Quantitative Methods in Chemistry

Week 8, Lecture 4

This week: Practice of Chromatography – HPLC, Gas Chromatography, Supercritical Fluid Chromatography, Detectors for analytes

This lecture: Detectors for analytes

Requirements from the detectors

- High sensitivity – able to detect nanogram or picogram of analyte is needed

- Selectivity – In certain applications, selective detection of one analyte over many others is needed.

- High signal-to-noise ratio – to clearly identify the presence of analyte in the eluent

- Low baseline noise – to discriminate the presence of analyte

- Fast response – Needed for the online or real-time detection of the analyte during the chromatographic separations

- Low Baseline drift

Points to be considered when using detectors

Signal

Noise level
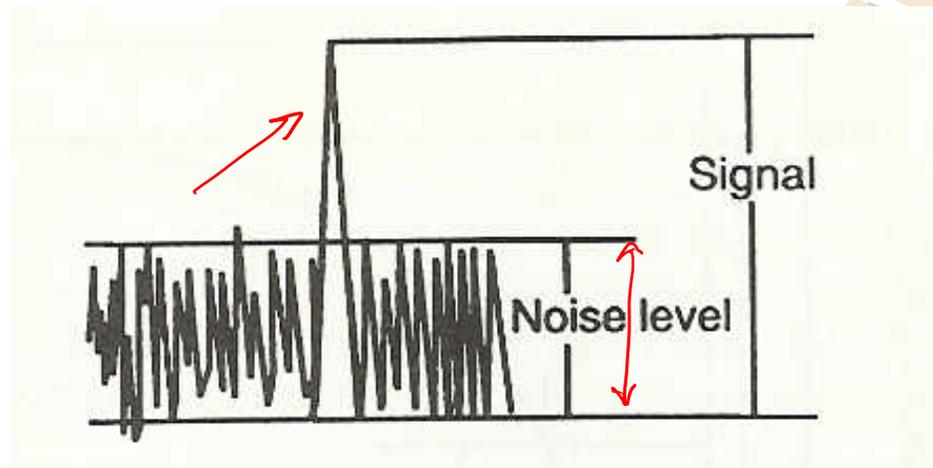
Signal-to-noise ratio

3σ

*fluctuations in the signal in absence of any analyte*
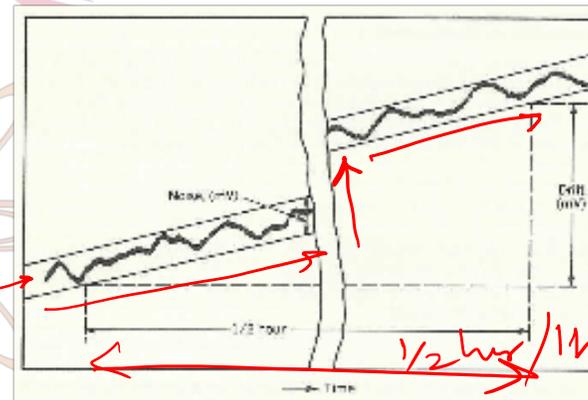
Drift of baseline with time

Profile got in presence of baseline drift

Stable baseline

$1/2$ hrs/1 hr

- Response Factor = Peak area/ Conc. Of Analyte

- Spectral sensitivity of the detectors

**Detector Dynamic Linear Range and Response Time**

Detector Response Time

exponential

$S(t) = S_o + (S_f - S_o) \cdot \exp(-t/\tau)$

Detector Response

low concin regime

high concin of analyte

Dynamic Linear Range

Concentration of the analyte

S_f

Detector response

S_o

τ
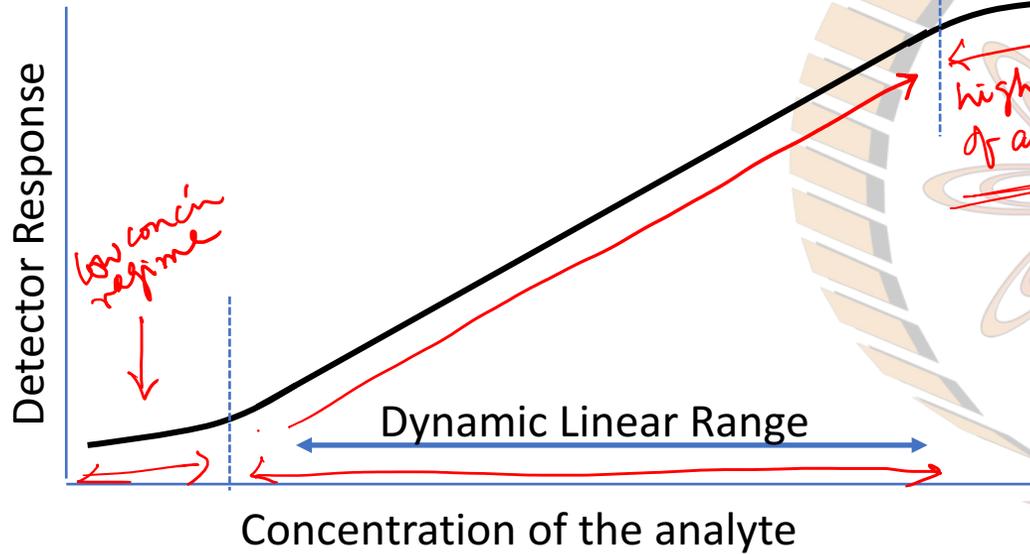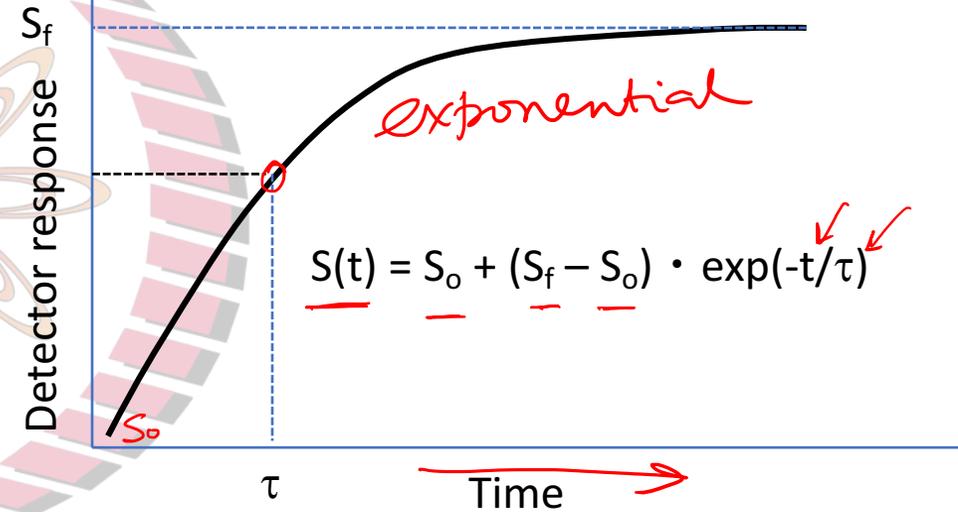
Time

Where τ = time taken by the signal to reach $1 - (1/e)$ = 63.2% of the final value. e = 2.718

$A \propto C$

$A < 1.0$

τ when $S_{(t)} = 0.632 \times S_f$

Low $\tau \Rightarrow$ Rapid detector response

Detectors in LC

UV/ vis detectors

Incident radiation
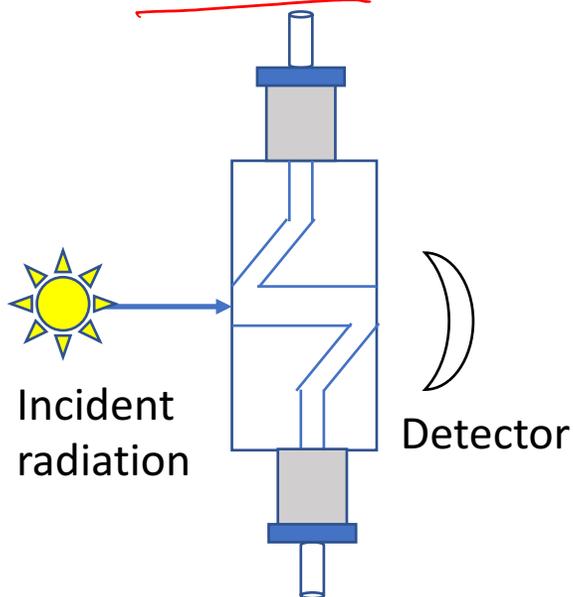
Detector

Refractive Index detector or Differential refractometer

Incident beam

Reference

Mobile phase

Mobile phase

Sample

Exiting beam

II → Analyte is present

Incident beam

Reference

RI (ref)

RI (sample)

Sample

Exiting beam
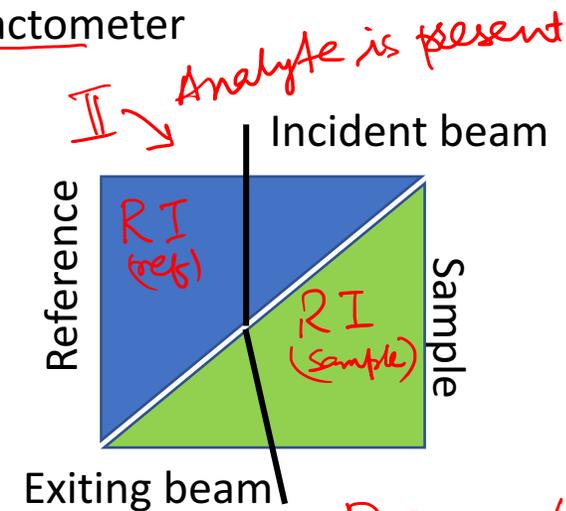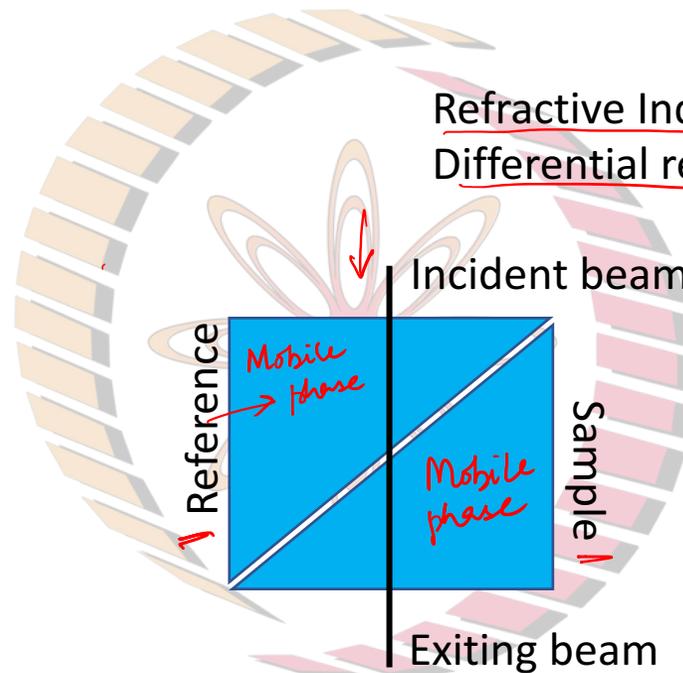
$RI_{ref} \neq RI_{(sample)}$

Universal detector
μM conc. range detection

Detectors in GC

Flame Ionization Detector (FID)

Labels in diagram: Ion Collector, Power supply (−, +), H$_2$ flame, O$_2$, H$_2$, Eluent from the column
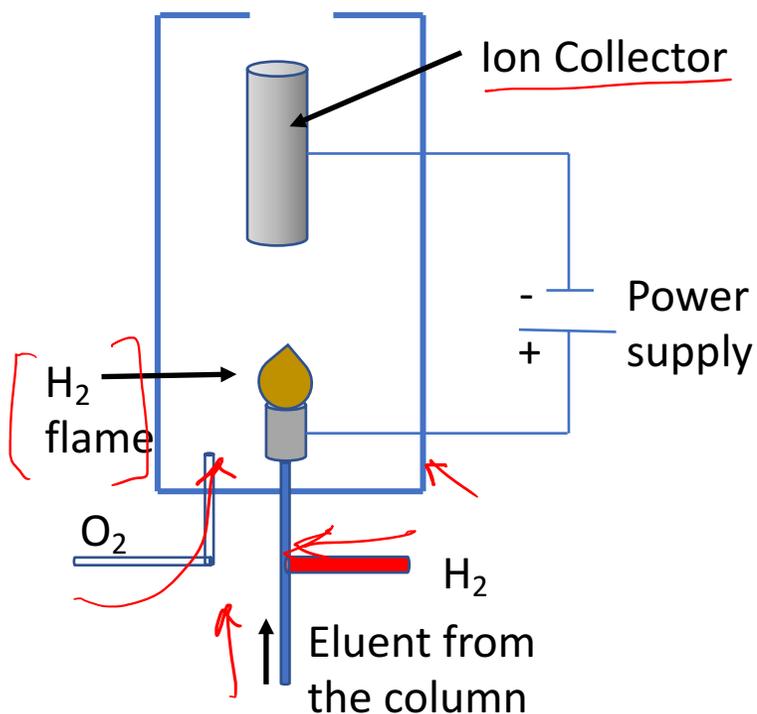
- A high temperature flame is used to pyrolyze the analyte molecules eluting out of the column.

- The ions thus generated are collected on an ion collector. This ion current resulting from the pyrolysis of analyte is used as the signal.

- A universal detector for all types of organic compounds. Has high sensitivity of upto ng (ppb levels), large linear dynamic range, and is also less prone to contamination because everything is burnt out!

- It can't be used in SFC with added organic additives to increase the polarity of the mobile phase. It is **destructive** detector!

Thermal Conductivity Detector

Carrier Gas   Column Eluent

Filaments (handwritten labels on diagram)
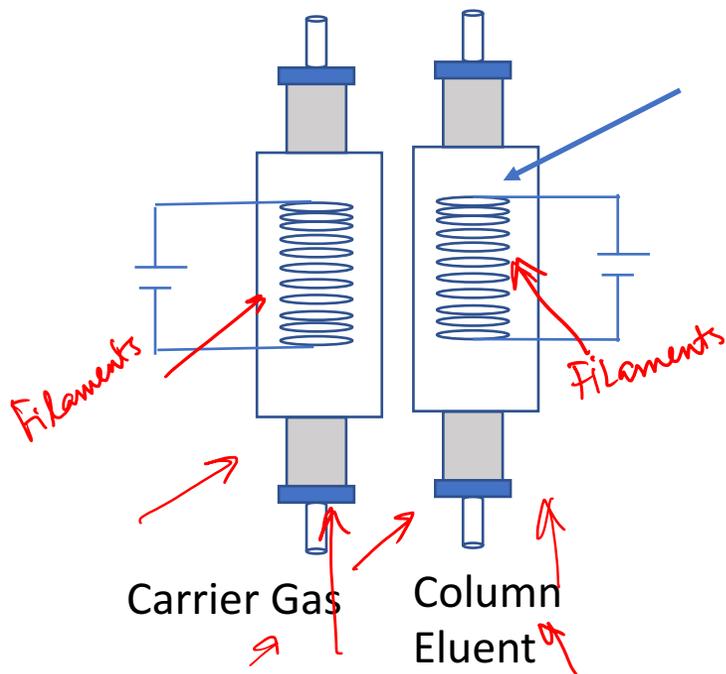
Filament heated by current flow and cooled by gas flow.

Column eluent containing analyte will have a different cooling efficiency. This may require altering the current flowing through the filament to maintain the temperature.

Thermal equilibrium unless the eluent contains analyte (handwritten)

The change in the current flow with regards to the reference cell being purged with only carrier gas is recorded as the signal for this detector.

$I_{ref} - I_{sample}$ vs time (handwritten)

Requirement: Constant flow of the carrier gas and column eluent. Heat conductivity values of the carrier gas should be kept in mind.

Advantages: Universal, Non destructive

Disadvantage: Lower sensitivity than FID (ug or ppm levels)

Electron Capture Detector

Column
Effluent
(dry)

hollow
cylinder

Air
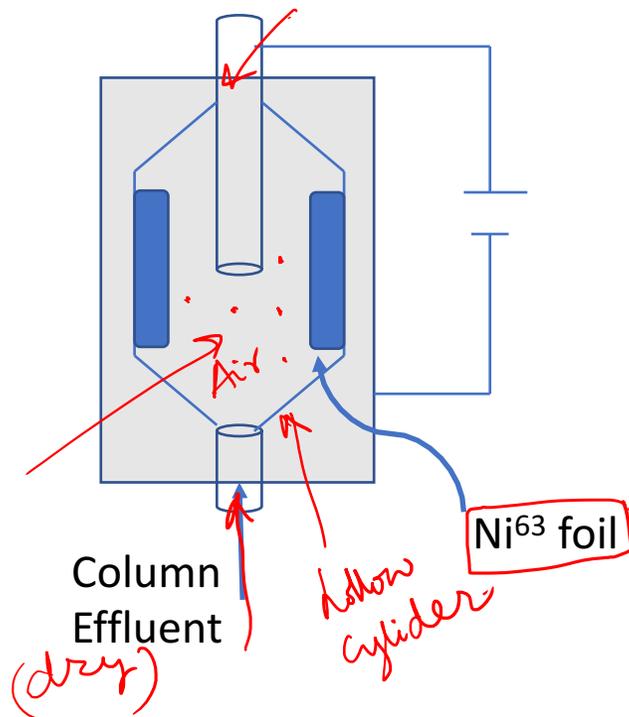
Ni^{63} foil

- Uses a mildly radioactive Ni^{63} foil to cover the inside of a hollow cylinder.

- The β-radiation from Ni^{63} ionizes the air between the two electrodes.

- The resulting ions are collected on the positive ion detecting electrode.

- The presence of analytes containing halide residues absorb the β-radiation and also quench the ions present in the air.

- ↓Baseline signal => ↑analyte containing halide residues.

- Advantages: Most sensitive detector – can detect picogram (or ppt) level analytes.

- Disadvantages: Only for halide containing organics, sensitive to moisture!