Chemistry 4631

Instrumental Analysis

Lecture 24

Gas Chromatography

Introduction

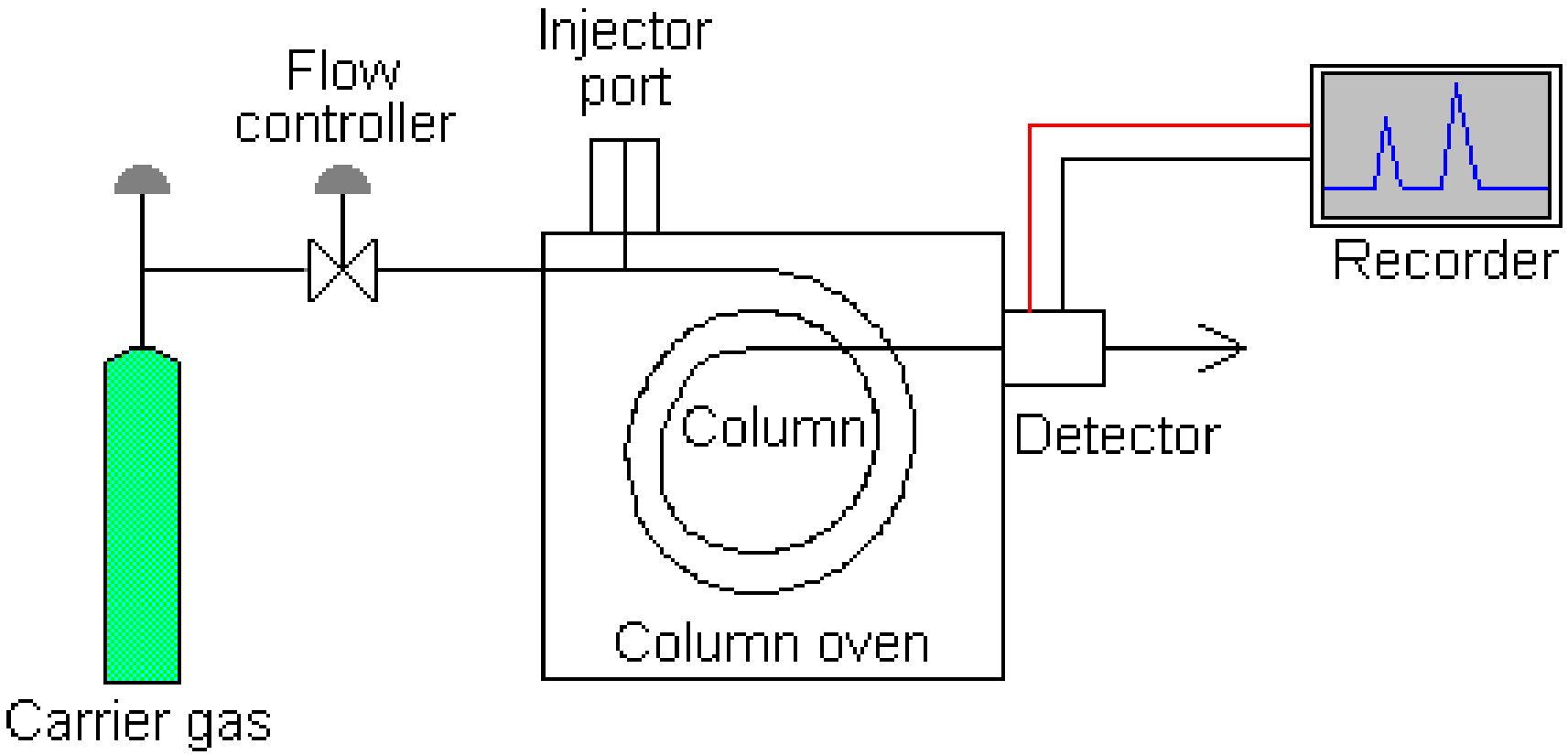
GC covers all chromatographic methods in which the mobile phase is gas.

It may involve either a solid stationary phase (GSC) or a liquid stationary phase retained on a solid solvent (packed column) or a column wall, such as in an open tubular column (GLC).

With the exception of a few specialized areas (i.e. inorganic gases) GLC is used.
Open tubular columns are the most popular.

Gas Chromatography

Instrumentation



Gas Chromatography

Instrumentation

Carrier Gas (Mobile Phase)

- Carrier gas usually consist of He, N, H or a mixture of argon and methane. The function of the gas is to carry the sample through the system.

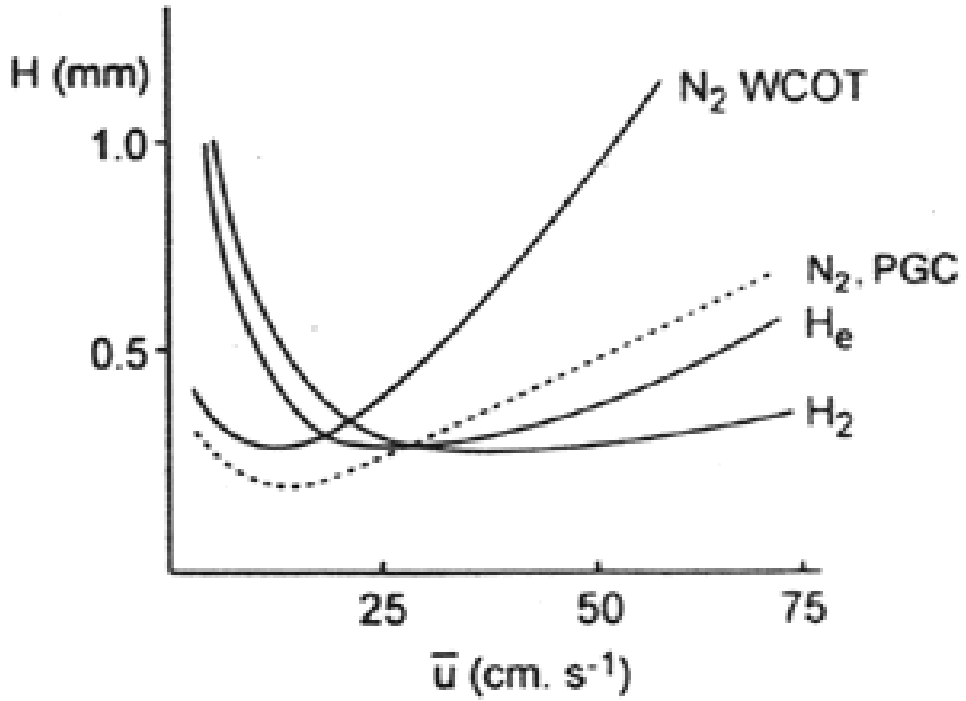
- The carrier gas must be:
  - inert toward the sample
  - dry
  - thermally stable
  - safe
  - cost effective
  - compatible with the detector

- He and N are the most popular carrier gases in GC.

Gas Chromatography

Instrumentation

The most efficient separations are achieved with N_2 as a carrier gas. This can be seen with the following van Deemter curve:



Gas Chromatography

Instrumentation

- **N_2 has a greater molecular weight and smaller diffusion coefficient – so lower β term, but must sacrifice analysis time. Best efficiency is at 8-10 cm/s.**
- **H and He have better analysis time w/ a small sacrifice in efficiency.**
  He → 16-20 cm/sec H → 35-40 cm/sec
- **To reduce deterioration of the stationary phase and to lessen detector noise – high purity gas needs to be used. For this reason oxygen and moisture traps in the carrier gas lines are used.**

Gas Chromatography

Instrumentation

The flow of gas is described by two variables

- **- the flow rate (measured in ml/min)**
- **- pressure drop between the injection port inlet and detector outlet**

Carrier gas is regulated by a flow controller – newer instruments use electronic programmable flow controllers.

Gas Chromatography

Instrumentation

Sample Injection

- Peak widths are influenced by the efficiency of the injection process. The shorter the length of the column occupied by the injected sample, the shorter the band as it begins and completes the chromatographic process.
- The critical function of the injection process is to introduce the sample so that it occupies the shortest possible length of column.

Gas Chromatography

Instrumentation

Sample Injection

Syringe Technique

- Universal method of introduction is with a microsyringe through a septum.

- Reproducibility with gas samples is poor since the volume of gas is temperature dependent – use of a sampling valve increases precision. Most samples are injected as liquids.

Gas Chromatography

Instrumentation

Sample Injection

Syringe Technique

Several techniques are used to inject the sample:

- **A vaporizing injection can retain the sample in the needle when introduced into the injection port. Most common and simple but poorest method.**
- **Variations include hot needles, solvent flush (or air), cold needles and filled needles.**

Gas Chromatography

Instrumentation

Sample Injection

Syringe Technique

- **Hot needle - sample in barrel only (temperature allowed to equilibriate).**
- **Cold needle - sample in barrel only (immediate injection).**
- **Filled needle - sample in barrel and needle.**
- **Solvent flush - solvent + sample + solvent or solvent + air + sample + air.**

Gas Chromatography

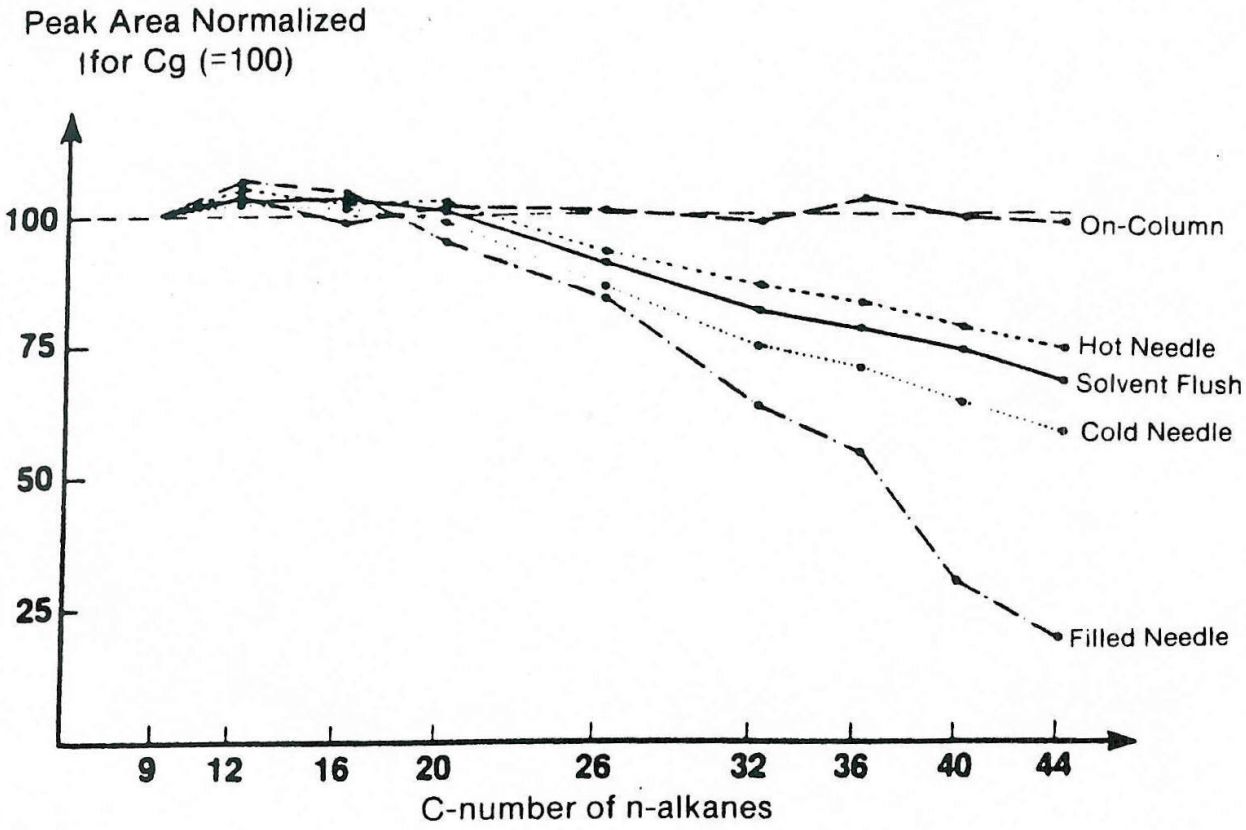


Fig. 3.5. Discrimination of *n*-alkanes obtained by different injection techniques using a split injection (1 μl; split ratio 1:15) and injection port temperature of 350°C. Methods of syringe handling are described in the text. Reproduced with permission from Grob and Neukom (1979). *J. High Resol. Chromatogr., Chromatogr. Comm.*, **2**: 15.

Gas Chromatography

Instrumentation

Sample Injection

Split Injection

- **First open tubular column injection technique used.**
- **Sample is injected using solvent flush or hot needle technique and after evaporation and mixing with carrier gas, the sample is split into two unequal portions – the smaller one passes to the column while the rest is vented to waste.**

Gas Chromatography

Instrumentation

Sample Injection

Split Injection

Dynamic Splitting

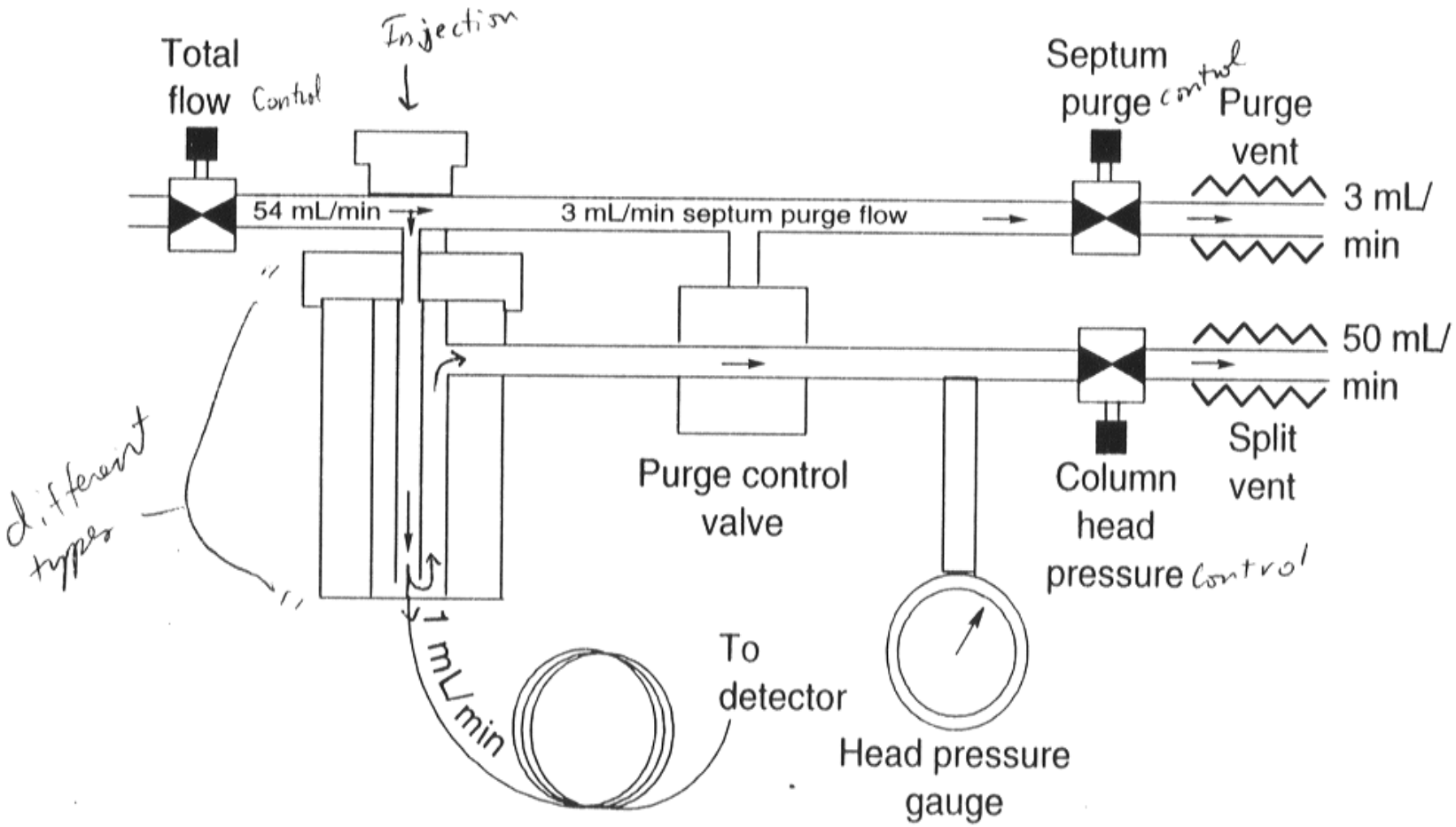
- Evaporation, mixing and splitting of the sample in a flowing stream – most common.

Why split? – capillary columns have a limited sample capacity.

Gas Chromatography

Instrumentation

Figure 8.2 Split inlet of the HP5890 GC. *(Courtesy of Hewlett-Packard Company.)*



Gas Chromatography

Instrumentation

Sample Injection

Split Injection

Total carrier gas flow into the inlet is split into three portions as it passes the inlet port.

- 1st portion – 1 to 3 ml/min – passes past the septum to sweep away contaminates from the septum to purge vent.
- 2nd and 3rd portion then flow into the inlet of the injection port.
- At the bottom of the injection port a split occurs
  - a very small portion flows down into the column
  - » ~ 1 ml/min
  - the rest flows out the split vent

Gas Chromatography

Instrumentation

Sample Injection

Split Injection

So ~90% of the sample is thrown away, however for quantitative analysis the proportion of the sample analyzed must be known.

- Split Ratio = $\frac{\text{split vent flow + column flow}}{\text{column flow}}$
- Split ratios range from 10:1 to 500:1.

For our figure:

Split Ratio = $\frac{50+1}{1}$ = 51:1

Gas Chromatography

Instrumentation

Sample Injection

Split Injection

- The smaller the column the higher the split ratio used to keep from overloading the column.
- Disadvantage: split inlets have a high probability of suffering from sample discrimination. So it is important to select the appropriate liner. (Variables – molecular size, polarity of analytes, injected volume, diameter of split liner, viscosity)

Gas Chromatography

Instrumentation

Sample Injection

Splitless Injection

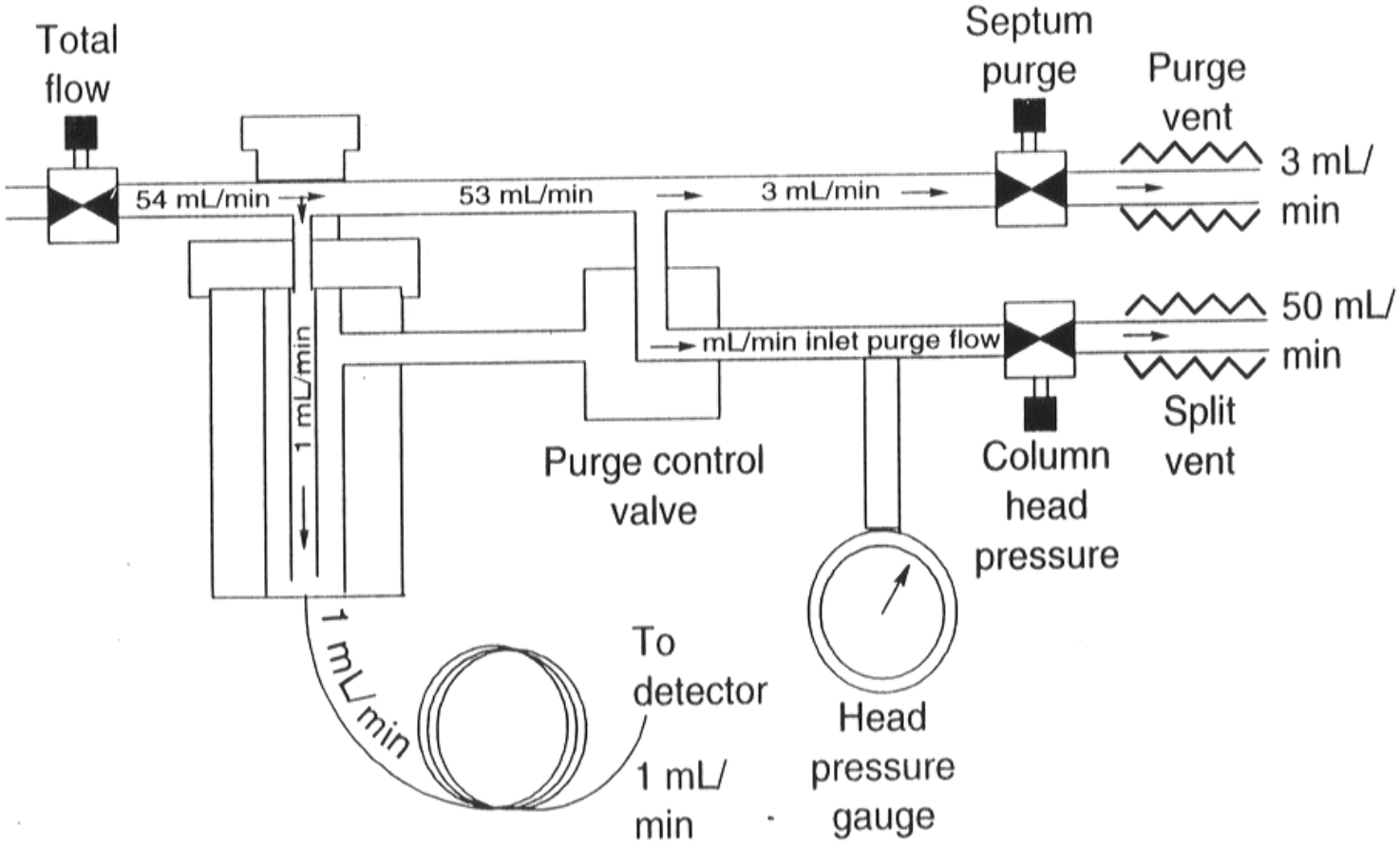
- For ultratrace analysis, very complex samples with wide range of boiling points – splitless injection is better.

- There are two types
  - evaporation and trapping (PTV – programmed temperature vaporizer)
  - cold-on-column injection or direct on column

Gas Chromatography

Instrumentation

Figure 8.3 Splitless configuration. *(Courtesy of Hewlett-Packard Company.)*



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Sample Injection

Splitless Injection

- For splitless – a large volume (1-5 ml) of dilute sample is introduced. The carrier gas velocity is lower for splitless than for split.
- Residence time of sample in injection port liner is longer for splitless mode (15 s) than for split mode (less than 1 sec).

Gas Chromatography

Instrumentation

Sample Injection

Splitless Injection

- Splitless work best for bonded phase columns since a high solvent load is placed on the column.
- Cold-on-column injection reduces solute decomposition and discriminatory effects if the injection is rapid. One disadvantage is that non-volatile material in the sample will enter the column and remain there.
- So the programmed temperature vaporizer (PTV) was developed using a cold split/splitless injection port, which can be rapidly heated. Non-volatile materials remain in the inlet and discrimination from the needle is minimized since the port is initially cold.
- PTV is a universal injection system – program – split/splitless.

Gas Chromatography

Instrumentation

Sample Injection

Programmed Temperature Vaporizing (PTV)

- PTV is a universal injection system that can be used in split, splitless or direct mode.
- The initial inlet temperature is below the boiling point of all components including the solvent.
- After the sample is injected, the temperature of the inlet is programmed to increase at a high rate.
- Linearity up to C28 hydrocarbon.

Gas Chromatography

Instrumentation

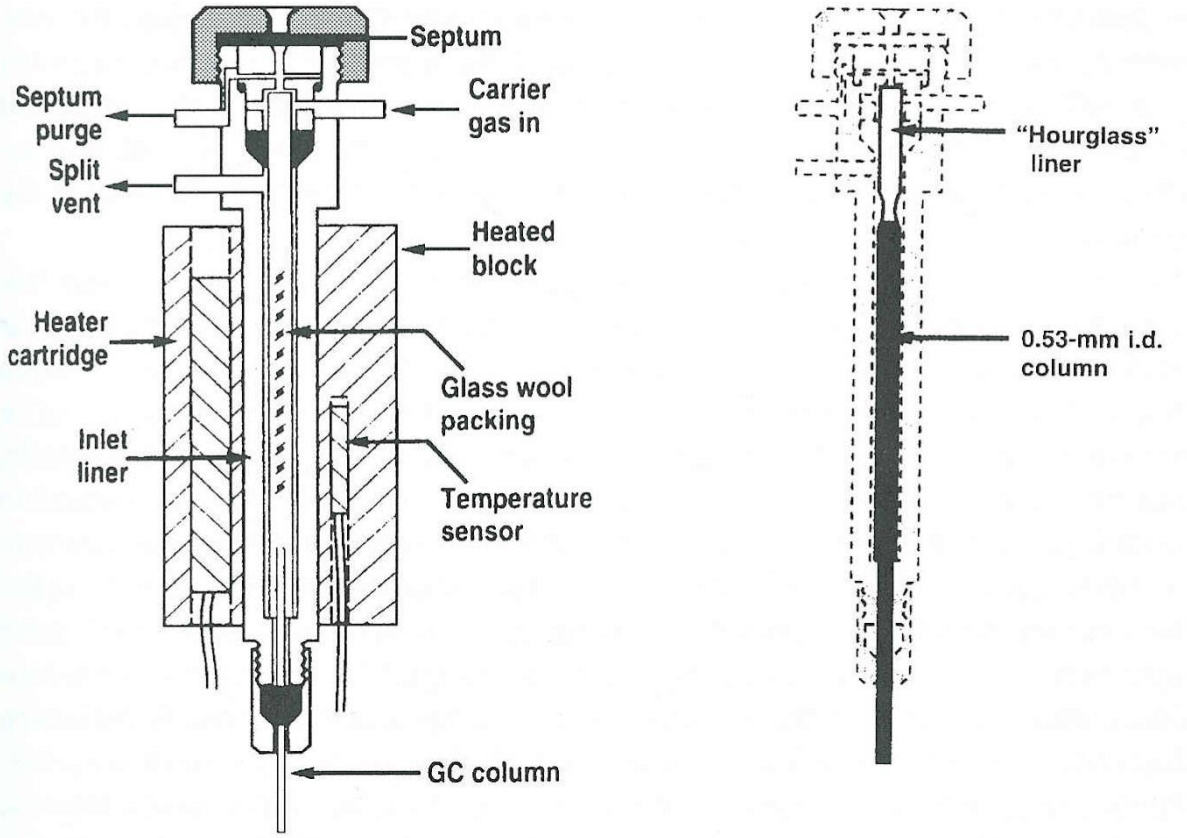


Fig. 3.7. Left, a Schematic representation of a PTV injector configured for split/splitless injection. The cooling coils were omitted for clarity. Right, the same injector modified for on-column PTV injection. The glass insert helps guide the needle directly into the column. *Taken from, J. Hinshaw, LC–GC, **10**:748 (1992)* with permission.

Gas Chromatography

Instrumentation

Sample Injection

Purge-and-Trap Method

- Effective way for sampling and analyzing low levels of volatile organic compounds from matrices such as drinking water, waste water, soil, and sludge.

- Preferred method for evaluation of water purity in the US using EPA methods. One method can quantitate 82 analytes at a detection limit of 0.1 ppb in a single analysis.

Gas Chromatography

Instrumentation

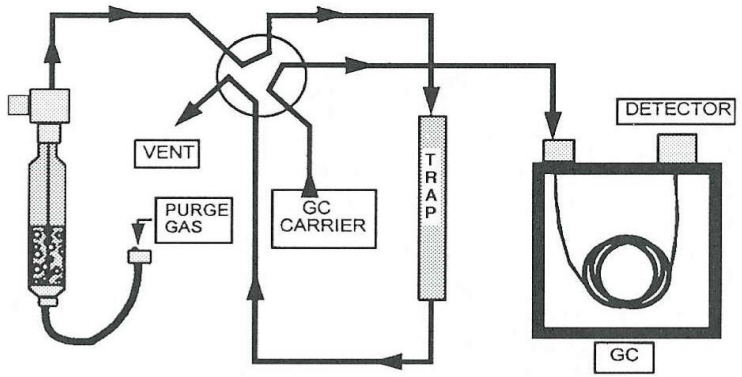
Sample Injection

Purge-and-Trap Method

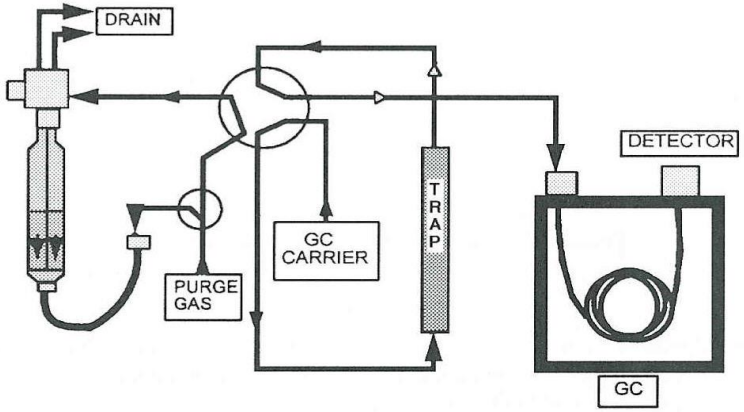
- A sample (liquid) is purged for a specific time and temperature with a purge gas, usually helium.
- The volatile analytes are swept by the purge gas to a trap and absorbed.
- The trap material (usually Tenax - 2,6-diphenylene-oxide polymer resin) is an absorbant material.
- After a specified trapping time, the trap is rapidly heated and the analytes are desorbed and swept into the GC column by the carrier gas.

Gas Chromatography

Instrumentation



PURGE STATE



DESORPTION & DRAIN

Fig. 3.16. Schematic representation of a purge and trap concentrator in the (top) purge, and (bottom) desorb modes. The six port valve is automated.

Gas Chromatography

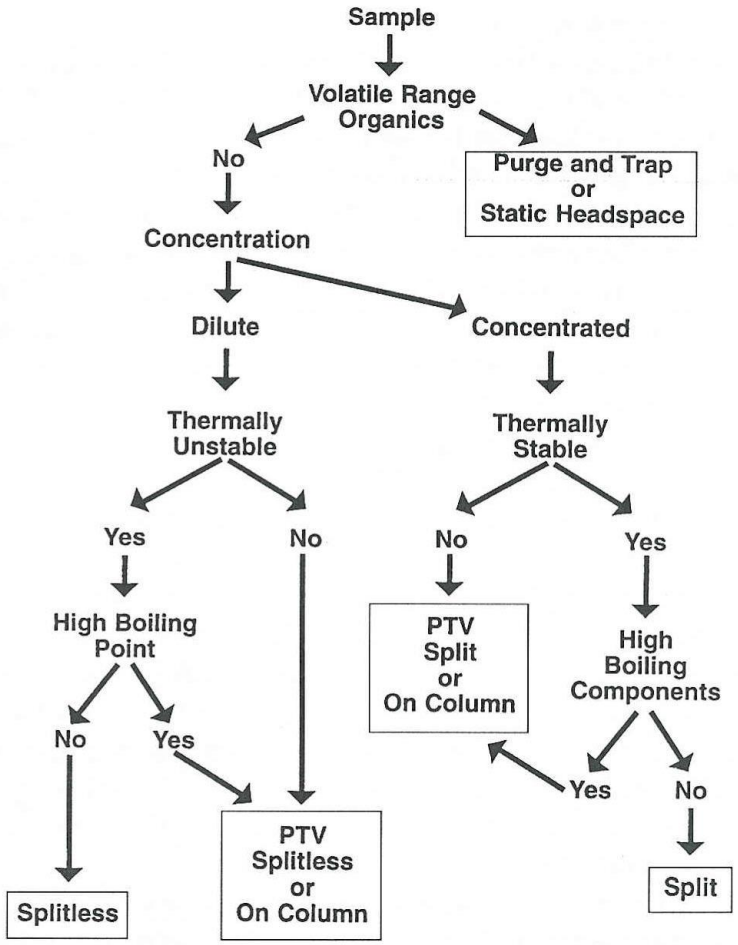


Fig. 3.19. A sample-based flow chart for selecting the injection mode. As an example, if the sample did not contain volatile range organics, was reasonably concentrated, thermally stable, and lacked high boiling components, the injection mode of choice is split.

Assignment

- Read Chapter 25
- HW13 Chapter 25: 1-8 and 10
- HW13 Chapter 25 Due 04/01/24

- Read Chapter 26
- HW14 Chapter 26: 1- 17
- HW14 Chapter 26 Due 04/03/24

- Read Chapter 27
- HW15 Chapter 27: 1-5, 11-19 & 21-23
- HW15 Chapter 27 Due 4/08/24

- Test 3 – PPT Lectures 15-21 - Friday April 5th