

GC Instruments

- Fairly simple instrumentation

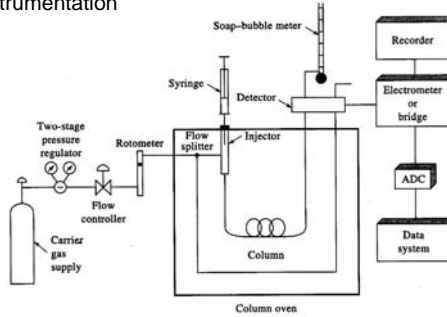


Figure 27-1 Schematic of a gas chromatograph.

- Maintaining constant average pressure is important!
 - Pressure controls flow rate
 - T influences retention (k')
 - Flow rate monitoring
 - Changing flow rate changes chromatogram (B/u)
 - Sometimes use Retention Volume (V_R)

GC Instruments - Sample Introduction

- Want small plug
 - Can doom the separation from the start!
- Most common: Direct injection (microflash vaporizer)
 - Inject and vaporize simultaneously
 - Need appropriate temperature
 - Ideally low dead volume
 - Fairly low maintenance
- More precise: Injection Loop
- Headspace and Purge-and-Trap methods
- SPME

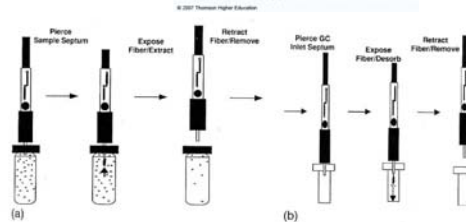
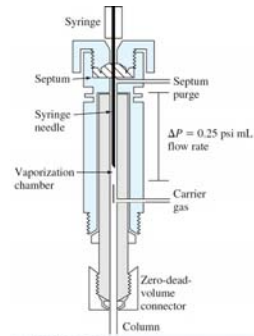


Figure 12.1 Diagrams of SPME (a) extraction sampling, and (b) GC desorption injection. (Used with permission from Supelco, Inc.)

GC Instruments - Sample Introduction

- Split/Splitless Injection
- Most common for capillary columns
 - Avoids overloading
- Split ratio is controllable by adjusting carrier gas flow through split vent.

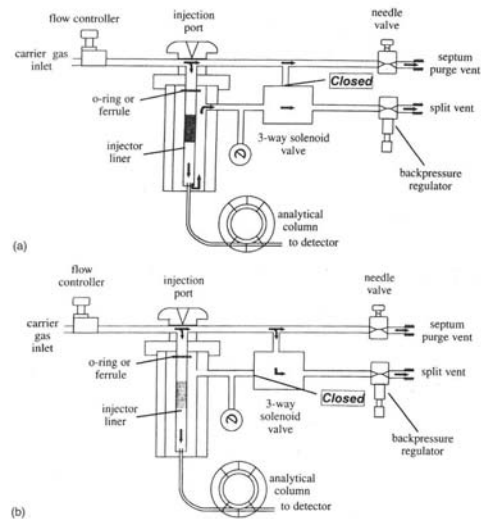


Figure 12.2 Diagram of GC flows for split and splitless injections: (a) split mode; (b) splitless mode. (Adapted with permission of Restek Inc.)

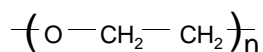
GC Instruments - Columns

- Two general classes: Packed and Open Tubular
 - three components: column, support, coating
- **Packed Columns**
 - Column materials: glass, metal (stainless), Teflon
 - few meters in length
 - few mm in diameter (i.d.)
 - Support Materials:
 - small particles, uniform (spherical) shape, porous, inert
 - Typically 100-300 μm diameter
 - Most common: diatomaceous earth
 - also polymeric materials
- **Capillary (Open Tubular) Columns**
 - Column materials
 - Small diameter (typically $<500 \mu\text{m}$)
 - metal, plastic, glass (FRAGILE)
 - More recently: Fused Silica - robust, flexible
 - Support methods:
 - Support-Coated OT:
 - Wall-Coated OT

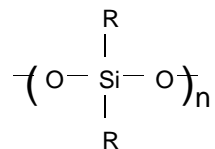
GC Instruments – Columns

Stationary Phase Materials

- **Gas-Liquid Chromatography (GLC)**
- Characteristics:
 - appropriate chemical nature (“like dissolves like”)
 - low volatility
 - thermal stability
 - chemical inertness
- Typical coatings (< 1 to several μm thickness):
 - Polyethylene Glycol (PEG, Carbowax)



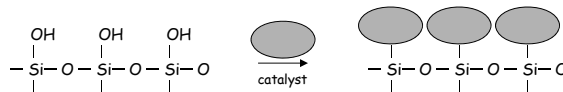
- Poly(dialkyl)silane:



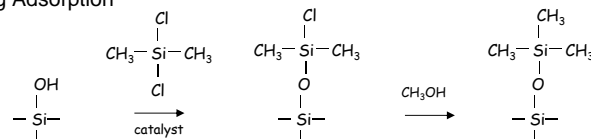
- Vary R groups to vary retention characteristics

GC Instruments - Columns

- Lifetime of column is limited by:
 - adhesion of liquid coating to stationary phase (bleeding)
 - irreversible adsorption of contaminants to column
- Minimizing bleeding
 - Cross-linking: on-column reaction
 - “Bonding”: Utilize surface chemistry of column (or packing)



- Minimizing Adsorption



- **Gas-solid Chromatography (GSC):**

- Typically porous solid adsorbed to walls (OT) or a porous solid support
 - molecular sieves
 - Porous polymers (beads or coatings)

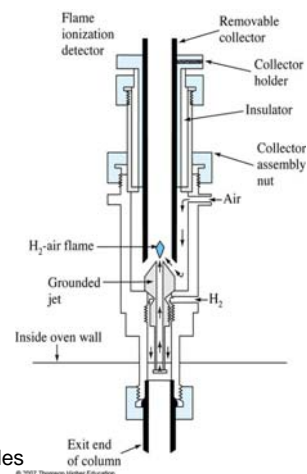
GC Instruments - Detectors

- Characteristics of a “good” detector
 - Sensitivity appropriate to sample
 - Large linear dynamic range
 - Useful at a range of temperatures
 - Rapid response time
 - Easy to use (idiot proof?)
 - Stable, Predictable response
 - Nondestructive (probably least important)

GC Instruments – Detectors

Flame Ionization Detector (FID)

- Column effluent is passed through a H₂-Air flame
 - Produces ions and electrons
- Charged particles are accelerated by voltage applied between jet and collector
 - results in current (pA)
- Number of ions depends on number of reduced (methylene) carbons in molecule
 - one molecule of ethane gives twice the signal of one molecule of methane
 - less sensitive for non-hydrocarbon groups
 - insensitive to H₂O, CO₂, SO₂ and other noncombustibles
- High sensitivity, good LDR (10⁷), low noise, destructive



GC Instruments - Detectors

Thermal Conductivity Detector (TCD):

- Element is electrically heated at constant power
 - Temperature depends on thermal conductivity of surrounding gas
- Measure conductivity (resistance) with respect to a “reference”
- Hydrogen and helium carrier gas provide best sensitivity
 - most thermally conductive
 - Organics are less so
 - when analyte comes off, filament temperature goes up, resistance goes down
- Poorer sensitivity than FID, but more universal
- Large LDR (10^5), non-destructive

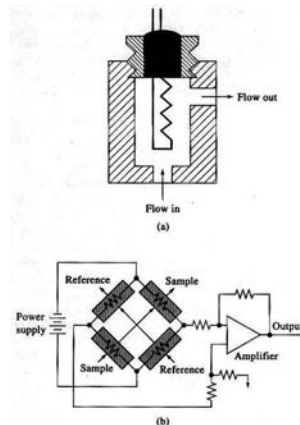


Figure 27-7 Schematic of (a) a thermal conductivity detector cell, and (b) an arrangement of two sample detector cells and two reference detector cells. (From J. V. Hinshaw, LC-GC, 1990, 8, 298. With permission.)

GC Instruments – Detectors

Electron Capture Detector (ECD):

- Carrier gas (and analyte) passes over β -emitter, resulting in ionization and e^- production
- Produces current between electrodes
- In the presence of other compounds (especially halogens, etc.) electrons are captured, causing decrease in current
- Most commonly used for halogenated organics (insecticides, etc.), small LDR (10^2)

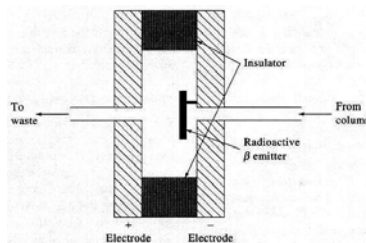


Figure 27-8 A schematic of an electron-capture detector.

Other Detectors:

- Atomic Emission
 - Microwave induced plasma, grating monochromator, diode array detector
- Mass Spectrometry Detection
- Thermionic Detector
 - Sensitive to phosphorous and nitrogen

Quantitative and Qualitative Analysis

- Qual.: Retention Index (Kovats Number)
 - Regardless of column, separation conditions, etc., define the retention index (RI) of a normal alkane as $100n$, where $n = \#$ of aliphatic carbons

$$RI = 100n$$

- RI for all other compounds will vary, depending on experimental conditions, but RI for n-alkanes is fixed.
- RI is related to retention time!

$$RI = 100 \left[n + (N-n) \frac{\log t'_r(U) - \log t'_r(n)}{\log t'_r(N) - \log t'_r(n)} \right]$$

- Useful for comparing multiple components in a separation

- Quant:
 - To a large degree, sensitivity is controlled by the detector, while selectivity is controlled by the separation conditions
 - Both need to work well to provide good accuracy and precision!

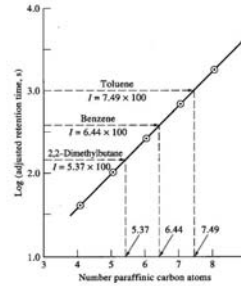


Figure 27-12 Graphical illustration of the method for determining retention indexes for three compounds. Stationary phase: squalane. Temperature: 60°C.

Two-dimensional GC

- Coupled GC columns
 - “Heart-cut” or “Comprehensive”
- Leads to improved qualitative (ID) information

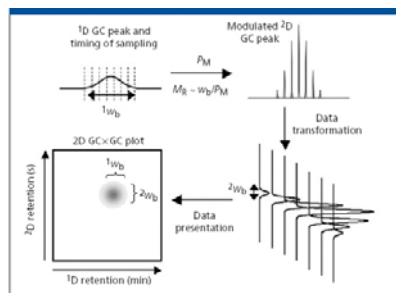


Figure 2: Modulation of a GC peak gives a series of peak pulses that are transformed into a format that can then be presented as a 2-D peak representation.

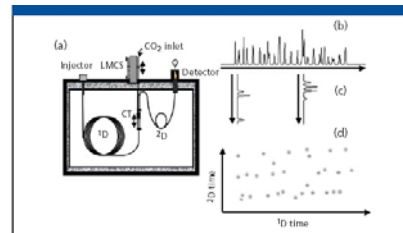


Figure 3: (a) A typical schematic of a GC x GC instrumental arrangement. (b) A 1-D chromatography separation has limited peak capacity (informing power). (c) Selected overlapping regions can be heart-cut to a second column which increases separation capacity for that zone. (d) The GC x GC experiment applies the 2-D separation power to the total chromatographic run, with a great increase in overall peak resolution and capacity.

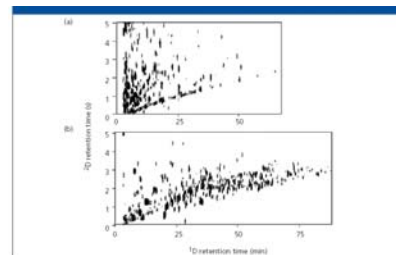


Figure 4: GC x GC analysis of the heptane of a coffee bean, sampled by using SPM. A nonporous column set (a) is not as effective as a porous polymer column set (b) in displaying the compound with best resolution and use of data separation space.