Hints for the Capillary Chromatographer

Vaporizing Split Injectors

*The following information on vaporizing split injectors was extracted from a seminar given by Dr. **Konrad** Grob for Restek on October 7 & 8 in Newark New Jersey. Future hints articles will include information on on-column and splitless injections.*

Evaporation from Split Injectors

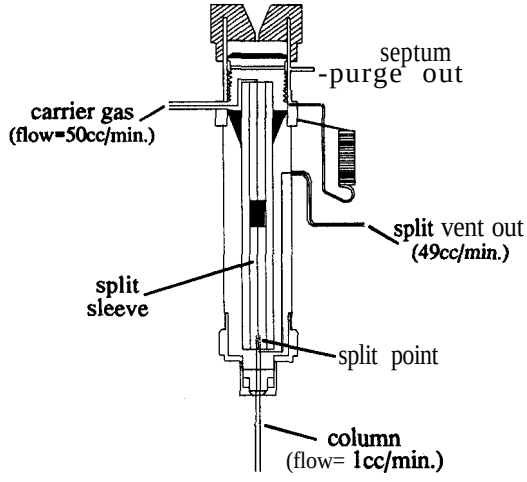
Split injectors function by dividing the sample stream into two unequal parts as shown in Figure 1. Most of the sample stream is vented to the atmosphere whereas a small part is delivered to the capillary column. For example, a 50 to 1 split ratio directs forty-nine parts of the sample out of the split vent and directs one part onto the column. Proper quantitation requires that the composition of the split streams be uniform. However, mass or molecular weight discrimination is common with split injectors. Typically, split injections cause the low molecular weight compounds to preferentially enter the column. Factors that influence mass discrimination include:

- Completeness of sample evaporation inside the injector chamber
- Syringe needle temperature during injection
- Length of heated syringe needle
- Speed of injection
- Syringe handling technique
- Evaporation from heated needle
- Design of gas supply system
- Column temperature during injection
- Sample solvent
- Non-volatile sample material

Sample evaporation consumes much more energy and time than commonly thought. It can easily take more than a second for a solvent to evaporate in the injector sleeve. Evaporation is seldom an "instantaneous" process. For evaporation to occur, a liquid must first cool the surface before it can intimately contact it and vaporize. Some samples evaporate in the gas phase after being nebulized. These samples hardly touch injector surfaces. This is why a small plug of wool in the injector is an excellent idea to ensure evaporation. The low thermal mass of the wool fibers allows them to rapidly cooled below the solvent's boiling point. After the solvent is vaporized, the site is rapidly heated and the solutes evaporate. Wool may not be sufficiently inert for all samples, causing adsorption or degradation of certain solutes. Therefore, other types of splitter devices are often used.

Liquids don't appear to actually touch the surfaces of the injector liner when evaporating. They jump around like a drop of water splashed on a hot griddle. This repulsion of a liquid from a hot surface is known as the Liedenfrost phenomenon. The Liedenfrost phenomenon is the reason why baffle or dimple sleeves do not allow complete sample vaporization.

Figure 1 - Typical split injector shows carrier gas flow paths during a split injection



Formula for determining the split ratio:

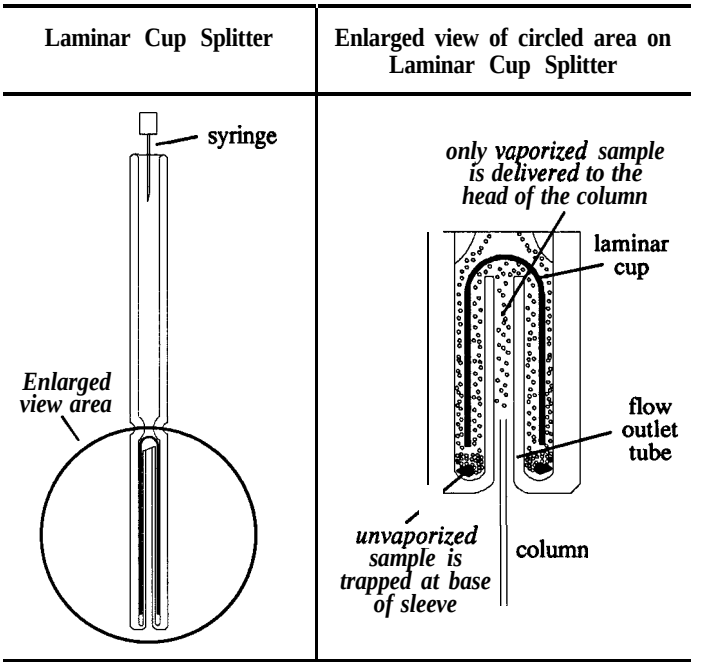
$$\text{Split ratio} = \frac{\text{Column Flow + Vent Flow}}{\text{Column Flow}}$$

The liquid sample simply slides around the obstructions and never touches the surface. Grob found that the best inlet sleeve design to promote complete vaporization is the laminar cup splitter (Figure 2). Larger injections (up to 5µl) can be made with the laminar splitter without allowing unvaporized sample to reach the split point. It was originally thought that the abrupt reversal of sample flow in the inlet sleeve was the key to good vaporization. However, Grob's experiments show that increased evaporization efficiency is promoted by the narrow channels between the laminar cup and insert walls. Sample evaporation has nothing to do with the reversal of the flow path. The first change in the flow direction forces the unvaporized sample droplets to sit at the base of the sleeve prior to the opening of the laminar cup. The remaining liquid sample will "dance" in this zone until vaporization is complete. Then the vaporized sample will enter the cup and complete its travel to the split point at the column inlet. Other inlet sleeve designs allow unvaporized sample droplets to enter the column and increase discrimination effects.

Syringe Needle Temperature Affects **SampleVaporization**

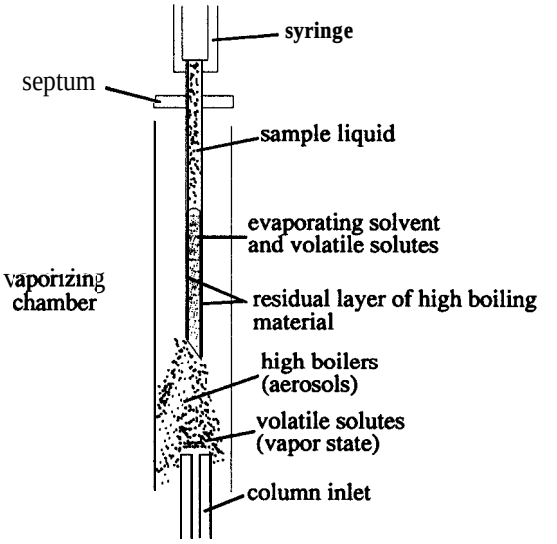
Grob found higher repeatability with the hot needle technique. This technique is performed by filling the syringe barrel with sample and solvent, holding the needle inside the hot injector for several seconds, and then rapidly depressing the plunger to expel the sample through the hot needle. This technique creates a high vapor pressure in the needle, thus allowing most of the sample to be expelled in the liquid phase which mini-

Figure 2 - Experiments by Grob determined that the laminar cup splitter is the best inlet sleeve for split analysis.



The sample travels through the narrow channels between the outer wall of the sleeve and the laminar cup. Unvaporized liquid is trapped at the bottom of the sleeve and "dances" around until all liquids evaporates Then the vapors travel inside the cup and reverse directions again until they reach the splitpoint.

Figure 3 - Needle discrimination can be avoided by the hot needle technique or by rapidly injecting using fast autosamplers.



High mass discrimination is caused by high molecular weight compounds sticking to the syringe needle wall after the solvent and the volatile compounds are evaporated. Low mass discrimination is caused by a higher proportion of low boiling compounds being forced into the column bore during the initial injection vaporization period and through the septum purge via backflash. By the time the high boilers are vaporized the pressure surge has returned to normal and the sample stream becomes more uniform,

mizes discrimination during evaporation. The hot needle technique also facilitates the job of the injector sleeve to vaporize the sample since it nebulizes the liquid. This technique is better performed on an instrument designed to deliver uniform heat from the bottom to the top of the injector. With a normal (- 1 second) injection, the high boilers stick to the syringe wall and do not fully vaporize, contributing to high mass discrimination.

Alternatively, rapid cool needle injections can be used to minimize mass discrimination. This technique requires an autosampler capable of extremely fast injection (150 millisecond residence time) and an instrument designed with a cool injector head. The needle enters the injector, introduces the sample, and is removed before the solvent starts evaporating inside the needle. The use of high boiling solvents and lower injector temperatures decreases needle discrimination from a cool rapid injection.

Sample Vaporization/Recondensation Affects Split Ratio

A pressure wave forms during a split injection as the 2µl liquid sample forms 400-800µl of vapor. This pressure wave can cause a deviation of the true split ratio as the amount of gas leaving the split vent changes during the injection. This amount of deviation is influenced on whether the injector is head pressure or back pressure controlled. Dr. Grob prefers head pressure controlled injectors to minimize this problem. Recondensation into a column kept below the boiling point of the solvent or into cool split lines can also compound the problem of obtaining a true split ratio. As the vaporized sample recondenses, the volume of gas decreases and split ratio changes. Since the vaporization process of the solute takes many seconds, less of the high molecular weight sample compounds enter the column, thus increasing mass discrimination if solvent recondensation occurs. The use of charcoal traps between the split vent controller (either a needle valve or back pressure regulator) and the injection port also causes recondensation and are not recommended. The sample adsorbs onto the charcoal bed and significantly decreases the gas volume in the injector during the critical time. (Note - a charcoal trap downstream of the split vent exit does not affect quantitation because the sample condensation occurs independent of the split ratio control pneumatics.) Because of these problems, analysts should not quantitate using split ratio values.

A multiple internal standard technique overcomes many of the problems associated with split injectors. By using internal standards that elute in the beginning, middle, and end of the chromatogram, problems such as mass discrimination or split ratio variation are minimized. External standard quantitation must be performed carefully. All parameters affecting the split ratio must be held constant including: column temperature, split flow or split ratio, sample volume, sample solvent and matrix, and flow rates.

For more information about Split Vaporizing Injectors, read Dr. Grob's newly revised book ***Classical Split and Splitless Injection in Capillary GC*** (Restek cat.# 2045 1). ■