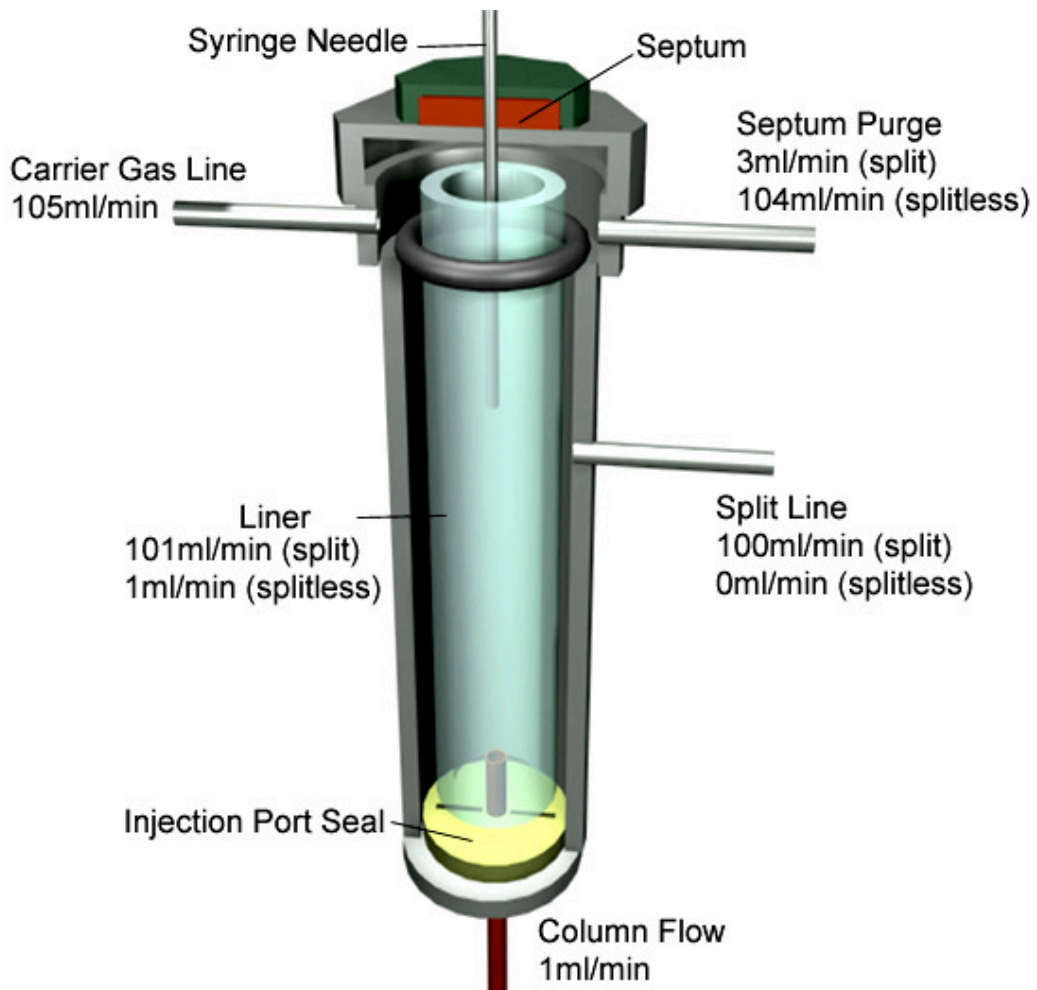
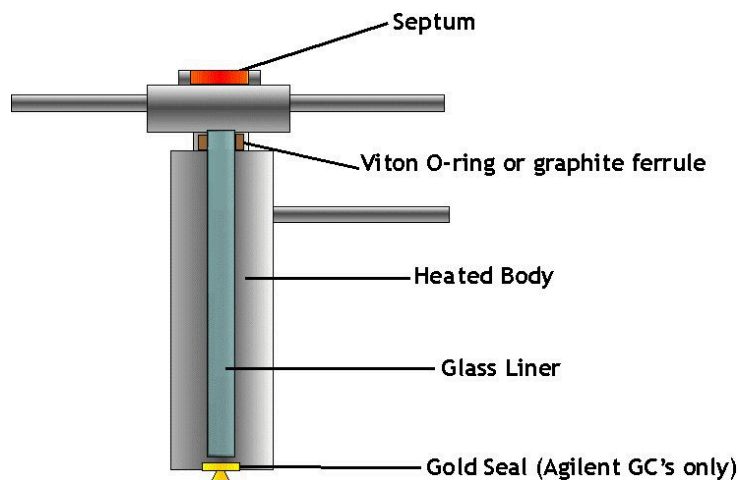


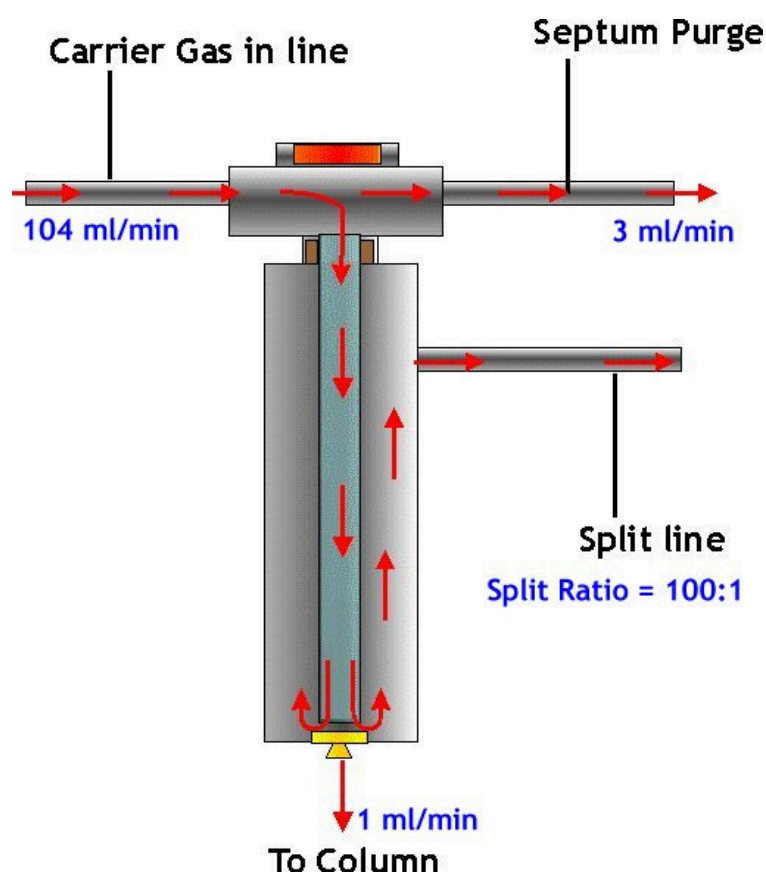
## Spilt / Splitless Injectors



This injector is in common use with capillary GC columns and has two discrete operating modes - split and splitless. A schematic of this injector is shown below:



## Split mode



This mode is used where the analyte concentration in the sample is high (i.e. we are not limited in terms of the amount of analyte). As the stationary phase in capillary chromatography has a limited **capacity\*** it is often necessary to restrict the amount of each analyte that is introduced into the column. In split mode only a fraction (determined by the user) of the vaporised sample is allowed to enter the column - the remainder being directed to waste. The ratio (or fraction) of the amount of sample that enters the column compared with the amount of sample that is discarded (via the split line - often referred to as the 'split flow') is called the **split ratio**:

$$\text{Split ratio} = \frac{F_{\text{column}}}{F_{\text{split} + \text{column}}}$$

The split ratio will have an effect on the shape of the chromatographic peaks and the sensitivity of the analysis. Therefore it is important to ensure that both the column flow and the split flow are accurately set and verified.

## Fundamental Gas Chromatography

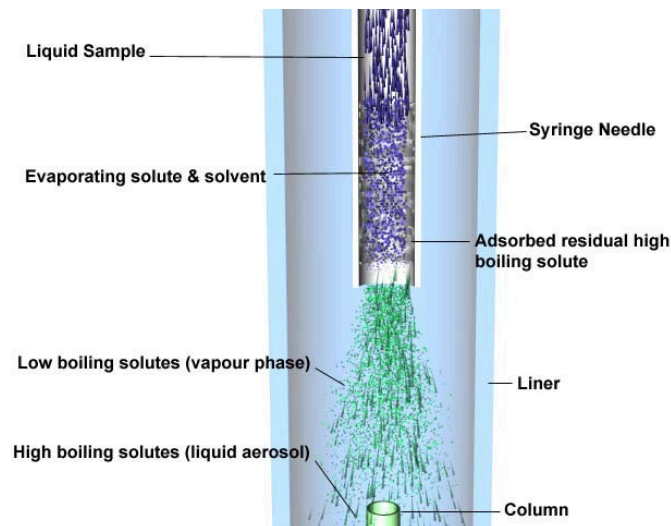
Split injection has some drawbacks:

- Thermally labile analytes may **decompose** in the injector
- **Discrimination** processes may occur in which high boiling analytes do not reach the column with the same efficiency as low boiling analytes

\*capacity - is a measure of the amount of analyte which can be introduced onto a stationary phase without the peak shape deteriorating significantly.

## Sample Discrimination

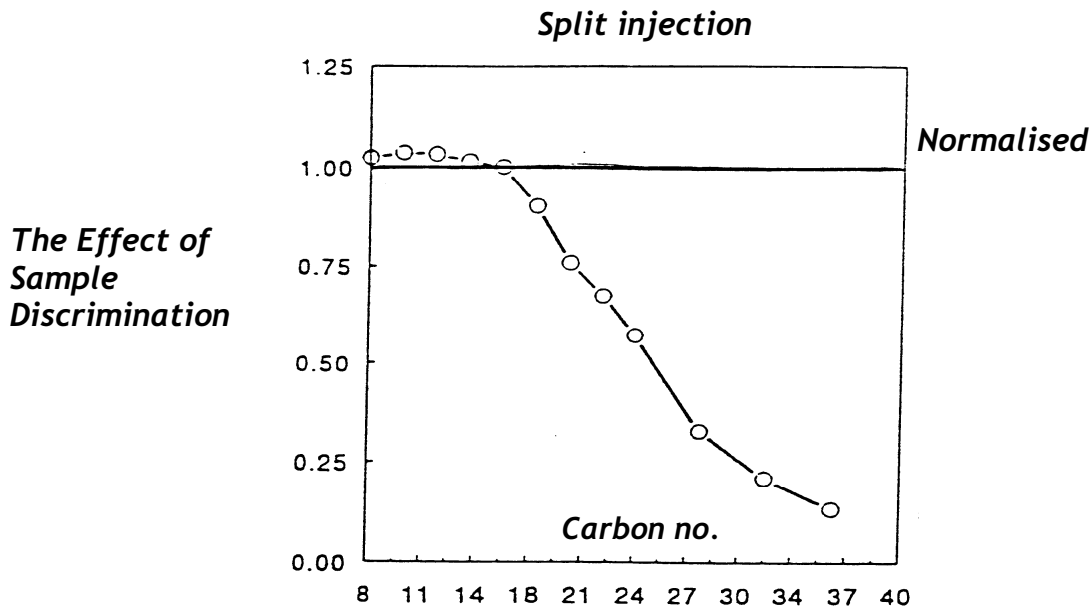
Sample discrimination is caused by condensation of high boiling point components on or in the syringe needle, when placed in the hot injector.



- High boiling point components vaporise at a slower rate and therefore do not enter the column with the vapour plug. They may bleed from the injector over an extended period giving broad peaks or a rising baseline.
- The higher boiling components may also condense on or in the syringe just before it is removed from the injection port.
- In splitless injection the higher boiling compounds which are slowly vaporising from the liner may be ejected from the injection port as the split vent is opened to eject the excess solvent.

It can be seen from the diagram below that as the carbon number increases (and sample volatility decreases), the amount of sample going onto the

column falls off rapidly. By the time C25 is reached, then less than 50% actually gets out of the injector and analysed.



Sample discrimination can be minimised by using either **fast** or **slow** injection.

That is:

- Allow the higher boiling components to evaporate fully from the inner or outer surface of the injection syringe needle by allowing the needle to remain in the inlet longer - bringing the needle up to the temperature of the inlet (slow injection technique).
- Increase the speed of injection (using an autosampler) so that the injected sample is in the liquid form as it passes through the syringe and is expelled into packing within the liner - i.e. well away from the syringe outer surface. By having packing in the liner that 'wipes' the syringe tip as it leaves the inlet - then this will also reduce the degree of injection inlet discrimination (fast injection technique).

### Peak width depends on Split Ratio:

Low Ratio (say 1:5)	High Ratio (say 1:100)
<ul style="list-style-type: none"> <li>• Large peaks</li> <li>• Broad peaks</li> <li>• Column easily overloaded</li> </ul>	<ul style="list-style-type: none"> <li>• Small peaks</li> <li>• Narrow peaks</li> <li>• Higher relative LOD</li> </ul>

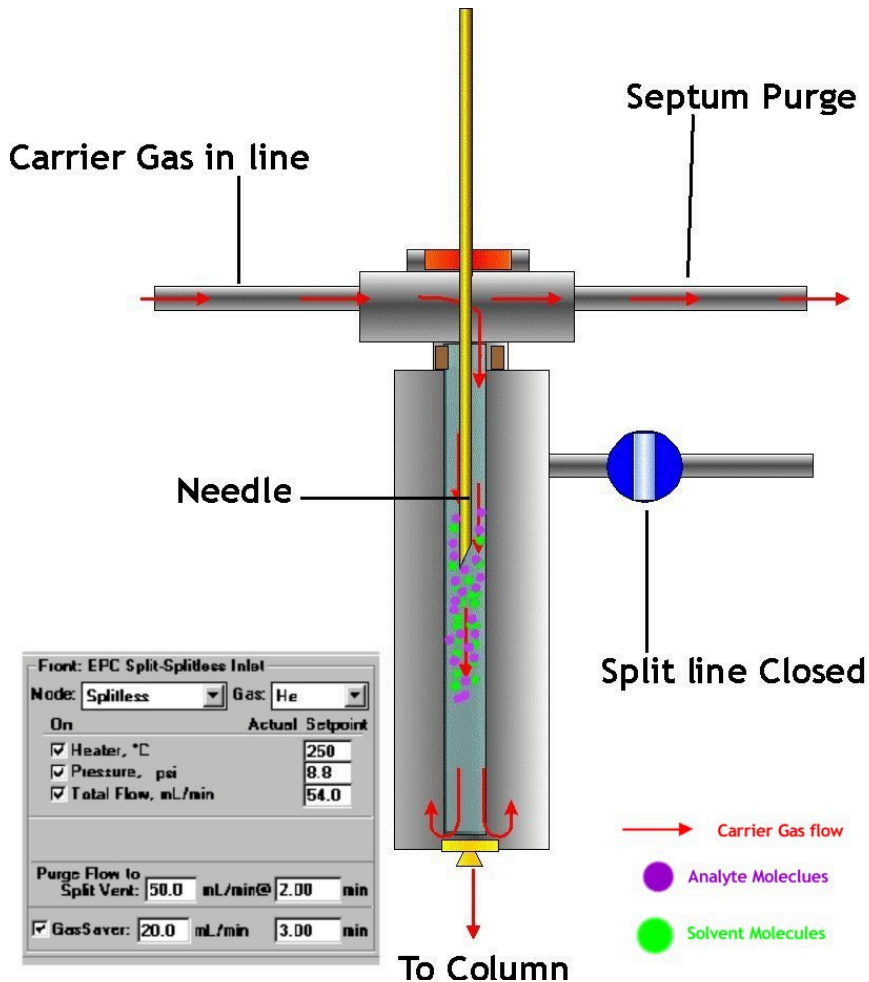
### Advantages and Limitations of Split Injectors:

Advantages	Limitations
<ul style="list-style-type: none"> <li>• Simple to use</li> <li>• Simple column temperature conditions</li> <li>• Can inject high sample concentrations</li> <li>• Protects column</li> </ul>	<ul style="list-style-type: none"> <li>• Cannot use for trace analysis</li> <li>• Components can suffer thermal degradation</li> <li>• Technique suffers from 'sample discrimination'</li> </ul>

## Splitless mode

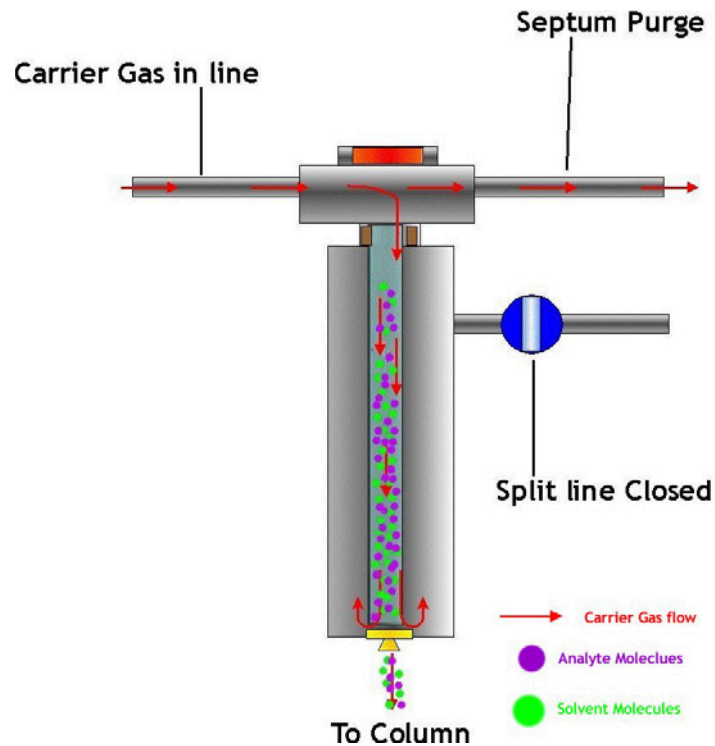
This mode is used where the analyte concentration is low (i.e. analyte is limited and the sample concentration is low). This injection mode uses the same hardware as split injection but the split flow is initially turned off so that the entire vaporised sample enters the inlet end of the capillary column.

The sample is injected into a hot injector where it is vaporised,

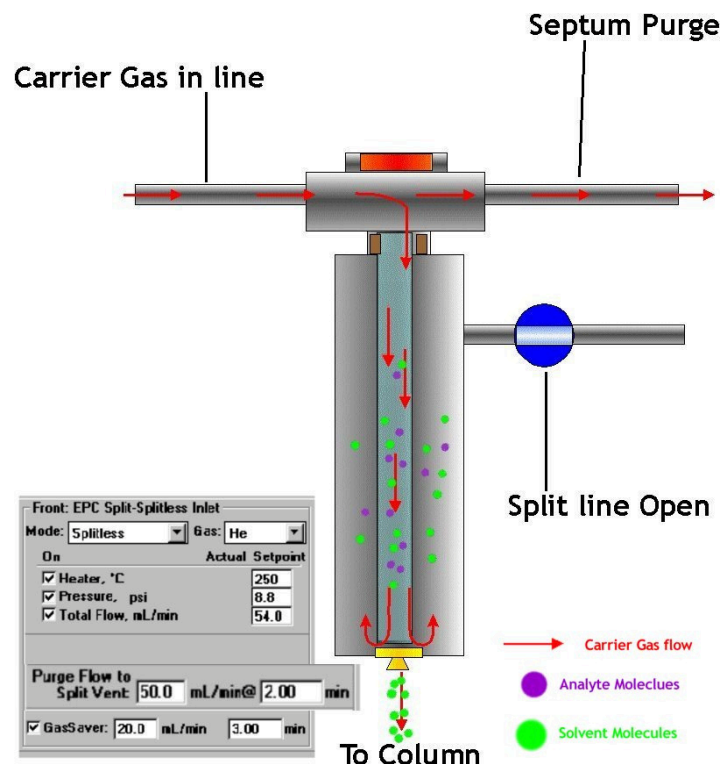


## Fundamental Gas Chromatography

The analyte and solvent molecules then move with the carrier gas onto the column:

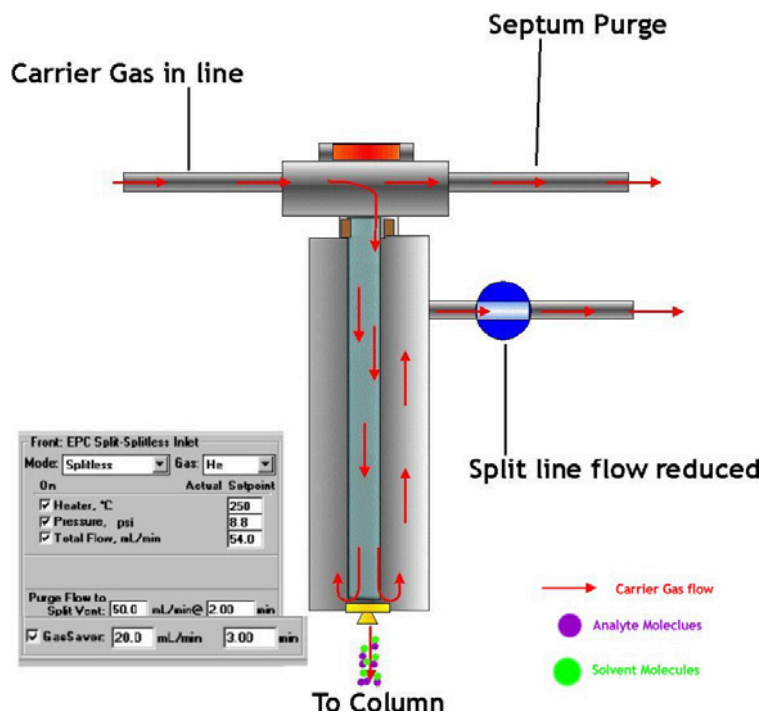


To help clear out the injector and ensure a stable and flat baseline in the chromatogram, the split line is turned on after a user-defined time and any components remaining in the injector are discarded to waste:



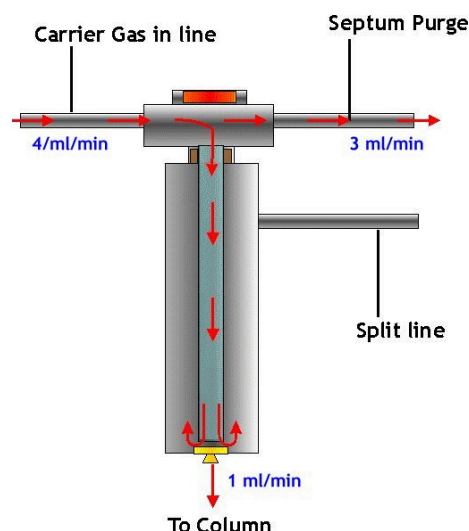
## Fundamental Gas Chromatography

To help preserve the gas supply the flow down the split vent line is often reduced at a user defined time once the liner has been cleared:



The peak shape, sensitivity and baseline appearance in splitless injection are determined by several parameters, which should be accurately set and verified. These parameters include:

- Column flow
- Initial oven temperature
- Split 'on-time' (the time after injection when the split flow is turned on)
- Split flow rate once the split flow is initiated



## Solute Focusing

Splitless injection produces broad peaks if the sample is injected at high initial column temperatures. We therefore need to use solute focussing to eliminate this.

In splitless injection the split vent is closed temporary, usually for about 30 seconds. Unfortunately a 30 second splitless time would give a minimum peak width of about 30 seconds if the GC were run isothermally. We therefore need to condense or focus the sample to reduce the initial peak width.

Solute focusing involves re-concentrating the sample at the head of the column. An appropriate temperature programme is used. Two methods of solute focusing can be used, depending on the volatility of the solutes, and these methods are referred to as Cold Trapping and use of the Solvent Effect.

## Solute Focussing

- Need to re-concentrate sample at front end of the column
- Use appropriate temperature programme

### COLD TRAPPING:

- Concentrates high BP components
- Need column start temperature at 150°C below BP of components

### SOLVENT EFFECT:

- Concentrates low BP components
- Need column start temperature at ~20°C below BP of the solvent

The mechanism of both Cold trapping and the Solvent Effect is demonstrated in the series of diagrams below.

# Fundamental Gas Chromatography

