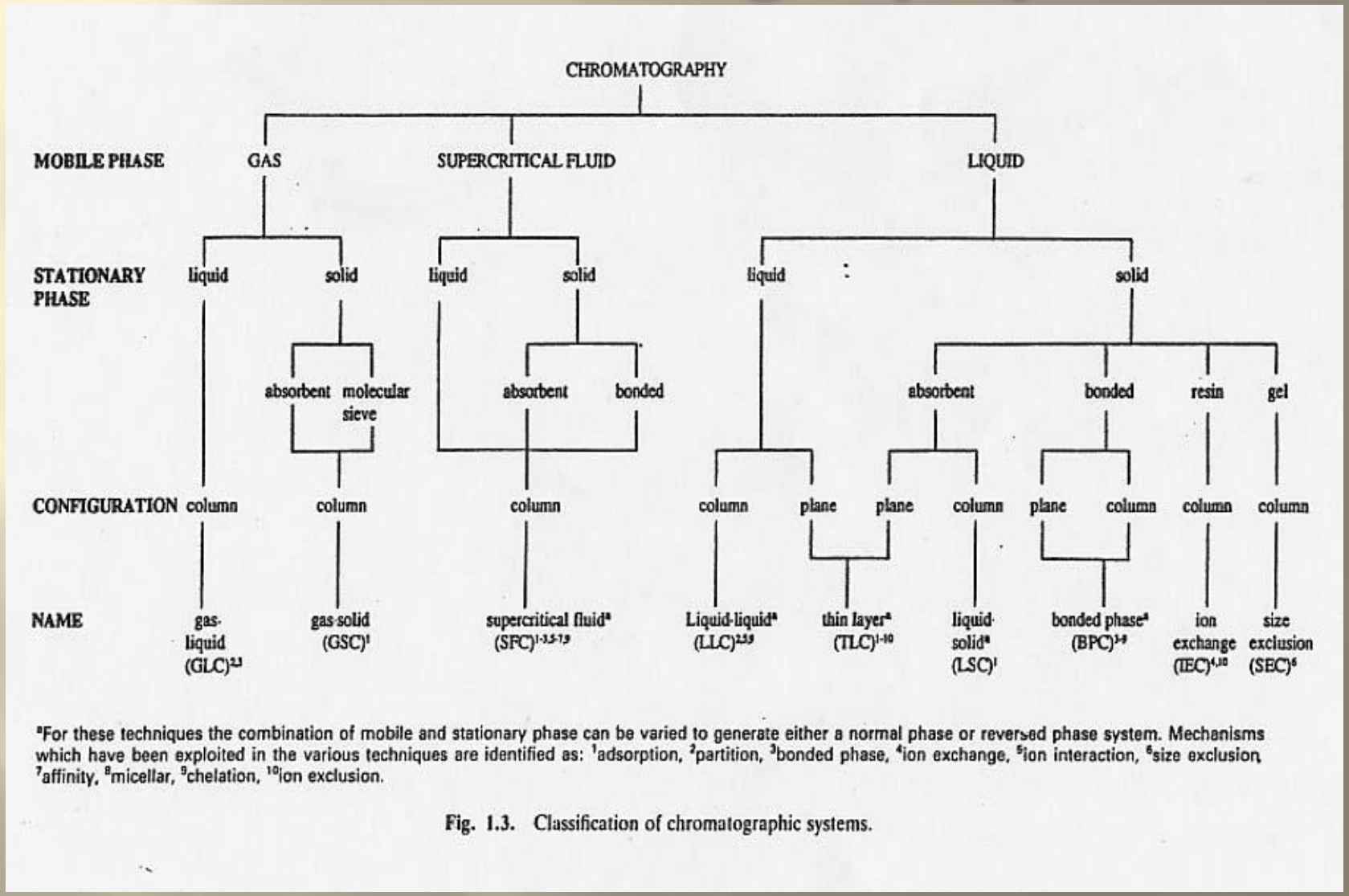
CHEMISTRY 5570

Advanced Analytical Chemistry

Lecture 15

Chromatography

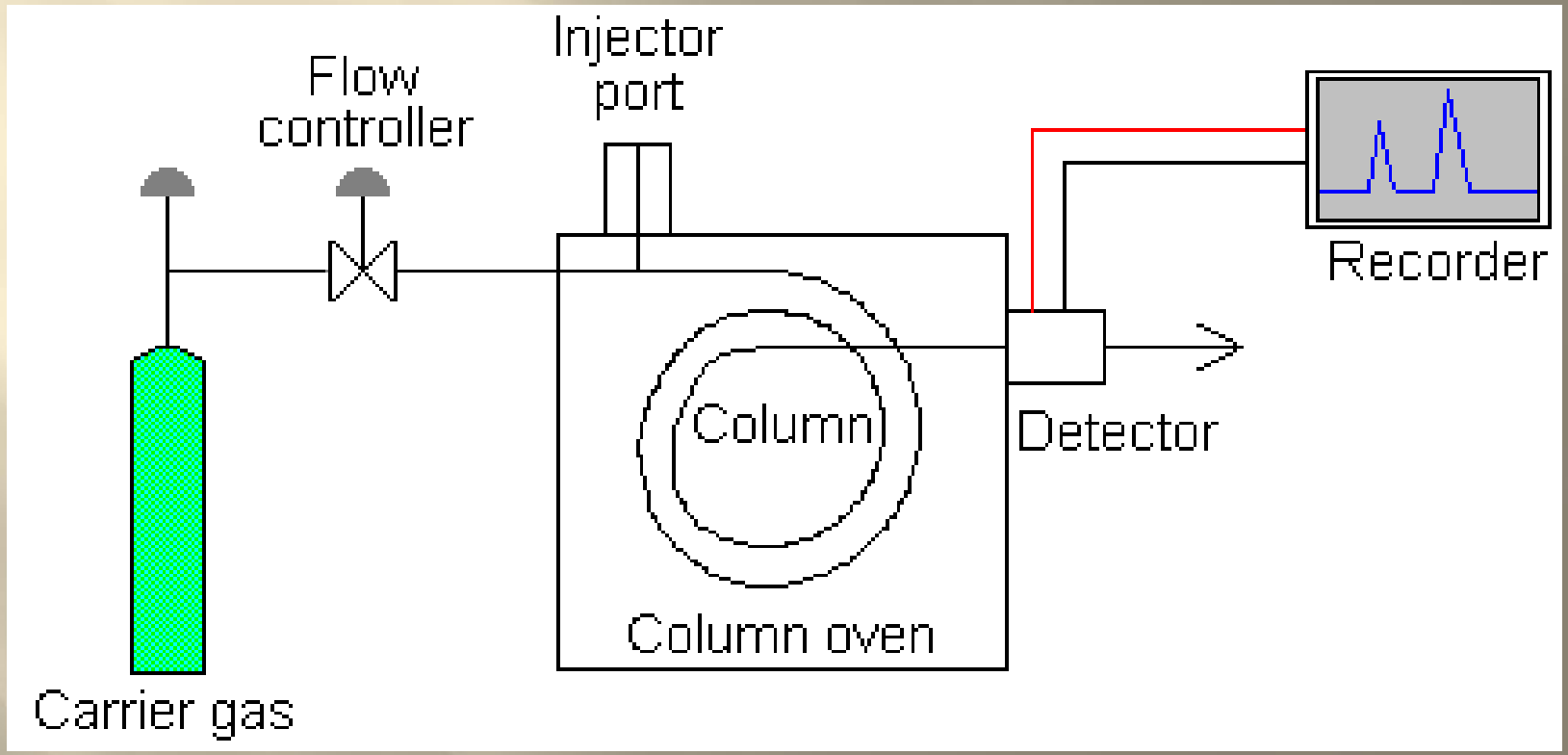


[a]For these techniques the combination of mobile and stationary phase can be varied to generate either a normal phase or reversed phase system. Mechanisms which have been exploited in the various techniques are identified as: [1]adsorption, [2]partition, [3]bonded phase, [4]ion exchange, [5]ion interaction, [6]size exclusion, [7]affinity, [8]micellar, [9]chelation, [10]ion exclusion.

Fig. 1.3. Classification of chromatographic systems.

Chromatography

Gas Chromatography – Columns



Chromatography

Gas Chromatography

Detectors

Monitors the column effluent and produces an electrical signal that is proportional to the amount of analyte eluted.
The output signal is recorded as signal intensity versus time.

In principle, any physical or physicochemical property of the carrier gas which deviates from the properties of the carrier gas plus analyte can serve as the basis of detection.

Chromatography

Gas Chromatography

Detectors

Over 100 detectors have been invented, but relatively few are in common use.

The criteria to consider when selecting a detector are: sensitivity, noise, minimum detectable quantity/detection limit, detection time constant or response time, and selectivity.

Chromatography

Gas Chromatography

Detectors

A non-selective detector responds to all compounds except the carrier gas, a selective detector responds to a range of compounds with a common physical or chemical property and a specific detector responds to a single chemical compound.

Detectors can also be grouped into concentration dependent detectors and mass flow dependent detectors.

Chromatography

Gas Chromatography

Detectors

The signal from a concentration dependent detector is related to the concentration of solute in the detector, and does not usually destroy the sample Dilution with make-up gas will lower the detectors response. (i.e. TCD, ECD, PID)

Mass flow dependent detectors usually destroy the sample, and the signal is related to the rate at which solute molecules enter the detector. The response of a mass flow dependent detector is unaffected by make-up gas. (i.e. FID, AFID, FPD)

Chromatography

Detectors

Common Detectors:

- **Thermal Conductivity Detector (TCD)**
- **Flame Ionization Detector (FID)**
- **Electron Capture Detector (ECD)**
- **Alkali Flame Ionization Detector (AFID)**
- **Flame Photometric Detector (FPD)**
- **Photoionization Detector (PID)**
- **Mass Spectrometry Detector (MS)**

Chromatography

Gas Chromatography

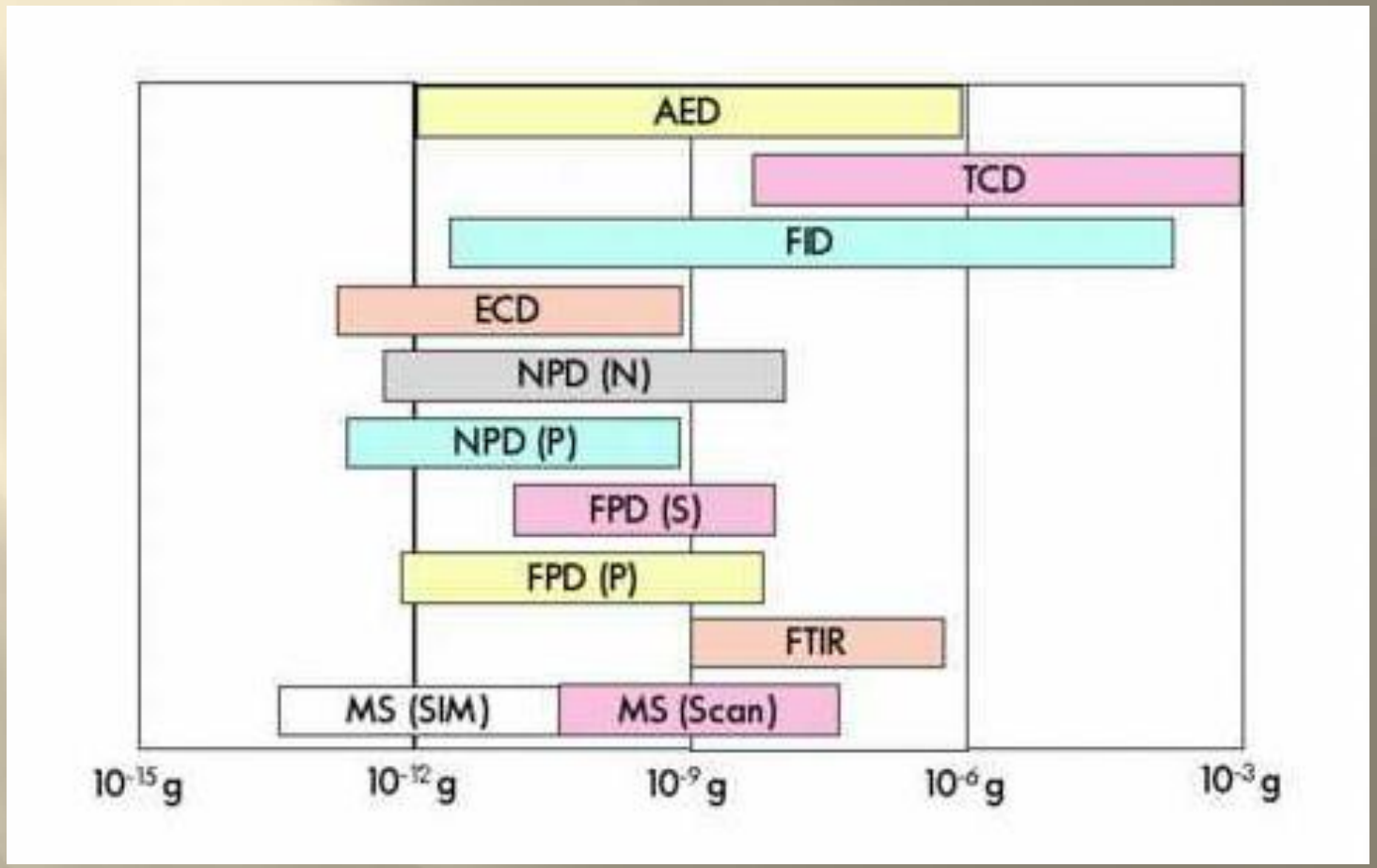
Detectors

Table 3.17 Classification of the most common gas chromatographic detectors.

Detector	Response	Optimal detection limit	Linear range	Classification
TCD	Organic and inorganic solutes	10^{-9} g ml^{-1}	10^4	Concentration; nondestructive
FID	All organic solutes except formic acid and formaldehyde	10^{-12} g ml^{-1}	10^7	Mass flow-rate; destructive
ECD	Halogenated and nitro compounds	10^{-16} mol ml^{-1}	10^3–10^4 (pulsed)	Concentration; nondestructive
AFID	P- or N-containing solutes	N:10^{-14} g s^{-1} P:10^{-13} g s^{-1}	10^3–10^5	Mass flow-rate; destructive
FPD	P- or S-containing solutes	S:10^{-10} g s^{-1} P:10^{-12} g s^{-1}	S:10^3 P:10^5	Mass flow-rate; destructive

Chromatography

Detectors



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Gas Chromatography

Detectors

Thermal Conductivity Detector (TCD)

- **First detector commercially available for GC, overall universal detector.**
- **General Purpose, Nondestructive**
- **Measures change in resistance of a wire based on variations in the thermal conductivity of the eluent.**

Filament – Pt, Pt alloy, W or W alloys.

Chromatography

Gas Chromatography

Detectors

Thermal Conductivity Detector (TCD)

Filaments are mounted in two flow channels, one reference, the other analytical. Filaments are heated and excess gas is carried away by the gas flow at a rate dependent upon the thermal conductivity of the gas. Thermal equilibrium is established for the carrier gas.

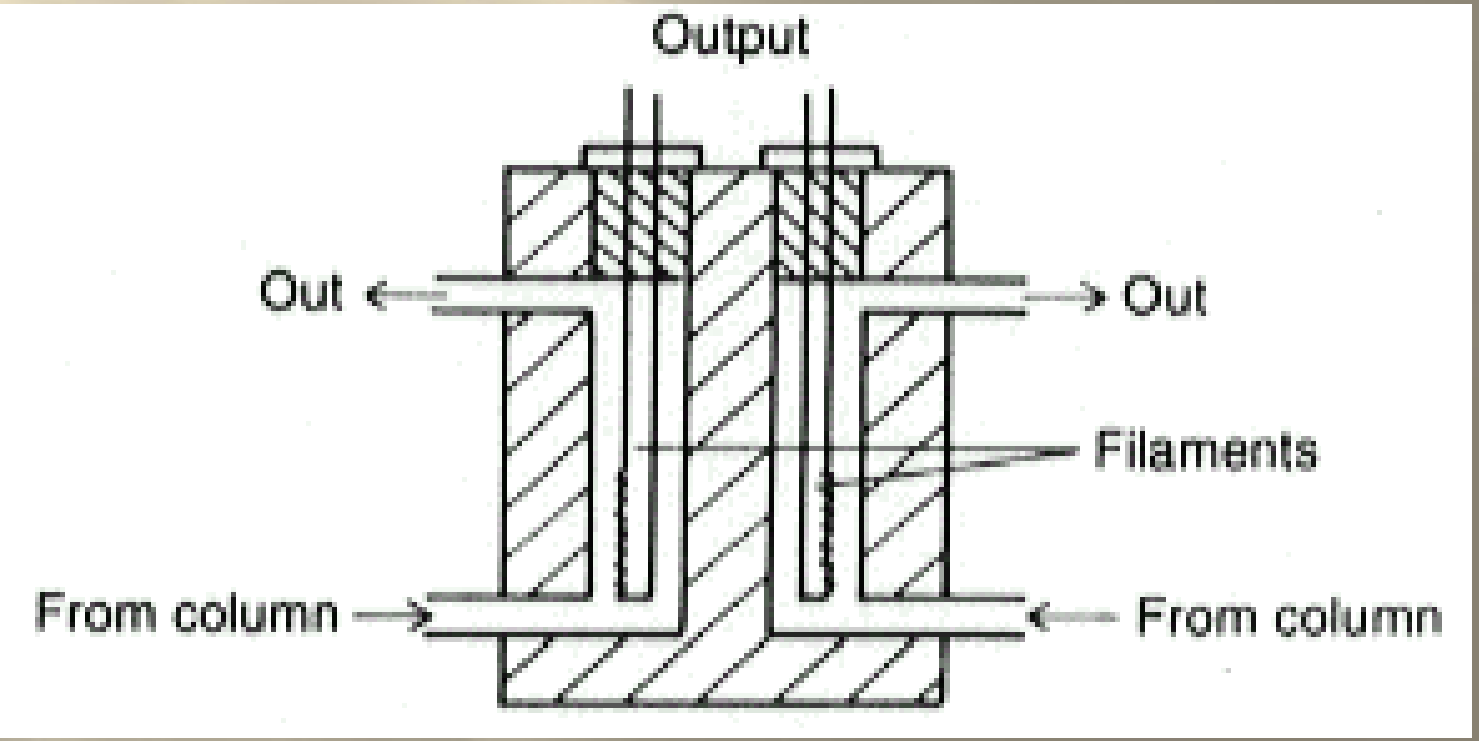
When only gas flows all resistors have the same value and there is no voltage difference measured. When a solute elutes from the column, resistance increases and a voltage difference is measured. Any changes in room temperature or column bleed affect each side the same and cancel each other out.

Chromatography

Gas Chromatography

Detectors

Thermal Conductivity Detector (TCD)



Chromatography

Detectors

Thermal Conductivity Detector (TCD)

When a solute passes through the analyte channel, the thermal conductivity of the carrier stream is changed and the rate of heat loss will change for the filament. This causes the temperature and thus the resistance of the filament to change. The signal is a difference in current from the reference.

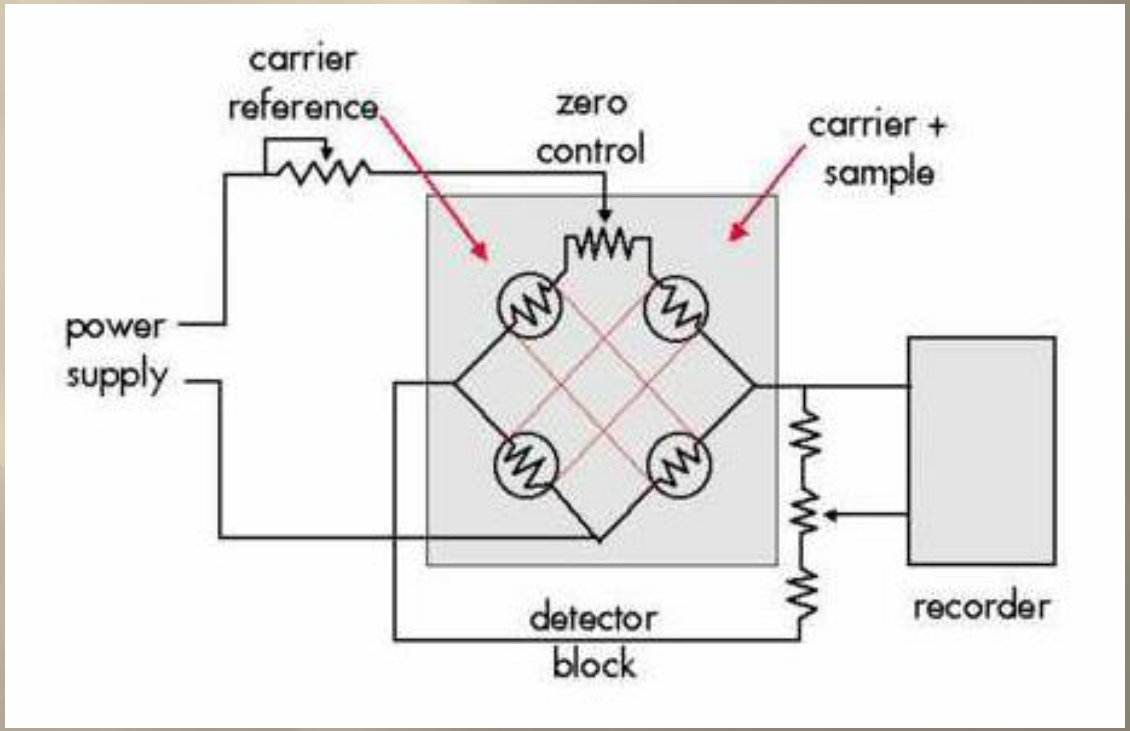
For newer detectors the current flowing through the filaments is adjusted electronically to maintain a constant temperature and the change in applied potential is monitored (V = IR). Bridge circuit used is a Wheatstone Bridge.

Chromatography

Gas Chromatography

Detectors

Thermal Conductivity Detector (TCD)



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Gas Chromatography

Detectors

Thermal Conductivity Detector (TCD)

Species	Thermal Conductivity (10^5 cal/cm sec ^oC)
hydrogen	49.93
helium	39.85
nitrogen	7.18
ethane	7.67
water	5.51
benzene	4.14
acetone	3.96
chloroform	2.33

Chromatography

Gas Chromatography

Detectors

Thermal Conductivity Detector (TCD)

TCD responds to any compound, regardless of structure, whose thermal conductivity differs from that of the carrier gas.

It is a standard detector for determination of inorganic gases – H_2, O_2, N_2, CS_2 and H_2O.

Most analytes have low thermal conductivities, so the highest sensitivity is attained by using a carrier gas of very high thermal conductivity → H or He (usually a 10 factor increase)

Chromatography

Detectors

Thermal Conductivity Detector (TCD)

Linear dynamic range 10^3 or sometimes higher.

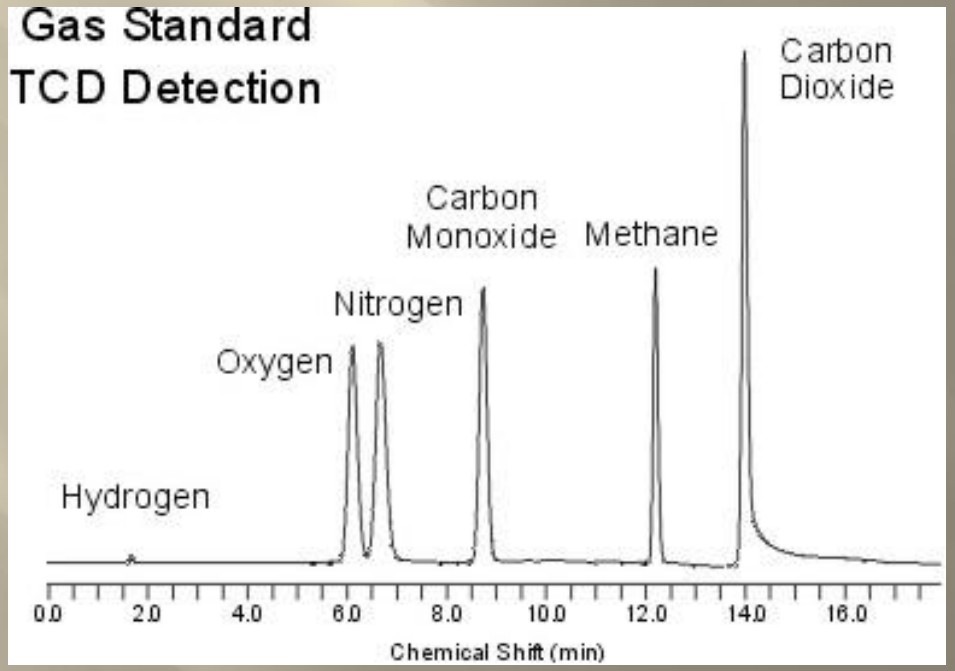
TCD is housed (heated) separate from the column oven → because temperature control is crucial.
Also filament must be protected from O_2 while hot.

TCD is classified as a concentration/nondestructive detector. The response is proportional to the relative concentration of analyte in the carrier gas (i.e. mass of solute per unit volume of carrier gas).

Chromatography

Gas Chromatography

Detectors
Thermal Conductivity Detector (TCD)



Chromatography

Detectors

Flame Ionization Detector (FID)

FID is the standard workhorse detector for the GC.

It is specific, destructive, has a wide linear range and a limit of detection of 5 pg carbon/second.

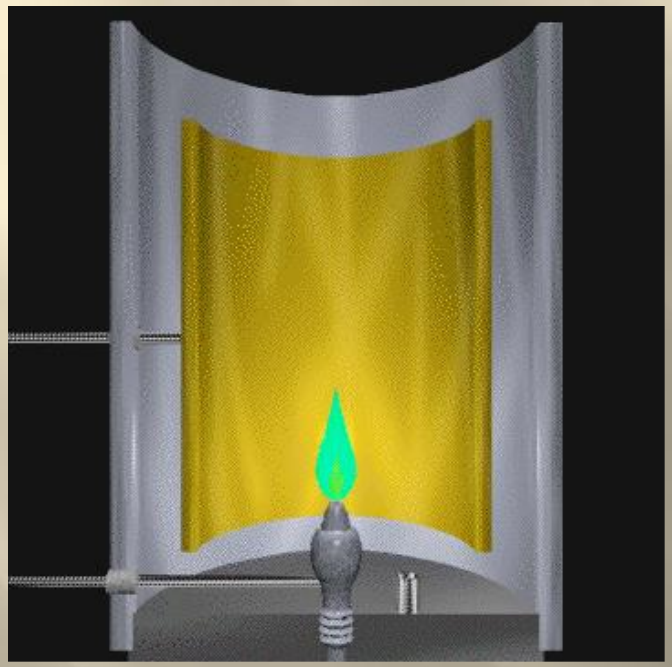
Production of ions in a flame result in a current that can be measured.
A make-up gas may be required to maintain an optimum flow - capillary columns.

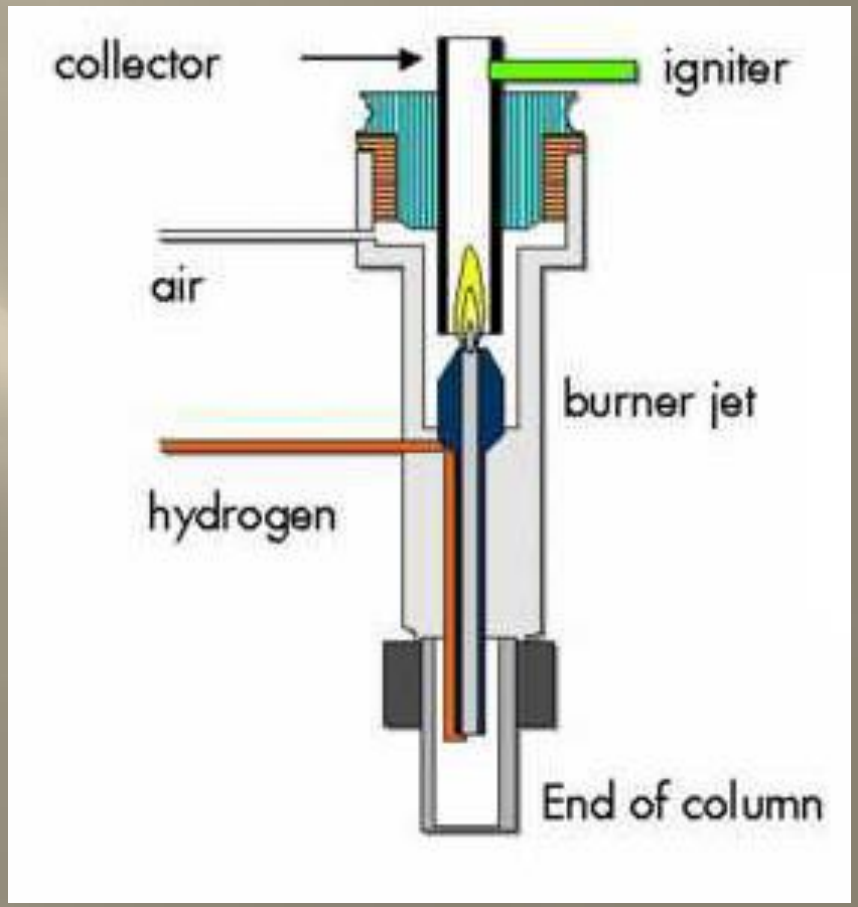
It has a stainless steel jet which allows carrier gas to mix with H_2 gas and flow to a microburner tip, which is supplied by a high flow of air for combustion.

Chromatography

Detectors

Flame Ionization Detector (FID)





Chromatography

Detectors

Flame Ionization Detector (FID)

Ions produced by combustion are collected at a pair of polarized electrodes to give a signal (increase in current).

This current is amplified and recorded. The ionization efficiency is low but sufficient enough to give excellent sensitivity and linearity.

For organic compounds the signal is a proportional to the total mass of carbon and hydrogen in the analyte (Oxygen and halogens affect this response).

There are compounds with little or no FID response, i.e. noble gases, NH_3, H_2O, CO_2, N_2, O_2.

Chromatography

Detectors

Flame Ionization Detector (FID)

FID is a mass flow detector – it depends directly on flow rate of carrier gas, produces a signal proportional to the absolute mass of solute vapor reaching the detector per unit time. The area response for a compound does not change with small changes in carrier flow.

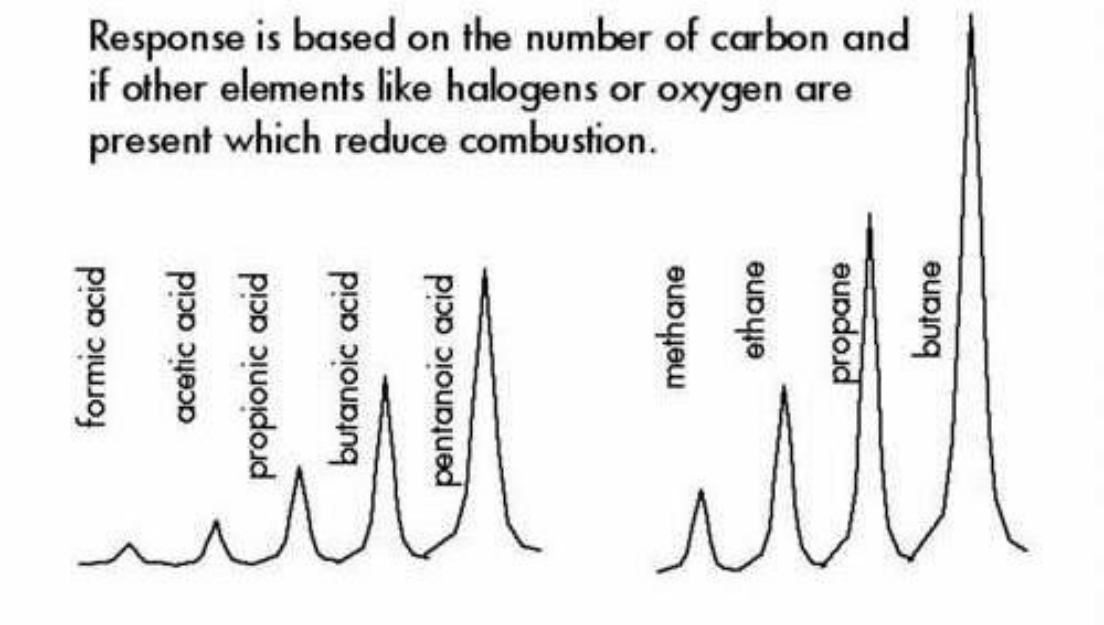
The response units are coulombs/gram of carbon.

Chromatography

Detectors

Flame Ionization Detector (FID)

The effective carbon number (ECN) has been developed to estimate the relative response for any compound.



Chromatography

Detectors

Flame Ionization Detector (FID)

TABLE 5.3 Contributions to Effective Carbon Number

Atom	Type	Effective Carbon No. Contribution
C	Aliphatic	1.0
C	Aromatic	1.0
C	Olefinic	0.95
C	Acetylenic	1.30
C	Carbonyl	0.0
C	Nitrile	0.3
O	Ether	−1.0
O	Primary alcohol	−0.6
O	Secondary alcohol	−0.75
O	Tertiary alcohol, esters	−0.25
Cl	Two or more on single aliphatic C	−0.12 each
Cl	On olefinic C	+0.05
N	In amines	Similar to O in corresponding alcohols

Chromatography

Detectors

Flame Ionization Detector (FID)

Aliphatic carbon → C-C-C-C
Aromatic carbon → benzene
Olefinic carbon → alkene
Acetylene carbon → H-C≡C-H
Carbonyl carbon → aldehyde, ketone, carboxylic acid
Nitrile → CN
Ether oxygen → (ROR')
Primary alcohol → CH_3CH_2OH
Secondary alcohol → $(CH_3)_2CHOH$
Ester or 3rd → $(CH_3)_3COH$

Chromatography

Detectors

Flame Ionization Detector (FID)

Example:

ECN of n-propanol
$OH\text{-}CH_2\text{-}CH_2\text{-}CH_3$
3 aliphatic carbons and one primary alcohol oxygen
ECN = (3 x 1.0) + (1 x –0.6) = 3 + (-0.6) = 2.4

Butyric acid
$CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH$

ECN = (3 x 1.0) + (1 x 0.0) = 3.0

Chromatography

Detectors

Alkali Flame Ionization Detector (AFID)

Also known as the Thermionic Ionization Detector (TID) or Nitrogen-phosphorous Detector (NPD).

Chromatography

Detectors

Alkali Flame Ionization Detector (AFID)

It is a modified FID – a constant supply of an alkali metal salt (i.e. Rubidium chloride) is introduced into the flame.

A ceramic or silica lead is coated with the alkali metal salt and placed between the flame jet and ion collector.

The bead is heated between 600 – 800°C. The alkali salt volatizes (positive ion produced) and passes into the flame and is ionized.

The ions in the flame create a constant standing current.

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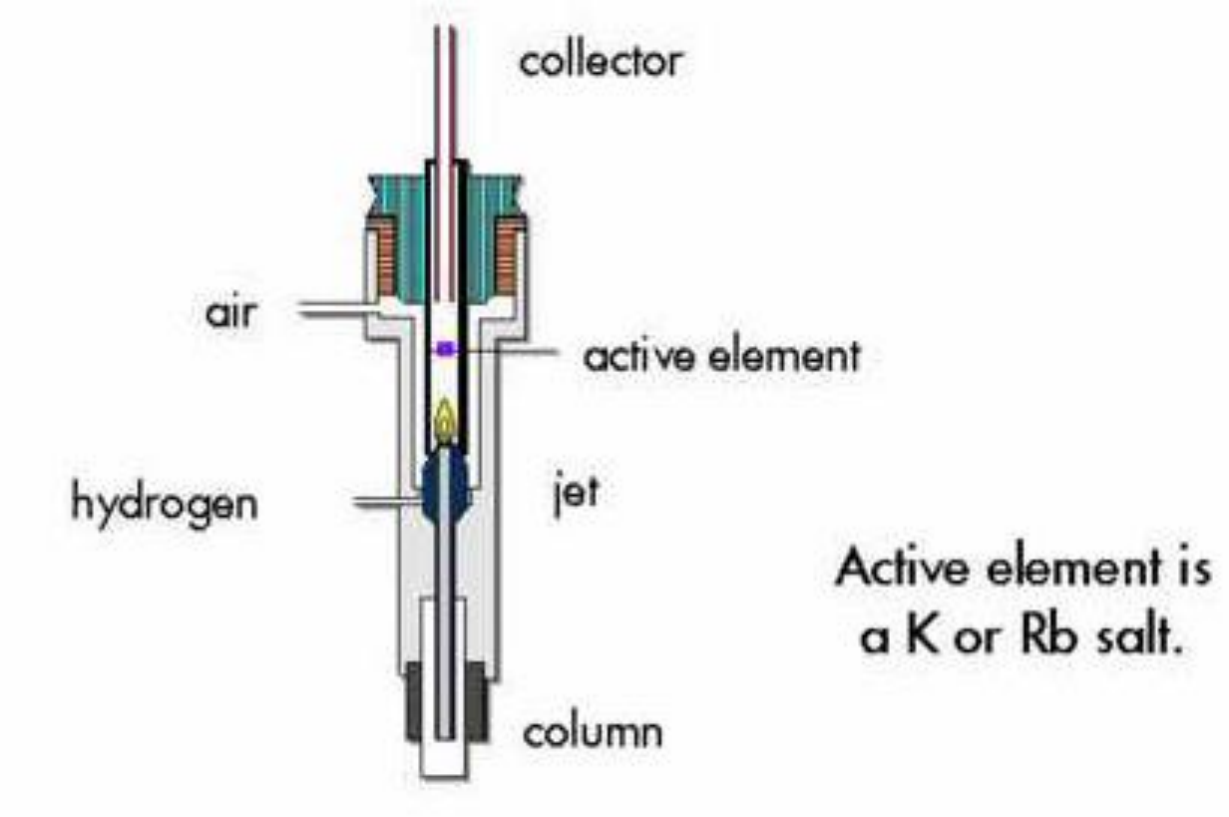
Detectors

Alkali Flame Ionization Detector (AFID)



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Detectors

Alkali Flame Ionization Detector (AFID)

- Instead of a flame, a low temperature plasma of H_2 can be used.
- AFID is selective to compounds containing nitrogen and phosphorous.
- Silylated compounds contaminate the AFID.
- Bead lifetimes are low – 100-1000 hours operating time.

Mechanism unknown.

Chromatography

Detectors

Electron Capture Detectors (ECD)

Most widely used of the selective detectors due to its high sensitivity to organohalogen compounds of environmental interest. (polychlorinated biphenyls, pesticides…)

Requires higher expertise and experience to achieve consistent results.
Consists of a chamber containing a radioactive source (usually ^{63}Ni, occasionally ^{3}H).

^{63}Ni can be used up to 380°C, without too much loss of radioactive material.

Chromatography

Detectors

Electron Capture Detectors (ECD)

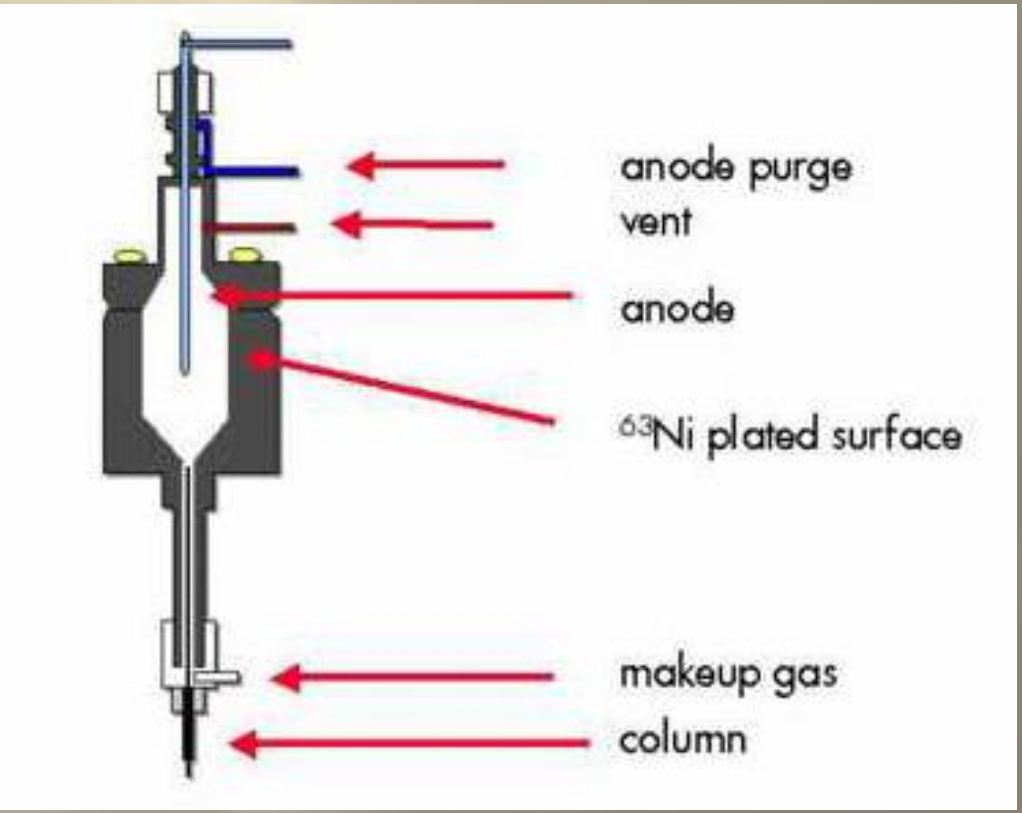
Traditional construction is a parallel plate design – more recent type is a concentric tube design with lower dead volume, shape optimizes the electron capture process.

Radioactive source emits high energy β particles capable of ionizing the carrier gas to produce secondary thermal electrons. Each β particle produces 100 – 1000 thermal electrons by collision.

Chromatography

Detectors

Electron Capture Detectors (ECD)



Chromatography

Detectors

Electron Capture Detectors (ECD)

The thermal electrons produced are collected at an anode that has a potential of ~50 V. This is the background or standing current. When an electrophilic analyte enters the detector it collides with a thermal electron and reduces the background current by either a dissociative or non-dissociative reaction.

$AB + e^- \rightarrow AB^-$ (nondissociative capture, favored at lower temperatures)

$AB + e^- \rightarrow A + B^-$ (dissociative capture, favored at higher temperatures)

Chromatography

Detectors

Electron Capture Detectors (ECD)

So the fast-moving electrons are replaced by slow-moving analyte ions which have a higher probability of recombining with the positive carrier gas to form neutral molecules.

$$AB^- + N_2^+ \rightarrow AB + N_2$$

ECD's are easily contaminated so water and oxygen must be removed from the carrier gas, low bleed columns are essential, and samples must be dilute to avoid saturation.

Chromatography

Detectors

Atomic Emission Detector (AED)

Element-selective detectors that utilize plasma, which is a partially ionized gas, to atomize all of the elements of a sample and excite their characteristic atomic emission spectra.

Chromatography

Detectors

Atomic Emission Detector (AED)

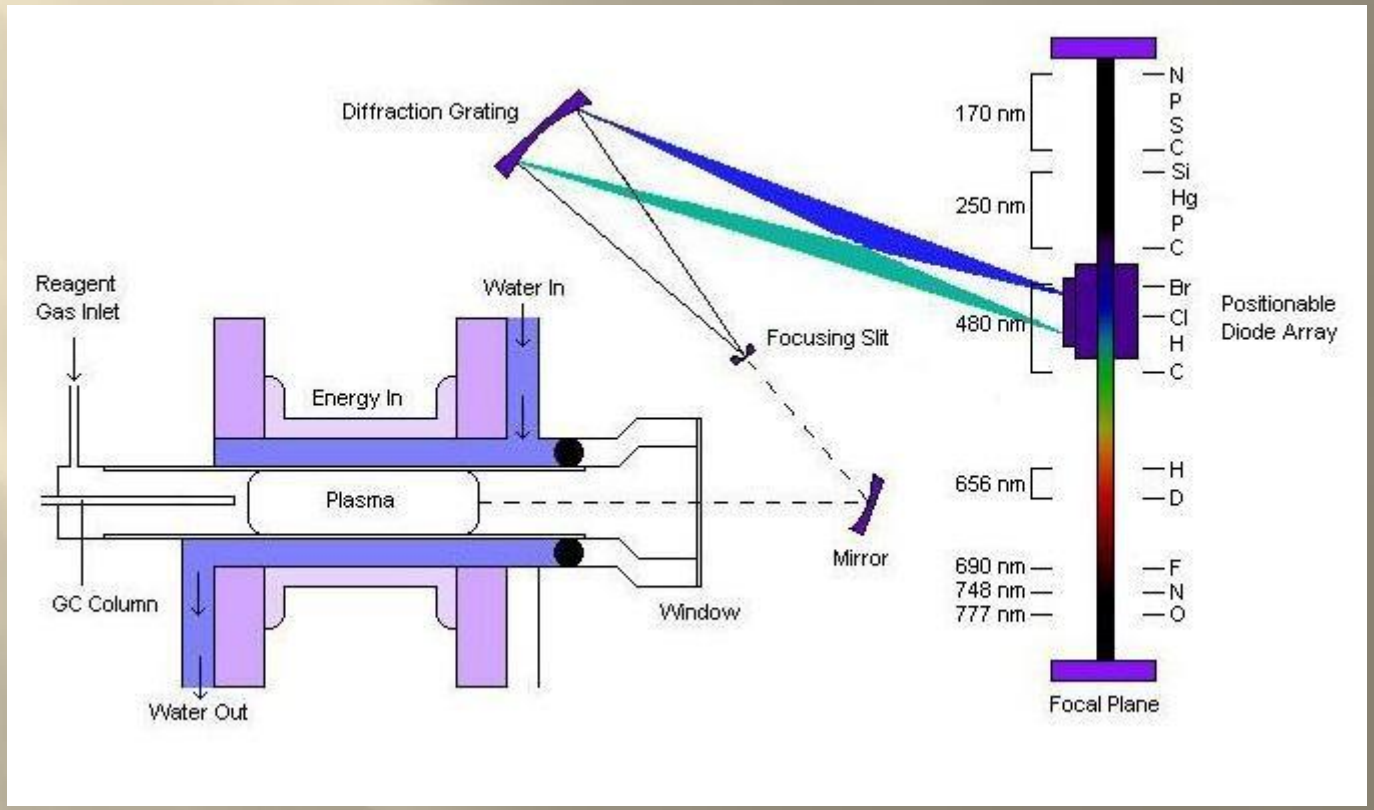
The components of the Atomic emission detectors include

1) an interface for the incoming capillary GC column to a plasma chamber, or
2) a microwave chamber,
3) a cooling system,
4) a diffraction grating with associated optics, and
5) a position adjustable photodiode array interfaced to a computer.

Chromatography

Detectors

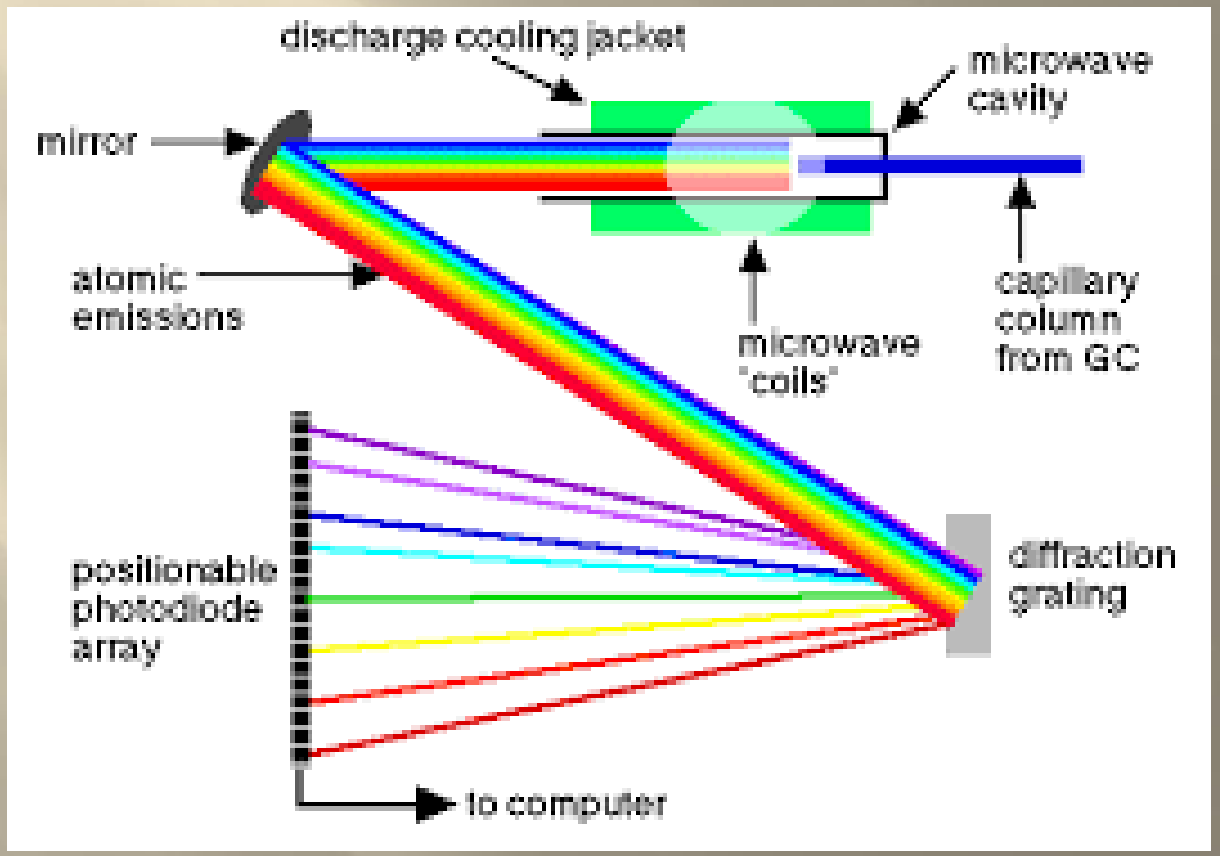
Atomic Emission Detector (AED)



Chromatography

Detectors

Atomic Emission Detector (AED)



Chromatography

Detectors

Atomic Emission Detector (AED)

Advantages

Measure many elements at once

Potentially can measure 70 or more elements

Disadvantages

Uses Helium carrier gas to carry the sample through the GC.

Uses a Helium plasma which requires very high purity He due to its sensitivity.

A reagent gas is sometimes used to improve the sensitivity of the AED by preventing the deposit of soot on the lamp or discharge tube.

He is also commonly used in GC-AED at the exit of the column to increase the flow rate into the detector.

Chromatography

Detectors

Flame Photometric Detector (FPD)

- **Directly measure photons produced during combustion of species.**

- **Destructive detector**

- **Limits of detection ~20 pg S/sec**
  ~0.9 pg P/sec

- **Linear range 10^4**

Chromatography

Detectors

Flame Photometric Detector (FPD)

Specific detector for sulfur or phosphorous (sub ng levels) used mostly for pesticides.

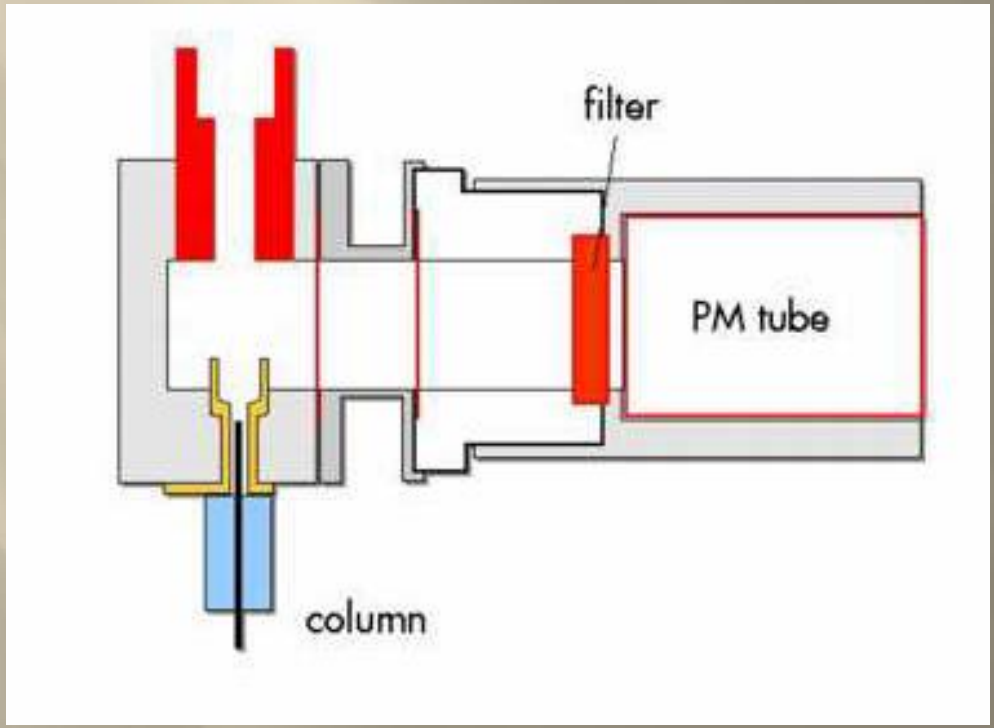
Combustion of phosphorous and sulfur compounds – produce excited species – HPO* and S_2*, which emit at 526nm and 394nm, respectively.

Response is linear for phosphorous but non-linear for sulfur (varies as the species of the amount of sulfur present).

Chromatography

Detectors

Flame Photometric Detector (FPD)



Chromatography

Detectors

Flame Photometric Detector (FPD)

1st Flame combust and decompose solvent molecules (can quench sulfur emission).

The elected species passes into a flame or plasma inside a shielded jet which produces atoms and molecules species.

The atoms and molecules are in an excited state and when they return to the ground state, they emit at wavelengths characteristic of the atomic line or molecular band.

Chromatography

Detectors

Photoionization Detector (PID)

Specific detector for compounds ionized by UV.
UV light is used to directly ionize the sample.
The resulting current is measured.

Nondestructive

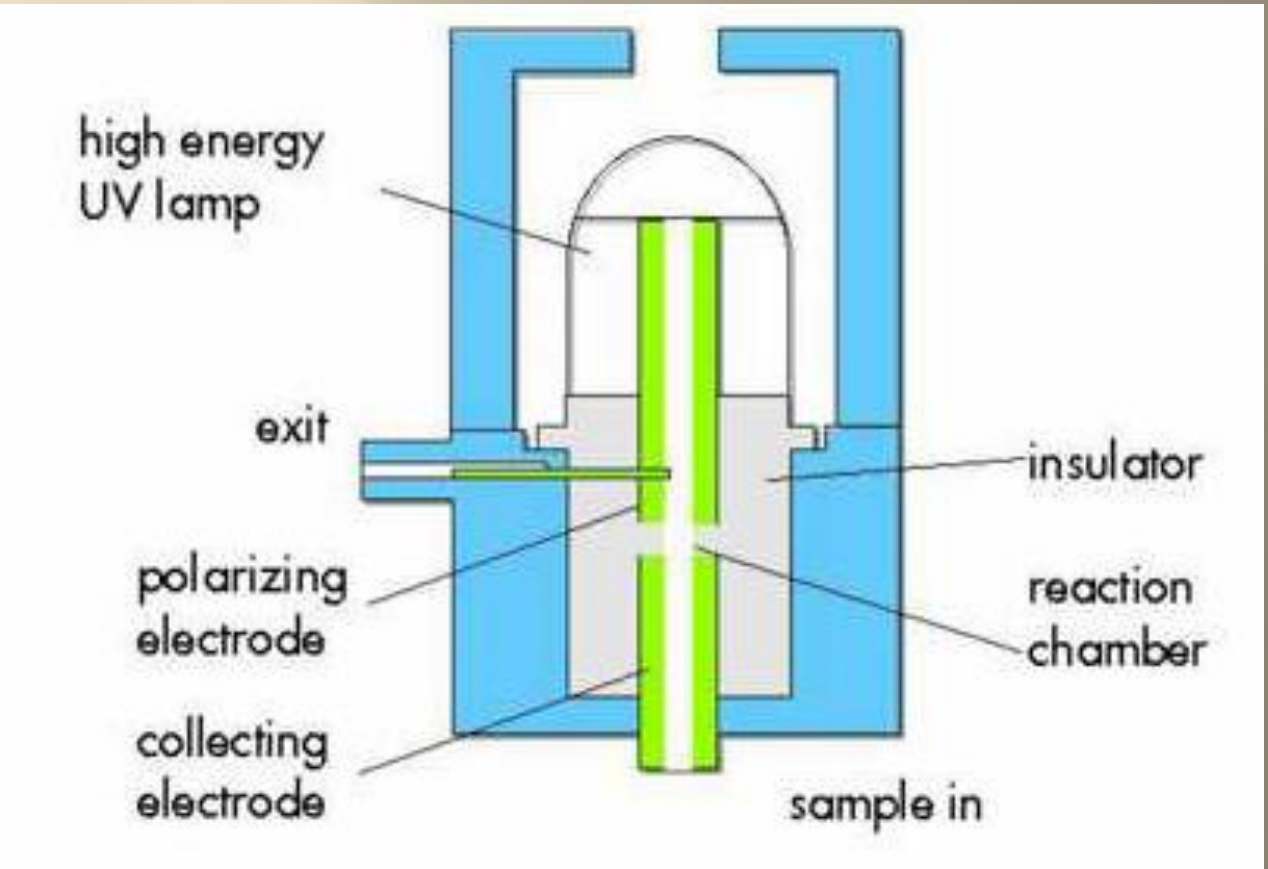
Limit of detection - 2 pg carbon/sec

Linear Range - 10^7

Chromatography

Detectors

Photoionization Detector



Chromatography

Detectors

Photoionization Detector

Since only a small (very reproducible but basically unknown) fraction of the analyte molecules are actually ionized in the PID chamber, this is considered a nondestructive GC detector.

Therefore, the exhaust port of the PID *can be* connected to another detector in series with the PID. In this way data from two different detectors can be taken simultaneously, and selective detection of PID responsive compounds augmented by response from another detector.

Chromatography

Detectors

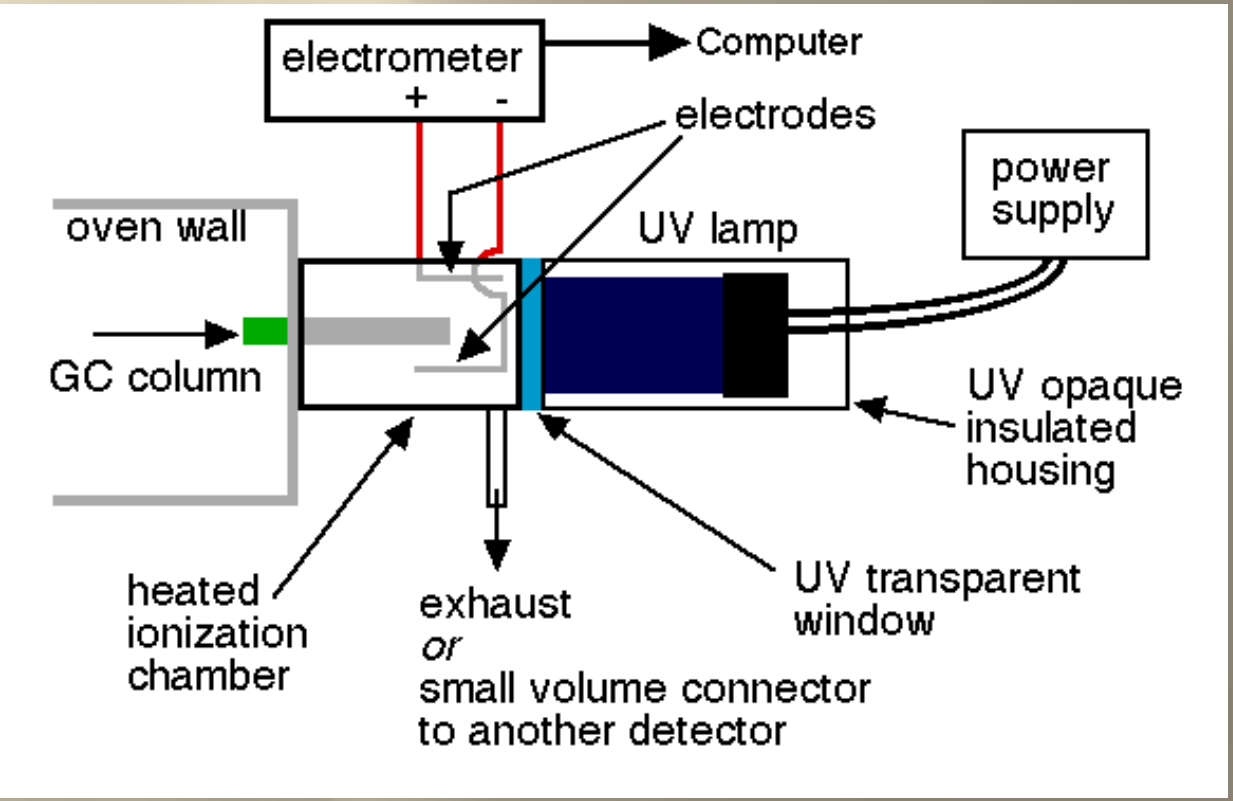
Photoionization Detector

The major challenge here is to make the design of the ionization chamber and the downstream connections to the second detector as low volume as possible so that peaks that have been separated by the GC column do not broaden out before detection.

Chromatography

Detectors

Photoionization Detector



Assignment

Chem 5570