Gas Chromatography

1. Introduction

2. Stationary phases

3. Retention in Gas-Liquid Chromatography

4. Capillary gas-liquid chromatography

5. Sample preparation and inlets

6. Detectors

(Chapter 2 and 3 in The essence of chromatography)

Detectors

1. Thermal conductivity detector (TCD): Bulk physical property

2. Ionization Detectors:

3. Optical Detectors

4. Electrochemical detector

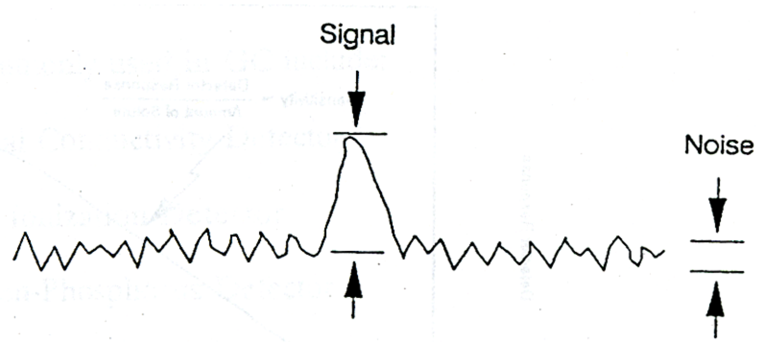
5. Spectroscopic detectors (Chapter 9)

1. The Basics for Detectors:

a. Minimizing extra-column band broadening

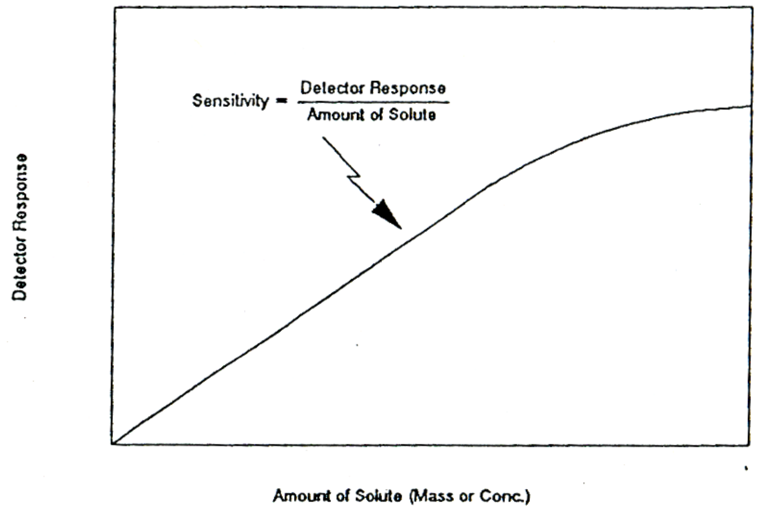
b High-sensitivity detection

(1) Limit of Detection: what is the smallest amount of solute to be detected?

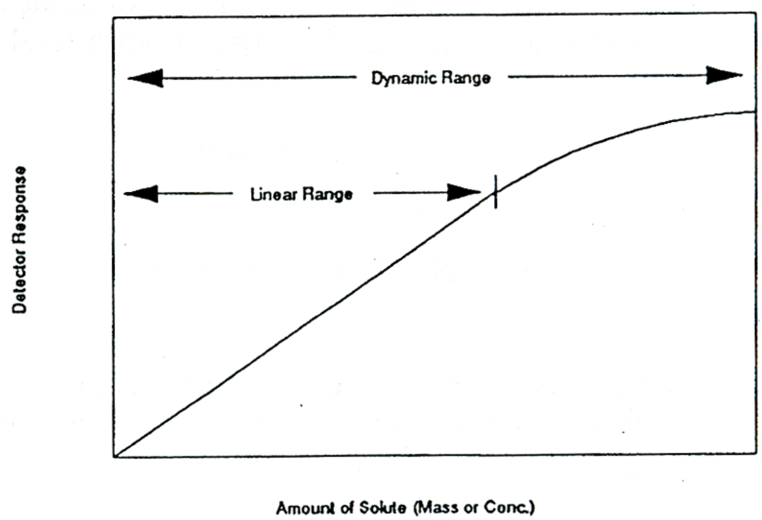


S/N >3

(2) Sensitivity: How small of a change in mass or concentration can be detected?
How fast its signal changes with a change in the amount or concentration of solutes



(3) Linearity or dynamic range: what mass or concentration range can be detected?



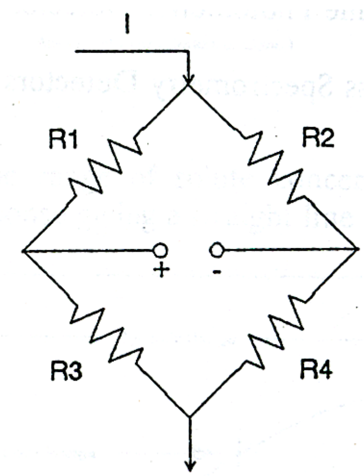
(4) Selectivity: What compounds are to be detected (all or a few)?

i. A universal detector is one which shows a response for all solutes

ii. A selective detector is one which responds to only certain types of solutes.

2. Thermal Conductivity Detector (TCD)

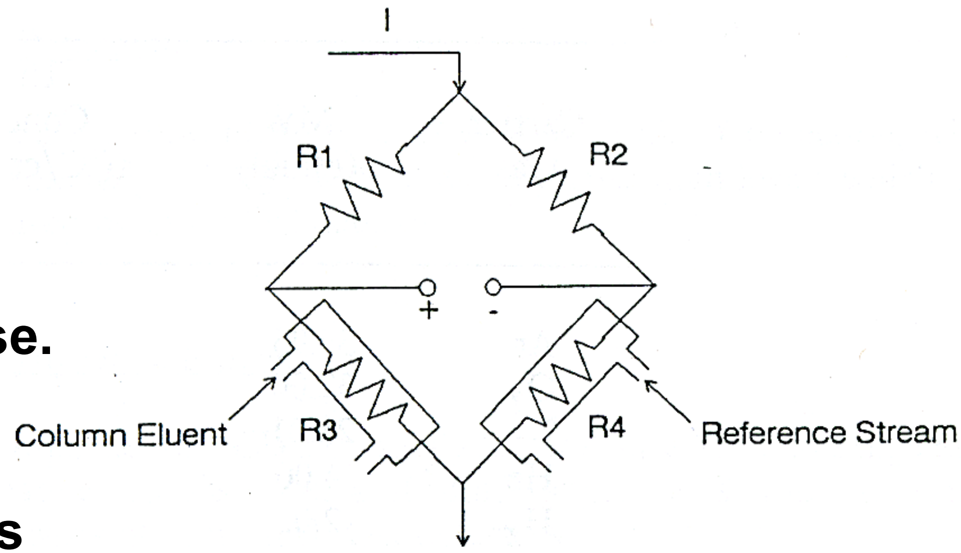
a. Detector design of TCD is based on an electronic circuit known as Wheatstone bridge.



b. When a current is applied, the voltage between pints (+) and (-) in the circuit will will be zero as long as the following relationship is true:

$$R_1/R_2 = R_3/R_4$$

c. In a TCD, one of these resistors is placed in contact with mobile phase leaving the column and another in a reference stream containing only pure mobile phase.



d. As current is passed through the circuit, the wire in the resistors are heat. For those in contact with the mobile phase and reference stream, some of this heat is removed.

Thermal Conductivity of Common Carrier Gases

Carrier Gas	MW (g mol)	Thermal Conductivity ((°C/cm sec)$^{-}$ x 10^{-5})
Ar	39.95	5.0
O_2	32.00	7.7
N_2	28.01	7.3
He	4.00	38.8
H_2	2.02	49.0

e. Temperature changes leads to resistance changes of resistors.

f. Most compound separated in GC have thermal conductivity of 1-4 X 10^{-5}.

f. Selectivity:

The response of a TCD is about the same for all compounds. Exceptions include low MW compounds (<40 MW), which may show higher responses.

g. Limit of detection: ~10^{-7} M

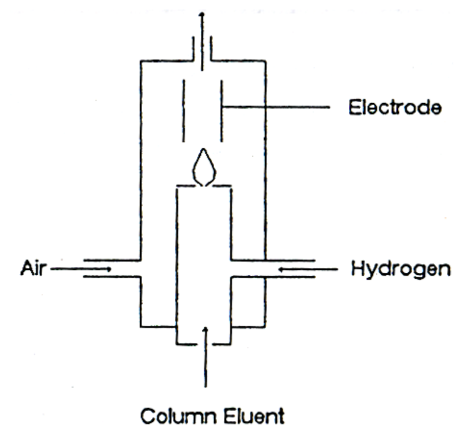
f. Linear range: a 10^3-fold range; dynamic range: a10^5-fold range

3. Ionization Detectors:

a. Flame Ionization detector (FID)

i. The FID is the most common type of GC detector (universal detector).

ii. The FID measures the production of ions when a solute is burned in a flame. These ions are collected at an electrode and create a current, allowing the solute to be detected



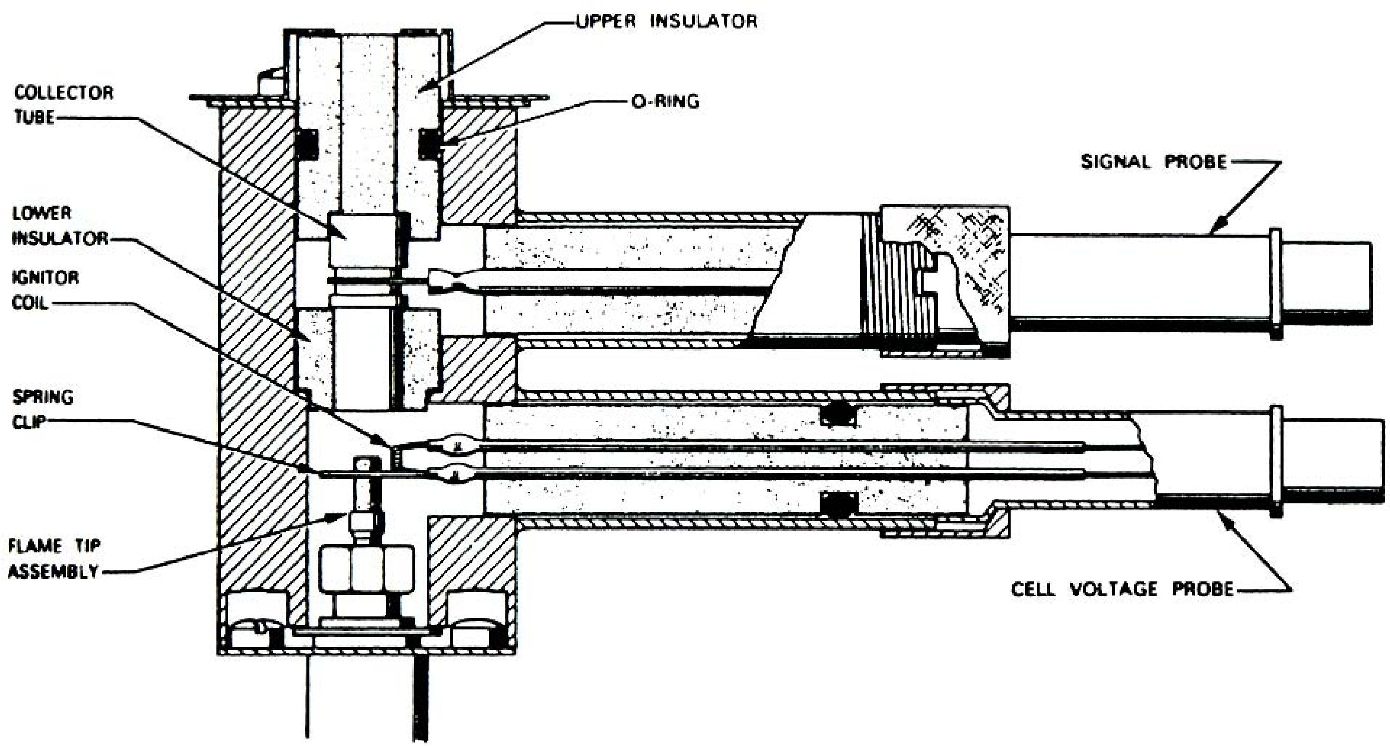


Figure 3.19. Cross-sectional view of a flame ionization detector. (©Varian Associates).

iii. A hydrogen/air flame is commonly used in FID since on ionic species are usually produced by this fuel mixture. This gives rise to a zero background current.

Table 3.3
Contributions of structure to the response of the flame ionization detector

Atom	Type	Effective carbon number
C	Aliphatic	1.0
C	Aromatic	1.0
C	Olefinic	0.95
C	Acetylenic	1.30
C	Carbonyl	0
C	Carboxyl	0
C	Nitrile	0.3
O	Ether	-1.0
O	Primary alcohol	-0.5
O	Secondary alcohol	-0.75
O	Tertiary alcohol	-0.25
N	In amines	Similar to O in alcohols
Cl	On olefinic C	-0.05
Cl	Two or more on aliphatic C	-0.12 per Cl

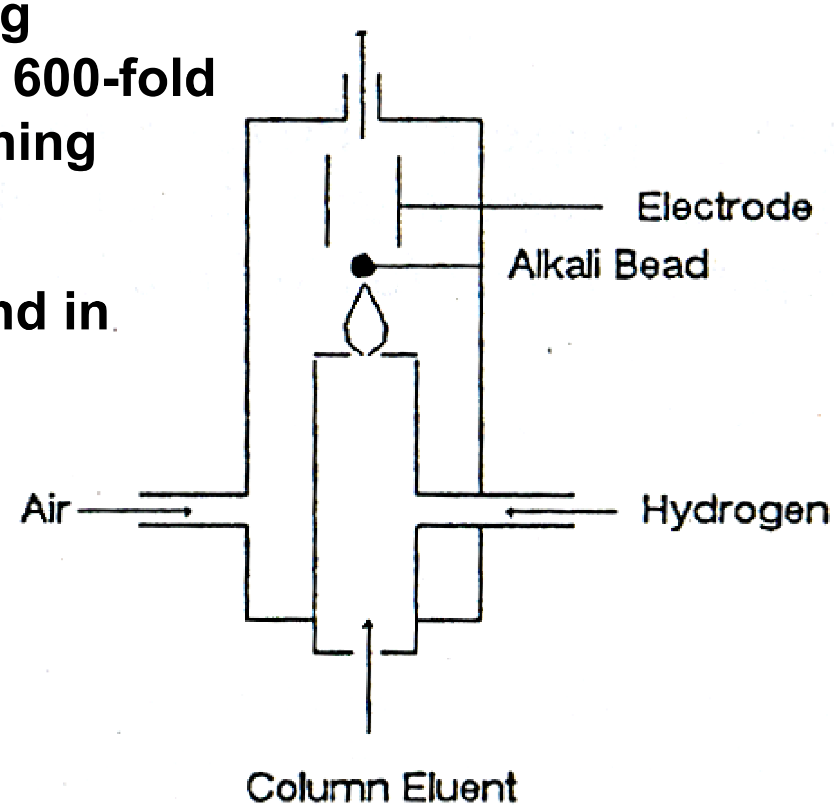
iii. Limit of detection: ~ 10^{-10} M

iv. Linear range: a 10^{5}-fold range; dynamic range: a10^{7}-fold range

b. Nitrogen-phosporus detector (NPD) Flame Ionization detector (FID)

i. The NPD is also known as an alkali flame ionization detector (AFID)

ii. A NPD is based on the same basic principles as an FID. However, a small amount of alkali metal vapor in the flame, which greatly enhances the formation of ions from nitrogen and phosphorus-containing compounds. The NPD is about 300-fold more sensitive that an FID in detecting nitrogen-containing compounds, and 600-fold More sensitive in phosphorus-containing compounds



iii. Applications: Organophosphate and in drug analysis For determination of amine-containing or Basic drugs.

iv. Limit of detection: ~ 10^{-10} M

v. Linear range: a 10^{6}-fold range

c. Electron capture detector (ECD)

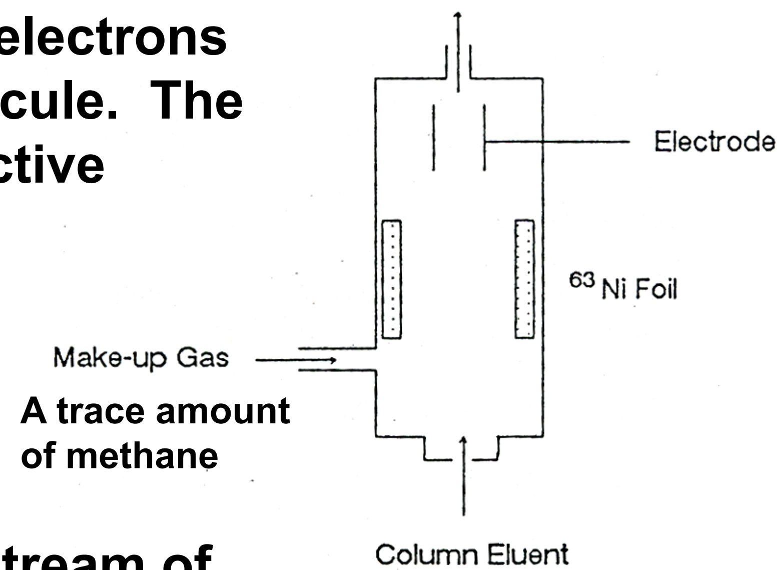
i. The ECD is a radiation-based detector selective for compound containing electronegative atoms, such as halogen.

ii. Principle:

(i) An ECD is based on the capture of electrons by electronegative atoms in a molecule. The electrons are produced by a radioactive source, such as ^{3}H and ^{63}Ni.

$$N_2 + \beta^- \longrightarrow N_2^+ + e^-$$

$$Ar_2 + \beta^- \longrightarrow Ar_2^+ + e^-$$



(ii) In the absence of solute, a steady stream of these secondary electrons is produced that goes to a collector electrodes and produce a current

(iii) As a solute with electronegative atoms elute from column, the solute Capture some of the secondary electrons, reducing the current.

iii. **Applications: An ECD is selective for any compounds with electronegative atoms such as halogen (I, Br, Cl, F), and sulfur-containing compounds.**

iv. **Limit of detection: 10^{-14} M to 10^{-16} M**

v. **Linear range: a 10^3 to 10^4-fold range**

Table 3.4
Relative response of the electron-capture detector to various organic compounds

General organic compounds	Relative response	Fluorocarbon compounds	Relative response
Benzene	0.06	$CF_3CF_2CF_3$	1.0
Acetone	0.50	CF_3Cl	3.3
Di-n-butyl ether	0.60	$CF_2{=}CFCl$	1.0×10^2
Methylbutyrate	0.90	CF_3CF_2Cl	1.7×10^2
1-Butanol	1.00	$CF_2{=}CCl_2$	6.7×10^2
1-Chlorobutane	1.00	CF_2Cl_2	3.0×10^4
1,4-Dichlorobutane	15.00	$CHCl_3$	3.3×10^4
Chlorobenzene	75.00	$CHCl{=}CCl_2$	6.7×10^4
1,1-Dichlorobutane	1.1×10^2	CF_3Br	8.7×10^4
1-Bromobutane	2.8×10^2	$CF_2ClCFCl_2$	1.6×10^5
Bromobenzene	4.5×10^2	$CF_3CHClBr$	4.0×10^5
Chloroform	6.0×10^4	$CF_3CF_2CF_2I$	6.0×10^5
1-Iodobutane	9.0×10^4	CF_2BrCF_2Br	7.7×10^5
Carbon tetrachloride	4.0×10^5	$CFCl_3$	1.2×10^6

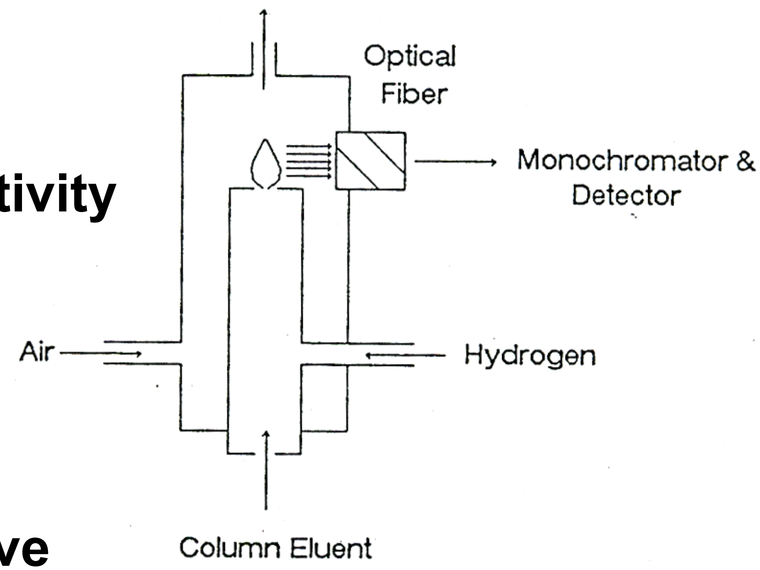
4. Optical Detectors

a. Flame photometric detector (FPD)

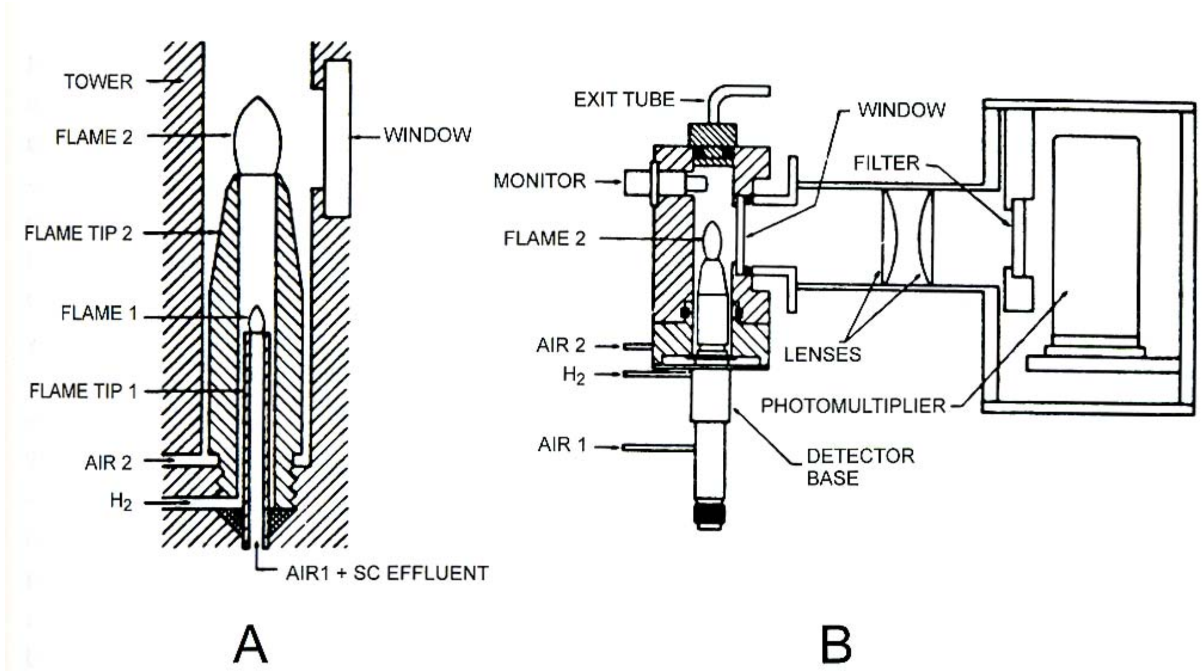
i. The FPD is a selective detector usually used for phosphorus- and sulfur-containing compounds.

ii. Principle:

The FPD is based on the release of light from excited atoms in a flame. The selectivity Of an FPD comes from the detection of Light at an emission wavelength Characteristic for the element of interest.



Iii By including a collector electrode above The flame, the same detector can be used both As an FPD and FID.



iii. Applications: An FPD is selective for any compounds containing any atoms emitting light in the wavelength monitored. It is usually used for detecting phosphorus- and sulfur-containing compound, which emit light at 526 and 394 nm respectively.

iv. Limit of detection: 10^{-14} M

v. Linear range: a 10^4 for phosphorus, and a 10^3-fold range for sulfur

b. Atomic emission detector (AED)

Excitation source: plasmas (i.e., inductively coupled argon plasmas

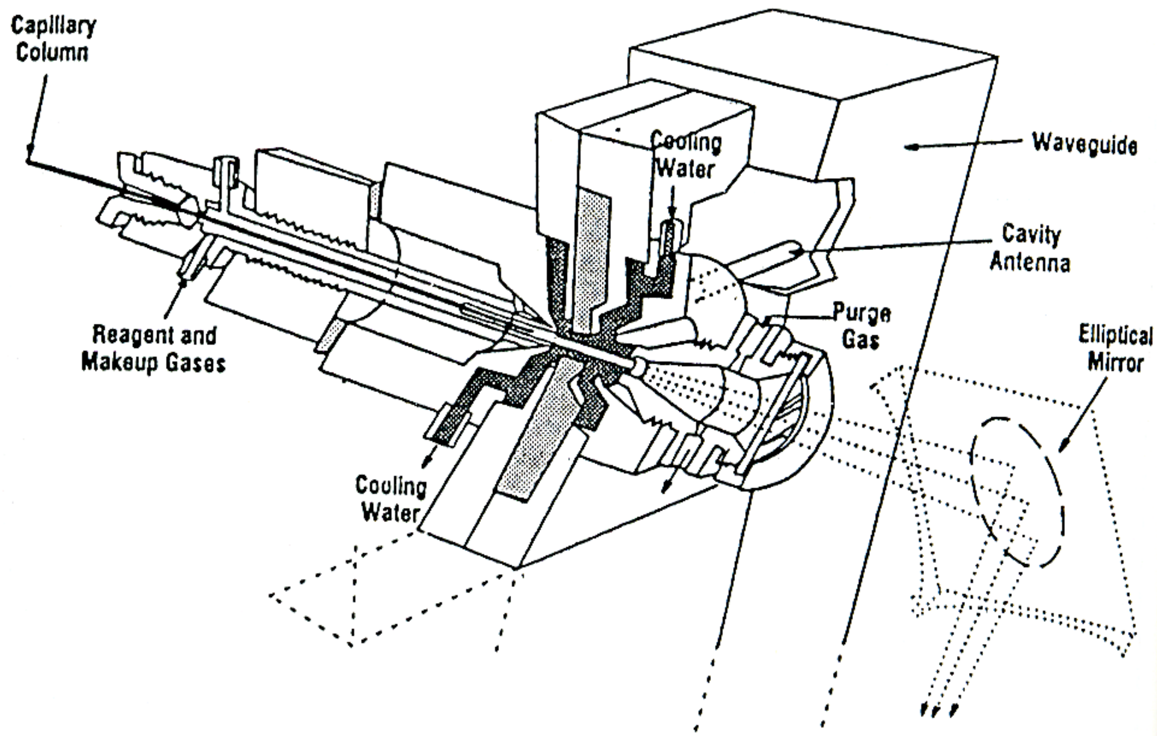
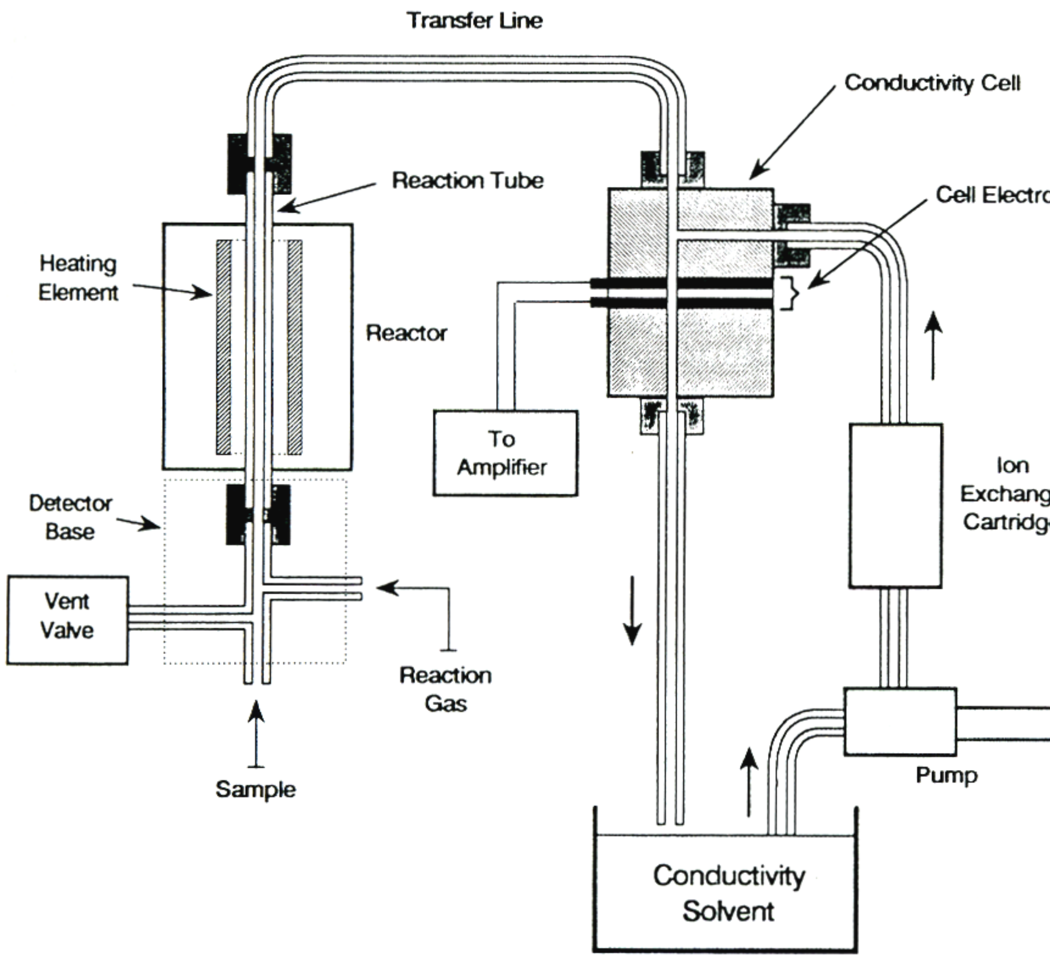


Table 3.5
Response characteristics of the atomic emission detector to different elements

Element (X)	Wavelength	Minimum detectable amount (pg/s)	Selectivity (g X/g C)	Linear range
C	193.1	2.6		2×10^4
H	486.1	2.2		6×10^3
Cl	479.5	39	2.5×10^4	2×10^4
Br	470.5	10	1.1×10^4	1×10^3
F	685.6	40	3.0×10^4	2×10^3
S	180.7	1	3.5×10^4	1×10^4
P	177.5	1	5.0×10^3	1×10^3
N	174.2	15	2.0×10^3	4×10^3
N	388	15	8.0×10^5	1×10^4
O	777.2	50	3.0×10^4	3×10^3
Sn	303.1	0.5	3.0×10^4	1×10^3
Se	196.1	4	5.0×10^4	1×10^3
Hg	253.7	0.1	3.0×10^6	1×10^3

5. Electrochemical detector

Electrolytic conductivity detector (ELCD). The ELCD is used primarily As an element-selective detector for halogen-, sulfur- and nitrogen-Containing compounds.



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