Sample Evaporation in Hot GC Injectors

by Dr. Konrad Grob

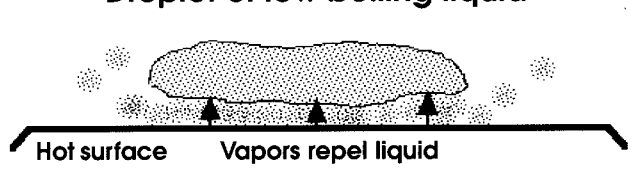
Is sample evaporation in a hot GC injector something you have to think about? Injector temperatures seem to guarantee almost instant evaporation of solutions in volatile solvents. However, appearances are deceptive. Not even vaporization of the solvent is ensured, and as long as not all of the solvent is evaporated, sample components cannot evaporate. Sample liquid "raining" onto (or rather, by) the column entrance is not wanted.

THE LEIDENFROST PHENOMENON

The problem of solvent evaporation has to do with the short time available for sample evaporation inside the injector and the Leidenfrost phenomenon. Have you ever seen what happens to a droplet of water falling onto a hot electric cooking plate? Was there the sharp hiss and the water was vaporized? No! The droplet became flat as a small disk and hovered a fraction of a millimeter above the plate. It may have moved nervously, jumping around the hot griddle. Evaporation took many seconds. If this experiment was repeated with a drop of edible oil, you'd observe a totally different behavior: the oil dropped onto the plate, adhered to it, and evaporated more rapidly than the water –although (or rather because!) the boiling point is much higher.

According to the "Leidenfrost phenomenon", liquids cannot touch a surface with a temperature above their boiling point because evaporation forms a cushion of vapor preventing contact. The higher the surface's temperature is above the boiling point of the liquid, the more rapid evaporation occurs. But, since more vapor is formed, the liquid is repelled further above the surface.

Figure 1: The Leidenfrost phenomenon: a cushion of vapor repels liquids from surfaces the temperature of which is above their boiling point.



The solvent vapors separating the sample liquid from the hot surface of the injector liner have two important effects. First, they render the liquid highly mobile–it glides away from hot surfaces. Secondly, they insulate the liquid from the hot surface. Since heat transfer is the time-determining step of evaporation, low boiling liquids may evaporate slower than higher boiling ones.

TIME AVAILABLE FOR EVAPORATION

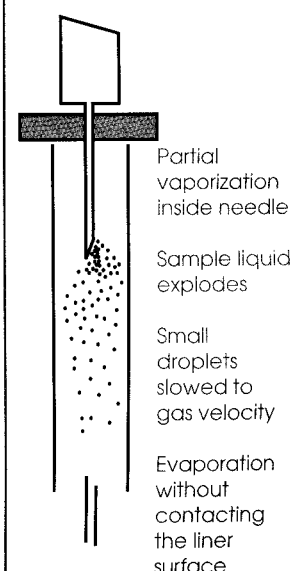
The time required for evaporating the sample (first of all the solvent) is determined by the transfer of the heat consumed. For 2 µl of hexane, it was calculated as several hundred milliseconds[1], while 2 µl of water require several seconds. Is this time available? It depends on how the sample liquid moves through the injector.

During manual injection, the plunger is depressed at a speed of around 1-2 m/s. However, as the liquid enters the narrower needle, it is accelerated to 15-30 m/s (some 50-100 km/h) and leaves the needle at this same speed at least. Fast autosamplers cause it to exit at speeds even far above those fast cars can achieve. If the injector liner is empty and the sample continues to travel at this speed, the column is reached in far less than 0.1-3 m/s–which is 100-10,000 times less than needed for sample evaporation. To achieve full vaporization, the sample liquid must be slowed or stopped above the column entrance.

NEBULIZATION OF THE SAMPLE LIQUID

If samples are injected by a technique involving a hot syringe needle, partial evaporation inside the needle often nebulizes them. The resulting fine droplets are rapidly slowed to the gas velocity and reach the column after several hundred milliseconds only (depending on the gas flow rate). Visual experiments have confirmed that most organic solvents are nebulized when injected by the hot needle

Figure 2: Sample evaporation involving nebulization at the needle exit.

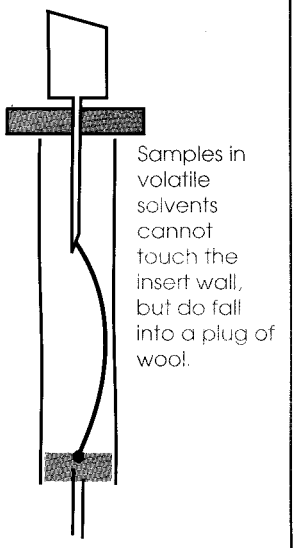


method (preheating the needle inside the injector before rapidly depressing the plunger). Nebulization in an empty liner provides gentle evaporation in the gas phase hardly involving any contacts with adsorptive and maybe dirty surfaces. Even high boiling, polar, and labile components are vaporized rather well.

STOPPING SAMPLE LIQUID BY PACKING MATERIAL

Nebulization does not occur with fast injection auto-samplers. The sample liquid forms a thin band, like water running from the tap, and moves almost without resistance. It must, therefore, be stopped above the column entrance by other means, which is all but simple because of the Leidenfrost phenomenon.

Figure 3: Non-nebulized sample liquid must be stopped, e.g., by glass or quartz wool.



Heat consumption by evaporating liquid cools the source of the heat. If cooling is strong enough to reduce the surface temperature to the sample (solvent) boiling point, the liquid can contact the surface. This occurs with obstacles of a low thermal mass, such as glass or quartz wool. The liquid cools the nearest fibers it encounters and falls into the wool just as children jump into a haystack. Hanging in these fibers, the sample forms an island with a temperature corresponding to the solvent boiling point until the solvent is evaporated.

The smallest amount of wool which forms a short plug without major gaps (1-3 mg) serves the purpose. Additional amounts merely aggravate the problems–adsorption and degradation of labile compounds. There are two concepts for placing the packing–situated near the exit of the inserted needle, the packing will always receive the liquid and the solutes will always evaporate from its surface. This renders the process reproducible, but susceptible to the activity of the packing. Placed just above the column entrance, the packing rather serves as a safety net: nebulized samples will evaporate in the gas phase above the packing and pass the latter easily (adsorptive surfaces have less effect on passing vapors than on material evaporating from them). If the sample is only partially nebulized or not at all, the packing acts as a net underneath the acrobat in the circus. Packings of low thermal mass would be the most convincing solution to sample evaporation if they were inert.

Recently, Restek sent us some carbon material (Carbofrit™) with the suggestion to test it as liner packing. Initially, I didn't even want to try it because carbon is usually highly retentive and catalytically active. As we nevertheless gave it a chance, we were highly surprised…it exhibited low retentive power and good inertness.

LINERS WITH OBSTACLES

Injector liners containing solid obstacles, such as baffles or an inverted cup (Jennings cup), were conceived to enhance mixing the sample vapors with the carrier gas and stop "shooting" sample liquid. The inverted cup forces the gas flow to reverse directions twice, which seemed to guarantee that non-evaporated sample material would not pass. There was no solid proof, however, because it is difficult to derive from chromatograms what happened inside the injector. Recent visual experiments provided more direct evidence. Because of the Leidenfrost phenomenon, the sample liquid is able to curve around hot solid obstacles and change direction rather sharply. For instance, it performed perfect slalom around the baffles, hardly being slowed. When the obstacles stop the sample liquid, it is for different reasons than what the originators thought. The main effects are due to the fact that liquids are hindered to enter narrow channels (again, the Leidenfrost phenomenon). The inverted cup of the Hewlett-Packard liner usually stopped the sample liquid, provided the sample volume did not exceed 1.5 µl. The most effective liner was, however, the "laminar liner" from Restek[2].

CONCLUSIONS

There are three principal concepts to achieve sample evaporation:

1. Sample evaporation in the gas phase of an empty liner provides the most gentle conditions, but presupposes partial evaporation inside the needle.
2. Well designed obstacles stop "shooting" sample liquid.
3. Packings with low thermal mass render vaporization most reliable, but evaporation occurs from a surface.

All three concepts may turn out best suited. You have to try.

1. *J. High Resolut. Chromatogr. 15 (1992) 190*
2. *J. High Resolut. Chromatogr. 16 (1993) 429*