure in the vaporization chamber, pushing the vapour into all accessible cavities. The easiest means of expansion usually involves returning into the carrier gas supply line. When pressure decreases again, the vapour returns. However, a substantial proportion of high-boiling and adsorptive solute material remains within this line as only a short section (if any) of the latter is heated. Solute material may slowly return when the split exit is opened again, then being split, with the effect that most material is lost for the analysis. Often solutes of intermediate volatility return during subsequent runs, creating "memory" effects. It is obvious that no optimal quantitation is possible under such conditions.

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CONCEPT OF THE TEST

The problem of too small vaporization injectors was recognized a long time ago, and it is difficult to understand why many instrument manufacturers have not solved the problem in the meantime. Some appear to hope that the pressure increase in the injector will keep the vapour together and others rely on the recondensation of the solvent in the column inlet, accelerating the vapour transfer. To our knowledge, neither of these theories has been checked experimentally, and in our experience their effects are too weak to prevent injector overflow. Rather than believing or not believing, the operator should check himself whether the injector has a sufficient capacity for housing the sample for the volume injected and using a particular (possibly too short) syringe needle. The test is simple, taking hardly 5 min. It is based on the detection of solvent vapour leaving the septum purge exit during splitless injection. The gas flow through the septum purge line passes the top end of the injector insert and carries away sample vapour if the insert overflows. As this gas flow does not pass through the vaporization chamber, vapour stored within the glass insert of this chamber are not affected.

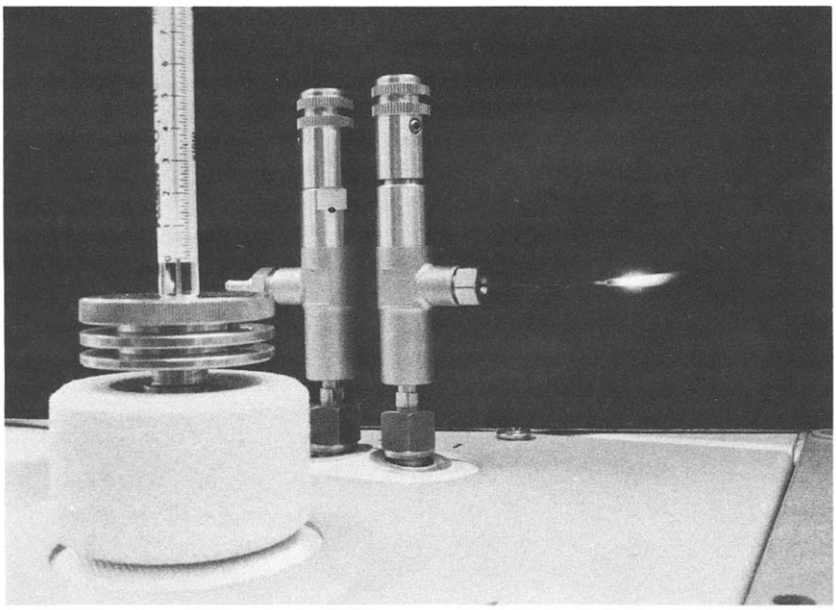

Fig. 1. Flame on the septum purge exit indicating back-flushing of sample vapour. Conventional vaporizing injector (Carlo Erba) on the left. Behind are the two needle valves of the split line (left) and the septum purge (right). The short fused-silica capillary mounted in the exit of the septum purge needle valve is not visible, but the glowing tip of the latter, free of polyimide coating, can be seen. The flame was photographed about 1 s after injecting 3 μl (reading 2 μl on the barrel of the syringe) of diethyl ether into the large (1 ml) injector insert, using a 70 mm long syringe needle. Injection of a 2-μl volume produced only a small, weakly yellow flame, indicating a small loss by back-flow. This allows the conclusion that (under the conditions applied) the injector had the capacity to take 2 μl of diethyl ether.

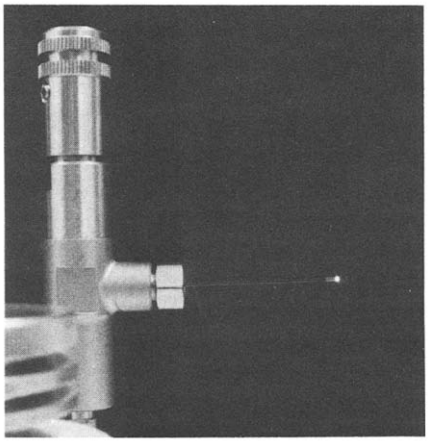

Fig. 2. Glowing of the fused-silica capillary tip in the small flame photographed *ca.* 15 s after an injection as shown in Fig. 1. The flame burns sample vapour backwards leaving the injector insert by diffusion. After opening the split exit, purging the injector, a flame is no longer visible.

EXPERIMENTAL

The GC carrier gas must be hydrogen. The septum purge exit is equipped with a short piece of 0.25–0.32 mm I.D. fused-silica capillary, as shown in Fig. 1. The septum purge flow-rate is adjusted to *ca.* 10–30 ml/min and the hydrogen at the tip of the fused-silica line is lit. As long as pure hydrogen leaves this exit, the flame is colourless, visible only as a weak glow at the tip of the fused-silica capillary. However, the flame turns yellow as soon as hydrocarbons are mixed with the hydrogen. Large dead volumes within the septum purge exit line disturb the experiment, as do needle valves and lines kept far below the boiling point of the solvent (the solvent recondenses and re-evaporates over extended periods of time, giving a wrong picture of the duration of back-flushing of sample vapour).

We assume that an injection is carried out by the "hot needle" technique, involving withdrawal of the sample liquid into the barrel when introducing the needle. During the introduction of the first part of the needle, the flame usually turns slightly yellow for a short period owing to solvent eluted from the tip of the syringe needle into the septum purge zone of the injector (vapour of sample liquid coating the needle wall). When the tip of the needle enters the vaporization chamber, eluted vapour is flushed towards the column and the flame becomes colourless again. Injection of the sample, and here we assume an excessively large volume, causes the flame immediately to turn yellow (Fig. 1), indicating back-flushing due to the pressure wave. The flame rapidly returns to a weak yellow colour, persisting for several tens of seconds. This is due to solvent (and solute material?) slowly diffusing backwards out of the injector insert. Sometimes these small amounts of solvent are only observed by a more intense glow of the fused silica (Fig. 2), caused by the higher temperature of the flame. On opening the split exit and flushing the injector chamber, the flame becomes colourless again and the glow is the same as before the injection.

The results of the test depend on many factors. Of course, losses are reduced by

reducing the sample volume injected. Losses through the septum purge also depend strongly on the length of the syringe needle, determining whether or not the available injector volume is fully used. Further, they depend on the sample solvent, the column inlet pressure, the column flow-rate and the column temperature (recondensation effect).

The experiment fails with solvents that do not create yellow flames, *e.g.*, methanol. Aromatic solvents produce the most intensely bright flame and allow the most sensitive detection of the back-flow. However, as solvents of smaller molecular size and higher densities form considerably larger vapour clouds per unit volume of liquid injected, they do not represent "tough" cases.

CONCLUSIONS

Back-flushing of sample vapour as detected by the above test causes immediate loss of sample material if the septum purge remains open during splitless injection. Closure of the septum purge exit prevents immediate loss, but does not represent a convincing solution to the problem, as overflowing vapour is forced into the carrier gas supply system, from where it returns incompletely and selectively, causing losses and "memory effects". Therefore, the injection volume should be reduced to a level that keeps the losses by back-flow small. Unfortunately, many analysts will find that on their equipment even the smallest sample volume that they can inject produce a considerable back-flow. The internal volume of the injector should be around 1 ml[1]; larger volumes make sample transfer from the injector into the column difficult[2]. Usually the possibilities of enlarging the vaporization chamber of conventional split–splitless injectors are limited, mostly being restricted to the use of injector glass inserts with thin walls, which allow the injector cavity to be exploited as efficiently as possible.

A more quantitative study on losses through back-flow and a more detailed discussion of the consequences will be published elsewhere.

REFERENCES

1 K. Grob, *Classical Split and Splitless Injection*, Hüthig, Heidelberg, 1986; 2nd ed., 1988.
2 K. Grob, Jr. and A. Romann, *J. Chromatogr.*, 214 (1981) 118.