Sample Introduction Techniques for GC

(Injectors & Injection Techniques)

Customer Support Centre
Shimadzu Asia Pacific Pte. Ltd.
Singapore
2006

Outline

Objective: to learn about GC injectors and basic sample introduction techniques for Shimadzu GC

Topics

- Injectors for GC
- Basic injection techniques
- General tips on injection techniques

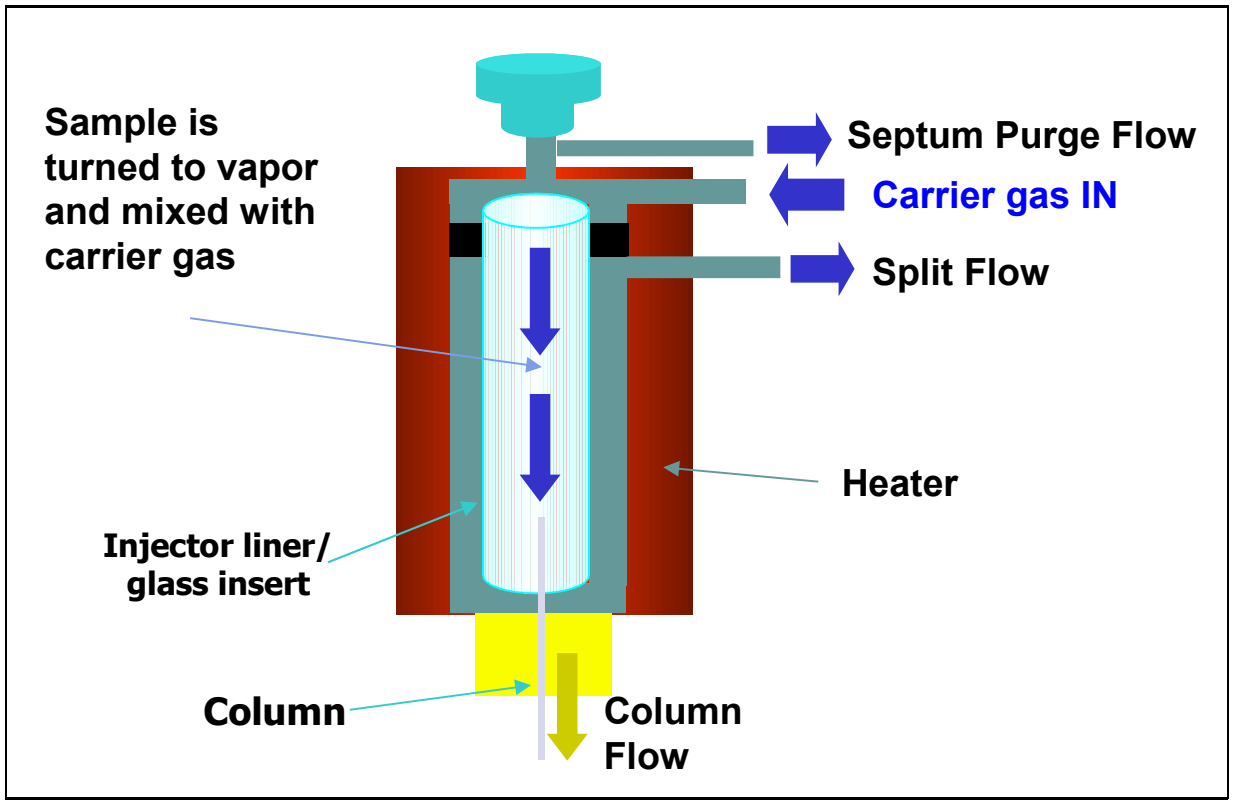
Sample Introduction

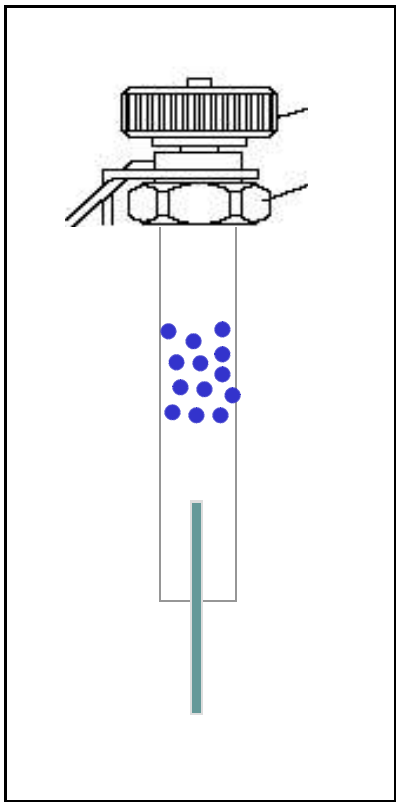
- Purpose: to introduce a representative portion of sample into the column in a reproducible way, while minimizing sample band width

- Goal: The sample must not be chemically altered, unless desired (e.g. derivatization); no contamination, degradation or discrimination

Basic GC Injector Structure

- Sample is introduced to the column through the GC injector, by using
  - Syringe injection
  - Autosampler injection
  - Valve injection

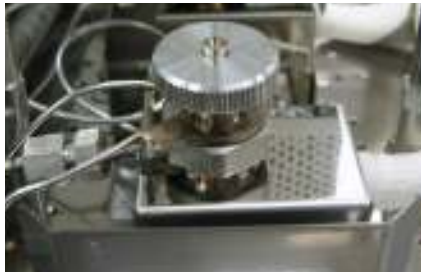


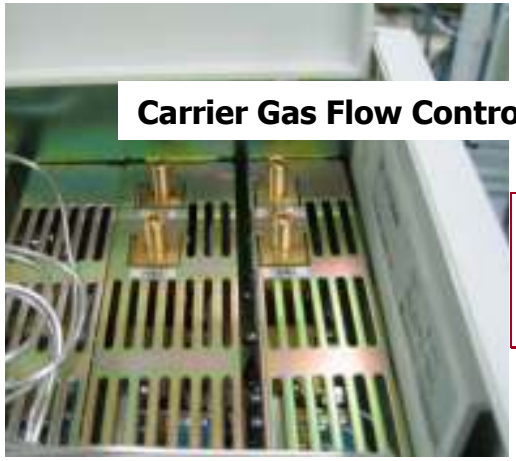


GC Injectors

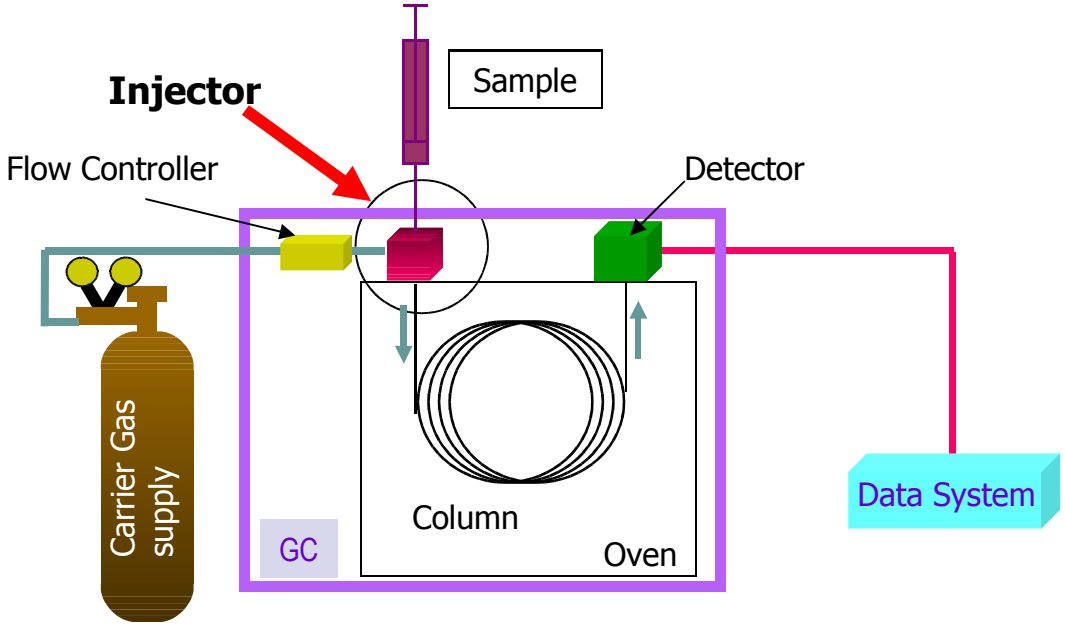
- **Four types of injectors:**
  - Split/splitless injector
  - Direct injector
  - Programmed Temperature Vaporization injector (not in GC-2014)
  - On-Column Injector (not in GC-2014)
  - Packed Injector (not in GC-2010)
- **OCI and PTV share the same injector main body and occupies one injector position for Shimadzu GC**
  - Can be used as OCI or as PTV as needed without major hardware modification
- **Carrier gas supplied to the injector is controlled electronically by using electronic/digital flow controllers**

Split/splitless injector





Electronic Flow Controllers



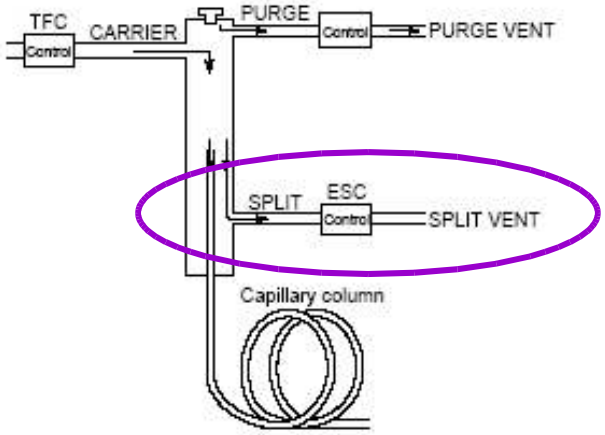
GC Injection Techniques

- Types of GC injection techniques
  - Vaporization injection: sample is instantaneously vaporized upon injection (injector temperature between 140 °C to 350 °C, depending on application)
  - Cold injection: sample is injected at relatively cool injector temperature (e.g. 50 °C)

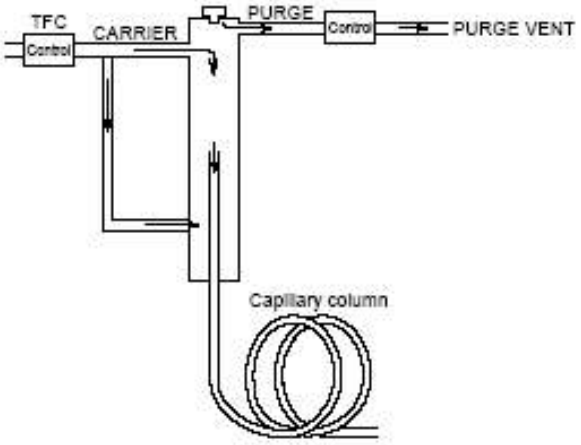
Vaporization Injection Techniques

- Split/splitless injection (most commonly used)
  - Carrier gas flow is split out to column, SPLIT VENT and PURGE VENT
  - Suitable for narrow bore to wide-bore capillary columns

- Direct (wide-bore) injection
  - Carrier gas flow is split out to column and PURGE VENT
  - No split flow line
  - Nearly the entire amount of sample injected is introduced to the column
  - Suitable for wide-bore capillary column (column I.D. 0.53mm)
  - Peaks are usually broader than that obtained by split/splitless (lower resolution)



Split/splitless injector



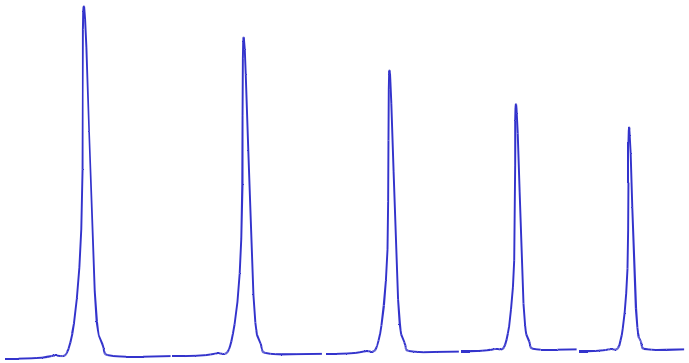
Direct (wide-bore) injector

Cold Injection Techniques

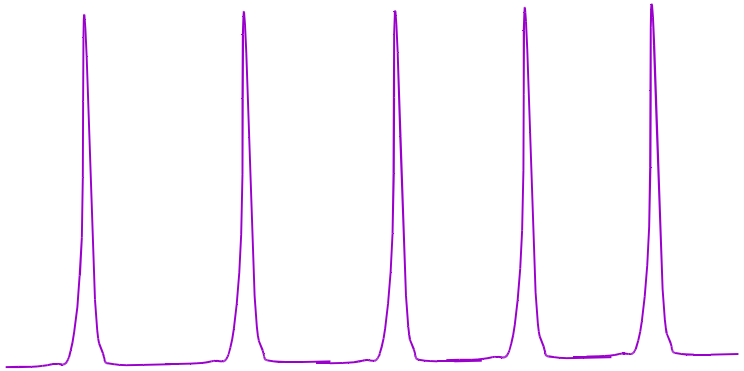
- On-Column Injection (OCI)
  - Sample is introduced directly onto the column
    - Requires special syringe (needle narrows at the tip) and a 0.53 mm I.D. column
  - Injection temperature can be programmed
  - No split flow is used (direct mode)
  - Advantages over vaporization injection
    - Reduced decomposition of thermally labile compounds
    - Reduced injector discrimination for compounds with high boiling points
- Programmed Temperature Vaporization (PTV) injection
  - Sample is introduced through a PTV glass insert
    - No special syringe is required
    - Not necessary to use 0.53 mm I.D. column
  - Injection temperature is programmed with a rapid heating rate (e.g. 250 ^{o}C/min)
    - Lower injector thermal mass allows rapid heating and cooling
  - Split flow is there and can be programmed
  - Advantages are the same as OCI
  - Additional advantage: larger volume of injection is possible
    - Use packing option of glass insert
    - Use split flow program

Injector Discrimination

Injection of mixture of compounds with equal concentrations but a wide boiling point range



- Vaporization Injection
  - Lower peak area for compounds with higher boiling points



- Cold Injection

Split / Splitless Injection Modes

- Split injection
  - Only a portion of the sample injected is introduced to the capillary column
  - Majority of sample is vented (split) to waste
  - Typically used in major/minor component analysis
  - Typically used for higher concentration samples (higher ppm range)
  - Used in Fast GC to obtain narrow peaks

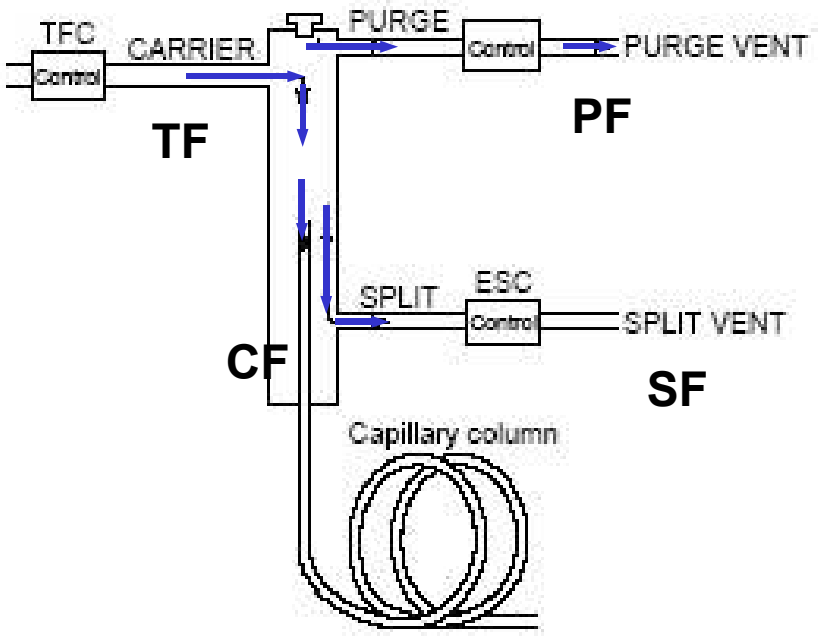
  - High pressure (pulsed) split injection
    - Pressure pulse contains sample expansion and transfers analytes to the column faster

- Splitless injection
  - Majority of sample is put onto the column
  - Relies on solvent or thermal effects for peak shape
  - Typically used in trace analysis

  - High pressure (pulsed) splitless injection
    - Pressure pulse contains sample expansion and transfers analytes to the column faster

Split Injection

- Sample vapor mixed with carrier gas, then flows with the carrier gas:
  - A small flow goes into the column (typically, 1-4 mL/min)
  - A much larger flow (typically 10-100 mL/min) goes out from the split vent
- SPLIT RATIO (SR) is the parameter that determines the amount of sample that goes into the capillary column
- PURGE FLOW (PF) is normally set at a low value (typically 3 to 5 mL/min)



$$\text{Split Ratio} = \frac{\text{Split Flow (SF)}}{\text{Column Flow (CF)}}$$

$$\text{Total Flow} = \text{Split Flow} + \text{Column Flow} + \text{Purge Flow}$$

Splitless Injection

- Two main steps in Splitless Injection:
  - Sampling Time
  - After Sampling Time

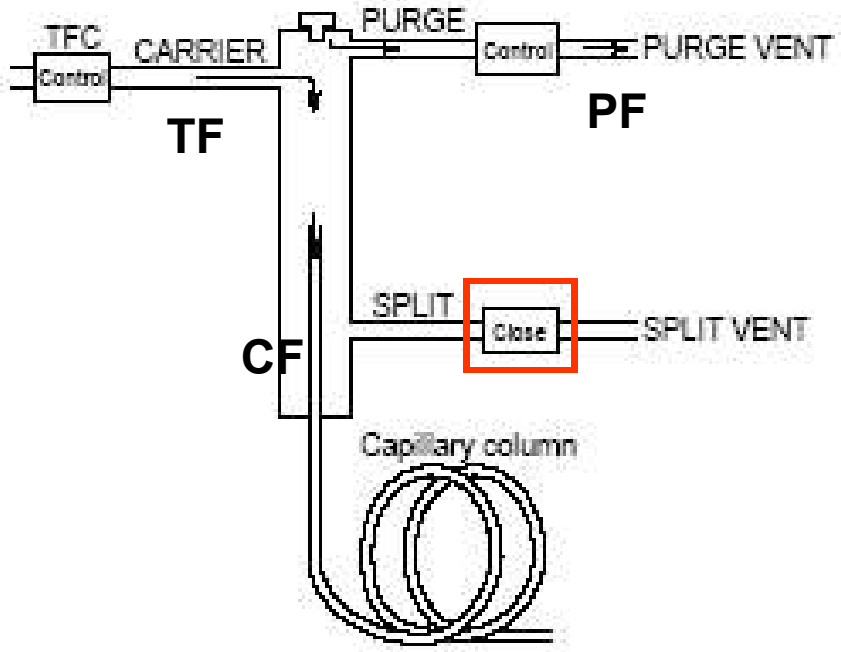
- SAMPLING TIME is the parameter that determines the amount of sample that goes into the capillary column
  - Sampling time is usually set to 2 min maximum

- SPLIT RATIO still needs to be set
  - Split Ratio is set to give Split Flow of about 20 to 30 mL/min
  - e.g. For column flow of 1 mL/min, set Split Ratio = 20 to 30

Splitless Injection (During Sampling Time)

- Split flow line is closed for a period of time called Sampling Time
  - No gas flows through the split vent
  - Almost all of sample vapor goes into the column

- To obtain good peak shapes: Column temperature should be set to a low value (guideline: 10 °C below the solvent boiling point)

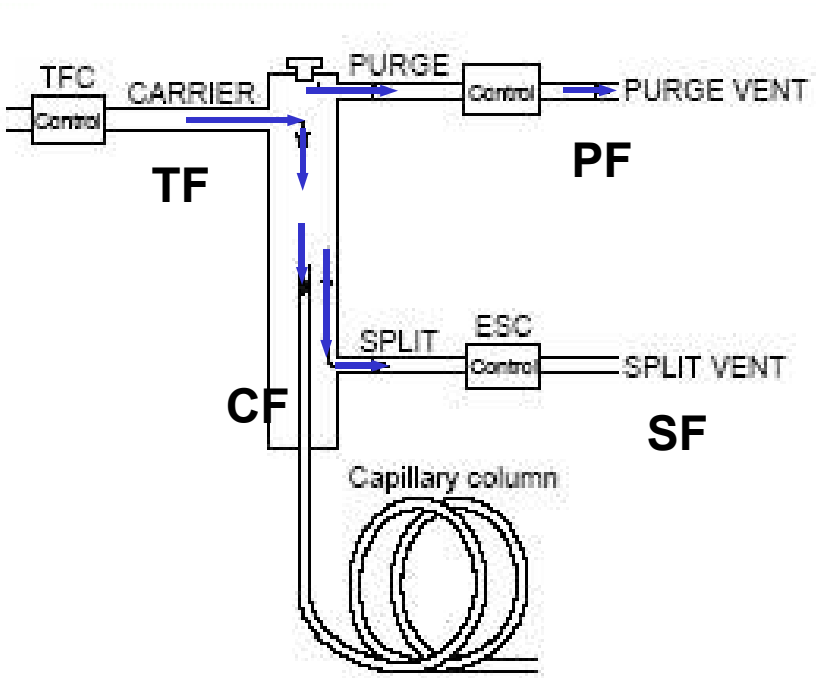


Total Flow = Column Flow + Purge Flow

Splitless Injection (After Sampling Time)

- Split flow line is re-opened to purge out the remaining solvent vapor from the injector

- If purging is not done, solvent peak will interfere with the analysis results



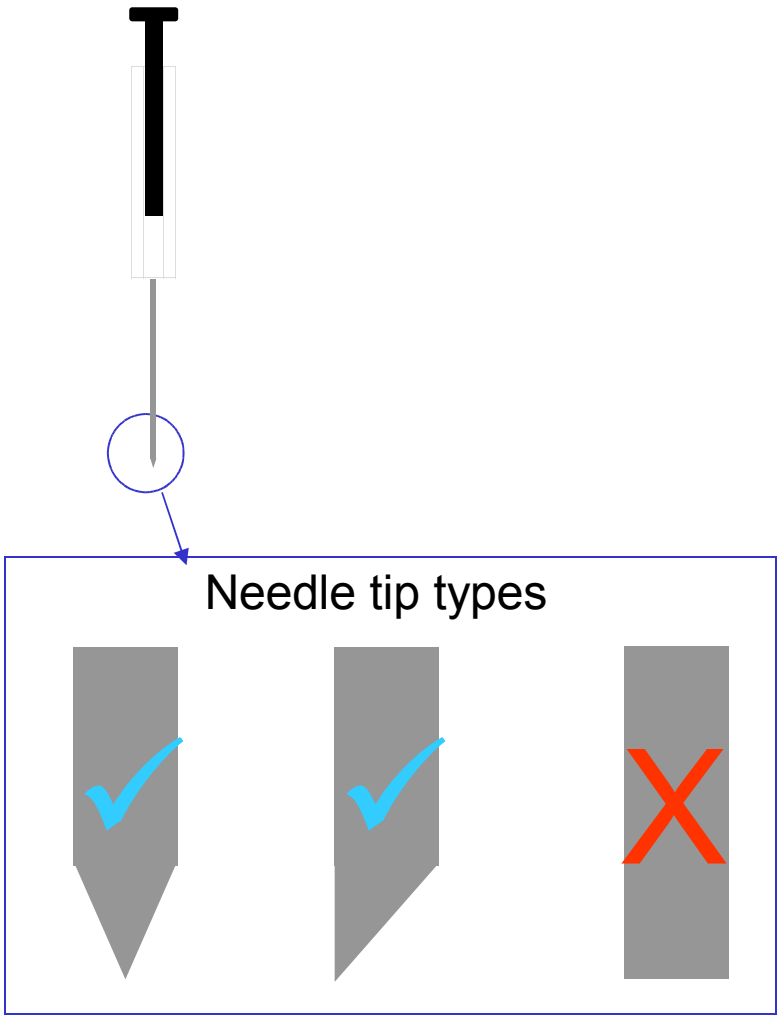
GC Sample Injection Devices

- Samples that is introduced into the GC injector must be in the form of liquid or gas – and not solid

- Sample is most commonly injected in liquid form by using liquid microsyringe
- Gas injection using gas-tight syringe or gas sampling valve is commonly used in certain applications

- For solid samples, the sample must be pre-treated to convert it into liquid or gas form
  - Chemical means (e.g. dissolve sample in solvent)
  - Heating/incubation of sample (e.g. headspace extraction)
  - Thermal decomposition (e.g. pyrolysis)

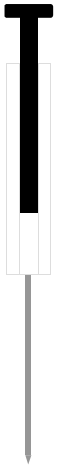
Injection Using Syringe



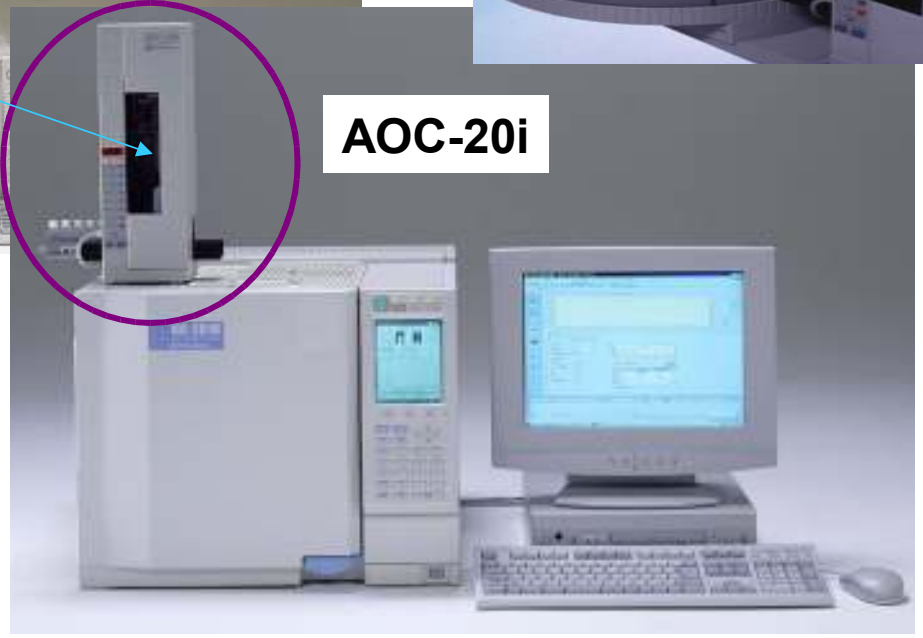
- GC syringe must have pointed needle

Liquid Injection Device

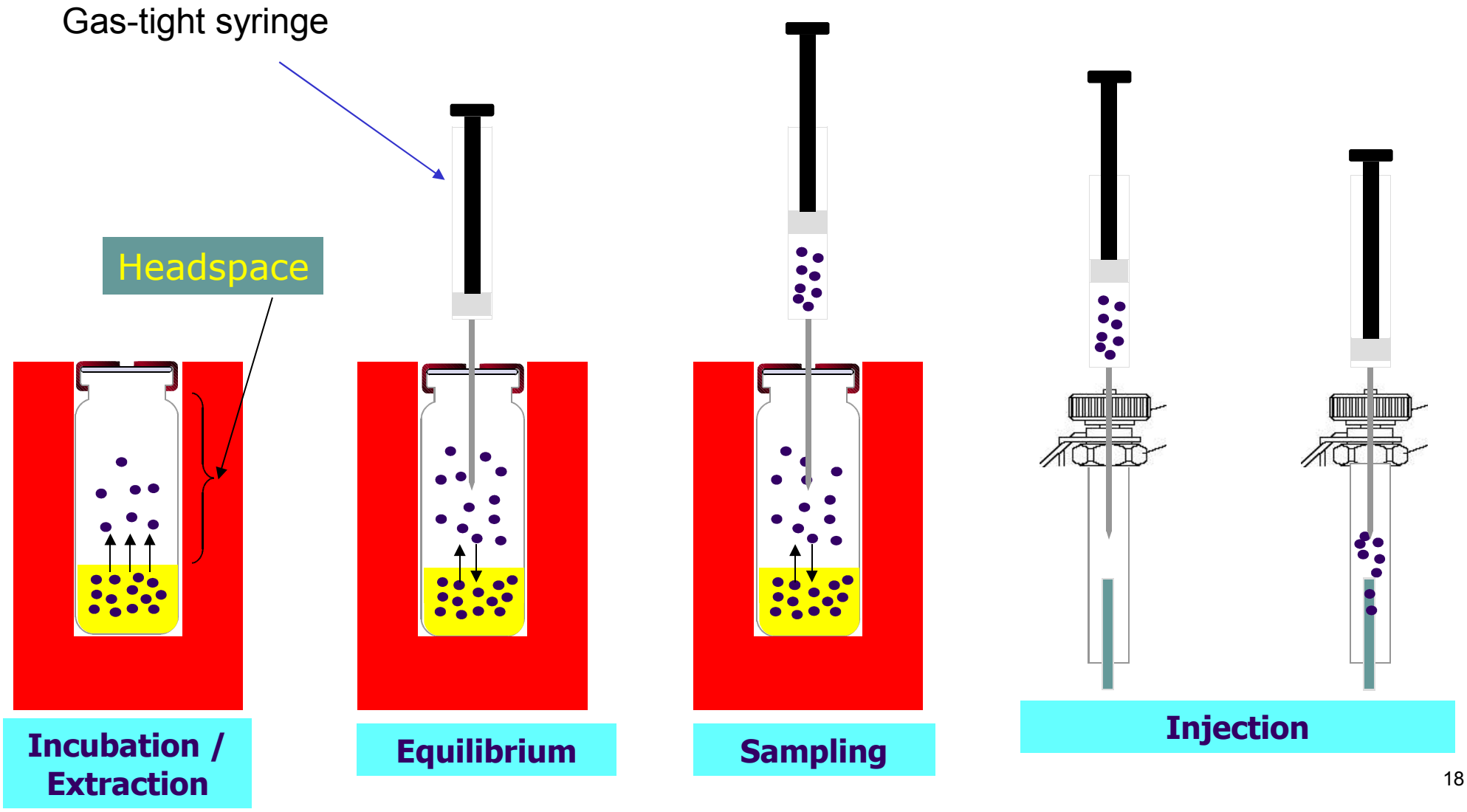
Liquid microsyringe



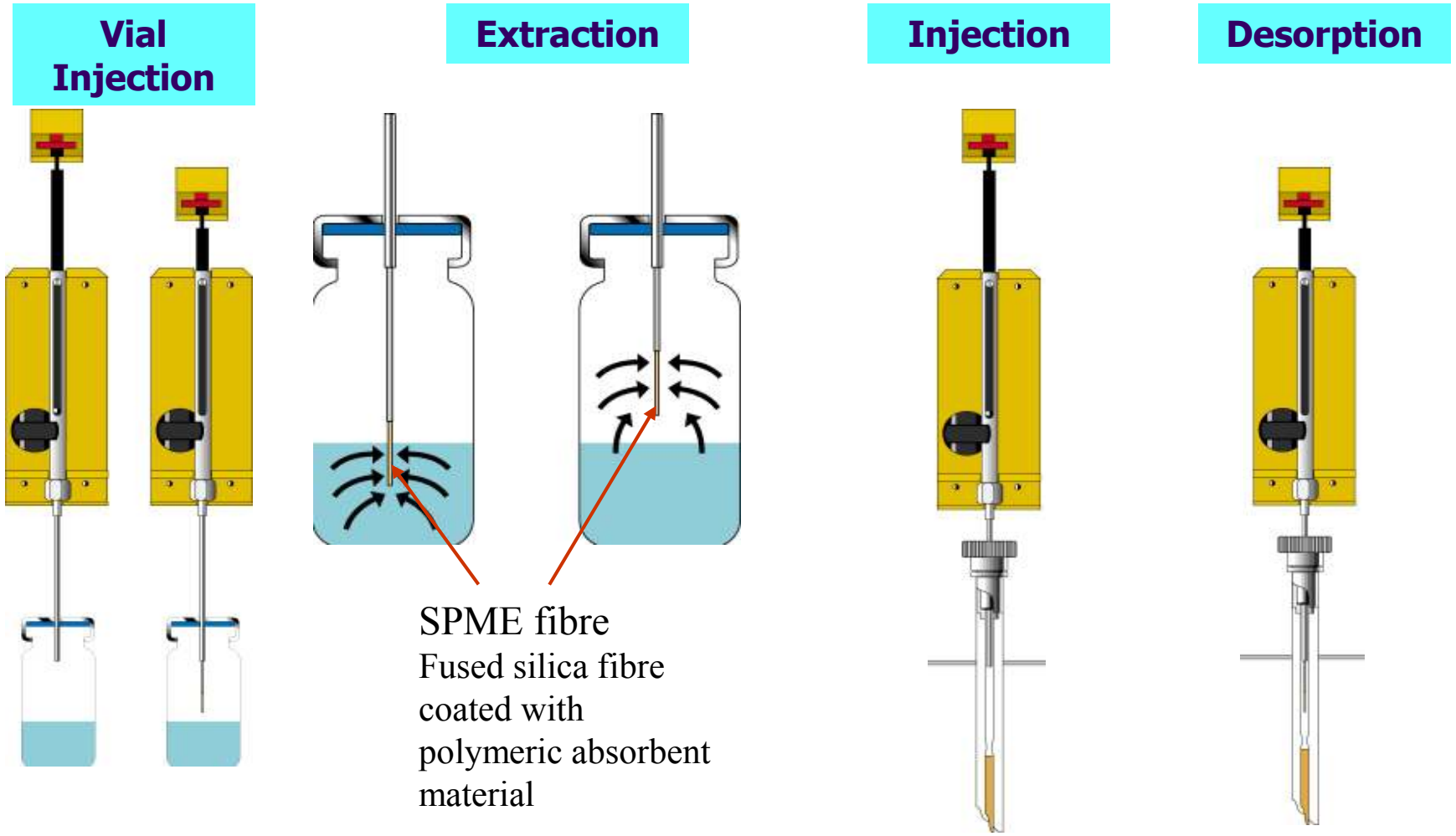
Automatic liquid injector / samplers



Headspace (HS) Extraction/Injection



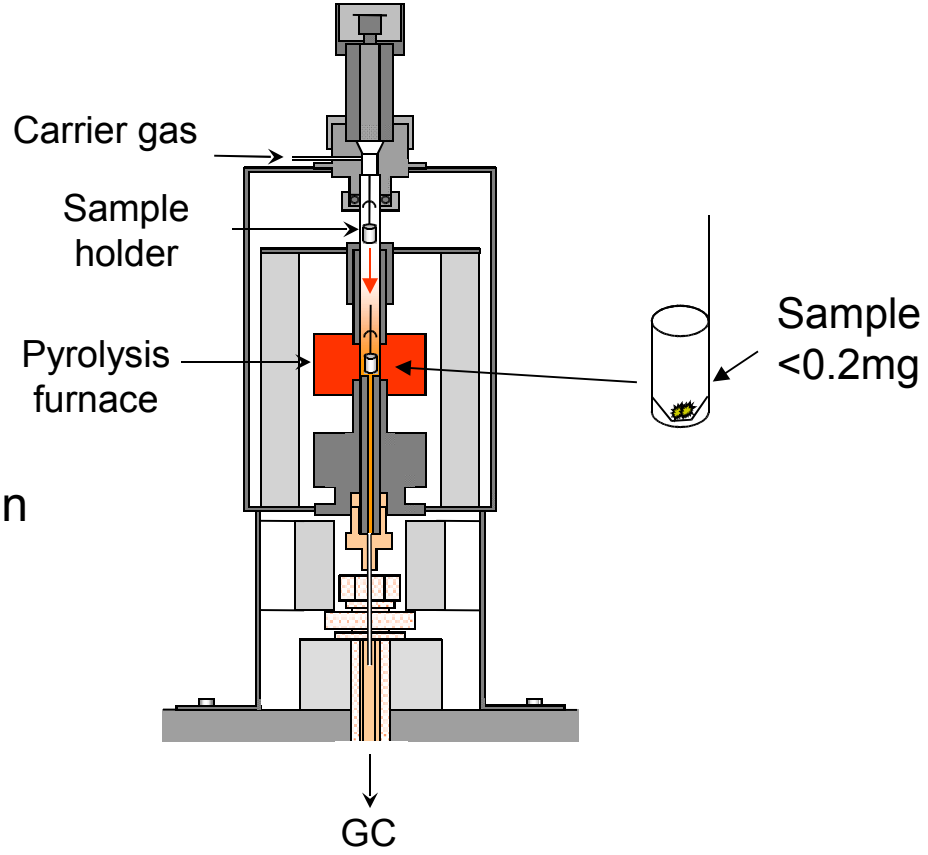
SPME (Solid Phase Micro-Extraction)



HS & SPME Auto-sampler

Pyrolysis

PY-2020iD Pyrolyzer Unit



- Sample is heated at/above 500 °C in the absence of oxygen (pyrolyzed)
- Sample molecule is thermally decomposed to give smaller, more volatile molecules
- Suitable for samples with very high molecular weight like polymeric materials

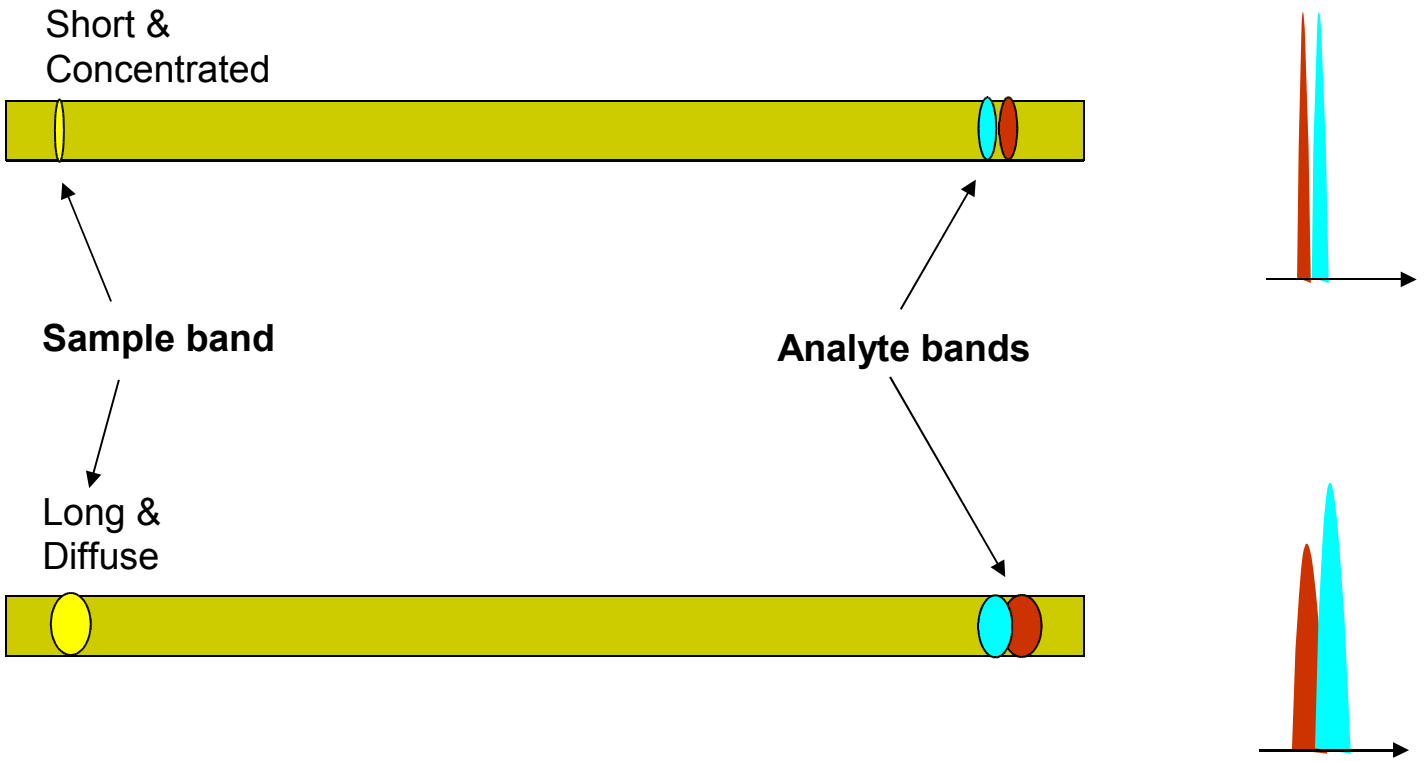
General Tips on Injection Techniques

Sample Introduction

- Purpose: to introduce a representative portion of sample into the column in a reproducible way, while minimizing sample band width

- Goal: The sample must not be chemically altered, unless desired (e.g. derivatization); no contamination, degradation or discrimination

Influence of Injection Efficiency on Sample Band Width



Glass insert

- Purpose:
  - Provides an “inert” space for liquid samples to be vaporized uniformly and transferred to the column
  - Improve peak shape (fast transfer of sample vapor)
  - Etc…
- Liquid-gas phase change involves a significant change in volume
- Gaseous sample volume depends on:
  - Temperature of injector
  - Column inlet pressure
  - Solvent type

Choosing a suitable glass insert

- Consideration for the best chromatography:
  - Glass insert volume
  - Glass insert deactivation / treatment
  - Special features (e.g. glass wool, silica wool, taper, etc.)

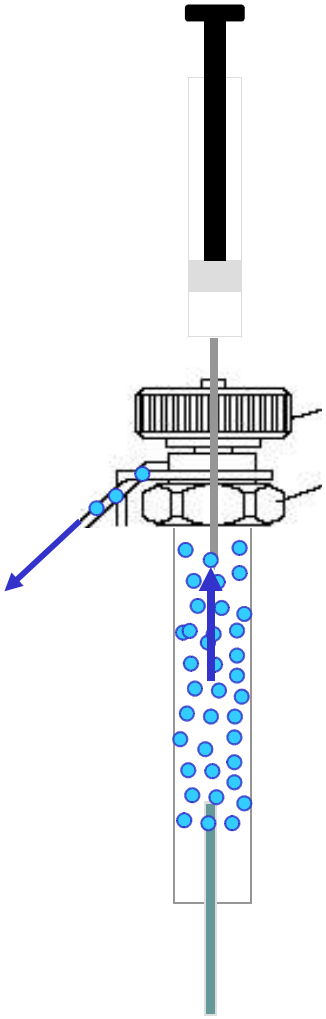
- Also consider:
  - What type of injector is used in your GC
  - The application itself and the types of glass inserts and injection techniques used for it

Split Splitless	On-column	Programmable Temperature Vaporization (PTV)

Volume of glass insert

- Glass insert volume must be sufficient to accommodate the sample vapor
- Important especially for polar solvents with large vapor volumes
- If sample vapor volume exceeds the glass insert volume, sample may “backflash” (flow back) into carrier gas supply lines, and cause ghost peaks and reproducibility problems

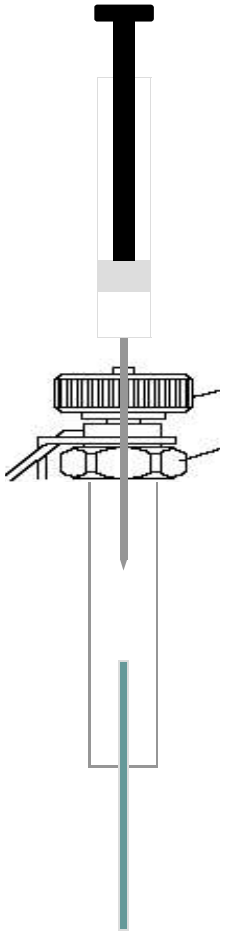
Backflash



- Sample expands in the injector
- If sample vapor volume exceeds the insert's volume, some sample flows out of the injector from the top of glass insert
- Sample will condense on the cool areas (e.g. carrier gas line)
- Condensed sample will be dislodged in the next injections or by the carrier gas, then sample enters the column as ghost peaks

Injection volume

- 1-2 microlitre or less for organic solvents
- 0.5 microlitre for water



Glass insert deactivation

- Minimize possibility of active sample components from adsorbing on active sites on the glass insert or glass wool surface
- Unwanted sample adsorption leads to tailing peaks and loss of response for polar compounds
- Deactivation of borosilicate glass inserts is often done with a silylating reagent, e.g. dimethyldichlorosilane (DMDCS)

Glass insert wool

- Amount, size and placement must be consistent for consistent results
- Can be broken upon installation into the glass insert, thus exposing active sites
- Glass insert deactivation with glass wool plug in place is ideal

Placement of wool in glass insert

- Near top of glass insert
  - Wipes sample from syringe needle
  - Can improve injection precision
  - Helps to prevent backflash

- Near bottom of liner
  - Helps in vaporization of high MW components
  - Increases mixing

Microsyringe

- Reproducibility of liquid injection also depends on the quality of maintenance of the microsyringe, among other things