Hints for the Capillary Chromatographer

Operating Hints for Split and Splitless Injection Systems

Split Injectors

Split injectors function by instantaneously vaporizing the sample, sweeping that vaporized stream around the column inlet end, and allowing a portion of the sample to enter the column inlet while the majority of the sample is swept away exiting the split vent. Split injection systems are used for concentrated samples or those which may be split by a ratio of fifty to one (or greater) and still be detected. For FIDs, sample component concentrations above 500ug/ml are generally analyzed in the split mode because a 1ul injection split fifty to one delivers approximately 10ng on-column.

Split injection modes are the easiest to use and offer the most repeatability from injection to injection. They are also ideal for dirty samples since the contaminants can be pre-filtered in the sleeve (through wool, beads, or a glass screw) thus preventin~column contamination. The primary drawback of a split injection is molecular weight discrimination when the high and low boiling components are deiivered in unequal proportions to the head of the column. Often, the low molecular weight components exhibit enhanced area counts and the high molecular weight components show reduced area counts. Because the discrimination is minimal and repeatable, the quantitative accuracy for most samples is acceptable. However, for samples which contain very low and very high molecular weight compounds, (i.e., from C5 to C50), mass discrimination can be significant enough to warrant the use of other injection techniques such as Cold On-column or Programmable Vaporizing Injectors.

Split Injector Sleeve Designs
Many different sleeve designs are available which attempt to overcome the

Table 1 - Split Injector Sleeve Designs

Split Sleeve with Wool

The wool provides a high surface area to allow rapih vaporization of the sample and deliver a uniform mist to the spiit point.

Benefits:
- low cost
- simple to manufacture

Drawbacks:
- glass wool is adsorptive
- high maintenance requirements

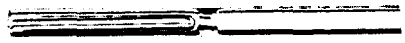
Cup Splitter

The sample ffows through a mini funnel and smashes into a glass cup. The flow path then inverts twice before reaching the split point. Use glass wool or beads for dii samples containing non-active compounds.

Benefits:
- tortuous flow path aids in sample vaporization
- minimizes molecular weight discrimination

Drawback
- difficult to clean

Laminar Cup Splitter



The sample flows through a smal1 orifice and smashes against the head of a glass cup, rather than inside the cup. Then the sample travels around the outside of an elongated cup before the flow is inverted twice.

Benefits:
- best splitter sleeve for high molecular weight compounds
- laminar flow profile pmvides highest resolution
- easy to clean

Drawbacks:
- costly to manufacture

Cyclosplitter

Provides an excepdonal vaporization surface by swirling the sample through a cylindrical, glass screw channel. The cyclone sample pathway provides a large area for sample vaporization,

Benefits:
- ideal for dii samples
- allows many injections of dirty samples before cleaning is required
- easy to clean

Drawback:
- no known drawbacks

limitations of split injectors such aa poor linearity and susceptibility to contamination. (See Table 1.)

Splitless Injectors*

Most split injectors can operate in the splitless mode. Splitless injection modes are used for samples containing trace components that can not be detected if split. The splitless mode is necessary for sample concentrations lower than 50ug/ml (for FIDs). Splitless injectors instantaneously vaporize the sample in the injection port chamber. However, they initially operate in a direct injection mode where the majority of the sample vapor cloud is slowly forced into the column inlet. Then, after approximately thirty seconds to one minute, a solenoid valve opens the split vent and purges excess solvent from the injection port chamber. The choice of solvent and oven temperature profiles must be carefully optimized to properly focus the sample band and provide good quantitation.

Splitless injection modes can be less repeatable and leas quantitative than other injection techniques if the solvent focusing technique and other parameters are not carefully optimized. Splitless injections are not recommended when operating the GC oven isothermally or when the initial starting oven temperature is above the solvent's boiling point. Usually, the oven temperature is set 20°C below the solvent's boiling point to focus the solutes. Then, the oven is rapidly pmgrammed up in temperature to release the sample in a tight band. Splitless injections can be used for dirty samples if the inlet sleeves are packed with glass wool. Just like split injectors, they suffer from molecular weight diirimination where the high and low boiling components are delivered in unequal proportions to the head of the column. Since the injection chamber is swept shortly after the sample injection, splitless injections are not 100% efficient. The majority of the sample vapor cloud reaches the column inlet with only a negligible amount of sample lost through the split vent Gooseneck sleeves, which better contain the sample vapors, are available in an attempt to improve inertness and reduce breakdown of active compounds.

Table 2 - Splitless Injector Sleeve Designs

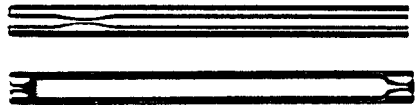
Straight Tube Design

Use for samples containing a narrow molecular weight distribution and not prone to thermal decomposition. Wool packing aids in vaporization of high molecular weight compounds and minimizes discrimination.

Benefit:
- **lowcost**

Drawbacks:
- **decomposes active compounds such as endrin & DDT**
- **prone to high molecular weight dis&mination**

Gooseneck



Ideal for samples with thermally liable or high molecular weight compounds.

Benefits
- **increases splitless efficiency**
- **deceased breakdown of active compounds such as endrin & DDT**
- **chamber contains sample vaporization cloud**

Drawback:
- **higher cost than straight tube splitless sleeves**

Figure la - 4mm ID splitless sleeve without wool exhibits fronting peaks

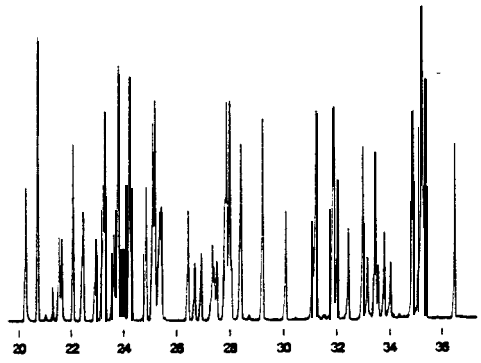
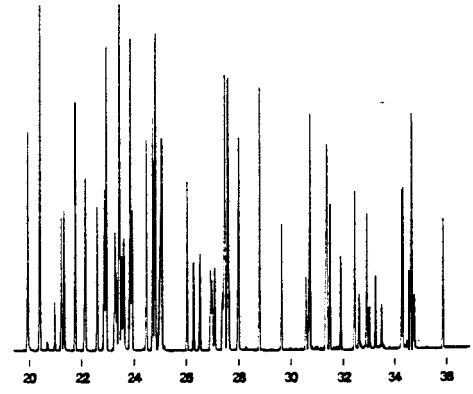


Figure lb - 4mm ID splitless sleeve with wool eliminates fronting peaks by aiding in sample vaporization



Splitless Injector Sleeve Designs

Because spiitless injections slowly transfer the sample to the column, sleeves do not need high surface areas for rapid vaporization except when using rapid auto injectors. These auto injectors require sleeves packed with glass wool to improve sample vaporization. Without wool, the sample is not completely vaporized, resulting in fronting peaks (Figure la). By adding a plug **of** wool, fronting can be reduced or eliminated (Figure lb). The sleeve should be packed with wool if samples contain a lot of non-volatile residue. Use 2mm ID sleeves for sample volumes less than 2u1 and 4mm ID sleeves for sample volumes exceeding 2u1. (See Table 2.)

Turn the page for more helpful hints?

As an **alternative to splitless* **injections,** *direct injections with a* **Uniliner can** *improve* the ***selectivity of high molecular weight compounds. {See The Restek Advantage, VoL 2. No. 2, p.10)***

Helpful Hints for Operating Inlets

Regardless of the type of injection port or GC you are using, obtaining a good seal between the sleeve and inlet is critical for proper operation. Otherwise, peak tailing and loss of sensitivity occurs. Review the flow diagram in your instrument manual and determine where the critical seal is located for your particular inlet.

HP GCs: The critical seal for HP GCs is at the top of the inlet sleeve. Rubber o-rings usually make a leak-tight seal on both split and splitless sleeves, but they must be changed frequently to maintain their sealing integrity. Graphite o-rings are used for HP injection port temperatures greater than 260°C. However, the HP inlet design does not allow adequate torque to be placed on o-rings and they can be prone to leaks if they do not closely match the sleeve OD. In addition, two different sized graphite rings must be used depending on the sleeve type. Use 6.35mm ID graphite rings for split sleeves or$JniRners and 6.5mm ID o-rings for splitless sleeves. Using the wrong sized graphite o-ring will greatly degrade c@matograpbic performance.

HP GCs also use a metal disk to seal at the base of the inlet. This disk must be cleaned or replaced periodically to prevent sample residue build-up which causes adsorption of active compounds.

Varian GCS: Varian GCs use a conventional l/4" ferrule to seal the sleeve in the middle of the injection port body. This ferrule is tightened by turning the slotted cap located just under the septum nut. Either a Vespel or graphite ferrule can be used. Whatever type of ferrule is used, it should be frequently replaced to ensure a leak-tight seal with the sleeve. Use a micro hook tool to pull the fetrule from the injection port body. Prior to replacing the ferrule, slide it over the inlet sleeve to make sure it fits tightly. If the l/4" ferrule slides too easily, then the ferrule ID should be reduced by pre-swaging. Pre-swage the ferrule by inserting it inside any unused l/4" Swagelok-type fitting and tightening the fitting one turn past fmger-tight. Since there is no tubing for the ferrule to bite against in the l/4" fitting, the fetrule ID will compress. Now, remove the ferrule from the fitting and slide it over the inlet sleeve, it should fit tightly and make a leak-tight seal in the injection port.

Split sleeves are 72mm long and use a spring at the injector port base. The spring should be removed when the longer (74mm) double-slotted splitless sleeves are used. Periodically replace or clean the spring and base injection port fittings to prevent sample residue from adsorbing active sample components. Also, make sure the injection port knife edge is sharp enough to cut the septum, or septum lealcs will occur.

Perkin-Elmer GCs: The Sigma series injectors seal by compressing the tapered sleeve outlet onto a graphite ferrule through a spring-loaded metal sleeve located at the injector base. Frequently replace the ferrule and check for scratches and malformations to ensure a proper seal. Auto system sleeves seal at the top of the injection port Make sure the ferrule fits tightly against the sleeve or poor chromatographic performance will result.

Shimadzu GCs: The 9A GC uses sleeves that are 128mm long and maintains a seal using a 5mrn graphite ferrule at the base of the injector double nut fitting. The 14A GC uses sleeves that are 99nun long which seals at the top of the injector using a 5mm graphite ferrule. Make sure the ferrule seals tightly around the sleeve prior to installation or poor chromatographic performance will result with both 9A and 14A GCs. Compress the ferrule by placing it on the inlet sleeve and tightening the sleeve onto a packed column injection port with a 5mm packed column nut.

Protection Against Dirty Samples Using Packed Inlet Sleeves

Non-volatile residue, salts, pyrolizates, septa fragments, and other sample contaminants can be carried from the inlet sleeve to the column and degrade chromatographic performance. Fused silica wool, glass beads, or a glass screw (Cycle) will trap dirt in the inlet and prevent column damage. Packed inlets also aid in sample vaporization and decrease splitter discrimination. However, because of the high surface area, packed inlets can also increase the adsorption of active sample components. Use packings sparingly. One centimeter of fused silica wool or beads is sufficient for most dirty samples. A fused silica wool puller/inserter can be used to insert and position the wool in the sleeve. Position the wool so that it is appmxi-mately lcm from the end of the needle tip when the syringe is inserted in the injector.

Questions about sleeves? They may be answered in our new sieeve bulletin.

Call the wizards at 800-356-1688 for firther details.