Detectors used in Gas Chromatography

The type of detector used is based upon the sensitivity and nature of the compound to be detected. An ideal detector should have following characteristics;

I. Rapid response
II. Highly sensitive
III. A wide range of linear response
IV. Should be stable
V. Low noise
VI. Simple, inexpensive, ?safe
VII. Low detection limit

Different types of detectors used in G.C are given in table. Their brief introduction, instrumentation and uses are discussed briefly.

1. Flame ionization detector
2. Thermal conductivity detector
3. Electron capture detector
4. Thermionic specific detector
5. Flame photometric detector
6. Photo ionization detector
7. Mass spectrometers
8. chemi luminesence detector
9. atomic emission detector

1. Flame ionization detector:

The efflux from the column is mixed with H and air and ignited. Organic compounds burning in the flame produce ion and electrons which can conduct electricity through the flame. A large electric potential is applied at the burner tip and the collector electrode is located above the flame. The current resulting from Pyrolysis of any organic compound is measured. *FID's are mass sensitive instead of concentration sensitive* .this give the advantage that changes in mobile phase flow rate do not effect the detector's response. It has almost all ideal characteristics except it destroys the sample and hence sample can not be used for further analysis. A typical FID is shown in the figure.
Detection range is up to 100pg.

2. Thermal conductivity detectors:

A TCD consists of an electrically heated wire or thermistor. The temperature of the sensing element depends upon the thermal conductivity gas flowing around it. Changes in electrical conductivity when solute displaces some of carrier gas causes a temperature rise in the element which is sensed as a change in resistance. *TCD is not as sensitive as others but it is non-specific and non-destructive.*

Instrumentation:

Two pairs of TCD are used in gas chromatographs. One pair is placed in the column effluent to detect the separated components and other is placed before the injector or in reference column. The resistance of two sets of pairs is then arranged in the bridge circuit. The bridge circuit then allows amplifications of the resistance changes due to electrolyte passing over the sample thermo conductors and does not amplify changes in resistance that both sets of detectors produce due to flow rate fluctuations etc.

Sensitivity is up to 1ng and is of universal selectivity.

3. Electron capture detector:

The ECD uses a radioactive β emitter usually ^{63}Ni to ionize the some of the carrier gas and produce a current between a biased pair of electrodes. When an organic compound that contain an electronegative functional groups, such as: halogens, phosphorus, and nitrogen groups pass by the electrodes and reduced the current measured between the two electrodes. The ECD is as sensitive as the FID but has the limited dynamic range and finds its greatest application in analysis of the halogenated compounds.
The range of sensitivity is up to 50pg.
It is used for the halides, nitrates, peroxides, anhydrides, organometallics etc.

4. Thermionic specific detector:

It is also called as *Nitrogen-phosphorus detector*. It is modified form of FID that shows increased response to compounds containing nitrogen and phosphorus. It consists of a standard FID with an electrically heated bead of solid alkali compounds such as rubidium silicate suspended in the area above the flame assembly. In the presence of excess air, plasma is formed in the area of the bead. This produces a large number of ions from nitrogen and phosphorus containing compounds, that area then detected at the collection electrodes as in FID. The mechanism of action is not understood fully, but its sensitivity for nitrogen and phosphorus containing compounds is 10^3 to 10^4 times greater than for organic compounds. It also has importance in the analysis of pesticide residue.
It has sensitivity range of 10pg.

5. Flame photometric detector:

The determination of sulfur and phosphorus compounds is a job of FPD. The device uses the chemi luminescent reaction of these compounds in a hydrogen/air flame as a source of analytical information that is relatively specific for the substances containing these two kinds of atoms. The emitting species for sulfur compounds is excited S_2 with λmax = 349 nm. The emitted for phosphorus compounds is excited HPO with λmax= doublet 510 – 526 nm. In order to detect selectivity one or other family of compounds as it elutes from the GC column, an in? filter is used between flame and the photomultiplier tube, to isolate the appropriate emission land. *The drawback is that filter must have to change during run, if we want to analyze another different family of compounds.*

Instrumentation:

FPD includes the following important components for working as;

I. Combustion chamber
II. Fuel gas line
III. Exhaust chimney to remove combustion product
IV. Thermal filter to isolate only the UV-visible radiations

Without this, the IR emitted by the flames' combustion reaction would heat up the photomultiplier tube and increase its background signal. The PMT is also physically isolated/ insulated from the combustion chamber by using poorly conducting metals to attach the PMT housing, filter etc.
The physical arrangement of the components is as follows;

I. Flame chamber with exhaust
II. Permanent thermal filter (two IR-filters in same commercial design)
III. A removable phosphorus or sulfur filters (selective)
IV. Finally the photomultiplier tube

The sensitivity is of the order of 100pg.

6. Photo ionization detector:

The selective determination of the aromatic hydrocarbons or organo-hetero atom specie is the job of photo ionization detector (PID). This device uses UV light as a mean of ionizing analyte exciting from a G.C-column. The ions are then collected by electrodes. The current generated is therefore a measure of analyte concentration.

Theory:

If the energy of an incoming photon is high enough, photo excitation can occur to such an extent that an electron is completely removed from its molecular orbital i.e. ionization occurs.

$$R + h\nu \longrightarrow R^{+} + e^{-}$$

If the amount of ionization is reproducible for a given compound, pressure and light source then the current collected at the PID's reaction cell electrodes is reproducibly proportional to amount of that compound entering into the cell.

Instrumentation:

Since only a small fraction of analyte is ionized, so it is considered to be non destructive detector. So the exhaust part of PID's can be attached to another detector in series with PID's. In this way, data from the two detectors can be collected simultaneously.

The major challenge is to make the design of ionization chamber and down streams connections to the 2nd detector as low volume as possible, so the peaks that have been separated by the GC column do not broaden out before detection.

It is specific for;

Aliphatics, aromtics, ketones, esters, aldehydes, amines, heterocyclics, organo sulphurus and someorganometallics etc.

Lmit of detection is up to 2pg.

7. Mass spectrometers:

Mass spectrometers use the difference in mass to charge ratio (m/e) of ionized atoms or molecules to separate them from each other. So this technique is useful for the quantitation of atoms and molecules and for determining chemical or structural information about molecules.

Instrumentation:

In general mass spectrometer consists of;

I. An ion source
II. A mass selective analyzer
III. Ion detector

Since mass spectrometer create and manipulate gas phase ions, they operate in light vacuum system.The magnetic sector, quardrapole and time of flight designs also require extraction and acceleration ion optics to transfer ions from source region into analyzer.

Different mass analyzer designs are;

1) Fourier transformer MS
2) Ion trap MS
3) Quardrapole MS
4) Time of flight MS

8. Chemiluminescence detectors:

Chemiluminescence like atomic emission spectroscopy (AES), uses quantitative measurements of the optical emission from the chemical species to determine analyte concentration, however unlike AES, it is usually emission from energized molecules instead of simple excited molecules. The bands of light determined by this technique emanate from molecular emissions and are therefore broader and more complex than bands originating from atomic spectra. It can only be used for gaseous samples.

Its strength lies in the detection of electromagnetic radiations produced in system with very low background and on top of this, because the energy necessary to excite the analytes to higher electronic, vibrational and rotational states does not come from an external light source like a laser or lamp. *The problem of excitation source scattering is completely avoided. Its major limitation is the dark current of the photomultiplier tube necessary to detect the analytes' light emissions.*

In gas phase chemiluminescence, the light emission is produced by the reaction of an analyte and strongly oxidizing agent such as; fluorine or ozone etc.
The reaction occurs as a time scale such that the production of light is essentially instantaneous; therefore most analytical systems simply mix the analytes and reagents in small volume chamber infront of PMT. In case of GC, column is directly connected to the chamber.

Since as much as the energy of reaction should be used to excite as many of the analyte molecules as possible, loss of energy via gas phase collisions is undesirable and therefore a final consideration is that the gas pressure in the chamber is maintained at low pressure ($\simeq$ 1torr) to minimize effects of collisional deactivation.

9. ***Atomic emission detectors:***

This detector is more expensive than other available GC-detectors but is an extremely powerful alternative. The strength of AED lies in the detectors' ability to simultaneously determine the atomic emission of many of the analytes that elute from the GC column. As eluents come off the capillary column, they are fed into microwave powered plasma cavity where the compounds are destroyed and their atoms are excited by the energy of the plasma. The emitted light by the separated particles is separated into individual lines via photodiode array. The associated computer then sorts out the emission lines and can produce chromatograms made up of peak from eluents that ? only a specific elements.

Instrumentation:

The components of AED include

1) An interface for the incoming capillary GC- column to microwave induced plasma chamber.
2) The microwave chamber itself.
3) A cooling system for that chamber.
4) A diffraction grating and associated optics to focus then disperse the spectral lines.
5) A position adjustable photodiode array interfaced to a computer.