

Sample Evaporation in Splitless Injection : a problem ?



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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

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

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

