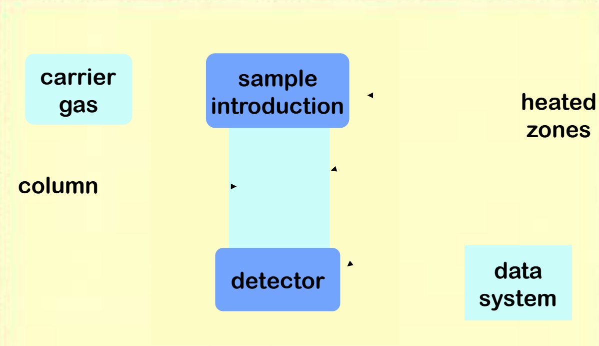
## Gas chromatography

First instrumental chromatographic method developed commercially.

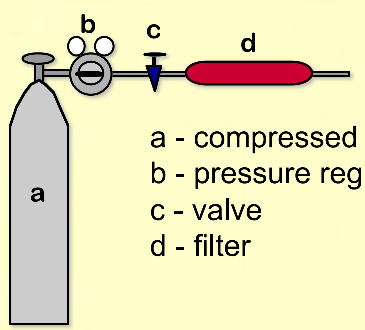
Reason - it is relatively easy to produce a stable flow and pressure for the mobile phase - carrier gas.

All that is really needed is a tank of compressed gas, pressure regulator and a valve.

## Schematic of a packed column gas chromatograph




## Flow control




a - compressed gas cylinder
b - pressure regulator
c - valve
d - filter

## Flow measurement

While flow is relatively easy to control, it still must be measured.

Bubble meters - post column or detector measurement of flow. Cheap and relatively accurate.

Rotameters - precolumn measurement of flow via position of ball floating in a calibrated glass tube.

## Flow measurement

### Electronic flow sensor

A modified thermal conductivity detector.

Permits continuous measurement of flow over a reasonably large range.

Must be calibrated for accurate flow measurement.

Response will also vary based on carrier gas used

## Injection methods

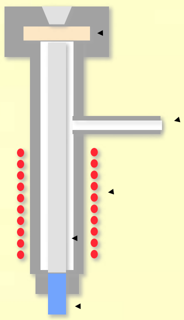
With packed column GC, this is a pretty simple portion of the system.

### Two basic approaches

Injection ports

Sampling loops / valves

## Injection port



**septum**

**carrier in**

**heat source**

**liner**

**column**

## Injection port

Purpose of port is to flash evaporate your sample and introduce it into the column.

$T_{INJ}$ > 50°C above $T_{column}$

Injection is through a septum.

Septum must be
stable at the $T_{inj}$
replaced regularly to maintain seal

## Injection port

**Liner.**

Provides a known area for the flash vaporization.

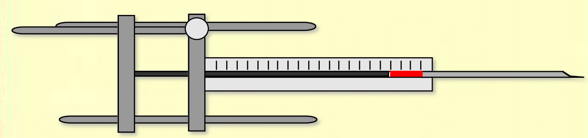
Typically made of glass although metal liners may be used. Some instruments don't have liners. Some columns will extend through the port, directly to the septum.

It can and should be replaced at regular intervals - all non-volatile materials and degradation products end up here.

## Syringes

Syringes are used to introduce a known volume of a liquid or gas samples .

Adapters can be used to help control the volume injected.



## Syringes

Various styles are available

Fixed needle
Removable needle
Several needle lengths and angles

Sample volumes from < 1 μl an up
Body loading
Through the barrel plungers

## Syringe filling

When filling, you must insure that there is no air in the syringe.

## Syringe injection

**Samples must be injected rapidly so that your sample is introduced as a small 'plug.'**

**By pulling back on the syringe after injection, you can measure how much sample remains in the needle.**

## Sample size

**Liquids**

0.1 - 10 $\mu$l is typical

**Gases**

0.5 - 5 ml is typical

Injection precision with a syringe is +/- 1%

## Gas sampling loops

Introducing a constant amount of a gas can be difficult with a syringe.

Gas sampling loops and valves offer a high precision (+/- 0.1%) means of introducing gases.

Equipment is relative inexpensive and only requires a constant temperature for easy use.

## Sampling loops

sample vent sample vent

column

carrier carrier

## Columns

- Heart of the separation process.
- Vast number of materials have been evaluated.
- It is usually best to refer to various catalogs as an up to date reference.
- Can be classified by tubing diameter and packing type.

## Types of columns

**Conventional**

1/8-1/4" OD, stainless steel or glass tube

6 - 20 feet in length

**Preparative**

> 1/4"

>10 feet in length

**Capillary**

0.1 - 0.5 mm ID

10 - 100 meters in length

## Types of columns

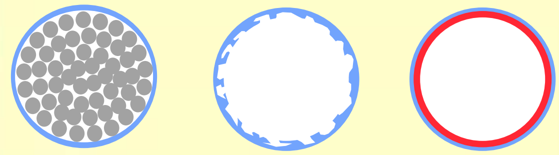
Columns

- Packed
  - porous packing
  - non-porous packing
    - Packed with porous layer
    - liquid coated
    - packed capillary
- Open tubular (capillary)
  - coated with porous layer
  - bound phase
  - liquid coated wall

## Types of columns

Packed

open (capillary)



bead column

porous layer

conventional

Porous Layer Open Tube

Wall Coated Open Tube

## Packed vs. capillary columns

| | Packed | Capillary |
|---|---|---|
| length, M | 0.5 - 5 | 5 - 100 |
| ID, mm | 2 - 4 | 0.1 - 0.7 |
| flow, ml/min | 10 - 60 | 0.5 - 15 |
| head pressure, psig | 10 - 40 | 3 - 40 |
| total plates | 4000 | 250,000 |
| capacity | 10μg/peak | 100ng/peak |
| film thickness, μm | 1 - 10 | 0.1 - 8 |

## Improved sensitivity

Because peaks remain narrower, the sensitivity is improved.

Packed

Both peaks have an area of 5000 units.

Capillary

Because the capillary peak is higher, you get a better S/N.

## Capillary columns

Available in two basic forms

**Coated** - simple coating on the inside of a fused silica tube

**Bonded** - chemically bound via a silane bond.

Both types are coated on the outside with a polyamide to reduce breakage.

## Column selection

Unless you're developing new packing materials or methods, the best starting point is to consult a chromatographic catalog.

They provide a wealth of information regarding cost, temperature limits, sample applications.

Another factor to consider, you must use the proper column called for by the 'standard' method (Ex. A specific EPA method.)

## Temperature programming

The column sits in an oven.

If the temperature is held constant during the entire analysis it is isothermal.

If you vary the temperature during the analysis, you typically use a temperature program.

Why bother?

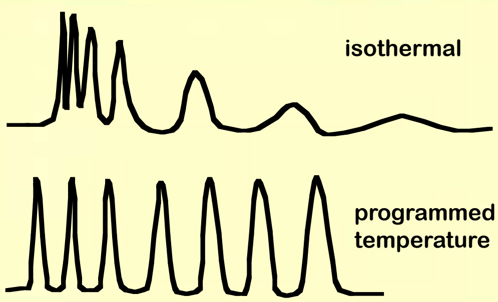
## Temperature programming

With homologues, the retention time increases exponentially with the number of carbon.

As $t_R$ increases, width increases and the height decreases, making detection impossible after a few peaks have eluted.

Since solubility of a gas in a liquid decreases as temperature goes up, we can reduce the retention of a material by increasing $T_{column}$.

## Example




## Temperature programming

Factors to consider:

- Variations in solubility of solutes
- Changes in volatility of solutes
- Stability of solutes
- Flowrate changes
- Stability of stationary phase

Must stay within $T_{min}/T_{max}$ of column.
Other factors are found experimentally.

## A temperature program

(c)

(b)

(a)

a - initial temperature and time

b - ramp (°C/min)

c - final hold time and temperature

Some GCs will allow for a more complex program.

## Temperature programming

General steps to create a program assuming that the separation is possible.

1. Determine initial temperature and time based on best possible separation of first first few peaks.

2. Repeat 1 for the last few peaks to find the best final temperature and time.

3. Experiment with various ramps to account for the rest of the components.

## Detectors

We need a way to measure our eluents as they evolve from the column.

Virtually every method of directly or indirectly observing eluents as been looked at.

We'll cover some of the more common types.

## Detectors

Each can be roughly classified based on

Destructive vs. nondestructive

General vs. some discrimination
vs. very discriminating

Let's start by reviewing some general concepts such as detection limit and sensitivity.

## Properties of a good detector

High sensitivity - possible selectivity

Rapidly respond to concentration changes

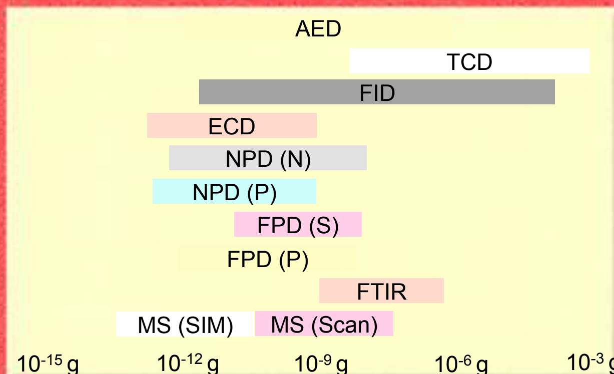
Large linear range

Stable with respect to noise and drift

Low sensitivity to variations in flow, pressure and temperature

Produces an easily handled signal

## GC detectors sensitivities and ranges




## Thermal conductivity detector

General purpose
Nondestructive
Limit of detection ~ 400 pg/ml carrier
Linear range ~ $10^6$

Mode of detection
Change in resistance of a wire based on variations in the thermoconductivity of the gas evolving from a column.

## Representative thermal conductivity values, 100°C

| Species | Thermal conductivity $10^5$ cal/cm sec °C |
|---|---|
| hydrogen | 49.93 |
| helium | 39.85 |
| nitrogen | 7.18 |
| ethane | 7.67 |
| water | 5.51 |
| benzene | 4.14 |
| acetone | 3.96 |
| chloroform | 2.33 |

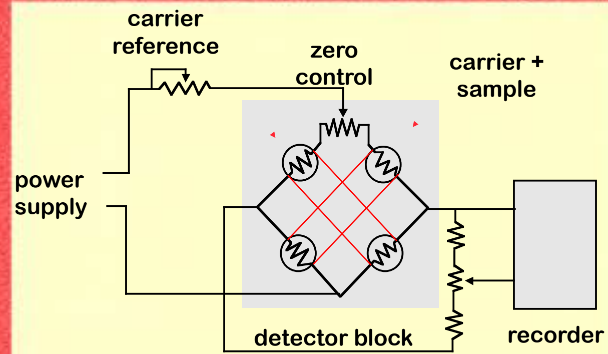
## Thermal conductivity detector

While hydrogen has the largest TC value, helium is commonly used - less reactive.

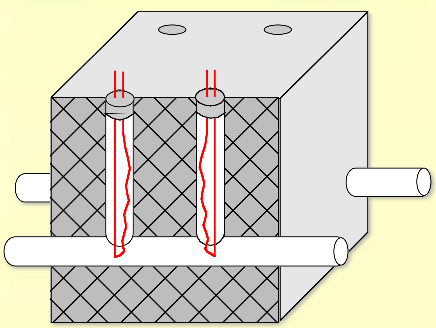
Hydrogen will give a negative peak when helium is the carrier gas.

Peak response is a function the the TC value for a species so you must standardize for each eluent of interest.

## Thermal conductivity detector




## Thermal conductivity detector



## Thermal conductivity detector

Dual channel detectors require both an analytical column and a blank column.
- accounts for response changes due to
  - variations in temperature
  - column bleed

Single channel TCD systems are available that correct for temperature variations.

## Flame ionization detector

Specific - sample must be combustible
Destructive

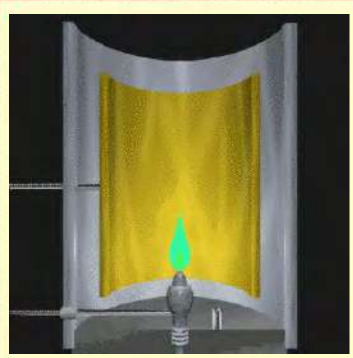
| | |
|---|---|
| Limit of detection | ~ 5 pg carbon / second |
| Linear range | ~ $10^7$ |

Mode of detection

Production of ions in a flame result in a current that can be measured.

A make-up gas may be required to maintain an optimum flow - capillary columns

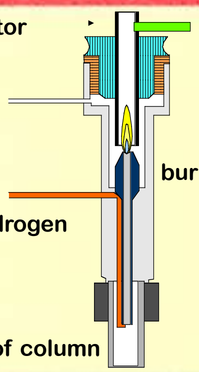
## Flame ionization detector



Sample components enter at the base of the detector. They mix with hydrogen and enter the flame.

Ions are produced that can be measured.

## Flame ionization detector




A make-up gas may also be present if capillary columns are to be used.

## Flame ionization detector

Compounds with little or no FID response

| | | |
|---|---|---|
| noble gases | $NH_3$ | $CS_2$ |
| $No_x$ | CO | $O_2$ |
| $H_2O$ | $CO_2$ | $N_2$ |

perhalogenated compounds
formic acid
formaldehyde

## FID response

Response is based on the number of carbon and if other elements like halogens or oxygen are present which reduce combustion.

formic acid
acetic acid
propionic acid
butanoic acid
pentanoic acid

methane
ethane
propane
butane

## Electron capture

Specific - sample must contain a gas phase electrophore

Non-destructive

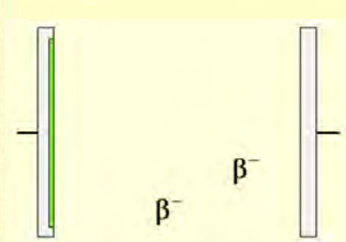
Limit of detection ~ 0.1 pg Cl / second

Linear range ~ $10^4$

Mode of detection

Absorption of $\beta$ particles by species containing halogens, nitriles, nitrates, conjugated double bonds, organometallics.

## Electron capture

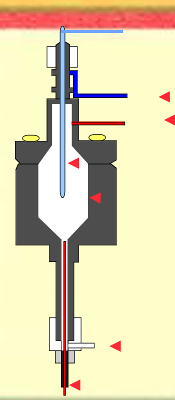



**$\beta^-$ are emitted by an $^{63}$Ni source.**

**Electrophores will absorb $\beta^-$, reducing the current.**

**This is the basis for the response**

## Electron capture



## Electron capture detector

Provides excellent trace analysis of

- halogenated compounds
- nitro group compounds
- eluents with conjugated double bonds

Most common use is environmental analysis of organochlorine pesticides

Major problem - detector is radioactive. Requires regular area testing and must be licensed.

## Electron capture detector

Relative responses

| | |
|---|---|
| $10^0$ | hydrocabons |
| $10^1$ | esters, ethers |
| $10^2$ | alcohols, ketones, monochlorides, amines |
| $10^3$ | monobromides, dichlorides |
| $10^4$ | anhydrides, trichlorides |
| $10^5$ - $10^6$ | polyhalogenated, mono and diiodo |