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SCHOOL OF ELECTRICAL & ELECTRONICS ENGINEERING

DEPARTMENT OF ELECTRONICS & INSTRUMENTATION ENGINEERING

UNIT – I -Analytical Instrumentation – SIC1304

I SAMPLING SYSTEMS

pH CONDUCTIVITY & DISSOLVED COMPONENT ANALYSER

Conductivity meters - pH meters - dissolved oxygen analyser, hydrogen analyser -sodium analyser - silica analyser and Sampling systems.

pH Measurement

pH is an abbreviation of "pondus hydrogenii" and was proposed by the Danish scientist.S.P.L. Sørensen in 1909 in order to express the very small concentrations of hydrogen ions.pH is a convenient measure of the acidity/alkalinity of an aqueous solution at a specified temperature (usually 25°C). It is measured on a continuous scale from 0 to 14. If the pH value is 7, the solution is neutral, if it is less than 7, the solution is acidic and if it is greater than 7, it is alkaline (base).

Measurement of pH is carried out for a wide variety of purposes such as , to test a sample against a legal requirement, to test a chemical against a specification, as part of an analytical method, monitoring and controlling biochemical and physiological reactions, process control in the chemical industry, environmental monitoring of waste and effluents.

pH is usually determined by electrochemical measurements, in which the potential of a pH electrode immersed in the test solution is measured. The pH electrode responds quantitatively and specifically to hydrogen ions even in the presence of other positive ions. The potential of the pH electrode is measured with respect to reference electrode using a pH meter. The pH meter comprises a high impedance electronic voltmeter. Such a voltmeter is required because the resistance of the electrochemical cell, which is a part of the pH measurement system, is very high (approximately $10^8\Omega$).

The electrochemical cell may be represented as:pH electrode/test solution to be measured//reference electrode The symbol // signifies the presence of a liquid junction between the test solution and the reference electrode.The pH value of a given solution is a measure of the activity of the hydrogen ion in that solution.The activity (concentration) of the hydrogen ion in solution is measured with a pH measuring system consisting of a glass electrode, a reference electrode and a pH meter. When the pH sensitive glass bulb is immersed in a solution, exchange equilibrium is established between the hydrogen ion and the ions in the glass. This equilibrium is the source of the potential measured. The potential which is measured varies with the hydrogen ion activity. The glass electrode alone is not sufficient to measure the potential, since a reference electrode is needed to complete the measuring

circuit. The reference electrode supplies a stable reference potential against which the potential from the glass electrode may be compared. The reference electrode provides a stable potential by surrounding an internal element with a known solution.

Glass electrode

Glass electrode is an ion selective electrode, sensitive, sensitive to H+ ions, so it is used to measure H+ ion concentrations. It is used with other reference electrodes to generate a potential difference.

Principle: A thin glass membrane is in contact with solutions of different H+ ion concentrations on its two sides, a difference in potential is developed across the membrane. The magnitude of potential difference depends on the difference in H+ ion concentration and hence the PH can be calculated.

Schematic of Glass electrode

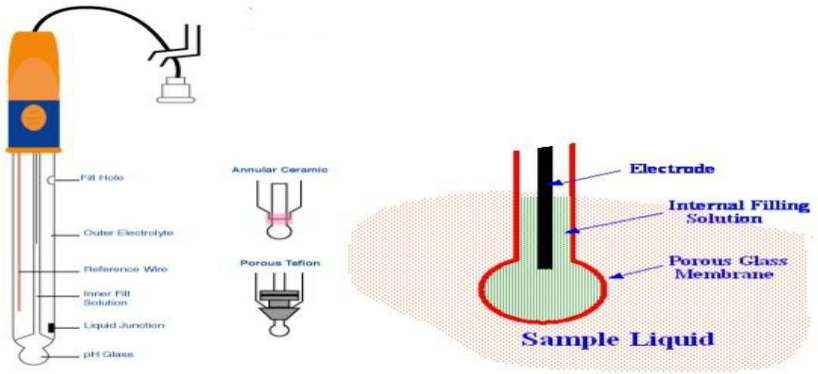

Figure No. 1:Glass Electrode

Construction: The glass electrode consists of the following parts

- pH glass
- outer electrolyte
- Inner fill solution
- Reference wire
- Fill hole
- Electrode (Silver chloride)

It is made up of a special glass of relatively low melting point and high electrical conductivity, in the form of a sealed glass tube filled with 0.1 M Hcl, a platinum wire is inserted into it, to make electrical contact. The glass electrode is represented as Pt; 0.1M HCL glass test H+ solution. The H+ ion concentration inside the electrode is constant. When this electrode is immersed into a solution of unknown H+, it becomes sensitive to the outside H+ concentration in the solution. Such sensitivity arises because of the difference between the H+ ion concentration inside and outside. A second electrode is necessary when measuring the electromotive force generated at the electrode membrane of a glass electrode. This other electrode, paired with the glass electrode, is called the reference

electrode. The reference electrode must have extremely stable potential. Therefore, it is provided with a pinhole or a ceramic material at the liquid junction. The Fill hole is used to fill the outer electrolyte.

Working: The difference in pH between solutions inside and outside the thin glass membrane creates electromotive force in proportion to this difference in pH. This thin membrane is called the electrode membrane. Normally, when the temperature of the solution is 30 ℃, if the pH inside is different from that of outside by 1, it will create approximately 60 mV of electromotive force. The liquid inside the glass electrode usually has a pH of 7. Thus, if one measures the electromotive force generated at the electrode membrane, the pH of the sample can be found by calculation.

Advantages: It can be used for the determination of PH of oxidizing agents, reducing agents viscous madia, in presence of proteins which interfere the other electrode etc. It can be used in the PH range of 0 to 12. It can be used in colored, turbid and colloidal solutions. It is simple to operate.

Disadvantages: Not used in ordinary potentiometer due to the high resistance of glass membrane.

Calomel electrode

The calomel electrode is a reference electrode based on the reaction between elemental mercury and mercury chloride.

Principle: A thin glass membrane is in contact with solutions of different concentrations on its two sides, a difference in potential is developed across the membrane. The magnitude of potential difference depends on the difference in concentration.

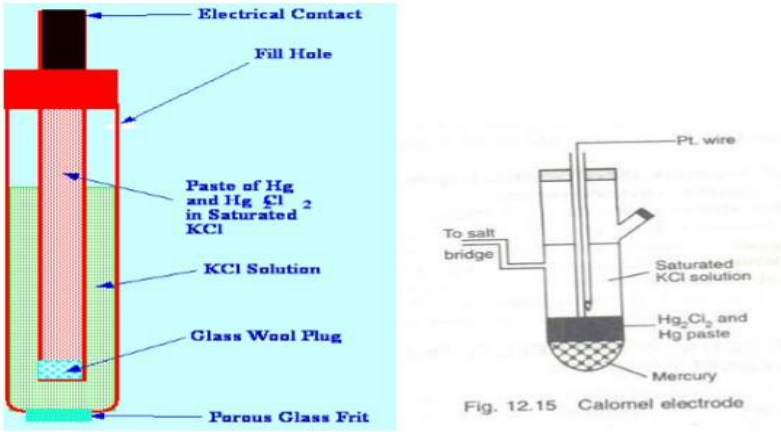

Figure No.2 : Calomel Electrode

Construction: It consists of an outer glass tube fitted with a frit at the bottom to permit electrical contact with the outside solution. In side there is another tube, the bottom of which is packed with

glass wool to allow further electrical connection between the contents of the inner tube and the contents of the outer tube.

The inner tube is packed with a paste of mercury and mercurous chloride dispersed in a saturated solution of potassium chloride. The electrode potential will depend on the concentration of the potassium chloride and, thus, the electrode potential must be reported together with the potassium chloride concentration. Thus, for the saturated calomel electrode the common reference voltage is +0.244 V. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 N, the electrode is known as normal calomel electrode (NCE) while for 0.1 N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE).

Working:

The electrode reaction when the electrode acts as cathode is:

The reduction potentials of the calomel electrodes on hydrogen scale at 298K are as follows:

Saturated

KC1= 0.2415 V , 1.0N KC1 =0.2800 V , 0.1N KC1= 0.3338 V

Calomel electrode acts as either anode or cathode w.r.to the other electrode connected to it.The electrode potential of any other electrode on hydrogen scale can be measured when it is combined with calomel electrode. The emf of such a cell is measured. From the value of electrode potential of calomel electrode, the electrode potential of the other electrode can be evaluated.

- **Advantages:** The calomel electrode is more realistic and more robust and is one of the common electrodes applied in corrosion analysis. It is comparatively low-priced.
- **Disadvantages:** The calomel electrode contains mercury, which poses health hazards

Silver/Silver Chloride Electrodes

Another common reference electrode is the silver/silver chloride electrode, which is based on the following redox couple between AgCl and Ag.

$$\mathrm{AgCl}(s) + e^{-}f \leftrightharpoons \mathrm{Ag}(s) + \mathrm{Cl}^{-}(aq)$$

As is the case for the calomel electrode, the activity of Cl^- determines the potential of the Ag/AgCl electrode; thus

$$E = E^{o}_{\mathrm{AgCl/Ag}} - 0.05916\log a_{\mathrm{Cl}^-} = +0.2223\ \mathrm{V} - 0.05916\log a_{\mathrm{Cl}^-}$$

When prepared using a saturated solution of KCl, the potential of a Ag/AgCl electrode is +0.197 V at 25°C. Another common Ag/AgCl electrode uses a solution of 3.5 M KCl and has a potential of +0.205 V at 25°C.

A typical Ag/AgCl electrode is shown in Figure, consists of a silver wire, the end of which is coated with a thin film of AgCl, immersed in a solution containing the desired concentration of KCl. A porous plug serves as the salt bridge.

The electrode's short hand notation is

$g(s) \mid AgCl(s), KCl(aq, a_{Cl^-} = x) \parallel$

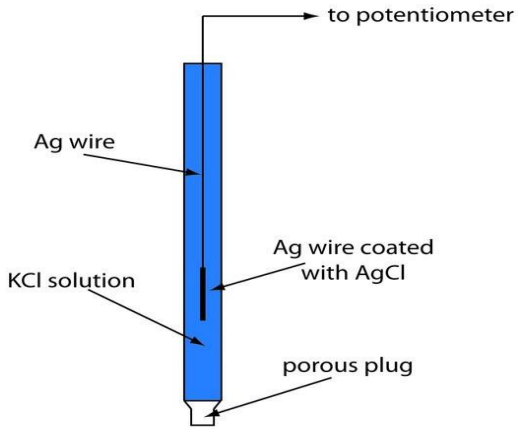

Figure No.3 : Schematic Ag/AgCl electrode

Because the electrode does not contain solid KCl, this is an example of an unsaturated Ag/AgCl electrode.

Selective ion electrodes

An ion-selective electrode (ISE), also known as a specific ion electrode (SIE), is a transducer (or sensor) that converts the activity of a specific ion dissolved in a solution into an electrical potential, which can be measured by a voltmeter or pH meter. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. The sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode.

Principle: The ion selective membrane selectively picks up certain ion to pass through it and creates a potential, which can be measured using a voltmeter.

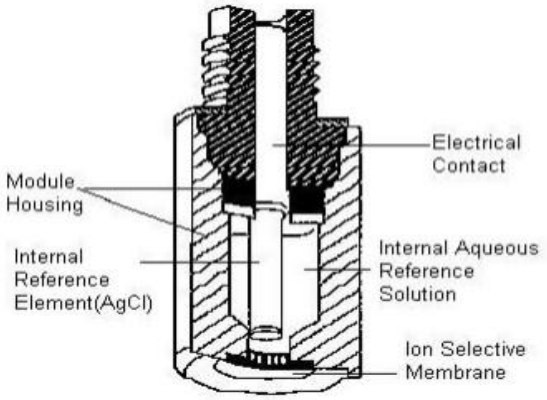

Figure No.4 :Schematic of Ion selective electrode

Types of Ion Selective Membrane:

Glass membrane: Glass membranes are made from an ion-exchange type of glass (silicate or chalcogenide). This type of ISE has good selectivity, but only for several single-charged cations; mainly H+, Na+, and Ag+. The glass membrane has excellent chemical durability and can work in very aggressive media. A very common example of this type of electrode is the pH glass electrode.

Crystalline membrane: Crystalline membranes are made from mono or poly crystallites of a single substance. They have good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response. An example is the fluoride selective electrode based on LaF3 crystals.

Ion exchange resin Membrane: Ion-exchange resins are based on special organic polymer membranes which contain a specific ion-exchange substance (resin). This is the most widespread type of ion-specific electrode. An example is the potassium selective electrode, based on valinomycin as an ion-exchange agent.

Construction: These electrodes are prepared from glass capillary tubing approximately 2 millimeters in diameter, a large batch at a time. Polyvinyl chloride is dissolved in a solvent and plasticizers (typically phthalates) added, in the standard fashion used when making something out of vinyl. In order to provide the ionic specificity, a specific ion channel or carrier is added to the solution; this allows the ion to pass through the vinyl, which prevents the passage of other ions and water. One end of a piece of capillary tubing about an inch or two long is dipped into this solution and removed to let the vinyl solidify into a plug at that end of the tube. Using a syringe and needle, the tube is filled with salt solution from the other end, and may be stored in a bath of the salt solution for an indeterminate period. For convenience in use, the open end of the tubing is fitted through a tight oring into somewhat larger diameter tubing containing the same salt solution, with a silver or platinum electrode wire inserted. New electrode tips can thus be changed very quickly by simply removing the older electrode and replacing it with a new one.

Working: An ISE (is immersed in an aqueous solution containing the ions to be measured, together with a separate, external reference electrode. The electrochemical circuit is completed by connecting the electrodes to a sensitive milli-volt meter using special low-noise cables and connectors. A

potential difference is developed across the ISE membrane when the target ions diffuse through from the high concentration side to the lower concentration side

Advantages: Inexpensive and simple to use , Wide concentration range , Unaffected by sample color or turbidity , Ideal for monitoring environmental pollution or water quality , Ideal for long term monitoring of changes in ion concentration

Standard hydrogen electrode

A Standard Hydrogen Electrode (SHE) is an electrode that scientists use for reference on all half-cell potential reactions. The value of the standard electrode potential is zero, which forms the basis one needs to calculate cell potentials using different electrodes or different concentrations.

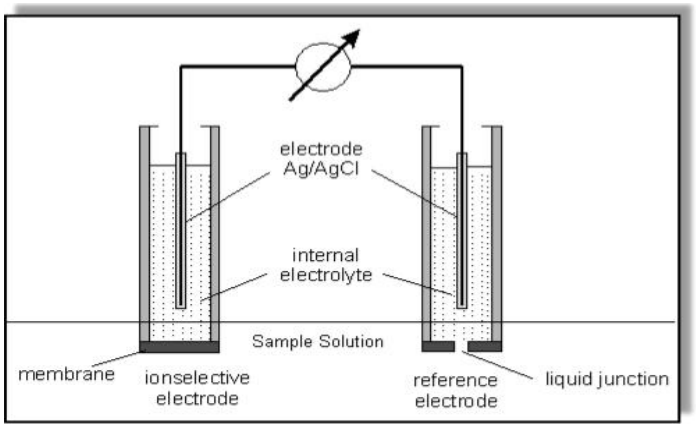

Figure No.5 :Schematic of Standard Hydrogen Electrode

Construction and Working:

SHE is composed of a 1.0 M H+ (aq) solution containing a square piece of platinized platinum (connected to a platinum wire where electrons can be exchanged) inside a tube.

During the reaction, hydrogen gas is then passed through the tube and into the solution causing the reaction: $2H^+ (aq) + 2e^- <==> H_2(g)$. First an initial discharge allows electrons to fill into the highest occupied energy level of Pt. As this is done, some of the H+ ions form H_2O + ions with the water molecules in the solution. These hydrogen and hydronium ions then get close enough to the Pt electrode (on the platinized surface of this electrode) to where a hydrogen is attracted to the electrons in the metal and forms a hydrogen atom. Then these combine with other hydrogen atoms to create $H_2(g)$. This hydrogen gas is released from the system. In order to keep the reaction going, the electrode requires a constant flow of $H_2(g)$. The Pt wire is connected to a similar electrode in which the opposite process is occurring, thus producing a charge that is referenced at 0 volts. Other standard electrodes are usually preferred because the SHE can be a difficult electrode to set up. The difficulty arises in the preparation of the platinized surface and in controlling the concentration of the reactants. For this reason the SHE is referred to as a hypothetical electrode.

Conductivity Meters

Electrical Conductivity (EC) meters measure the capacity of ions in an aqueous solution to carry the electrical current. As the ranges in aqueous solutions are usually small, the basic units of measurements are milliSiemens/cm (mS/cm) and microSiemens/cm (µS/cm).

Conductivity is used widely to determine the level of impurities in water supplies for domestic consumption as well as industrial use. Industries that employ this method include the chemical, semi-conductor, power generation, hospitals, textile, iron and steel, food and beverage, mining, electroplating, pulp and paper, petroleum and marine industries.

It is defined as the conductivity in ohms of a solution containing one gm equivalent of solute when placed between two sufficiently large electrodes, which are one cm apart. It is denoted by λ.

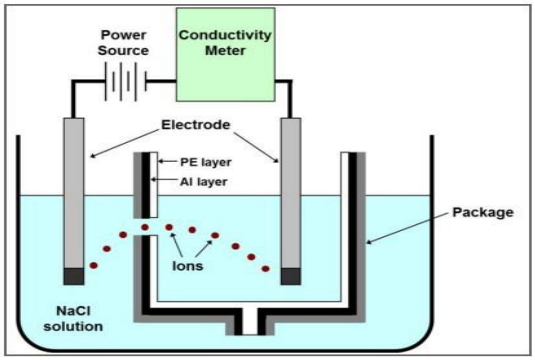

Figure No.6 :Conductivity Meter

The solution whose conductivity is to be determined is taken in a suitable cell, known as conductivity cell. These cells are made of quartz and are fitted with platinum electrodes. The electrodes usually consist of two sheets of platinum. In order to remove the polarization effects the electrodes are coated with finely divided platinum black, and these are called platinized platinum electrodes. The measurement of conductivity using a conductivity meter involves the measurement of cell constant of the conductivity cell. The cell is first calibrated with 0.1 N KCl solutions, following which the conductance of the unknown solution can be measured in mhos.

Conductivity is a parameter used to measure the ionic concentration and activity of a solution. If a solution has more salt, acid or alkali then its conductivity is greater. The unit of

conductivity is S/m, often also S/cm. The scale for aqueous solutions begins with pure water at a conductivity of 0.05 µS/cm (77 °F /25 °C). Naturally occurring waters such as drinking water or surface water have conductivity in the range 100 - 1000 µS/cm. At the upper end of the chart some acids and alkalines can be found.

Conductivity cell measurements are used for a wide range of applications such as the production of ultrapure water or determining the salinity of sea water.

Conductivity is measured by using a conductivity cell to make a measurement of the electrical resistance. The simplest kind of measuring cell used consists of two similar electrodes. An alternating voltage applied to one of the conductivity electrodes causes the ions in the solution to migrate towards the electrodes. The more ions in the solution mean the greater the current, which flows between the conductivity electrodes. The conductivity meter measures the current produced

by the conductivity cell and uses Ohm's law to calculate first the conductance of the solution and then by taking the cell data into account the conductivity.

Conductivity Cells are ideal for monitoring ground water, rivers, lakes, streams, swimming pools, and industrial water applications including juices, electroplating, and pharmaceutics also ideal for routine field measurements. Conductivity is measured in the field with a portable probe.

Table 1: Conductivity values

Aqueous Conductivities	
Solution	**µS/cm**
Totally pure water	**0.055**
Typical DI water	**0.1**
Distilled water	**0.5**
RO water	**50-100**
Domestic "tap" water	**500-800**
Potable water (max)	**1055**
Sea water	**56,000**
Brackish water	**100,000**

pH Meter:

To measure the pH of a test solution, a glass electrode is dipped into a test solution and another reference electrode generally calomel electrode is also connected with this solution by means of a salt bridge having potassium chloride. These 2 electrodes are connected to a potentiometer to measure the concentration of H^+ ions. When the glass surface is in contact with a solution, it generates an output potential which is proportional to the concentration of H^+ ions in the solution.

Commercially available modern pH meters can be classified broadly into two main types.

1. The direct reading type
2. The null detector type

Direct Reading type:

In this type pH meter consists of a combination electrode (ie both the measuring and reference electrode are placed in the solution whose pH is to be measured), electrometer and a galvanometer. The electrometer consists of 3 electrodes (anode, cathode and grid) which are fixed in an evacuated glass tube. The pH measuring glass electrode is connected to the grid and the anode is connected to a battery via the galvanometer. The cathode is connected to both the battery and the reference electrode. Due to high potential difference between the anode and cathode by battery electrons are emitted by the hot cathode and are attracted by the anode. Thus the electrons are start moving from anode to cathode. The grid is used for controlling the current flow.

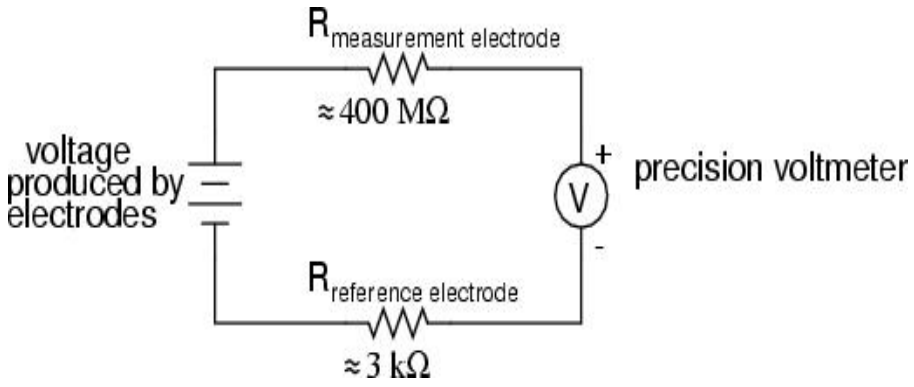

Figure No. 7: Direct Reading Type pH meter

Initially the instrument is calibrated by introducing it into a solution whose pH is known. Then it is introduced in the solution of unknown pH. Depends on the pH of a solution, glass electrode generates an output potential which is applied between the grid and the cathode of the electrometer. Change in potential causes change in current flow which is indicated directly by the galvanometer whose scale is calibrated in terms of pH.

Null detector type:

In this type pH meter consists of a combination electrode, electrometer and a galvanometer. The electrometer consists of 3 electrodes which are fixed in an evacuated glass tube. The pH measuring glass electrode is connected to the grid and the anode is connected to a battery via the galvanometer. The cathode is connected to both the battery and the reference electrode **through a potentiometer**.

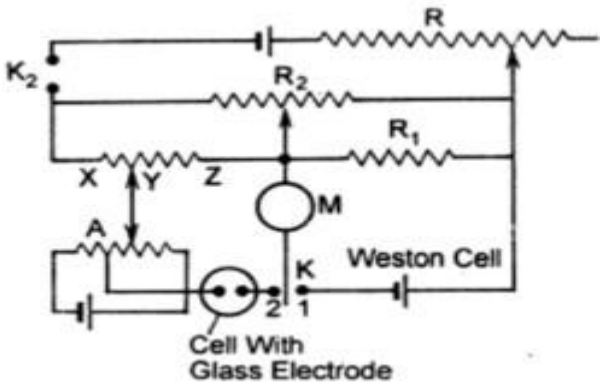

Figure No. 8: Null Detector Type pH meter

Initially the instrument is calibrated to read zero or null by introducing it into a solution whose pH is known. Then it is introduced in the solution of unknown pH. Depends on the pH of a solution, glass electrode generates an output potential which is applied between the grid and the cathode of the electrometer. So the meter is unbalanced. In order to balance the meter, an equal and opposite potential is applied from the potentiometric circuit.Under the null condition the meter is said to be balanced.then the voltage applied by a potentiometric circuit is measured which is proportional to unknown pH.

DISSOLVED OXYGEN ANALYZER

Introduction:

Oxygen analyzers are widely used in industries to detect the amount of oxygen present in the water in order to avoid corrosion in the metallic part of the boiler. The analyzer is based on the katharometer or thermal conductivity.

Principle:

The amount of oxygen in a closed space above water at a constant temperature depends upon the oxygen content present in the water only and does not depend on gas above the water.

Schematic of dissolved oxygen analyzer:

Construction:

The dissolved oxygen analyzer consists of

- Condensing section
- Transmitting section
- Analyzing section

The condensing section cools the sample water to be tested to 20 -25 0C. The sample water is made to flow in a coiled tube around which cooled water is passed. The Transmitting section consists of flow regulator, which regulates the cool water to be flowed into analyzing section. The heart of the analyzer is analyzing section. The analyzing section terminals are connected to the wheat stone bridge. The analyzing section consists of reference arm to which a platinum wire is connected. This platinum wire is exposed to inert hydrogen gas. The other platinum wire is made to expose to oxygen which is present above the water. This platinum wire is connected to the measuring arm.

Working:

(i) **Balancing the Bridge:** Initially the bridge would not be balanced. To balance the bridge the amount of hydrogen ions in the reference arm has to be adjusted. Until the balance is arrived, the sample should not enter the measuring arm. The arm is subjected to a standard solution which produces a constant oxygen rate. The sample is blocked from entering the contact tube by a water cock.

(ii) **Measuring dissolved oxygen:** Once the bridge is balanced, the water cock is opened and the sample water is allowed to flow through the measuring arm. The contact tube picks up the oxygen gas and it changes the temperature of the platinum wire placed in the contact tube and hence the current flows through the bridge. The amount of current flow gives the measure of dissolved oxygen present in the sample.

Dissolved oxygen refers to oxygen dissolved in water. Its concentration is expressed as the amount of oxygen per unit volume and the unit is mg/L. Biologically, oxygen is an essential element for respiration of underwater life and also acts as a chemical oxidizer. The solubility of oxygen in water is affected by water temperature, salinity, barometric pressure, etc. and decreases as water temperature rises.

Membrane electrode method

The membrane electrode method measures a diffusion current or reduction current generated by the concentration of dissolved oxygen or partial pressure of oxygen to obtain the concentration of dissolved oxygen. This method is not affected by the pH value of water being measured, oxidation and reduction substances, color, turbidity, etc. and the measurement method offers good reproducibility. If a sensor is inserted into water, an air layer forms on the membrane (Teflon membrane). The oxygen partial pressure (concentration) in the air layer is in equilibrium with the concentration of dissolved oxygen in the water. The membrane electrode method measures the oxygen concentration in the gas phase to indirectly obtain the concentration of dissolved oxygen in water.

There are two types of membrane electrode method: the galvanic cell method, and polarographic method. These methods differ only in the presence or absence of an external applied voltage and have the same performance, features, and usage method.

(1) Galvanic cell method

The membrane has high permeability to oxygen and is constructed so that the electrodes and electrolyte are isolated from the water being measured. The counter electrode is a base metal and the

working electrode is a noble metal and potassium hydroxide is used as the electrolyte. Oxygen passes through the membrane and is reduced on the working electrode, and so the method measures the reduction current flowing between both electrodes, which is proportional to the concentration of dissolved oxygen.

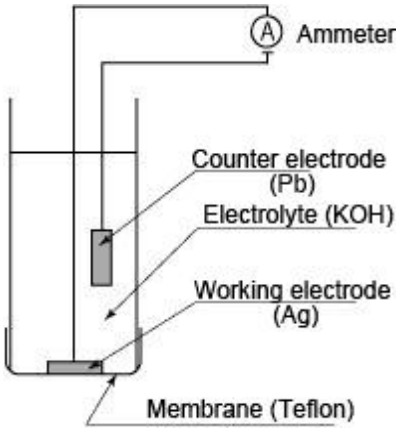

Figure No. 9: Galvanic Cell Method

(2) Polarographic method

The sensor construction is almost the same as that of the galvanic cell method. The counter electrode is silver-silver chloride and the working electrode is gold or platinum. When a voltage of 0.5–0.8 V is applied between both electrodes, oxygen that has permeated through the membrane

initiates a reduction reaction on the working electrode, causing a polarographic limiting current to flow which is proportional to the oxygen concentration. This method measures the concentration of dissolved oxygen based on this current value.

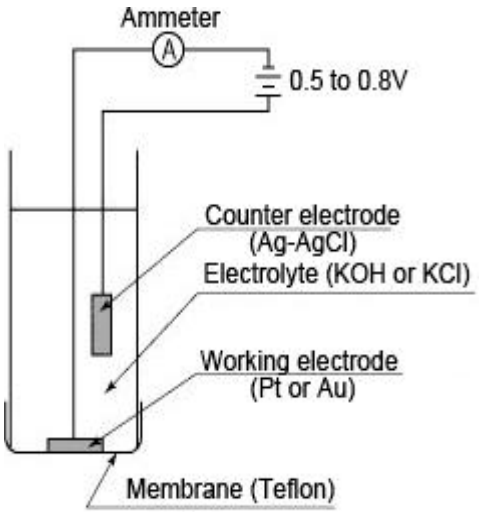

Figure No. 10: Polorographic Method

Sodium Analyzer

They are mainly used in thermal power plants for the determination of sodium ion concentration in the boiler water. This analysis is important because the excess of sodium will corrode the material in which it is passing.

Sodium Analyzer consists of overhead tank for storing the sample, standard solutions for calibrating the instrument, 3 way solenoid valves for allowing either sample or standard solution, Ammonia buffer for pH adjustment, reference and sodium ion specific electrode for concentration measurement, amplifier and indicator.

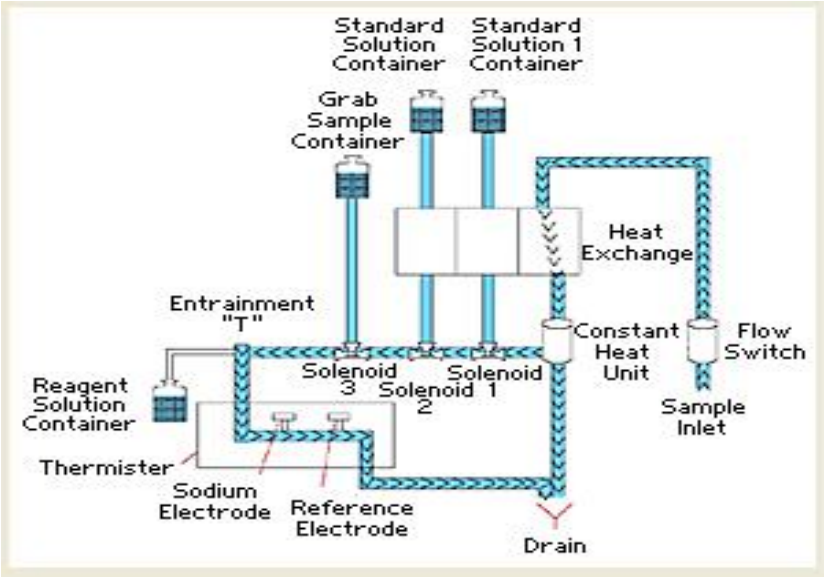

Figure No. 11: Sodium Analyzer

The sample to be analyzed is maintained in the constant head tank and allowed to reach the flow cell where the reference and ion selective electrodes are placed. The sample flow can be controlled by 3 way solenoid valve. The concentration of the sodium ion is measured with the help of electrodes. The output of the electrode is in terms of potential which is proportional to the logarithm of the sodium ion concentration in the solution. The potential value is amplified and it can be either indicated or recorded. The efficiency of the system can be improved by standardization and cleaning process.

Silica Analyzer

Silica presents in water and steam has the tendency to form deposition in the pipes and turbine blades which affects the efficiency of the equipment. Thus in turn reduce the efficiency of the entire power plant, hence continuous monitoring of silica is necessary

The analyzer is having two (reference and measuring) cuvettes, one lamp source and two photometers. The reference cuvette holding the reference solution whose concentration of silica is known and measuring cuvette holding the sample whose silica concentration is to be measured. The lamp source is placed between 2 cuvettes and the two photometers are placed on either side of the two cuvettes.

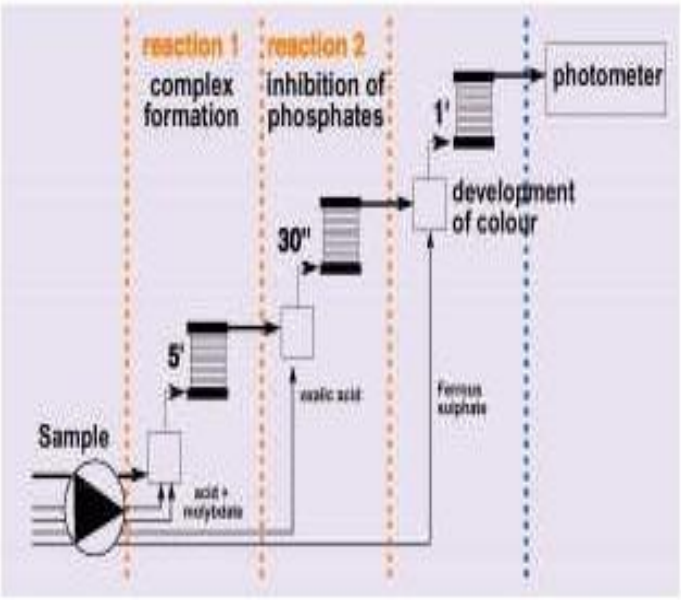

Figure No. 12: Silica Analyzer

Silica analyzer uses the colorimetric principle, where the added chemicals react with the silica to give a reaction product of a specific colour. The sample is prepared for analyzing by adding ammonium molybdate solution, sulphuric acid and a reducing solution with the sample. These are mixed well in the mixing vessel using stirrer and the flow rate of each is controlled by the valve which is placed on each line. After preparing the sample, the measuring cuvette is filled with the sample then the light source is allowed to pass through both the cuvettes. The transmitted light rays

are detected by the photo voltaic cells. The output of the 2 photo cells drives the differential amplifier and the amplified signal is read through the read out device.

Moisture Measurement

Moisture content has an important role in terms of quality, shelf life, process ability, pricing, weight…a seemingly endless list of attributes all of which are important to buyers, sellers, manufacturers, packagers, and users of products. Acceptable moisture content is determined by industry and trade associations and can be dictated or monitored by government agencies such as the Food and Drug Administration.

It is the responsibility of product manufacturers to institute processing procedures and perform quality tests to ascertain that their products' moisture content meets specifications.

Several methods are employed to determine or measure moisture content, some of which are complex, others relatively simple.

Following is a brief description of three techniques used for measuring moisture content.

Moisture Determination Methods

Thermogravimetric, chemical and spectroscopic techniques for moisture analysis.

Thermogravimetric Moisture Determination

Thermogravimetric moisture analysis calculates moisture content based on loss of weight on drying. Several methods are employed. As one example, halogen heaters are paired with an analytical balance that can be programmed to conduct measurements of small samples (in grams) under various scenarios including time, temperature and how heat is applied, also called the drying profile. The samples are dried until their weight is constant; the difference between starting and ending weight representing moisture content.

Some laboratory moisture balances use infrared heaters although these can take a longer time to reach the operating temperature necessary to conduct the analysis.

A disadvantage of both processes is that that the heat may cause decomposition of the samples, so care must be exercised. Both halogen and IR processes do not distinguish between water and other volatile constituents of the sample.

Microwave ovens (professional, not household) can accommodate larger sample sizes than a moisture balance but do not offer the high degree of temperature control found with moisture balances. Microwave drying is not suitable for samples with water content less than 2%.

Drying ovens use circulating hot air, sometimes under vacuum, to establish reference moisture content. They can process large samples and multiple samples at a time but can take hours to produce the data and are labor intensive. This method is frequently cited in laws governing determining moisture content in food.

Phosphorous pentoxide is a powerful and dangerous desiccant used as a drying agent for materials with which it does not react. In determining moisture content it is placed in a closed container along with the sample and heated. Its increase in weight is the measure of the water content of the sample.

The ***distillation method*** is favorably priced but requires solvents that can create disposal problems. In it the thermally separated moisture from the sample is measured. Distillation accuracy is average.

Chemical Moisture Determination

Karl Fischer titration (both coulometric and volumetric) is an accurate reference method for water detection vs. any volatile substance that is identified by thermogravimetric methods. It is based on a reagent that reacts with water and converts it into a non conductive chemical. Karl Fischer titration uses dangerous chemicals and requires skilled technicians to conduct the analysis.

The ***calcium carbide method*** of moisture determination, which has an attractive price, requires trained personnel as the method can form explosive materials through a chemical reaction. Calibration is required because not all water contained in the sample participates in the reaction.

Spectroscopic Moisture Analysis

Spectroscopic methods of determining moisture content include infrared (surface moisture), microwave (total moisture) and nuclear magnetic resonance (NMR) spectroscopy. These indirect measurement methods can be quite complex and/or time consuming because they require multiple samples for calibration. For that reason they are not widely used for moisture content quality control checks along packaging lines.

Absorption spectroscopy is a relatively simple method of passing light through a gas sample and measuring the amount of light absorbed at the specific wavelength. Traditional spectroscopic techniques have not been successful at doing this in natural gas because methane absorbs light in the same wavelength regions as water. But if one uses a very high resolution spectrometer, it is possible to find some water peaks that are not overlapped by other gas peaks.

The tunable laser provides a narrow, tunable wavelength light source that can be used to analyze these small spectral features. According to the Beer-Lambert law, the amount of light absorbed by the gas is proportional to amount of the gas present in the light's path; therefore this technique is a direct measurement of moisture. In order to achieve a long enough path length of light, a mirror is used in the instrument. The mirror may become partially blocked by liquid and solid contaminations, but since the measurement is a ratio of absorbed light over the total light detected, the calibration is unaffected by the partially blocked mirror (if the mirror is totally blocked, it must be cleaned).

A TDLAS analyzer has a higher upfront cost compared to most of the analyzers above. However, tunable diode laser absorption spectroscopy is superior when it comes to the following: the necessity for an analyzer that will not suffer from interference or damage from corrosive gases, liquids or solids, or an analyzer that will react very quickly to drastic moisture changes or an analyzer that will remain calibrated for very long periods of time, assuming the gas composition does not change.

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SCHOOL OF ELECTRICAL & ELECTRONICS ENGINEERING

DEPARTMENT OF ELECTRONICS & INSTRUMENTATION ENGINEERING

UNIT – II -Analytical Instrumentation – SIC1304

II.GAS ANALYZER

GAS ANALYSER

Thermal conductivity - thermal analyser - type Oxygen analyser - CO monitor - NOx analyser - H2S analyser - dust

and smoke measurement.

OXYGEN ANALYZER

PARAMAGNETIC OXYGEN ANALYZER

Oxygen is a paramagnetic gas and is attracted into a strong magnetic field. Because this measurement is a purely physical effect, nothing is consumed and in principle the cell has an unlimited life. However, contamination of the cell by dust, dirt, corrosives or solvents can lead to deterioration. Measurement range is typically 0.05% to 100% O2.The paramagnetic sensor utilizes the paramagnetic susceptibility of oxygen, a physical property which distinguishes oxygen from most other gases.The sensor incorporates two nitrogen-filled glass spheres mounted on a rotating suspension. This assembly is suspended in a strong magnetic field. The oxygen in the surrounding gas is attracted to the magnetic field, resulting in a force on the glass spheres. The strength of the torque acting on the suspension is proportional to the oxygen content of the surrounding gases.

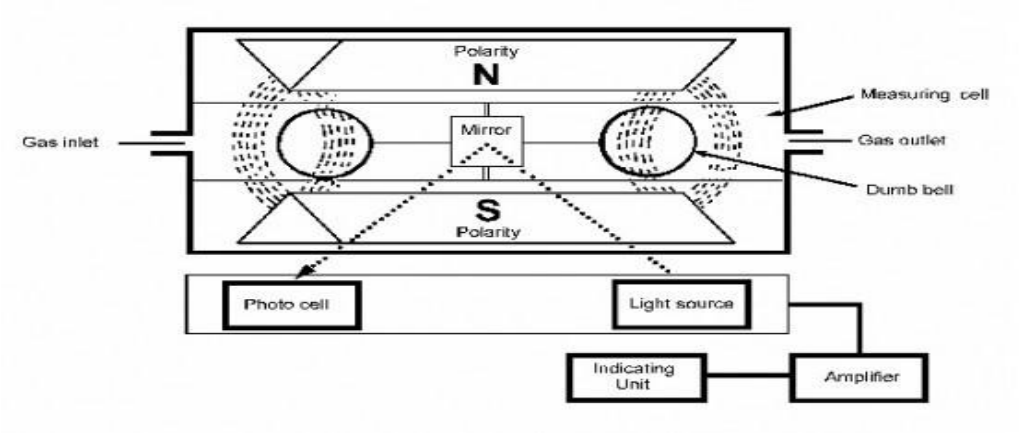

Figure No.1: Schematic diagram of Paramagnetic Analyser

Refer to above Figure no.1 the measuring system is 'null-balanced'. First the 'zero' position of the suspension assembly, as measured in nitrogen, is sensed by a photo-sensor that receives light reflected from a mirror attached to the suspension assembly. The output from the

photo-sensor is fed back to a coil around the suspension assembly. This feedback achieves two objectives.

First, when oxygen is introduced to the cell, the torque acting upon the suspension assembly is balanced by a restoring torque due to the feedback current in the coil. The feedback current is directly proportional to the volume magnetic susceptibility of the sample gas and hence, after calibration, to the partial pressure of oxygen in the sample. Therefore the current gives an accurate measurement of the concentration of oxygen in the gas mixture.

Second, the electromagnetic feedback 'stiffens' the suspension, damping it heavily and increasing its natural frequency, making the suspension resilient to shock. As the instrument uses an absolute measurement principle, once built and factory calibrated, it does not require any further factory calibration. Factory calibration consists of calibration of the electronics to accept the input signal from the detection cell and checking that the instrument then reads correctly on air, 20.9%. The instrument is then further checked for correct reading on 100% oxygen content. The paramagnetic analyzers may be used for measurement of oxygen at any level between 0-100% in gases or gas mixtures.

Types of Oxygen Analyzer

1. Magnetic wind method

The detector has two chambers, each of which has a heating wire element located at the center. A magnetic field is provided only on the measurement chamber. Once the gas under measurement is sent to the measurement chamber, oxygen is attracted by the magnetic field and then heated with the heating wire element. Thus, the magnetization factor decreases and a continuous flow of gas (magnetic flow) occurs. The magnetic flow cools the heating wire element as its intensity varies in proportion to the concentration of oxygen. Therefore, the resistance changes during this process are picked up as unbalanced voltage at the bridge to measure the concentration of oxygen. The magnetic wind type analyzer uses no movable part, making it highly resistant against vibrations and other similar effects. Such a relatively simple structure provides this analyzer with high durability. Carbon dioxide causes positive interference as the thermal conductivity varies greatly. If the concentration of CO2 is stable enough, the interference of CO2 is compensated for by applying electric compensation to the reading of CO2 or by taking any other effective means.

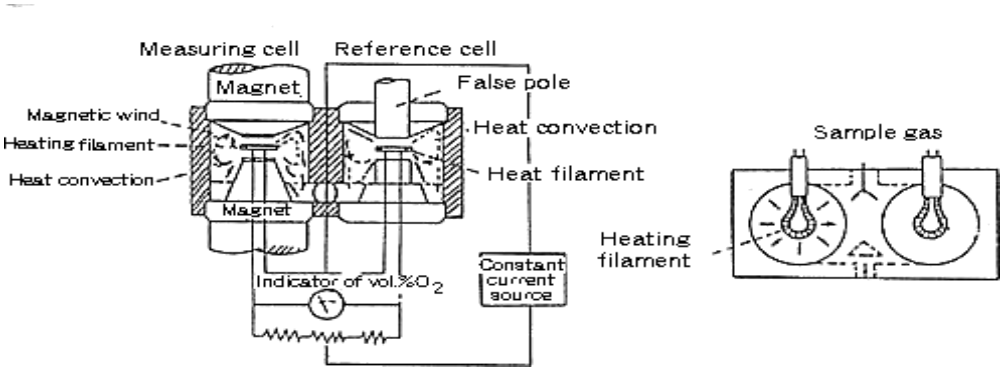

Figure No.2: Oxygen Analyser-Magnetic Wind Method

2. Magnetic force type

The magnetic force type oxygen analyzer is largely classified into the dumbbell type and the magnetic pressure type.

Dumbbell type

A non-magnetic dumbbell is suspended with a fine wire within a magnetic field. When the sample gas is introduced into the magnetic field, oxygen in the gas tends to approach the strongest part of the magnetic field while trying to push the dumbbell aside. This produces such force as pushes the dumbbell out of the magnetic field, causing the suspending wire to be twisted. This twist is detected as the movement of light from the reflective mirror secured at the center of the suspending wire. With this signal, current is sent to the exciting coil so that the wire is untwisted to the original state. The concentration of oxygen is measured from the intensity of this current. This method assures high linearity, minimizes the effects of coexisting gases, and provides high response. However, it is susceptive to mechanical shocks.

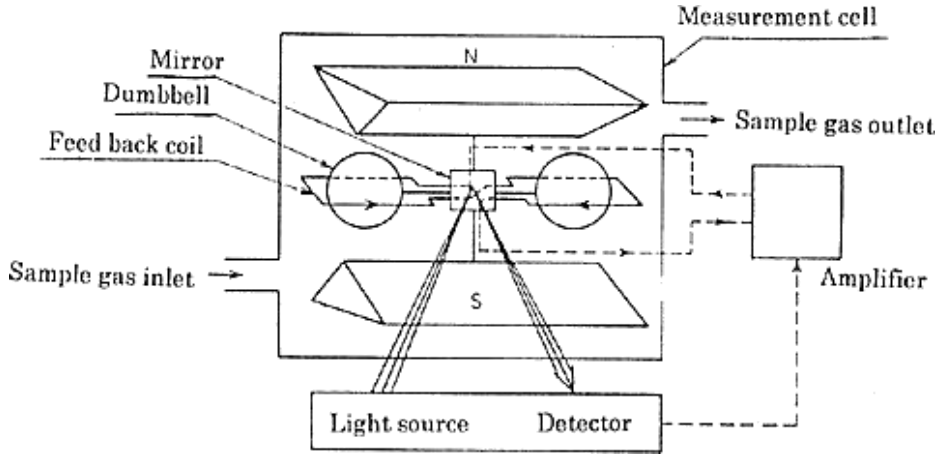

Figure No.3: Schematic diagram of Dumbbell Type Oxygen Analyser

Magnetic pressure type

When the sample gas is introduced into a magnetic field which is uneven due to magnetic poles, oxygen (paramagnetic material) in the sample gas is attracted toward the strongest part of the magnetic field, in which the magnetic poles have come closer to each other. A small amount of reference gas like pure nitrogen or air is externally supplied through a small hole made on one of the magnetic poles. The increase in pressure resulting from the attraction of oxygen is then detected with a capacitor microphone type detector or a mass flow sensor.

In order to ensure the stable detection of signals, the two magnetic poles are alternately excited to amplify alternating current. In this method, the effects of coexisting gases are relatively small and the zero point is stable. For this measurement, a reference gas is required.

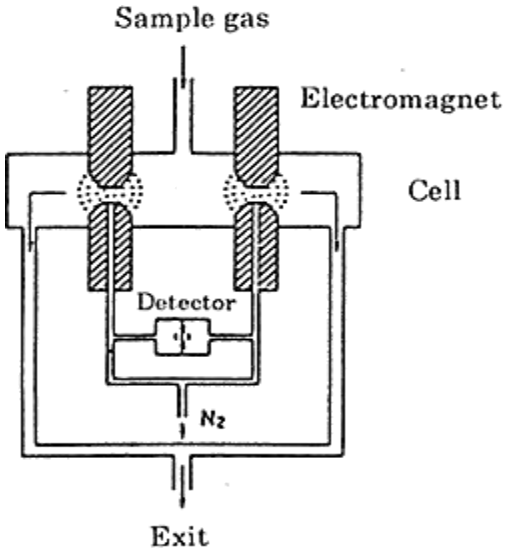

Figure No.4: Magnetic pressure type oxygen Analyser

3. Zirconia type

When stable zirconia (YHZ) obtained by adding CaO to ZrO2 is heated to more than several hundred degrees centigrade, the conductivity of oxygen ions increases. If a platinum electrode is installed on both sides of this element, oxygen ions move in accordance with the difference in the concentration of oxygen between the two electrodes, where electromotive force then occurs. The measured potential difference is in proportion to the logarithm of partial pressure ratio of oxygen. Therefore, the oxygen in the sample gas can be found by sending a reference gas to one of the electrodes. Since the measurement cell itself is at a high temperature, some of the relevant analyzers allow it to be inserted directly into the exhaust combustion gas. The zero calibration cannot be performed for such a gas as contains no oxygen, e.g, when an N2 gas cylinder is used. In such a case, an oxygen cylinder for about 10% of the range is used for this calibration.

In the case of the limiting current type analyzer, electric potential is applied between the zirconia electrodes. The oxygen concentration limited by gas dispersion holes is in a proportional relation with the limiting current and this current value is detected. This analyzer is easy to handle because it requires no reference gas, its output is linear, and the reading is stable even at around 21%.

For the zirconia type oxygen analyzer, since its element reaches a high temperature, the oxygen decrease involved in the oxidation and combustion of combustible gases becomes negative interference.

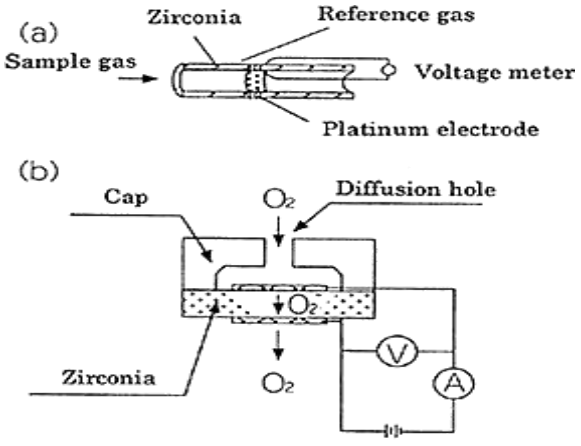

Figure No.5 : Zirconia type Oxygen Analyser

4.Electrode method

Galvanic cell method when a battery is made using a positive electrode of precious metal like Pt, a negative electrode of Pb, and an electrolyte solution of KOH, the reducing reaction of O2 occurs on the positive electrode as follows:

$$O2 + 2H2O + 4e- > 4OH^-$$

If negative resistance is properly chosen, the output in proportion to the oxygen concentration can be obtained. The dissipation and absorption of moisture inevitably occur through the diaphragm because the electrolyte solution is used. It is also inevitable that the electrodes deteriorate, e.g., as the activity of the working electrode catalyst diminishes. Despite of these drawbacks in relation to the maintenance, the relevant analyzer can be designed to be compact.

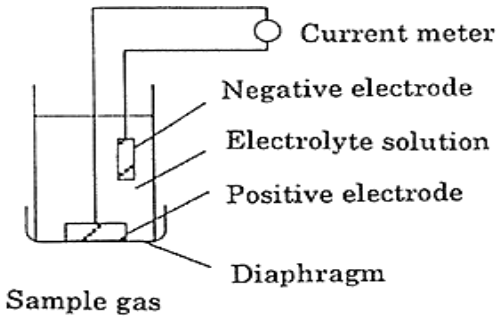

Figure No.6 :Galvanic cell type Oxygen Analyser

CO ANALYZER

An infrared gas analyzer (sensor) is typically used to measure the quantities of various gases. The basic principle to an infrared gas analyzer involves two chambers (one chamber being the reference chamber and the other chamber allowing for measurement of the type of gas and quantity). Infrared light of a particular frequency is emitted from one end of the chamber through to a series of gas chambers that contain given concentrations of different gases. As the photons from the infrared source pass through the different gas chambers, they excite symmetric and asymmetric vibrations in the gas molecules (i.e., the gas of interest will absorb some of the infrared radiation passing through the gas chamber). The detector, being the end chamber to this sensor, is responsible for converting the amount of infrared radiation absorbed by the gas into a voltage (e.g., the signal from the detector [end chamber] will change in response to varying levels of CO/CO2 in a given sample as shown in Figure No:7.

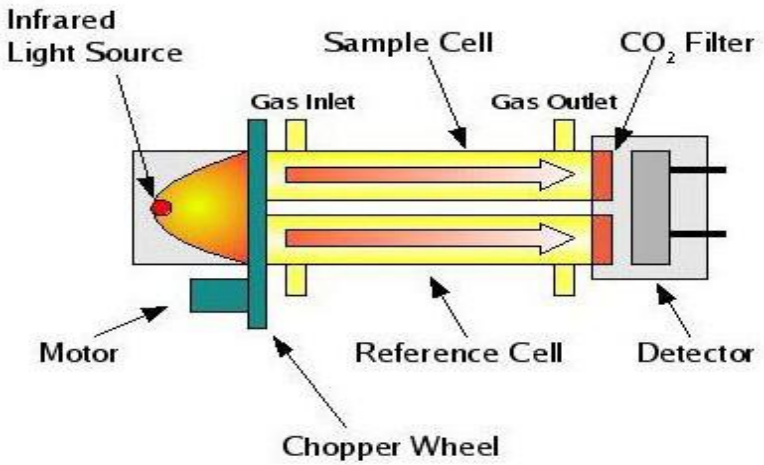

Figure No.7:Infrared CO Gas Analyser

Infrared gas analysers are standard detectors for the measurement of gas in any given environment. The accuracy of the detector is maintained by generating a constant signal known that the 'zero' point. This is based on the understanding that gas absorbs radiation in the same proportion. However, infrared energy absorption is proportional to the number of hydrocarbons present in a gas molecule, and with this analyser being the least sensitive to molecules with single bonds (i.e., CH4, a gas known to contribute to GHG emissions); it is, therefore, limited to the types of gases that can be monitored in the environment.

NO2 Analyzer

NO2 Analyzer utilizes the principle of chemiluminescence for analyzing the NO or NOX concentration within a gaseous sample.A chemi-luminescence detector (CLD) is the industry standard method of measuring nitric oxide (NO) concentration. The reaction between NO and O3 (ozone) emits light. This reaction is the basis for the CLD in which the photons produced are detected by a photo multiplier tube (PMT). The CLD output voltage is proportional to NO concentration.The light- producing reaction is very rapid so careful sample handling is important in a very rapid response instrument. The Cambustion Fast CLD uses a unique sampling system coupled with miniaturised CLD technology to give millisecond response times.

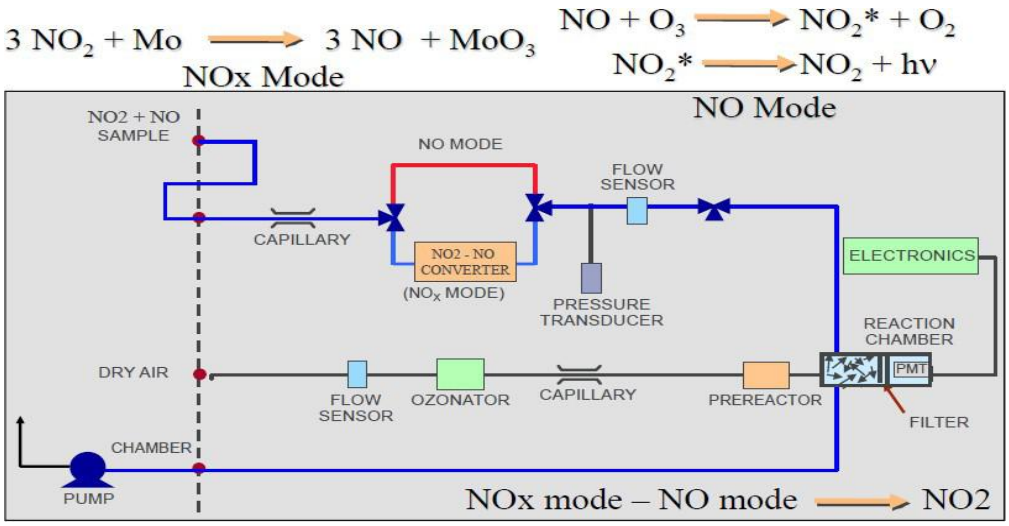

Figure No.8:NO2 Analyzer

In the NO mode, the method is based upon the chemiluminescent reaction between ozone and nitric oxide (NO) yielding nitrogen dioxide (NO2) and oxygen. Approximately 10% of the NO2 produced from this reaction is in an electronically excited state. The transition from this state to a normal state produces light which has an intensity proportional to the mass flow rate of NO2 into the reaction chamber. The light is measured by means of a photodiode tube and associated amplification electronics. In the NOX mode, NO plus NO2 is determined as above, however, the sample is first routed through the internal NO2 to NO converter which converts the NO2 in the sample to NO. The resultant reaction is then directly proportional to the total concentration of NOX. The entire sample, prior to the reaction chamber, is maintained at a temperature of 65°C. Analyzer is designed to continuously measure the total concentration of oxides of nitrogen within a gaseous sample. The gaseous sample can be ambient air, exhaust gases from an internal combustion engine, or exhaust gases from a combustion process.

Applications

Process Chemical Gas Analysis
Personnel Safety

Power Plant Stack De-Nitrification
Diesel Vehicle Emissions

Hydrogen sulfide (H2S) Analyzer

Hydrogen sulfide (H2S) is a clear, colorless, extremely toxic gas that has a rotten egg smell at low concentrations. The human nose can detect H2S at concentrations below 100 parts per billion.

Lead Acetate Tape

This method relies on the chemical reaction of H2S with lead acetate impregnated paper tape to form lead sulfide. The lead sulfide appears as a brown stain on the paper tape. A light source is used to illuminate the tape where the reaction is to occur and light detector is used to monitor the reflection of the source from the tape. A concentration of H2S can be determined by the rate of staining on the tape. Lead acetate tape can be used to measure total sulfur by mixing the sample stream with hydrogen and passing it through a quartz tube heated to 1000 o C. This process quantitatively converts sulfur bearing compounds to H2S which can then be measured at the tape. The lead acetate tape method is H2S specific, very sensitive, and has an equimolar response to sulfur when used in the total sulfur mode. Tape is typically linear up to 2000 ppm. Higher ranges can be achieved with dilution systems.

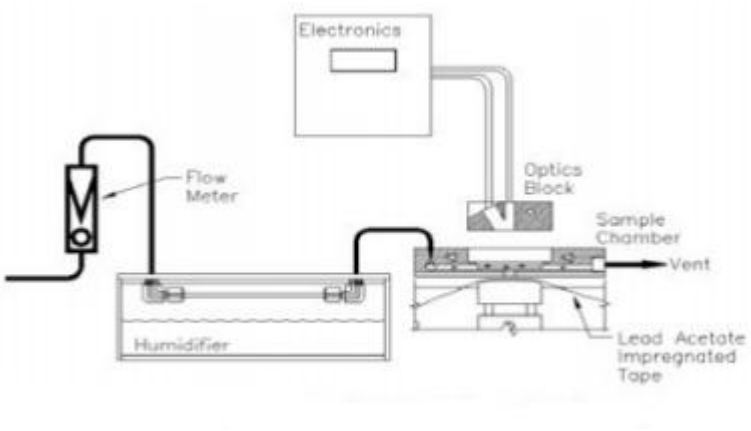

Figure No.9:Lead Acetate Tape Analyzer

Sulfur Chemiluminescence

This is a two step measurement process in which a small amount of sample is injected into a hydrogen rich flame or an enclosed combustion assembly. The hydrogen to air ratio combined with the presence of a vacuum allow for the formation of sulfur monoxide (SO) in the combustion assembly. The combustion gases from the flame or combustion assembly are then drawn under vacuum to a reaction cell where ozone from an ozone generator is continuously added. SO reacts with ozone to form an electronically excited state of sulfur dioxide (SO2) which releases ultraviolet (UV) radiation upon relaxation. The released UV radiation is detected with a photomultiplier tube and is linearly proportional to the amount of sulfur present in the sample. Sample can be injected directly to the analyzer to arrive at a total sulfur concentration. The addition of a chromatograph column prior to the detector allows for the measurement of individual sulfur compounds. The sulfur chemiluminescence detector is linear over a large range, very sensitive and has an equimolar response to sulfur compounds. This allows for the use of a single component, single point calibration which greatly simplifies the calibration process.

Flame Photometric Detector (FPD)

FPDs are generally employed as chromatograph detectors. The effluent from a chromatograph column is passed through a hydrogen rich, low temperature flame. Sulfur species are converted to S2 which becomes excited and emits radiation upon relaxation. The emitted

radiation is monitored by a photomultiplier tube. The FPD is very sensitive and selective to sulfur. Its response to sulfur is, however, non linear and non equimolar which makes it difficult to calibrate because several multi-component standards of varying concentration are required.

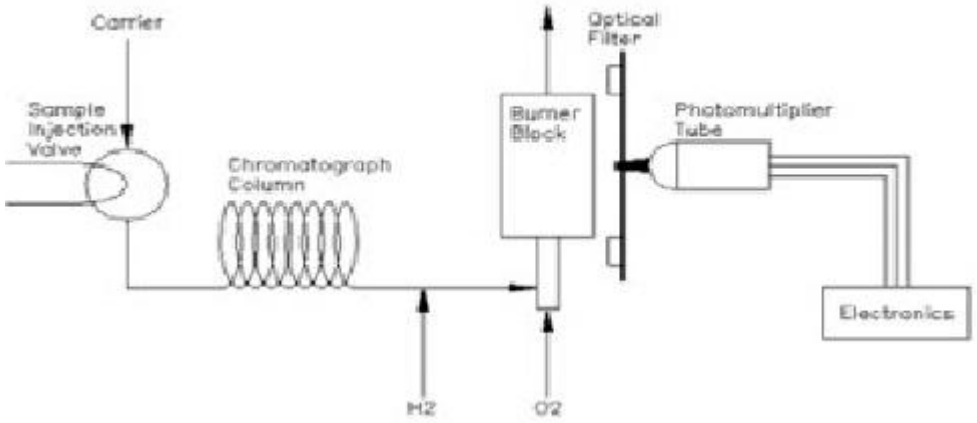

Figure No.10:Photometric Analyser

Ultraviolet (UV) Absorption

This method relies on the ultraviolet absorption characteristics of H2S. The optical system consists of a UV lamp as a source, a transparent sample cell through which the sample gas flows, and a single photomultiplier tube detector. In front of the detector is a motor driven beam splitter which alternately directs the source beam to a reference filter and a measurement filter. The measurement filter is selected to correspond to an absorbency peak of H2S while the reference filter is selected to correspond to some non-absorbing region of the spectrum for H2S. In this way the absorption of the sample can be measured and is proportional to the amount of H2S present in the sample. The UV absorption method is typically used at percentage levels of H2S, however, by lengthening the cell and pressurizing the sample in the cell, measurement at ppm levels is possible. This method is subject to strong positive interference from olefins and aromatic compounds. Chromatographic techniques are sometimes employed to separate the H2S from interfering species.

Dust and Smoke Measurement

Dust Mesurement

In power houses it is necessary to control the amount of dust into flue gases in order to comply with the requirements imposed by the municipal laws to control the pollution.

Types of dust monitoring instrument

1. Optical type flow dust monitor
2. Electrical type flow dust monitor
3. Electrostatic type flow dust monitor
4. Reflected type dust monitor

Optical type flow dust monitor

It consists of light source, photo detector and a glass plate. Initially a clean glass plate is placed in the flow path of the dust laden gas. After a particular time, the plate is analyzed by measuring the obscuration caused by the deposition of dust on the glass plate.

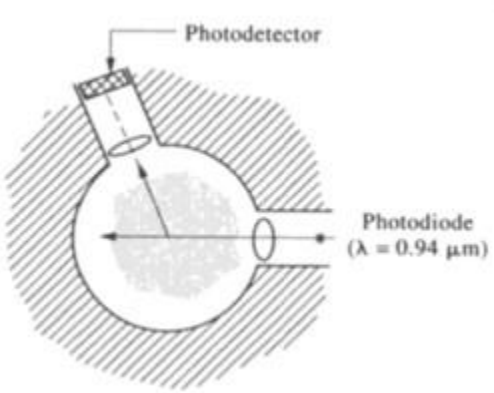

Figure No.11:Optical type flow dust monitor

In the analysis process, the dust collected glass plate is placed in between the light source and the photo cell. The light beam is allowed to pass through the glass plate and it is received by a photocell. The output of photocell decreases with increase in the dust on the glass plate which is proportional to the amount dust present in the gas.

Electrical type flow dust monitor

It uses the principle of charging to measure the amount of dust present in the flue gas. The instrument gets a sample of dust laden gas at a constant velocity and charges the dust electrically and then measures this charge. This charge will be proportional to the amount of dust present in the flue gas.

Electrostatic type flow dust monitor

It uses a tube made from special materials for the measurement of dust. The instrument withdraws a sample of gas at a constant velocity and imparts swirl to the gas and passes it through the tube. The swirling dust gives an electrostatic charge to this tube by friction. The measurement of this charge gives the measure of the dust in the flue gas.

Reflected type dust monitor

It measures the scattered light or reflected light. It consists of a lamp and a photocell both are mounted by side. The light from the lamp is allowed to pass into the duct through a small opening. While it passing through the duct laden gas some of the light will be reflected back on the photocell. Reflected light ray is directly proportional to the amount of dust present in the gas. The output from the photocell is amplified and is indicated by a indicator.

Smoke Measurement

There are two methods – optical method and ionization method

Optical Method

In this method, a known volume of air is continuously drawn through a filter paper for a period of one hour. The properties of the sample are measured by the reduction of light transmission through the filter. This reduction in light transmitted is a measure of the smoke. This method does not measure the absolute concentration or the deposited mass of particulates, rather it is an indicator of particulate matter suspended in the air.

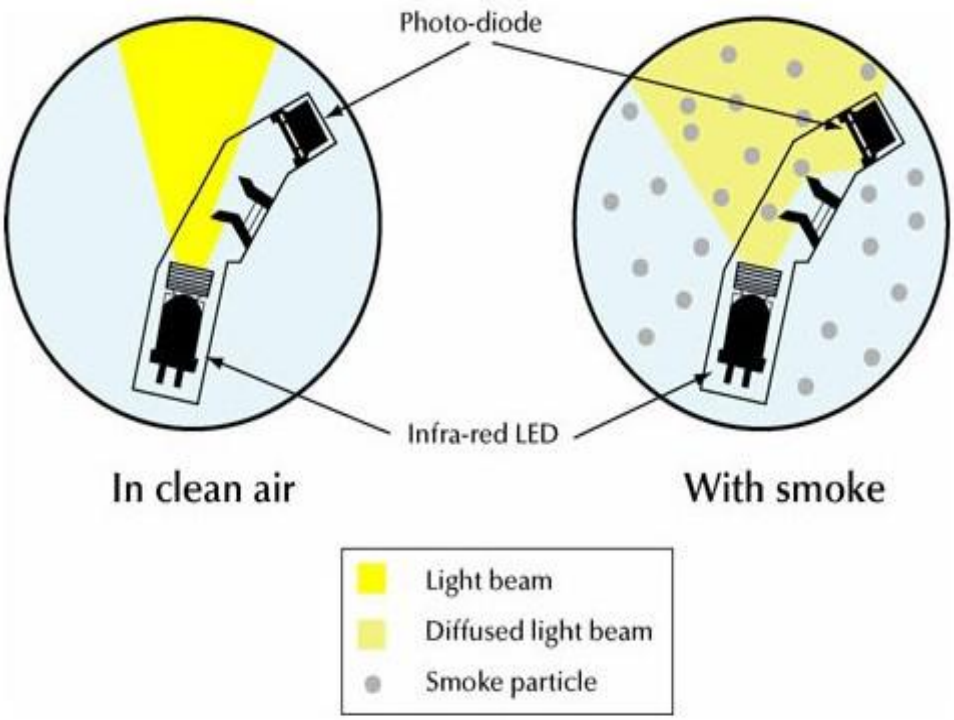

Figure No.12:Smoke Measurement using Optical Method

Ionization Method

It works on the principle of electrically charging the air within an open detector chamber. The charged air is a measure of the smoke. It is also called as fire alert ionization because it detects the outbreaks of fire at an earliest state.

It consists of the ionization chamber, integrating timer, charge detector and alarm. The ionization chamber is having a small radioactive source which irradiates the space between the electrodes with alpha particles. This creates ions of both positive and negative signs and moves towards the respective electrodes. The movement of ions constitutes the current flow.When compared with normal air ionized current, air with smoke produce less ionization current. This reduction in the electric current is a measure of smoke.

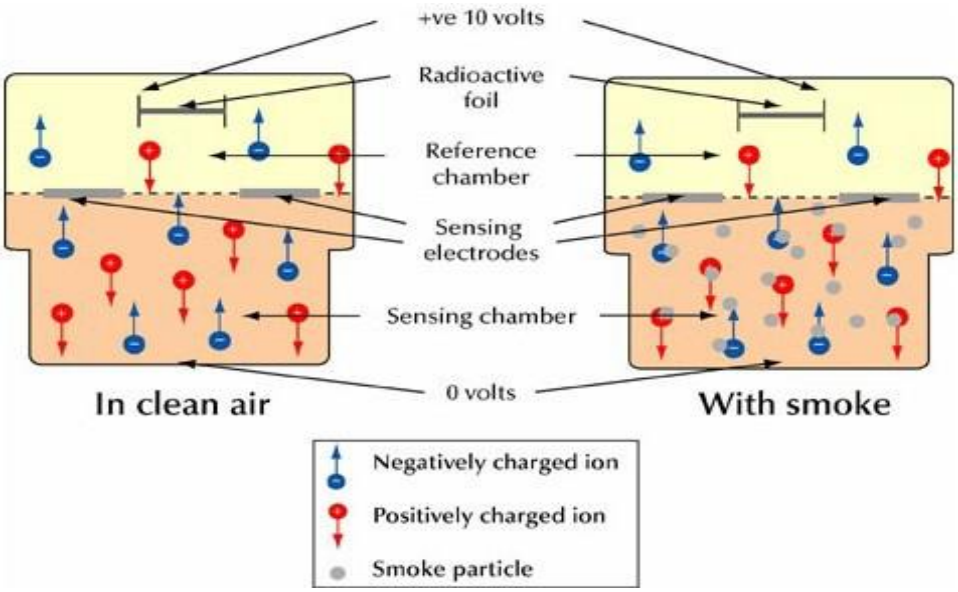

Figure No.13:Smoke Measurement using IonizationMethod

Thermal Conductivity Analyzer

Each gas has a known thermal conductivity - how well heat transfers through it. Thermal conductivity is measured with a sensor that employs four matched filaments that change resistance according to the thermal conductivity of the gas passing over it. The gas analyzer sensor uses four matched filaments that change resistance according to the thermal conductivity of the gas passing over it. These four filaments are connected in a Wheatstone Bridge configuration as shown below in Figure No.13.

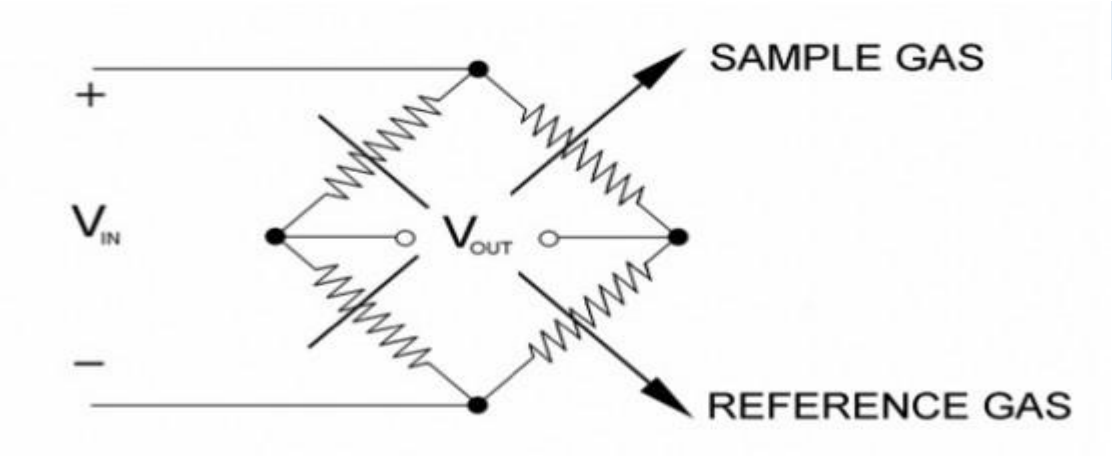

Figure No.13:Wheatstone Bridge of the thermal conductivity detector

When all four resistances are the same, VOUT is zero and the bridge is considered balanced. When zeroing, the reference gas is passed over all the filaments, the resistances will be the same (because filaments are matched) and the bridge is balanced. When the sample gas is passed over half of the bridge, then VOUT's value correlates to the content of the sample gas in the reference. The detector is a four element Katharometer having two elements situated in the reference gas and two elements in the sample gas shown in Figure No.14 below.

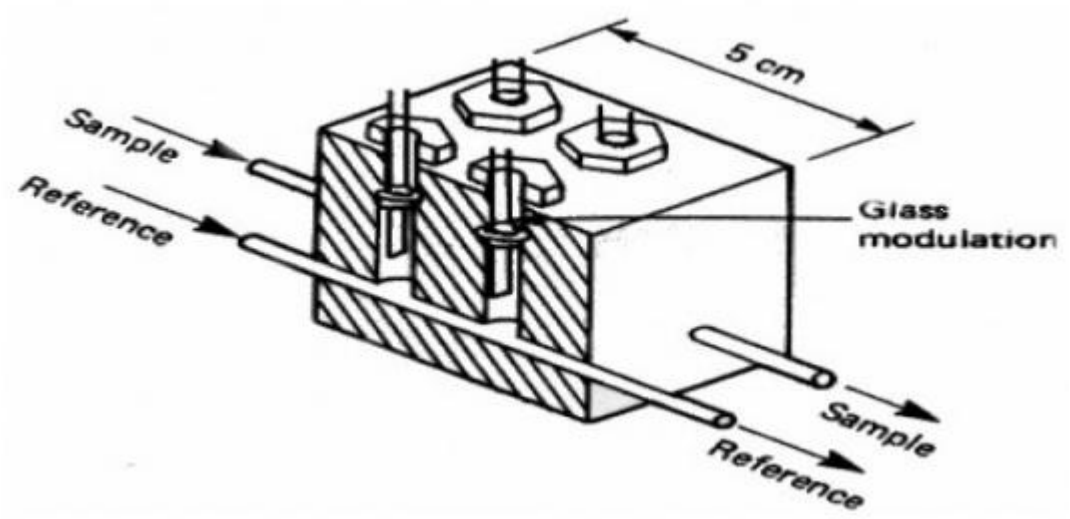

Figure No.14:Cut-away view of the thermal conductivity sensor

The four elements are electronically connected in a bridge circuit and a constant current is passed through the bridge to heat the elements. If each element is surrounded by the same gas, then the temperature and hence the resistance of each element will be similar and the bridge circuit will be balanced.

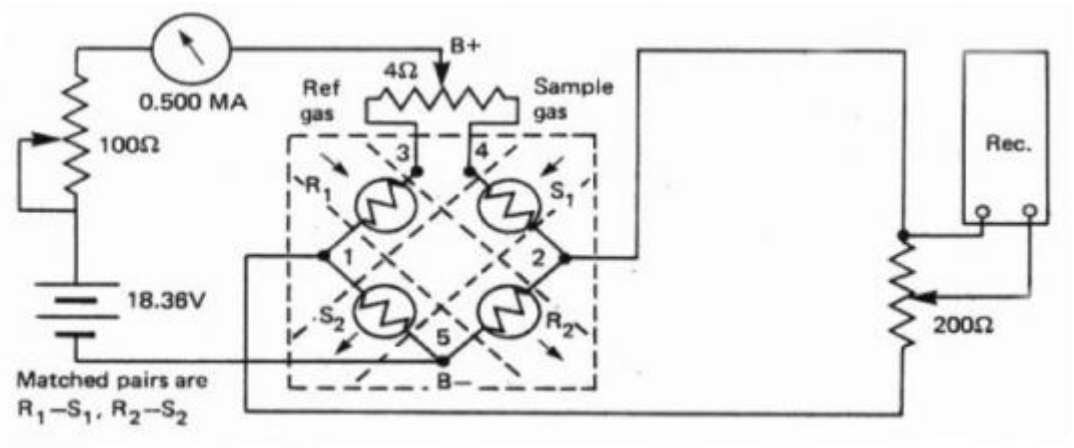

Figure No.15:Electrical diagram of the thermal conductivity sensor.

When the gas to be measured is introduced into the sample gas stream, the two Katharometer elements in this gas stream will be cooled to a greater extent than the two elements in the reference gas. The bridge circuit will be unbalanced, producing a signal voltage related to the measure gas content of the sample gas. Measure the gas sample content of a sample/reference mixture by comparing the thermal conductivity of the mixture with that of a reference. For example, hydrogen has a thermal conductivity which is approximately seven times greater than that of nitrogen, so small changes are readily detected. All other common gases have thermal conductivities similar to nitrogen so the method of measurement is fairly selective. Helium is the only other gas with a thermal conductivity comparable with that of hydrogen. Other gases that may be measured using this technique are:

- Carbon Dioxide
- Oxygen
- Argon
- Methane
- Sulphur Dioxide
- Ammonia

THERMAL ANALYZER

Thermal analysis measures physical or chemical changes in a material as a function of temperature. Two common complimentary techniques in this category are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These methods are typically used to determine the material properties of organic polymers as the sample is heated or cooled in a controlled manner or held isothermally for a specified time. Differential thermal analysis (DTA) is a method similar to DSC, but performed at higher temperatures for metals, minerals, ceramics, and glasses.

DSC - Differential scanning calorimetry measures heat flow to or from a sample as a function of temperature and time. A small portion of a sample is placed in an aluminum

pan and heated and/or cooled in a controlled manner. A reference material (usually an empty aluminum pan) simultaneously undergoes the same programmed time/temperature routine. Calorimetric measurements are made during the heating/cooling cycle. Two methods can be used for the calorimetric measurements. Differences in temperature between the sample and reference material can be measured as the same amount of heat energy (calories) is added to both. Or, differences in the amount of heat energy added to both are measured as the temperature for both the sample and reference are kept constant. In both cases, the heat flow and temperature of the sample are monitored in comparison to the reference material. The analysis is usually performed in an inert gas atmosphere, such as nitrogen. The amount of energy absorbed (endotherm) or evolved (exotherm) as the sample undergoes physical or chemical changes (e.g. melting, crystallization, curing) is measured in calories as a function of the temperature change. Any material reactions involving changes in heat capacity (e.g. glass transition) are also detected. The thermal cycle for DSC typically can range from less than -50°C to 300°C or greater. The principals for differential thermal analysis (DTA) are similar to DSC, but the temperature range for DTA can reach temperatures greater than 1500°C.

TGA - Thermogravimetric analysis continuously measures the weight of a sample as a function of temperature and time. The sample is placed in a small pan connected to a microbalance and heated in a controlled manner and/or held isothermally for a specified time. The atmosphere around the sample may consist of an inert gas, such as nitrogen, or a reactive gas, such as air or oxygen. The heating program may start in an inert atmosphere and then be switched to air at a certain point to complete the analysis. Weight changes observed at specific temperatures correlate to volatilization of sample components, decomposition, oxidation/reduction reactions, or other reactions or changes. Fourier transform infrared spectroscopy (FTIR) or mass spectroscopy (MS) may be used in conjunction with TGA to analyze and identify the evolved gases from constituents volatilized from the sample at specific temperatures.

DSC - By closely monitoring the heat flow and temperature, DSC can provide abundant information regarding a polymer material including: melting temperature, heat of fusion, glass transition temperature, curing temperature, heat of reaction, thermal history, and others. DSC is ideal for studying reversible reactions of thermoplastics such as melting-crystallization points and glass transition temperature. It is also used in the study of the kinetics of thermoset curing reactions, purity, heat capacities, and the effects of additives. Similarly, DTA analysis is used for determining the temperatures for melting and solid state phase transformations in metals, minerals, and ceramics.

TGA - As the TGA instrument measures the temperature and weight of the sample, thermally activated events are recorded. These events are expressed as weight loss or weight change for a given time or temperature. They may also be expressed as a rate of weight loss. The onset temperature for the weight loss is also recorded. These data correlate to and give information about such properties as: thermal stability, moisture or solvent content, additive or filler content, oxidation or decomposition temperatures and rate. Thermal events such as melting, glass transition, and other changes are not detected

because there is no change in sample mass associated with these events. Identification of the constituents driven off as evolved gases may be obtained when the TGA is used in conjunction with FTIR or mass spectroscopy.

APPLICATIONS DSC

Determination of melting temperature, heat of fusion, and glass transition temperatures
Analysis of polymer blends and copolymers

1. Comparison of two lots of similar polymers
2. Determination of cure temperatures/times for epoxies or other thermally-cured polymers
3. Reaction rate and temperature evaluation
4. Determination of thermal history, e.g. annealing, etc.
5. Volatile compound concentration
6. Plasticizer content
7. Inorganic filler content
8. Polymer thermal degradation profiles
9. Polymer thermal and/or oxidative stability
10. Identification of volatile components or thermal degradation products

SAMPLE REQUIREMENTS

DSC - Typically requires six to ten milligrams of sample. Samples may solids or liquids.

TGA - Typically requires twenty to thirty milligrams of sample. Samples may be solids or liquids.

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SCHOOL OF ELECTRICAL & ELECTRONICS ENGINEERING

DEPARTMENT OF ELECTRONICS & INSTRUMENTATION ENGINEERING

UNIT – III -Analytical Instrumentation – SIC1304

II .CHROMATOGRAPHY

CHROMATOGRAPHY

Gas chromatography - liquid chromatography -- high-pressure liquid chromatography - principles, types and applications detectors.

- **Chromatography** is the ability to separate molecules based on partitioning characteristics of a molecule to remain in stationary or mobile phase.**Chrome** (in Greek) means **colour** and **Graphy** means **Writing**
- **Principle of separation:** The mobile phase flows through the stationary phase and carries the components of the mixture with it. The migration velocity of different components is different hence the molecules in the mixture can be isolated.
- It is a technique for separation of a mixture. The components of a mixture are basically of two types of phases, mobile phase and stationary phase. The constituents of the mixture travel at different speeds thus enabling the separation.

Classification of Chromatography:

The primary classification of chromatography is based on the physical nature of the mobile phase. If the mobile phase is a gas then the chromatography is called gas chromatography. When the mobile phase is gas, the stationary phase can be a liquid (Gas-Liquid Chromatography) or a solid (Gas-Solid Chromatography).

If the mobile phase is a liquid, then the chromatography is called liquid chromatography When the mobile phase is a liquid, the stationary phase may be a liquid (Liquid-Liquid chromatography) or a solid (Liquid-Solid Chromatography)

Terms involved in chromatography

Chromatograph: The equipment used for separation using the technique of chromatography.
Chromatogram: The visual output of the chromatograph, typically a graph indicating the detectors ' response with respect to time.

Analyte: The component of the mixture which is required to be separated.

Eluent: The mobile phase of the mixture containing the analyte which enters the column
Eluate: The mobile phase which leaves the column.

Retention time is the characteristic time it takes for a particular analyte to pass through the system (from the column inlet to the detector).

Types of chromatography:

Column chromatography

Paper Chromatography

Thin Layer chromatography

Column chromatography: It is the most common type of chromatography employed. The column is usually a glass or metal tube that is constructed to withstand pressures applied across it. The column contains the stationary phase

The column is where the actual separation takes place. It is usually a glass or metal tube of sufficient strength to withstand the pressures that may be applied across it. The column contains the *stationary phase*. The *mobile phase* runs through the column and is adsorbed onto the stationary phase. The column can either be a *packed bed* or *open tubular* column.

Packed Bed Column

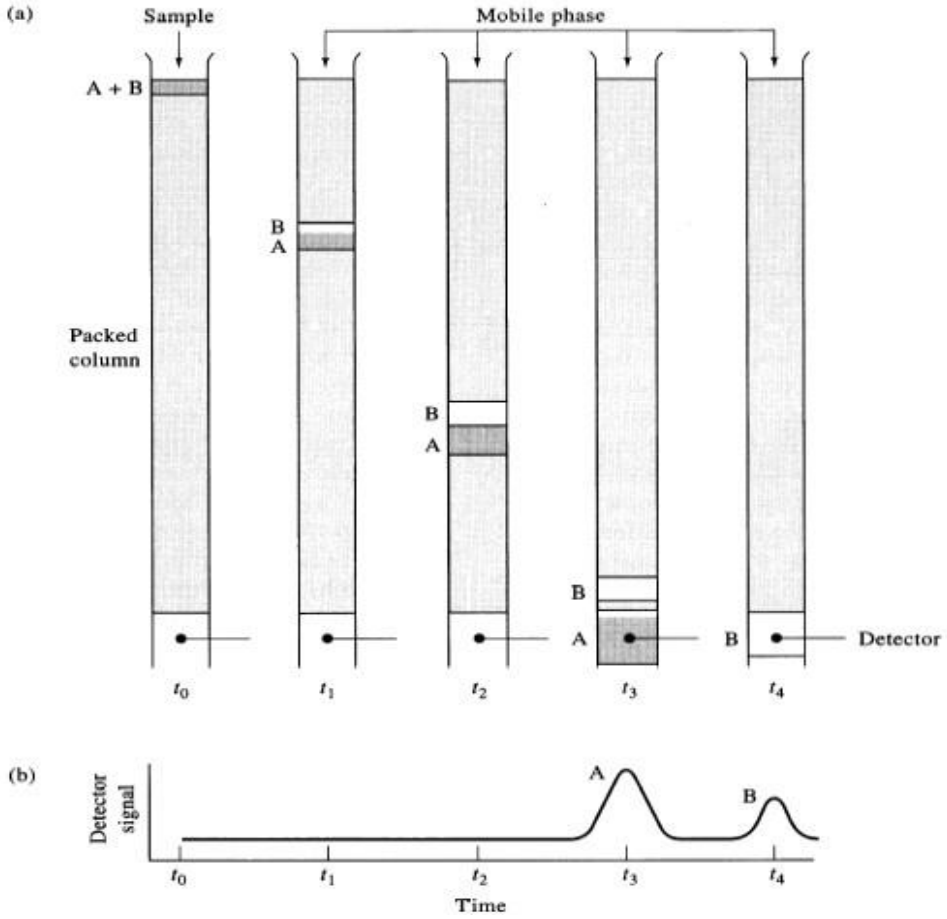
A packed bed column is comprised of a stationary phase which is in granular form and packed into the column as a homogeneous bed. The stationary phase completely fills the column.

Open Tubular Column

An open tubular column's stationary phase is a thin film or layer on the column wall. There is a pasageway through the center of the column.

The Mobile and Stationary Phases

The mobile phase is comprised of a solvent into which the sample is injected. The solvent and sample flow through the column together; thus the mobile phase is often referred to as the "carrier fluid." The stationary phase is the material in the column for which the components to be separated have varying affinities. The materials which comprise the mobile and stationary



phasesvary depending on the general type of chromatographic process being performed.

Figure No.1:Stages of Chromatography

Components:

Mobile phase: a solvent that flows through the supporting medium

Stationary phase: a layer or coating on the supporting medium that interacts with the analytes

Supporting medium: a solid surface on which the stationary phase is bound or coated

Gas Chromatography

The sample to be analysed or separated is vaporized and injected into the column. The mobile phase is a gas, usually an unreactive gas, like Nitrogen, flowing through the tube. The mobile phase carries the sample along the column. The column contains the stationary phase which is an involatile liquid adsorbed on the surface of an inert solid.

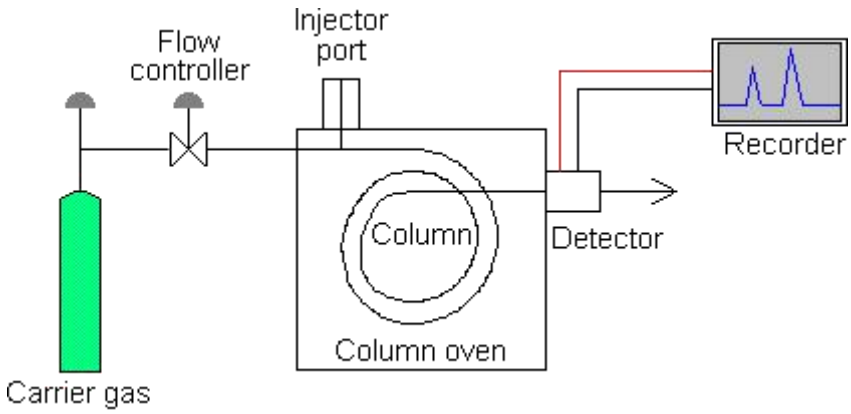


Figure No.2:Schematic diagrams of Gas Chromatograph:

Main Components of GC:

The main components of GC are Carrier gas, Sample injection port, Column, Detector and Computer.

1.Carrier gas

- Must have the following features:
- Must be chemically inert. Examples of carrier gas: N2, He, Ar, CO2 Must be Safe to use (non-inflammable)
- Must be of High purity.
- Carrier gas is chosen based on the detector used.
- Must be easily available
- Must be cheap

2.Sample injection port

The sample is injected into the column usually with the help of micro-syringes.If the sample is a liquid, then using micro-syringe, it is injected into the hot part of the column, where the sample vaporizes. The temperature of the sample port is usually maintained at a temperature higher (about 50°C higher) than the boiling point of the least volatile component of the sample.If the sample is a gas, then it is injected using a gaslight syringe or by 'stream splitter' also known as bypass system.

If the sample is a solid, then it is injected into the hot zone of the column using solid injection syringes. The sample is withdrawn into the needle by depositing it on the end of the plunger. The plunger is extended to place the sample into the column.

3. Columns

Two types of columns are used in Gas Chromatography: Packed Columns and Capillary column.

The columns contain tubing made of stainless steel or glass that may in the form of coiled, bent or straight. Packed columns are 1.5m to 10m in length with an internal diameter of 2 to 4 mm. The tubing contains a packing of solid support material coated with liquid or solid stationary phase.

Capillary columns have an internal diameter in the order of few tenths of millimeters and lengths are usually between 25 to 60 m. The capillary columns are usually made of fused silica with a coating of polyamide. The columns are so flexible that they can be wound into coils. The capillary columns can be one of two types; wall-coated open tubular (WCOT) or support-coated open tubular (SCOT). Wall-coated columns consist of a capillary tube whose walls are coated with liquid stationary phase. In support-coated columns, the inner wall of the capillary is lined with a thin layer of support material such as diatomaceous earth, onto which the stationary phase has been adsorbed. SCOT columns are generally less efficient than WCOT columns. Both types of capillary column are more efficient than packed columns.

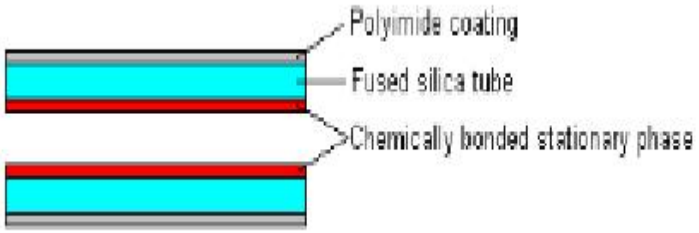


Figure No.3:Cross Section of Fused Silica open tubular column

Column temperature

It is essential that the column temperature be controlled to within tenths of a degree, which increases the precision. The optimum column temperature is dependent upon the boiling point of the sample. As a rule of thumb, a temperature slightly above the average boiling point of the sample results in an elution time of 2 - 30 minutes. Minimal temperatures give good resolution, but increase elution times. If a sample has a wide boiling range, then temperature programming can be useful. The column temperature is increased (either continuously or in steps) as separation proceeds.

4. Detectors

Detectors are transducers that convert physical quantity to an electrical signal. The detector is placed at the exit of the column. It provides a quantitative measure of the different constituents of

the sample. Detectors not only quantify the elute coming out of the column but also identifies them. Detectors can be grouped based on selectivity and on dependence. Based on selectivity, detectors are of three types: Non-selective (responds to all compounds except carrier gas), Selective (responds to a range of compounds with similarity in physical or chemical property) and Specific (responds to a single chemical compound)

Based on dependence, detectors can be concentration dependant or mass flow dependant. Concentration dependant detectors gives a response related to the concentration of the solute in the detector and does not usually destroy the sample, whereas mass flow dependant detectors give a response related to the rate at which the solute particles enter the detector. These detectors destroy the sample.

Table 1: Types of Detectors in Gas Chromatography

Detector	Support gases	Selectivity	Detectability	Dynamic range
Flame ionization (FID)	Hydrogen and air	Most organic cpds.	100 pg	10^7
Thermal conductivity (TCD)	Reference	Universal	1 ng	10^7
Electron capture (ECD)	Make-up	Halides, nitrates, nitriles, peroxides, anhydrides, organometallics	50 fg	10^5
Nitrogen-phosphorus	Hydrogen and air	Nitrogen, phosphorus	10 pg	10^6
Flame photometric (FPD)	Hydrogen and air possibly oxygen	Sulphur, phosphorus, tin, boron, arsenic, germanium, selenium, chromium	100 pg	10^3
Photo-ionization (PID)	Make-up	Aliphatics, aromatics, ketones, esters, aldehydes, amines, heterocyclics, organosulphurs, some organometallics	2 pg	10^7
Hall electrolytic conductivity	Hydrogen, oxygen	Halide, nitrogen, nitrosamine, sulphur		

An ideal detector must possess the following characteristics:

- Good sensitivity,reliability and reproducibility
- Quick response
- Must be stable and non destructive

There are six types of detectors that can be used in GC.

1. **Flame Ionization Detector:**

   Principle: The effluent from the column is mixed with hydrogen and air, and ignited. Organic compounds burning in the flame produce ions and electrons which can conduct electricity through the flame. A large electrical potential is

   applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured using a high impedance pico- ammeter, which is related to the mass of the elutes.

   Advantages:

- ❖ Very useful for analysis of organic compounds
- ❖ High sensitivity
- ❖ Low noise
- ❖ Reliable
- ❖ Easy to use
- ❖ Large linear response range

Disadvantages:

- ❖ Mass dependant detector and hence destroys the sample
- ❖ Requires flammable gases

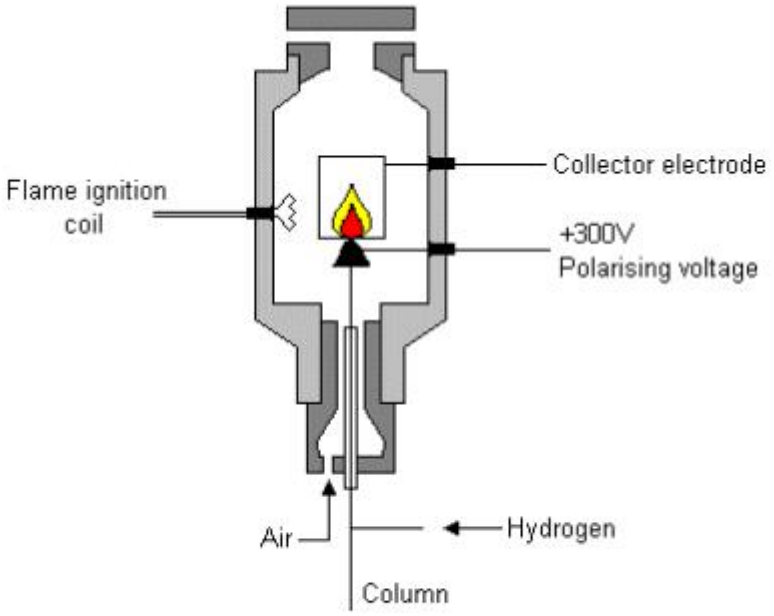


Figure No.4:Flame Ionisation Detector

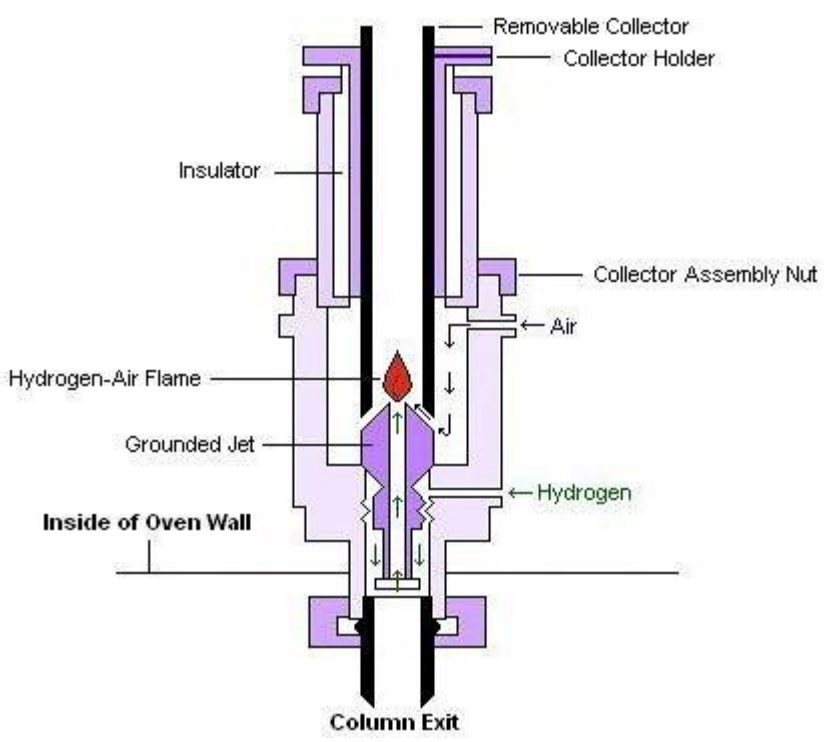


Figure No.5 :Schematic of a typical flame ionization detector.

Thermal Conductivity Detectors

Thermal conductivity detectors (TCD) works by measuring the change in carrier gas thermal conductivity caused by the presence of the sample, which has a different thermal conductivity from that of the carrier gas. Their design is relatively simple, and consists of an electrically heated source that is maintained at constant power. The temperature of the source depends upon the thermal conductivities of the surrounding gases. The source is usually a thin wire made of platinum or gold The resistance within the wire depends upon temperature, which is dependent upon the thermal conductivity of the gas.

TCDs usually employ two detectors, one of which is used as the reference for the carrier gas and the other which monitors the thermal conductivity of the carrier gas and sample mixture. Carrier gases such as helium and hydrogen has very high thermal conductivities so the addition of even a small amount of sample is readily detected.

Advantages:

1. Easy and simple to use.
2. Can be applied to inorganic and organic compounds.
3. Analyte can be collected after separation and detection

Disadvantages:

1. Low sensitivity.
2. Depends on flow rate and concentration.

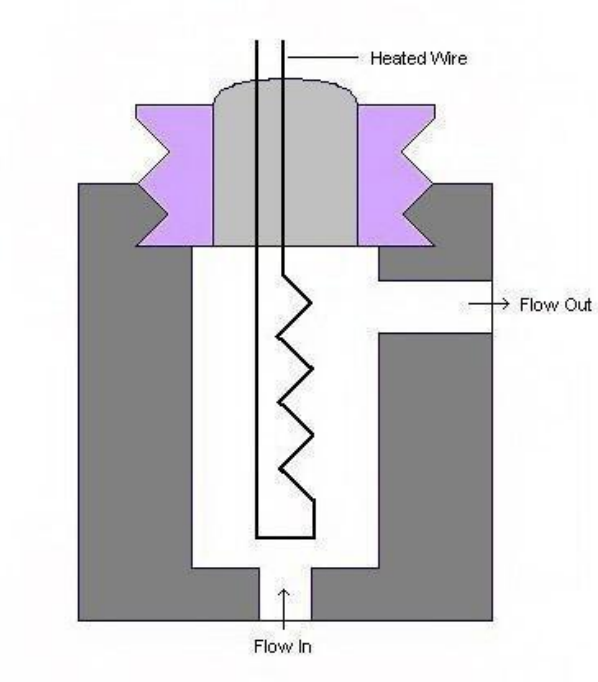


Figure No.6:Schematic of thermal conductivity detection cell

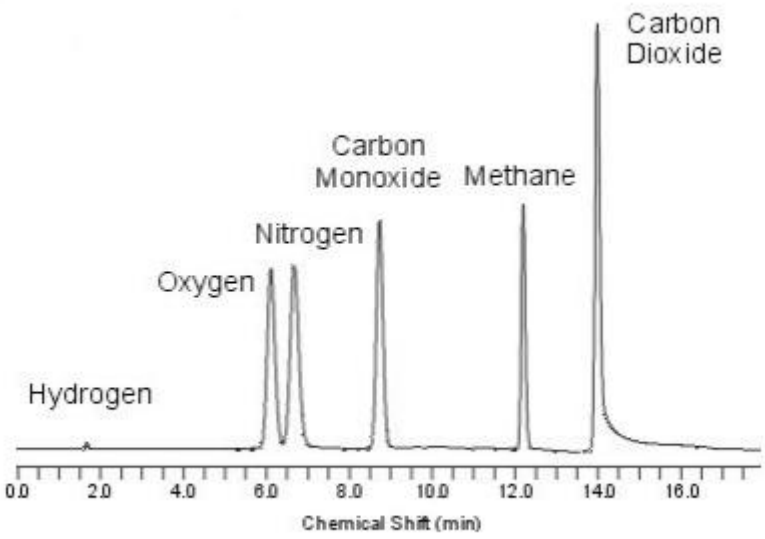


Figure No.7: Standard Chromatogram of a Mixture of Gases

Electron-capture Detectors

- Highly sensitive
- Used for detecting environmental samples as the device selectively detects organic compounds with moieties such as halogens, peroxides, quinones and nitro groups
- Best suited for detection of traces of chemicals such as in pesticides.

Working:

In the absence of organic compounds, a constant standing current is maintained between two electrodes. With the addition of organic compounds with electronegative functional groups, the current decreases significantly as the functional groups capture the electrons.

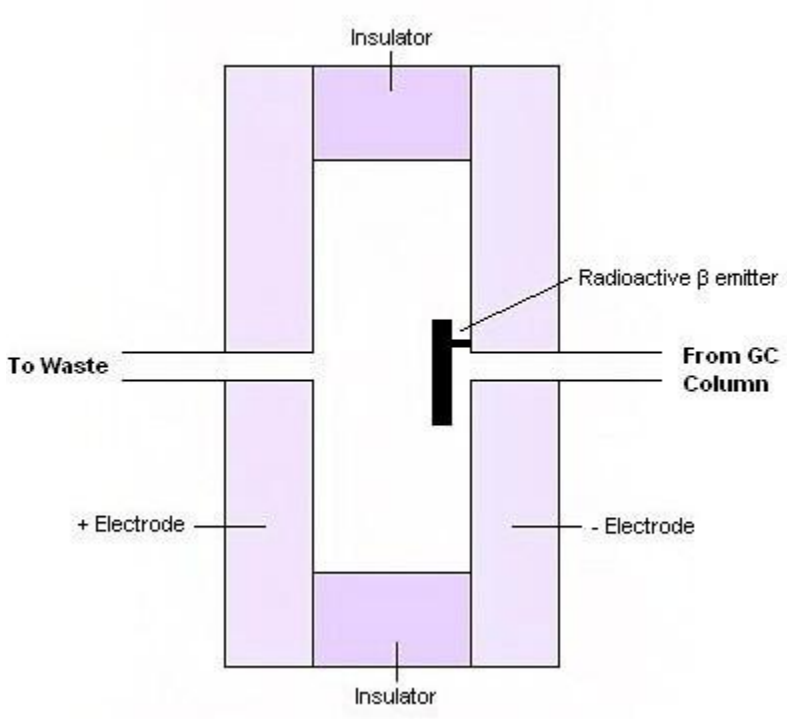


Figure No .8: Schematic of an electron-capture detector

Atomic Emission Detectors

Atomic emission detectors (AED) are 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.

There are three ways of generating plasma: microwave-induced plasma (MIP), inductively coupled plasma (ICP) or direct current plasma (DCP).

MIP is the most commonly employed form and is used with a positionable diode array to simultaneously monitor the atomic emission spectra of several elements.

Working:

The components of the Atomic emission detectors include

1) an interface for the incoming capillary GC column to induce plasma chamber

2) a microwave chamber,

3) a cooling system

4) a diffration grating that associated optics,

5) a position adjustable photodiode array interfaced to a computer.

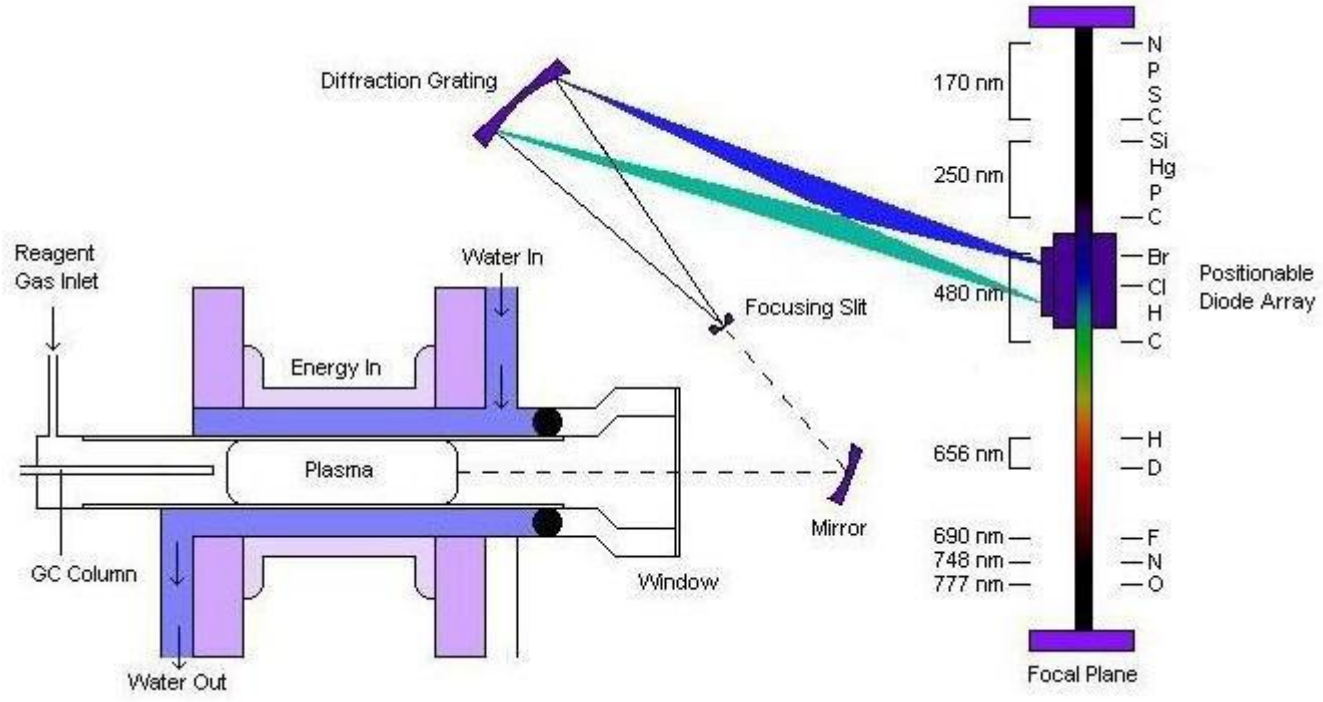


Figure No .9:Schematic of atomic emission detector.

GC Chemiluminescence Detectors

Chemiluminescence spectroscopy (CS) is a process in which both qualitative and quantitative properties can be be determined using the optical emission from excited chemical species.

The light source for chemiluminescence comes from the reactions of the chemicals such that it produces light energy as a product. This light band is used instead of a separate source of light such as a light beam.

Like other methods, CS also has its limitations and the major limitation to the detection limits of CS concerns with the use of a photomultiplier tube (PMT). A PMT requires a dark current in it to detect the light emitted from the analyte.

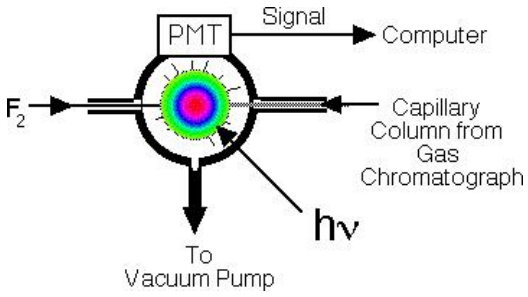


Figure No .10:Schematic of a GC Chemiluminescence Detector

Photoionization Detectors

Photoionization detector (PID) is a portable vapor and gas detector that has selective determination of aromatic hydrocarbons, organo-heteroatom, inorganice species and other organic compounds.

PID comprise of an ultrviolet lamp to emit photons that are absorbed by the compounds in an ionization chamber exiting from a GC column. Small fraction of the analyte molecules are actually ionized, nondestructive, allowing confirmation analytical results through other detectors.

PID is used commonly to detect VOCs in soil, sediment, air and water, which is often used to detect contaminants in ambient air and soil.

The disavantage of PID is unable to detect certain hydrocarbon that has low molecular weight, such as methane and ethane.

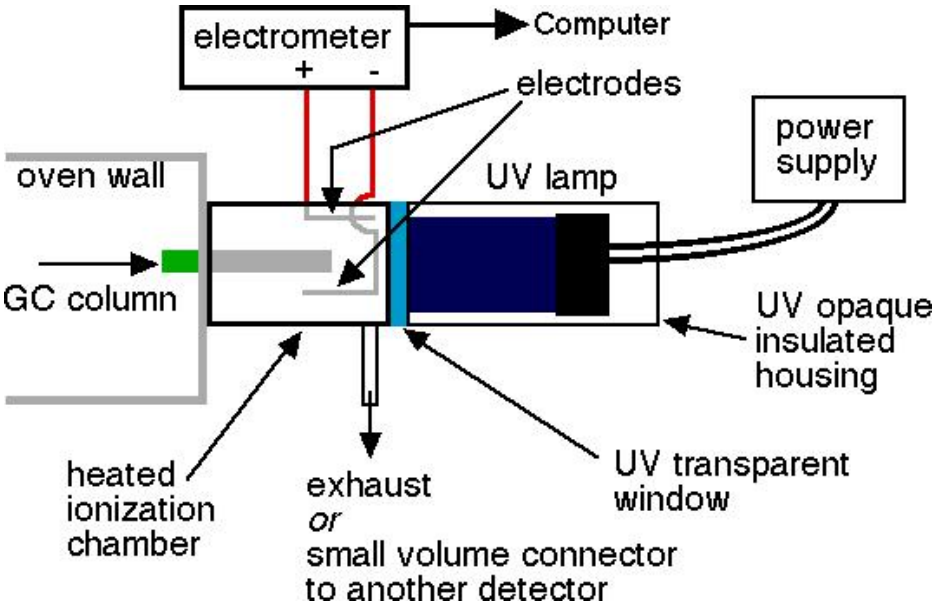


Figure No .11:Schematic of a photoionization detector

Disadvantages:

1. Not suitable for detecting semi-volatile compounds
2. Only indicates if volatile organic compounds are presents.
3. High concentration so methane are required for higher performance.
4. Frequent calibration are required.
5. Units of parts per million range
6. Enviromental distraction, especially water vapor.
7. Strong electrical fields Rapid variation in temperature at the detector and naturally occurring compounds may affect instrumental signal.

Liquid chromatography

Separation technique that involves the placement (injection) of a small volume of liquid sample into a tube packed with porous particles (stationary phase) where individual components of the sample are transported along the packed tube (column) by a liquid moved by gravity.The components of the sample are separated from one another by the column packing that involves various chemical and/or physical interactions between their molecules and the packing particles.The separated components are collected at the exit of this column and identified by an external measurement technique, such as a spectrophotometer that measures the intensity of the color, or by another device that can measure their amount.

HPLC (HIGH PERFORMANCE LIQUID CHROMATOGRAPHY)

Separation technique that involvesthe injection of a small volume of liquid sample into a tube packed with tiny particles (3 to 5 micron (μm) in diameter called the **stationary phase**) where individual components of the sample are moved down the packed tube (**column**) with a liquid (**mobile phase**) forced through the column by high pressure delivered by a pump.

In principle, LC and HPLC work the same way except the speed, efficiency, sensitivity and ease of operation of HPLC is vastly superior.

These components are separated from one another by the column packing that involves various chemical and/or physical interactions between their molecules and the packing particles.

These separated components are detected at the exit of this tube (**column**) by a flow-through device (**detector**) that measures their amount. An output from this detector is called a "**liquid chromatogram**".

Components of HPLC:

1. Pump:

The role of the pumpis to force a liquid (called the mobile phase) through the liquid chromatograph at a specific flow rate, expressed in milliliters per min (mL/min).

Normal flow rates in HPLC are in the 1-to 2-mL/min range.

Typical pumps can reach pressures in the range of 6000-9000 psi (400-to 600-bar).

During the chromatographic experiment, a pump can deliver a constant mobile phase composition (isocratic) or an increasing mobile phase composition (gradient).

2. Injector:

The injector serves to introduce the liquid sample into the flow stream of the mobile phase. Typical sample volumes are 5-to 20-microliters (μL).

The injector must also be able to withstand the high pressures of the liquid system.

An auto sampler is the automatic version for when the user has many samples to analyze or when manual injection is not practical.

Manual Injector:

- ❖ User manually loads sample into the injector using a syringe
- ❖ Then turns the handle to inject sample into the flowing mobile phase, which transports the sample into the beginning (head) of the column, which is at high pressure

Autosampler:

- ❖ User loads vials filled with sample solution into the auto sampler tray (100 samples) autosampler automatically
- ❖ measures the appropriate sample volume
- ❖ injects the sample
- ❖ then flushes the injector to be ready for the next sample, etc., until all sample vials are processed

3. Column:

The column's stationary phase separates the sample components of interest using various physical and chemical parameters.

The small particles inside the column are what cause the high backpressure at normal flow rates.

The pump must push hard to move the mobile phase through the column and this resistance causes a high pressure within the chromatograph.

Columns are packed with small diameter porous particles.The most popular sizes are: 5-μm, 3.5-μm and 1.8-μm

Columns are packed using high-pressure to ensure that they are stable during use, most users purchase pre-packed columns to use in their liquid chromatographs

These porous particles in the column usually have a chemically bonded phase on their surface which interacts with the sample components to separate them from one another , for example, C18 is a popular bonded phase.

The process of retention of the sample components (often called analytes) is determined by the choice of column packing and the selection of the mobile phase to push the analytes through the packed column.

4. Detector:
The detector can see (detect) the individual molecules that come out (elute) from the column.

A detector serves to measure the amount of those molecules so that the chemist can quantitatively analyze the sample components.

The detector provides an output to a recorder or computer that results in the liquid chromatogram (i.e., the graph of the detector response).

The most common are:

Spectroscopic Detection

Spectroscopy (MS): An MS detector senses a compound eluting from the HPLC column first by ionizing it then by measuring it's mass and/or fragmenting the molecule into smaller pieces that are unique to the compound.The MS detector can sometimes identify the compound directly since its mass spectrum is like a fingerprint and is quite unique to that compound.

Refractive Index Detection.

The ability of a compound or solvent to deflect light provides a way to detect it.

The **RI** is a measure of molecule's ability to deflect light in a flowing mobile phase in a flow cell relative to a static mobile phase contained in a reference flow cell.

The amount of deflection is proportional to concentration.

The RI detector is considered to be a universal detector but it is not very sensitive.

Fluorescence Detection:

Compared to UV-Vis detectors fluorescence detectors offer a higher sensitivity and selectivity that allows to quantify and identify compounds and impurities in complex matrices at extremely low concentration levels(trace level analysis).Fluorescence detectors sense only those substances that fluorescence

5. Computer:
Frequently called the data system, the computer not only controls all the modules of the HPLC instrument but it takes the signal from the detector and uses it to determine the time of elution (retention time) of the sample components (qualitative analysis) and the amount of sample (quantitative analysis).

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IV.SPECTRO PHOTOMETERS

Introduction

Many compounds absorb ultraviolet (UV) or visible (Vis.) light. The diagram below shows a beam of monochromatic radiation of radiant power P_0, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power P.

The amount of radiation absorbed may be measured in a number of ways:

Transmittance, $T=P/P_0$

% Transmittance, $\%T = 100\ T$

Absorbance,

$$A = \log_{10} P_0 / P A = \log_{10} 1 / T$$

$$A = \log_{10} 100 / \%T$$

$$A = 2 - \log_{10} \%T$$

The last equation, $A = 2 - \log_{10} \%T$, is worth remembering because it allows you to easily calculate absorbance from percentage transmittance data.

The relationship between absorbance and transmittance is illustrated in Figure No.1

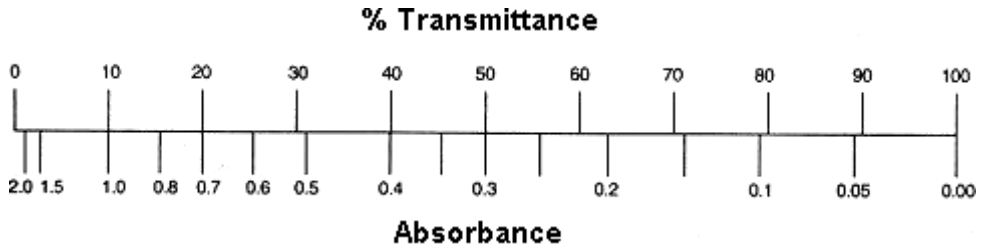

Figure No.1 : Relationship between absorbance and transmittance

So, if all the light passes through a solution without any absorption, then absorbance is zero, and percent transmittance is 100%. If all the light is absorbed, then percent transmittance is zero, and absorption is infinite.

The Beer-Lambert Law

The **Beer-Lambert law** states that there is a linear relationship between the concentration and the absorbance of the solution, which enables the concentration of a solution to be calculated by measuring its absorbance.

$A = \varepsilon lc$,where

A is absorbance,

ε is the molar extinction coefficient (which depends on the nature of the chemical and the wavelength of the light

used),
l is the length of the path light must travel in the solution in centimetres,

c is the concentration of a given solution.

The reason to express the law with this equation is because absorbance is directly proportional to the other parameters, as long as the law is obeyed.

Colorimeter

It is based on the Science of colour measurement. It is used in industries like paint, inks, plastics, textiles and cosmetics. It is also known as photometer.

Two types of colorimeter are available such as single beam and double beam photometer. A single beam instrument uses a single light path for both the reference and the sample. A double beam uses separate light paths for the reference and sample.

SINGLE BEAM PHOTOMETERS

Single beam photometers use the same light path for both the solvent (100 %T) and the solvent-sample. Typically, the light passes through a collimating lens that is directed at the entrance slit where the light is then passed through a filter. The unabsorbed light is passed through the sample holder, passes a closeable shutter (0 %T), to a photovoltaic cell which is attached to a readout device.

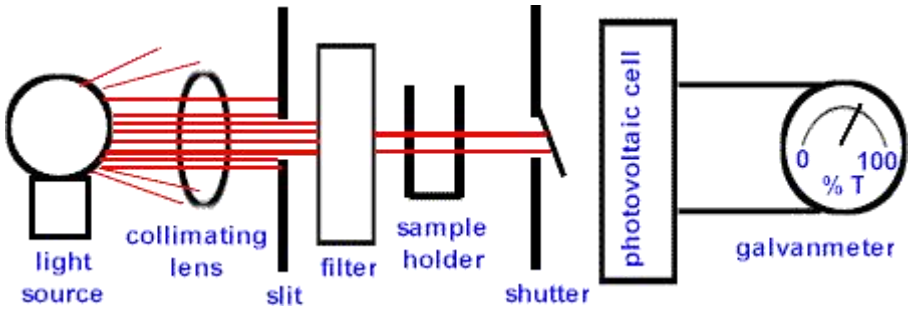

Figure No.2 : Schematic Diagram of Single Beam Photometer

A stabilized power supply is very important. Using a stabilized power supply avoids errors resulting from changes in the beam intensity during the time required to measure 100 %T and the %T of the analyte.

Normally, the process that is followed for the analysis of a sample at a predetermined wavelength (as per filter selection) is as follows:

1

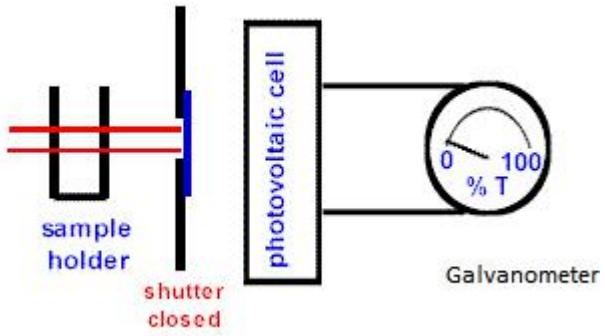

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Figure No.3 a : Calibration of Single Beam Photometer(Shutter Closed)

The shutter is closed to adjust the galvanometer to 0 %T.

2.

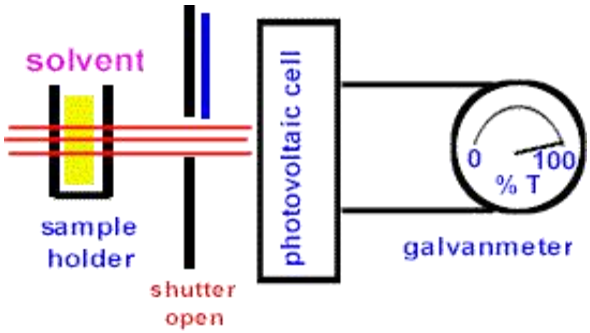


Figure No.3 b : : Calibration of Single Beam Photometer(Solvent)

The sample holder is filled with the solvent (blank), the shutter is opened and 100 %T is adjusted.

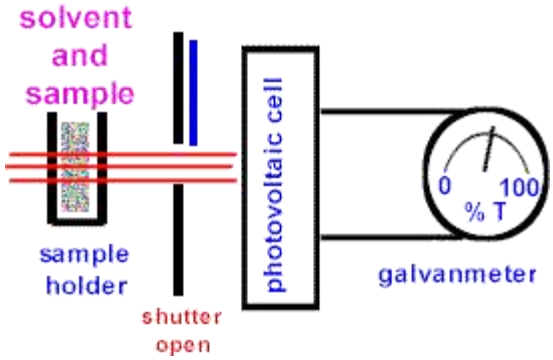


Figure No.3 c : Calibration of Single Beam Photometer(Shutter open with solvent & sample filled)

The sample is added to the sample holder and %T is read.

Advantages of single beam photometers

- low cost
- ease of operation

Disadvantages of single beam photometers

- variation in light intensity — errors in %T
- light beam not monochromatic — deviation from Beer's law
- %T and A are not "true" values
- not designed for spectral data

DOUBLE BEAM PHOTOMETERS

Double beam photometers split the light path into two segments. One segment is used as a reference and the other as the working path. This allows the instrument to make automatic corrections for variations in light intensity.

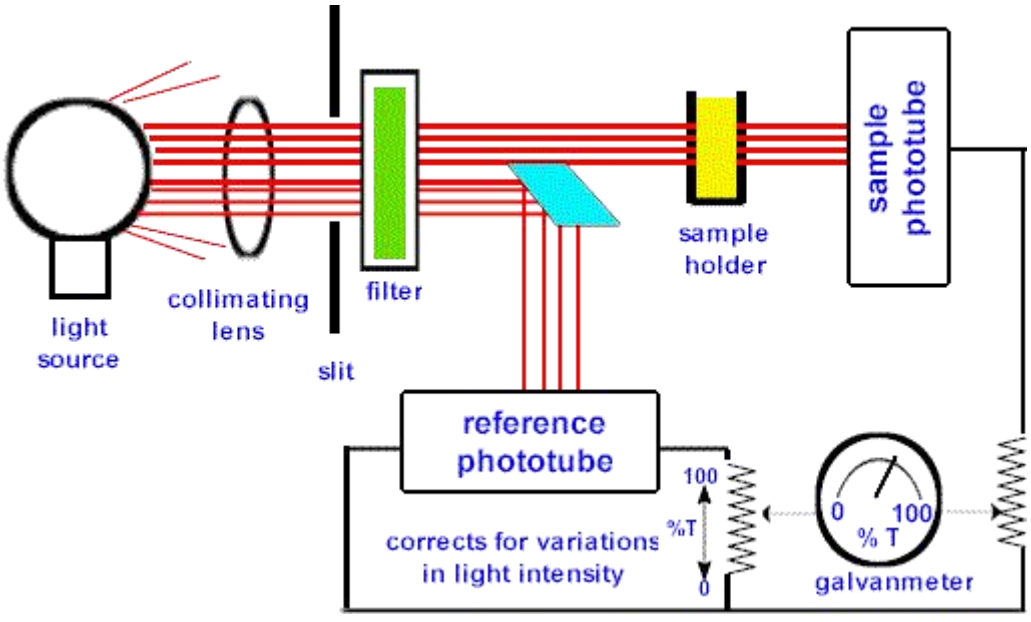


Figure No.4: Schematic diagram of Double Beam Photometer

When the voltages between the sample resistor (CD) and reference resistor (AB) are equal, no current flows through the galvanometer (null detector) since there is no voltage potential ddifference between the two resistors.

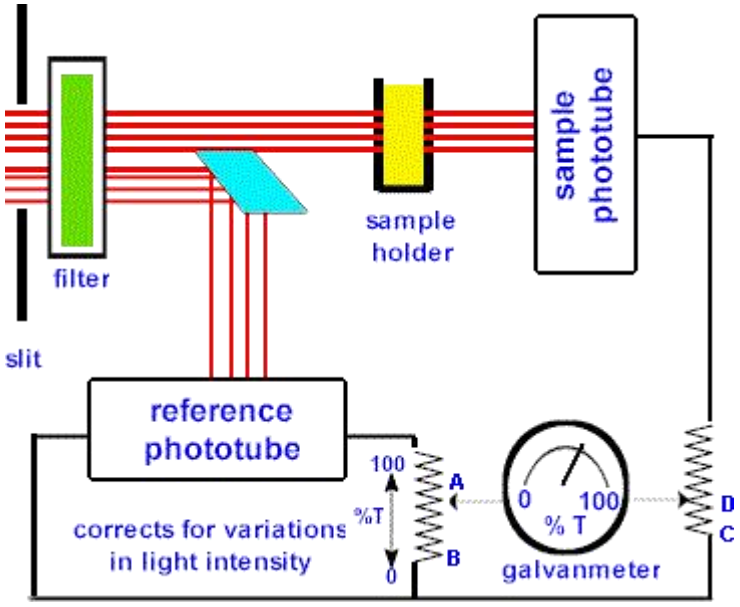


Figure No.5: Schematic diagram of Double Beam Photometer(without light source)

The 0 %T is set by moving contact A (between the meter and the reference resistor) to no resistance (contact B). The shutter is closed which blocks all light from hitting the phototubes. The null meter is mechanically set to read 0 %T since no current is produced by the phototubes.

100 %T is set by placing only the solvent in the sample container. The null meter's contact A (between the meter and the reference resistor) is set for maximum resistance (100 %T). The shutter is opened so that light does strike both phototubes (sample and reference). The null meter's contact D (between the meter and the sample resistor) is adjusted so that there is equal voltage difference between the two resistors (points AB and points CD). At that point, no current flows through the null meter and the meter reads 100 %T.

The analyte and solvent is now placed in the sample container. The analyte will absorb some of the light passing through it which reduces the intensity of the light striking the sample phototube. Since less light is striking the sample phototube, the phototube produces less current. Less current means less voltage across the sample resistor.

Now there is a voltage difference between the sample resistor (AB) and reference resistor (CD). Current now flows through the null meter (AD).

To compensate, contact A (between the null meter and the contact reference resistor) is moved downward until the voltages are once again equal and no current flows (AD). The %T is read directly from the meter.

Advantages of double beam photometers

- correction for changes in light intensity
- ease of operation

Disadvantages of single beam photometers

- light beam is not monochromatic — deviation from Beer's law
- %T and A are not "true" values

not designed for spectral data

SPECTROPHOTOMETERS

Spectrophotometers use monochromatic dispersion elements to vary the wavelengths.

- continuously variable wavelength selection
- light source is UV or VIS

Optical Path of Single Beam Spectrophotometers

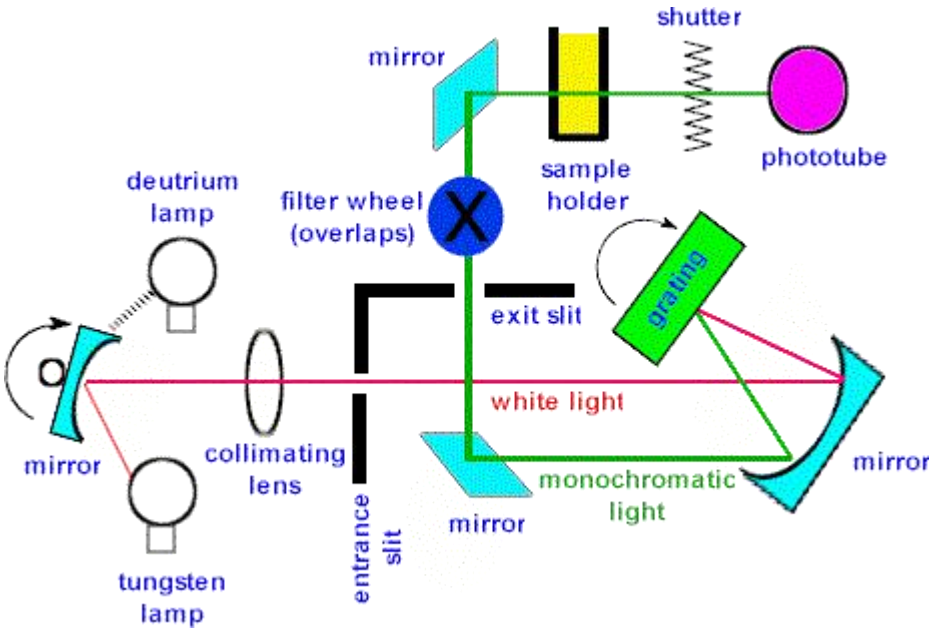


Figure No.6: Electronics of Single Beam Spectrophotometers

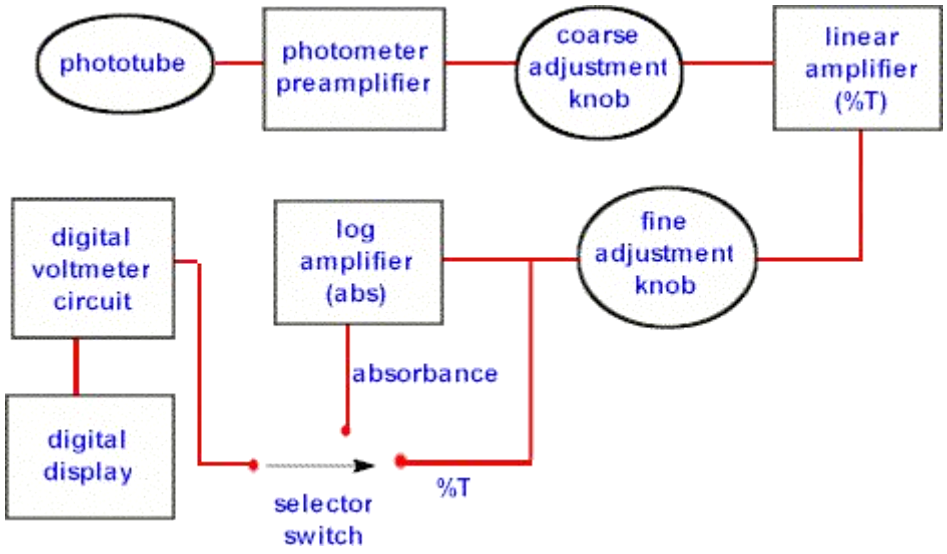


Figure No.7: Steps involved in single beam spectrophotometer

Steps for the use of a single beam spectrophotometer

1. Set the wavelength.

2. Select readout display to the desired mode (%T, A, Conc).

3. Set the readout display to 0 %T (no light) (shutter closed).

4. Insert the reference cell which contains the solvent and set the readout display to 100 %T (shutter open).

5. Insert the sample dissolved in the solvent and read %T from the display.

Advantages of single beam spectrophotometer

- Wavelengths easily selected
- Low cost

Disadvantages of single beam spectrophotometer

- Cannot easily be used for absorption spectra (point by point).
- Changes in light intensity cause variations in readout.
- Changes in solvent causes variations.
- Changes in wavelengths cause variations and % T and has to be reset at 0 %T and 100 %T.

DOUBLE BEAM SPECTROPHOTOMETERS

Double beam spectrophotometers use a beam chopper to separate the reference beam from the sample beam.

Beam Chopper

The chopper is divided into three equal segments. One segment is clear which will pass light through the wheel, one segment is mirrored which will reflect light along a different path, and the third segment is opaque so that no light is transmitted nor reflected.

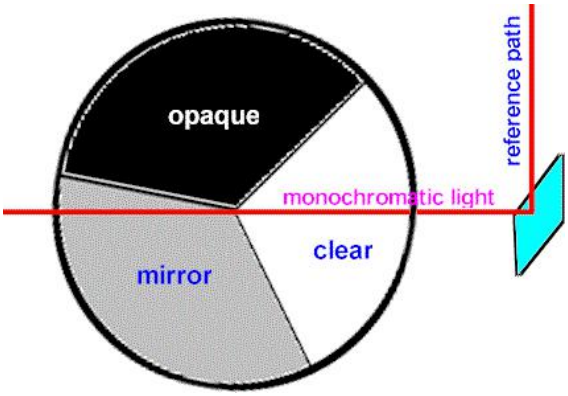


Figure No.8:Transmision of light through transparent region

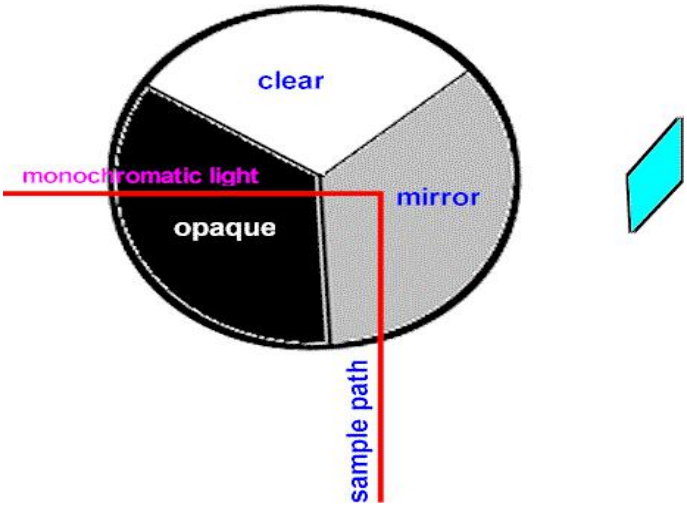


Figure No.9: Light incident on the mirror

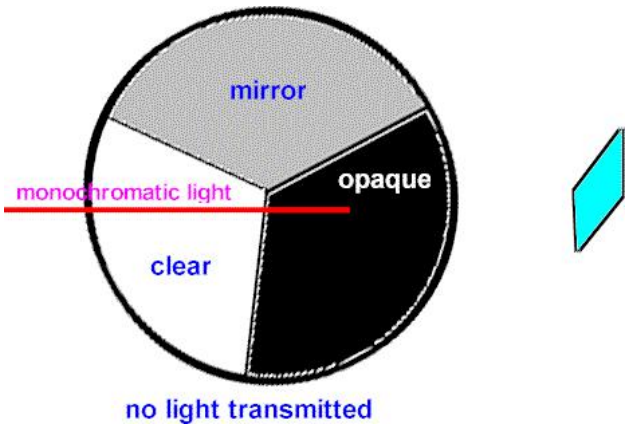


Figure No.10: Transmision of light through opaque surface

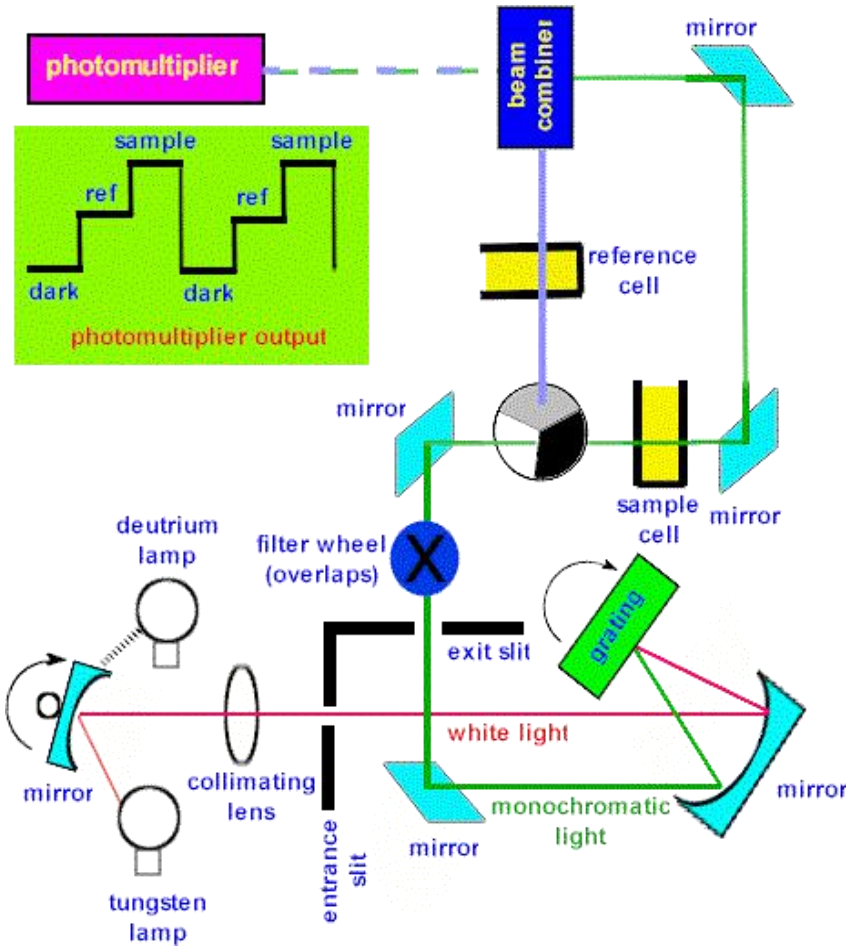


Figure No.11: Optical Path of Double Beam Spectrophotometers

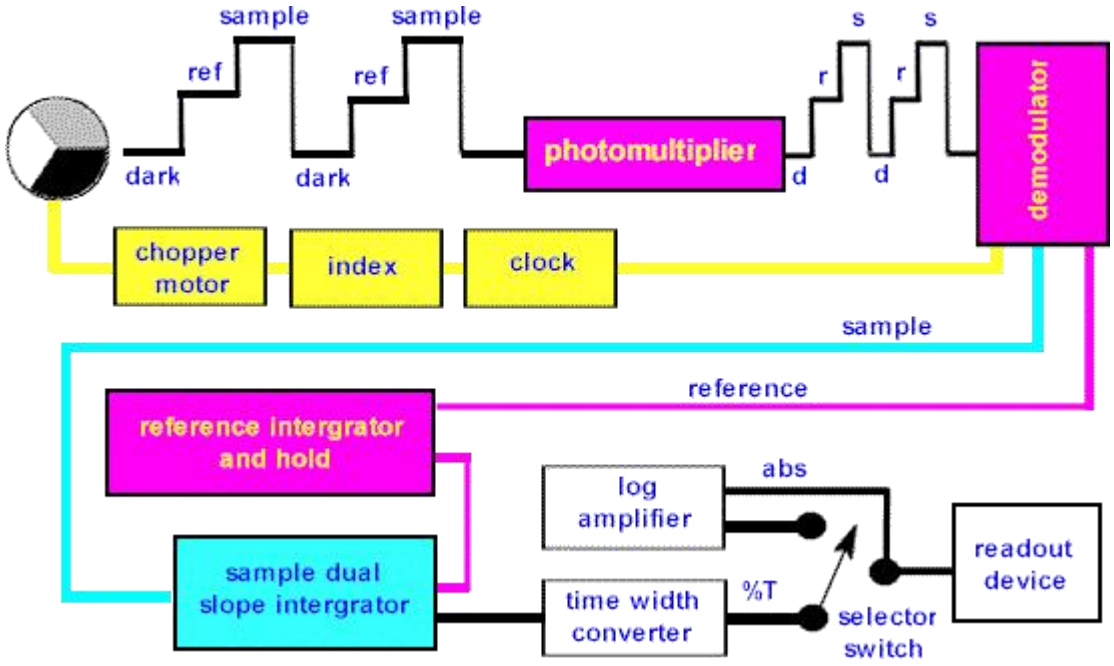


Figure No.12: Electronics of Double Beam Spectrophotometers

Advantages of double beam spectrophotometers

- speed of operation
- automatic compensation for variation in lamp output
- solvent absorption at various 8
- changes in detector sensitivity
- spectra scan

Disadvantages of double beam spectrophotometers

- cost is higher

SELECTIONS ON INSTRUMENT

Most instruments have various options and selections which can be made during an analysis.

The *mode* switch allows the operator to choose what data the readout gives . The three major choices are absorbance (a log amplifier converts transmittance to absorbance), % T, or directly into concentration units.

The slit adjustment allows the operator to adjust the slit width of the instrument.

For instruments which have gratings which can be automatically turned the scan speed (wavelength/min) can be adjusted. Higher scan speeds are used for surveys while slower speeds are used to look at areas in more detail.

The chart recorder is used to record the data of scan instruments. The paper speed and range (mv) can be adjusted to match the output of the spectrophotometer to give a spectra scan.

SPECTRA SCAN

Spectra scans have two coordinated: the X axis is normally wavelength, and the Y axis is either absorbance or transmittance. The resulting graph is called a spectra scan. A spectra scan is similar to a fingerprint of a compound.

PROBE TYPE PHOTOMETERS

Dipping type photometers use fiber optics to transport light.

The original light from a tungsten lamp travels down a fiber optic cable which is dipped into the solutions of interest.

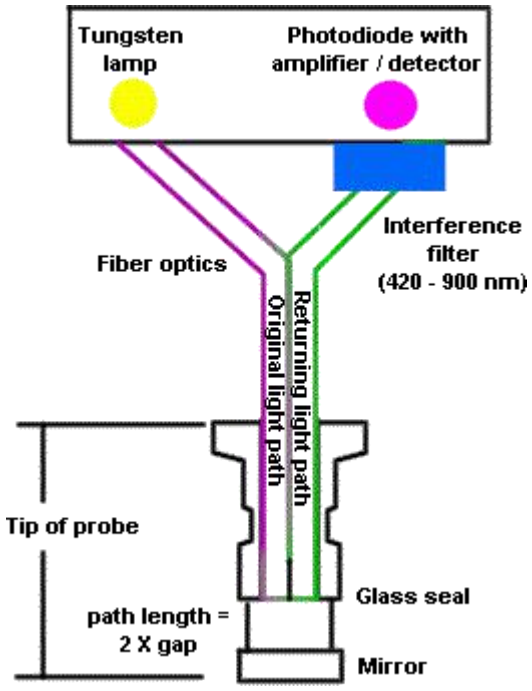


Figure No.13: Probe type photometer

The light then passes through the solution and a mirror reflects the light back to a return fiber optics cable.

The cell path length is 2 times the distance between the ends of the optical cable and the mirror. Interference filters are provided to select wavelengths.The reflected light is then passed through a photodiode with an amplifier and an electronic chopper which is synchronized with the lamp. This results in the detector not responding to extraneous light.

Infrared Spectrophotometer

Dispersive – Similar to UV/Visible dispersive spectrometer(prism/ grating)

- Non – Dispersive – Use interference filters, tunable laser sources like FTIR(Fourier Transform)
  - Types of IR Spectrometer
    - Near IR
    - Mid IR

Radiation Sources

- Globar rod:
  - A rod of silicon carbide 5 mm in diameter , 50 mm long
  - Self starting and has an temperature near 1300 deg C
  - Encased in a water cooled brass tube
- Nernst filament:
  - Brighter source above 1500 deg C
  - Used a mixture of zirconium, Yttrium and thorium
  - Have a negative temp. coefficient
- Nichrome Coil
  - Temperature to 1100 deg C
  - Simple; but, it is less intense than other IR sources

Detectors

- Bolometers
- Thermocouples
- Thermistors
- Golay Cell
- Pyroelectric Transducers
- Photoconductivity cell

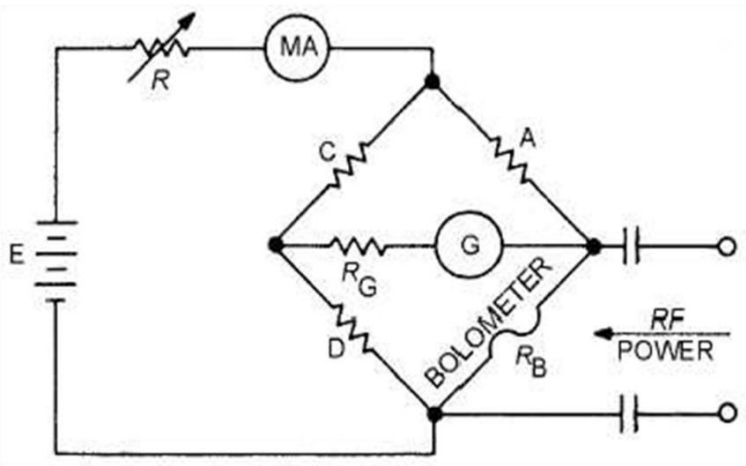


Figure No.14:Bolometers

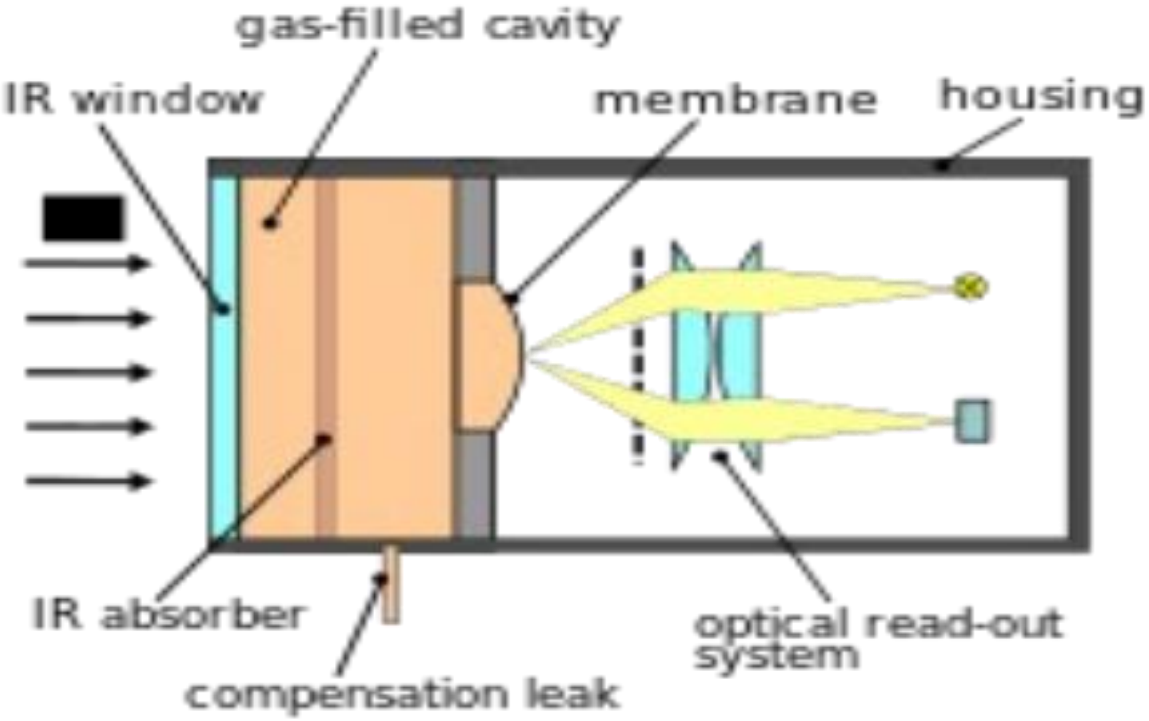


Figure No.15:Golay Cell

Fourier Transform Infra Red Spectrometer

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the coherence of a radiative source, using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation

Fourier transform infrared spectroscopy (**FTIR** is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR has made dispersive infrared spectrometers all but obsolete.

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer .The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a

Beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams "interfering" with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured, all frequencies are being measured simultaneously.Thus, the use of the interferometer results in extremely fast measurements.Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly. A means of "decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation.This transformation is performed by the computer which then presents the user with the desired spectral information for analysis

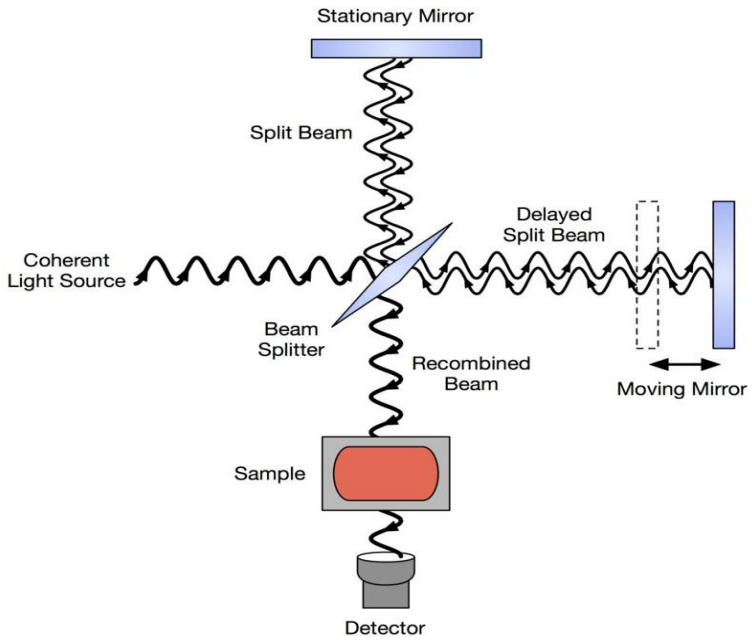


Figure No.16:Fourier Transform InfraRed Spectrometer

Atomic Absorption Spectroscopy

ATOMIC ABSORPTION

Atomic absorption measures metallic elements.The principle behind atomic absorption is the absorption of radiation by atomized atoms.The atomized atoms absorb only the radiation which will raise them to an excited energy level

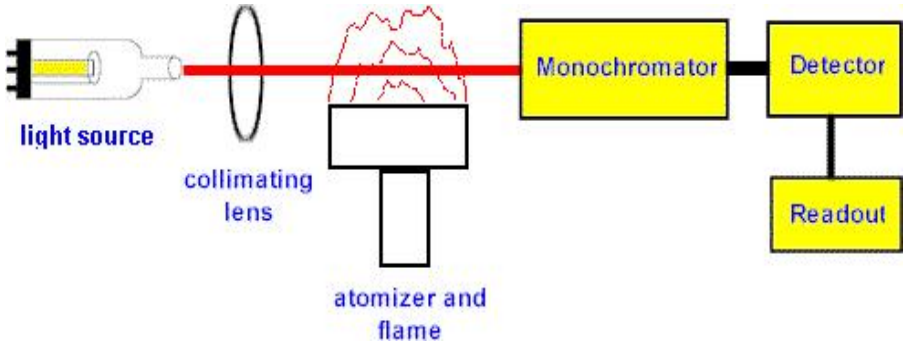


Figure No.17: Atomic Absorption Spectroscopy

EXCITED STATES (Energy Levels)

The energy levels of outer electrons are assumed to have a ground state energy of 0. These outer electrons can be excited and promoted to an excited state in which the outer electron has more energy than its ground state. These excited states are particular orbits that the outer electron can be raised to. Unless the exact amount of energy (E = hν) is supplied to reach one of these "particular orbits", the electron will not become excited. The more outer electrons the atom has, the more complex the spectra.

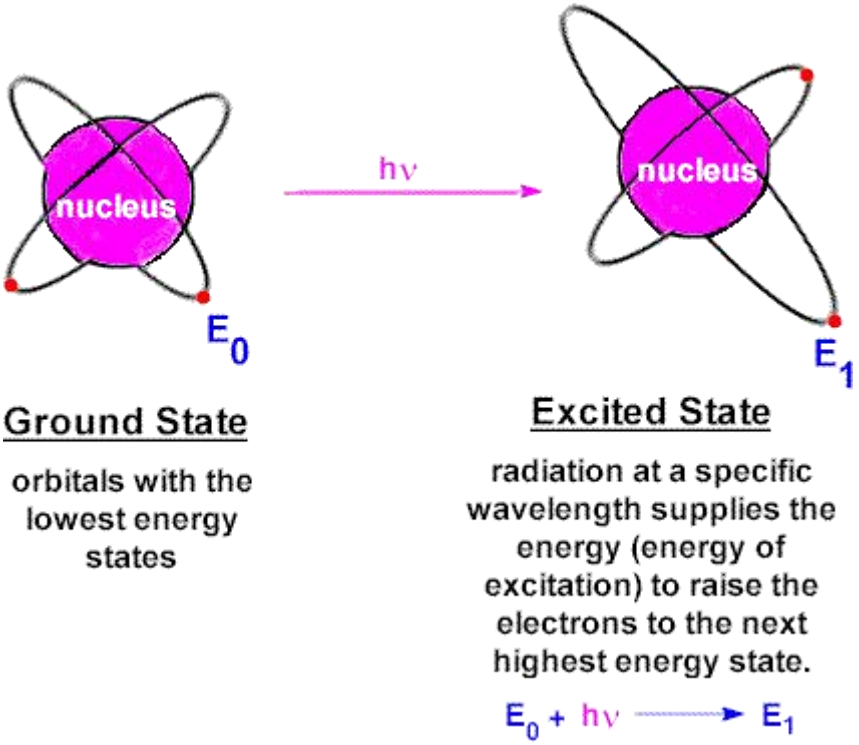
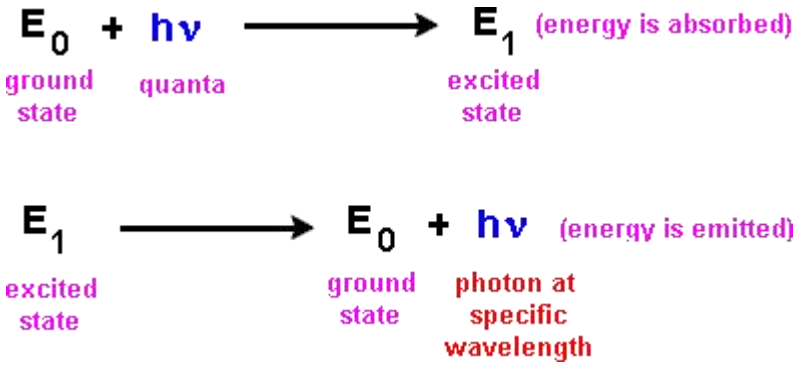


Figure No.18:Illustration of transition of an atom from ground state to excited state

Electrons within orbitals of the lowest energy are called ground state orbitals. Radiant energy at specific wavelengths (E = hc/l) can supply the exact amount of energy (energy of excitation) necessary to raise certain electrons to the next highest energy state. Radiation at any other wavelength is ignored.



The excited electron gives off energy at a specific wavelength when it rapidly returns to its ground state.

Radiant energy is supplied at a wavelength which will raise the ground state electrons to the excited state. The change in radiant energy before and after absorbance is measured.

ATOMIC EMISSION SPECTRA

At room temperature, all the atoms of a material are essentially in the ground state.

Excitation (promotion to higher orbitals) can be caused by flame, plasma, or electrical arc. The excitation is very brief before returning to the ground state E_1 v E_0 + hv which also emits a photon of radiation.Atoms are capable of absorbing radiation of wavelengths that match the energy levels needed for excitation if the atoms are in a hot gaseous medium.

ATOMIC BANDWIDTHS

Narrow absorption band widths are highly desirable since they reduce the chances of overlapping band widths.

EFFECTS OF TEMPERATURE ON ATOMIC SPECTRA

Temperatures can have a dramatic effect on the ratio of excited atomic particles and unexcited atomic particles.Emission spectra where quantitative values are being measured would be temperature sensitive (example: a 10^{o}C increase in temperature would increase the number of excited atoms by 4%).Absorption spectra would not be as effected since it measures unexcited atoms. Since the proportion of excited to unexcited atoms are say only 0.017% exact, a 4% change in that ratio (to 0.018%) would be inconsequential.But temperature fluctuations indirectly affect atomic absorption. Increased temperature increases the efficiency of the atomization process (total number of atoms in the vapor).Temperature variations influence the degree of ionization of the sample thus, the concentration of the non-ionized sample on which the analysis is based.

Electrons can also be excited by the energy in a flame. These excited electrons are in equilibrium to the ground state electrons in the flame. The equilibrium between the excited electrons and the ground state electrons is not dramatically effected by the temperature of the flame. The number of excited electrons increase with a temperature increase but remains constant at a specific temperature.

Table 1: Atomic State/ Number of Atoms with respect to temperature variations

Atomic State	Number of Atoms	
	3000 K	3500 K
Excited	1	30
Ground	999,999,999	999,999,970

The change in temperature does not significantly change the number of ground state electrons. Therefore, the system is stable in regard to temperature variations.

ATOMIZATION

The constituents of a sample must be converted to gaseous atoms in ionized atoms. This is a critical step. The sample introduction must be representative of the entire sample and reproducible.

Solutions are the most common type of sample used. These types of atomizers are pneumatic nebulizations, ultrasonic nebulizations and electro thermal vaporizations.

Nebulization is where the sample is converted to a fine mist of finely divided droplets but using a jet of compressed gas. The flow carries the sample into the atomization region.

ADVANTAGES

- Determine over 60 metallic elements
- Low detection limits
- Few interferences
- Easy sample preparation and instrument operation

DISADVANTAGES

- Chemical interferences (can be corrected).
- Not all elements can be determined (only metals).
- Analyze only one element at a time.

Nonmetals (Cl, Fl, O, Br, I, N) absorb radiation in areas not in the practical range of standard atomic absorption instruments, but these nonmetals can be determined indirectly.

For example, chlorides can be measured by reacting them with Ag^+ to form AgCl. One then measures the concentration of Ag to determine the chloride.

APPLICATIONS OF ATOMIC ABSORPTION SPECTROPHOTOMETRY

- Used in medical,food,agriculture,crime,metallurgy,clinical chemistry blood work,
- Pollution, and petroleum industries

Flame spectroscopy

The main objective of flame spectroscopy is to determine the concentration of alkali and alkaline earth metals in various samples. Scientists Bunsen and Kirchhoff showed that the radiation emitted from the flames depends on the characteristic element present in the flame. The potential of atomic spectroscopy in both the qualitative as well as quantitative analysis were then well established.. Atomic spectroscopy is an unavoidable tool in the field of analytical chemistry. It is divided into three types which are absorption, emission, and luminescence spectroscopy. The different branches of atomic absorption spectroscopy are (1) Flame photometry or flame atomic emission spectrometry in which the species is examined in the form of atoms (2) Atomic absorption spectrophotometry, (AAS), (3) Inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Photoelectric flame photometry, a branch of atomic spectroscopy is used for inorganic chemical analysis for determining the concentration of certain metal ions such as sodium, potassium, lithium, calcium, Cesium, etc. In flame photometry the species (metal ions) used in the spectrum are in the form of atoms. The basis of flame photometric working is that, the species of alkali metals (Group 1) and alkaline earth metals (Group II) metals are dissociated due to the thermal energy provided by the flame source. Due to this thermal excitation, some of the atoms are excited to a higher energy level where they are not stable. The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques. The subsequent loss of energy will result in the movement of excited atoms to the low energy ground state with emission of some radiations, which can be visualized in the visible region of the spectrum. The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques while the emitting radiation intensity is measured using the emission techniques. The wavelength of emitted light is specific for specific elements.The different parts of the flame spectroscopy is given below.

Source of flame:

A burner that provides flame and can be maintained in a constant form and at a constant temperature.

Nebuliser and mixing chamber:

Helps to transport the homogeneous solution of the substance into the flame at a steady rate.

Optical system (optical filter):

The optical system comprises three parts: convex mirror, lens and filter. The convex mirror helps to transmit light emitted from the atoms and focus the emissions to the lens. The convex lens

help to focus the light on a point called slit. The reflections from the mirror pass through the slit and reach the filters. This will isolate the wavelength to be measured from that of any other extraneous emissions. Hence it acts as interference type color filters.

Photo detector:

Detect the emitted light and measure the intensity of radiation emitted by the flame. That is, the emitted radiation is converted to an electrical signal with the help of photo detector. The produced electrical signals are directly proportional to the intensity of light.

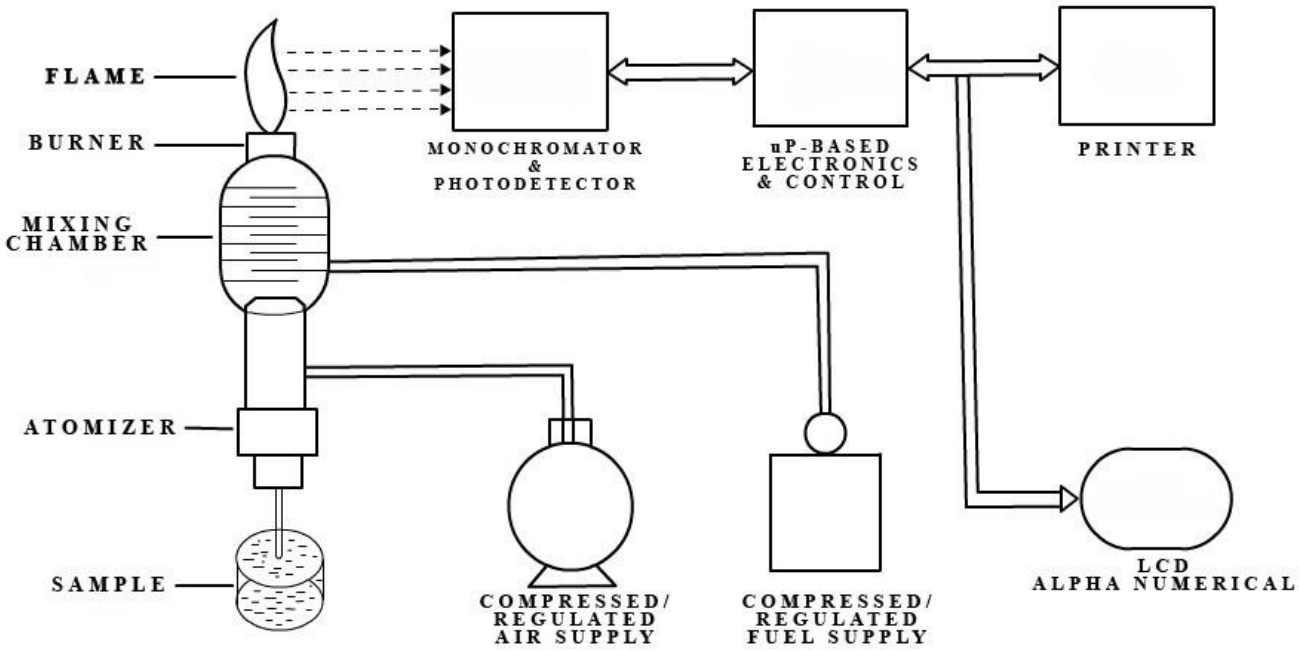


Figure No.19: A schematic representation of flame photometer

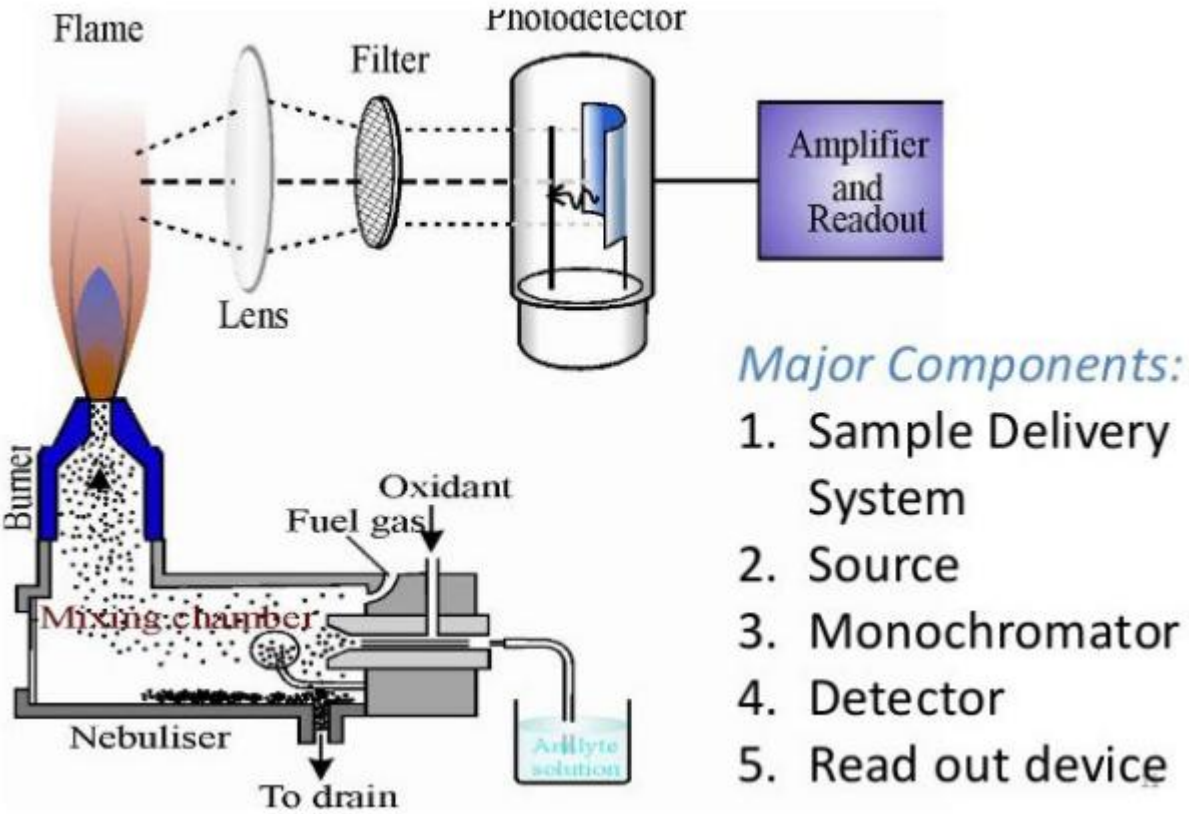


Figure No.20:Schematic diagram of Flame Spectrometer

Nebulisation:

The solution of the substance to be analyzed is first aspirated into the burner, which is then dispersed into the flame as fine spray particles.

A brief overview of the process:

The solvent is first evaporated leaving fine divided solid particles.

1. This solid particles move towards the flame, where the gaseous atoms and ions are produced.
2. The ions absorb the energy from the flame and excited to high energy levels.
3. When the atoms return to the ground state radiation of the characteristic element is emitted.
4. The intensity of emitted light is related to the concentration of the element.

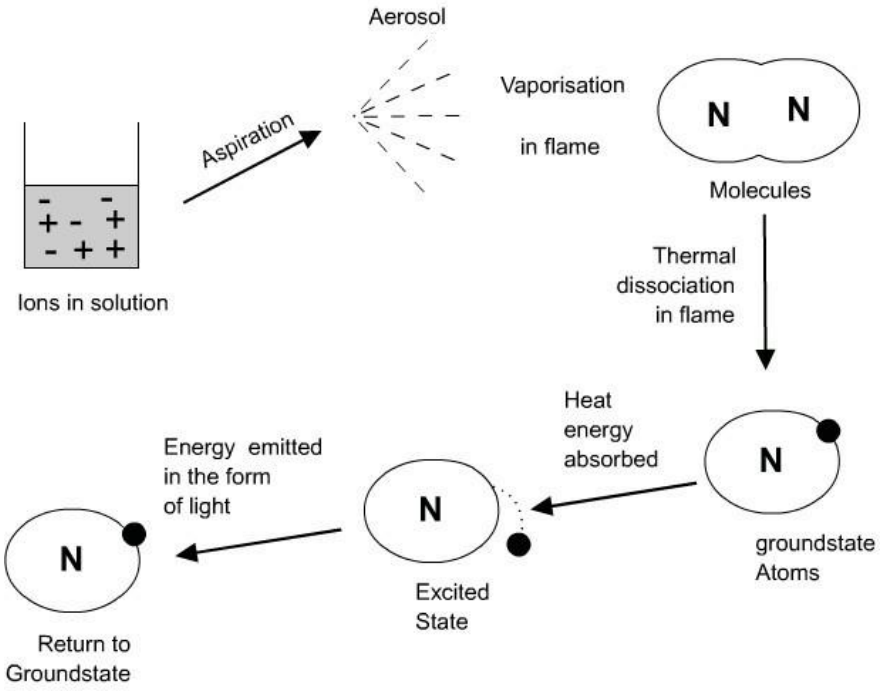


Figure No.21: Brief overview of the Flame Emission Spectroscopy

Events occurring in the flame:

Flame photometry employs a variety of fuels mainly air, oxygen or nitrous oxide (N_2O) as oxidant. The temperature of the flame depends on fuel-oxidant ratio.

The various processes in the flame are discussed below:

1. **Desolvation**: The metal particles in the flame are dehydrated by the flame and hence the solvent is evaporated.

2. **Vapourisation**: The metal particles in the sample are dehydrated. This also led to the evaporation of the solvent.
3. **Atomization**: Reduction of metal ions in the solvent to metal atoms by the flame heat.
4. **Excitation**: The electrostatic force of attraction between the electrons and nucleus of the atom helps them to absorb a particular amount of energy. The atoms then jump to the exited energy state.
5. **Emission process**: Since the higher energy state is unstable the atoms jump back to the stable low energy state with the emission of energy in the form of radiation of characteristic wavelength, which is measured by the photo detector.

The flame emissions of the alkali and alkaline earth metals in terms of the emission wavelength and the characteristic color produced by each element is shown in table 2

Table 2: Colour of the flame for different Elements

Name of the element	Emitted wavelenght range (nm)	Observed colour of the flame
Potassium (K)	766	 Violet
Lithium (Li)	670	 Red
Calcium (Ca)	622	 Orange
Sodium (Na)	589	 Yellow
Barium (Ba)	554	 Lime green

Applications:

Flame photometer has both quantitative and qualitative applications. Flame photometer with monochromators emits radiations of characteristic wavelengths which help to detect the presence of a particular metal in the sample. This help to determine the availability of alkali and alkaline earth metals which are critical for soil cultivation. In agriculture, the fertilizer requirement of the soil is analyzed by flame

test analysis of the soil. In clinical field, Na+ and K+ ions in body fluids, muscles and heart can be determined by diluting the blood serum and aspiration into the flame. Analysis of soft drinks, fruit juices and alcoholic beverages can also be analyzed by using flame photometry.

Advantages:

1. Simple quantitative analytical test based on the flame analysis.
2. Inexpensive.
3. The determination of elements such as alkali and alkaline earth metals is performed easily with most reliable and convenient methods.
4. Quite quick, convenient, and selective and sensitive to even parts per million (ppm) to parts per billion (ppb) range.

Disadvantages:

Moreover the flame photometer has a wide range of applications in the analytical chemistry, it possess many disadvantages which are explained below:

1. The concentration of the metal ion in the solution cannot be measured accurately..
2. A standard solution with known molarities is required for determining the concentration of the ions which will corresponds to the emission spectra.
3. It is difficult to obtain the accurate results of ions with higher concentration.
4. The information about the molecular structure of the compound present in the sample solution cannot be determined.
5. The elements such as carbon, hydrogen and halides cannot be detected due to its non radiating nature.

X ray spectroscopy

Energy-dispersive X-ray spectroscopy (**EDS**, **EDX**, or **XEDS**), sometimes called **energy dispersive X-ray analysis** (**EDXA**) or **energy dispersive X-ray microanalysis** (**EDXMA**), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic

structure allowing unique set of peaks on its X-ray emission spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons (see PIXE), or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the

two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured. Four primary components of the EDS setupare

1. the excitation source (electron beam or x-ray beam)
2. the X-ray detector
3. the pulse processor
4. the analyzer

Electron beam excitation is used in electron microscopes, scanning electron microscopes (SEM) and scanning transmission electron microscopes (STEM). X-ray beam excitation is used in X-ray fluorescence (XRF) spectrometers. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis. The most common detector now is Si(Li) detector cooled to cryogenic temperatures with liquid nitrogen; however newer systems are often equipped with silicon drift detectors (SDD) with Peltier cooling systems.

The identification of elements by X-ray methods is possible due to the characteristic radiation emitted from the inner electronic shells of the atoms under certain conditions. The emitted quanta of radiation are X-ray photons whose specific energies permit the identification of their source atoms. To understand this phenomenon, we must first look at how X-rays are generated.

When an electron beam of high energy strikes a material, one of the results of the interaction is the emission of photons which have a broad continuum of energies. This radiation, called bremsstrahlung, or “braking radiation”, is the result of the deceleration of the electrons inside the material..

Another result of the interaction between the electron beam and the material is the ejection of photoelectrons from the inner shells of the atoms making up the material. These photoelectrons leave with a kinetic energy (E-φ) which is the difference in energy between that of the incident particle (E) and the binding energy (φ) of the atomic electron. This ejected electron leaves a “hole” in the electronic structure of the atom, and after a brief period, the atomic electrons rearrange, with an electron from a higher energy shell filling the vacancy. By way of this relaxation the atom undergoes fluorescence, or the emission of an X-ray photon whose energy is equal to the difference in energies of the initial and final states. Detecting this photon and measuring its energy allows us to determine the element and specific electronic transition from which it originated .Herein lies the basis for XRF spectrometry, where elements may be quantitated based on the rate of emission of their characteristic X-rays from a sample that is being excited.

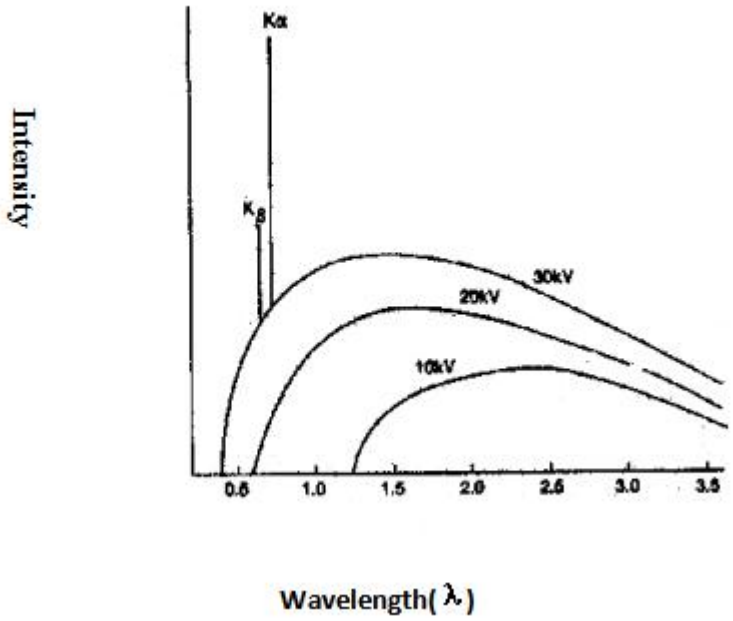


Figure No. 22:Intensity output from a Mo anode X-ray tube at different voltages

Any of the electrons in the inner shells of an atom can be ejected, and there are various electrons in the outer shells that can "drop" to fill the void. Thus there are multiple types of allowed transitions that occur which are governed by the laws of quantum mechanics, each transition having its own specific energy or line .

High energy electrons are not the only particles which can cause ejection of photoelectrons and subsequent fluorescent emission of characteristic radiation. High-energy X-ray photons can create the same effect, allowing us to excite a sample with the output of an X-ray tube or any source of photons of the proper energy. In fact, in some applications of XRF spectrometry, X-rays from a tube are used to excite a secondary, which emits photons that in turn are used to excite the sample.

When X-rays impinge upon a material, besides being absorbed, causing electron ejection and subsequent characteristic photon emission, they may also be transmitted or scattered. When an X-ray is scattered with no change in energy this is called Rayleigh scattering, and when a random amount of energy is lost the phenomenon is Compton scattering. Scattered X-rays are usually problematic in XRF, creating high levels of background radiation Since only the inner electron shells are involved in the emission of X-rays, the wavelengths are independent (within our ability to measure) of the state of chemical bonding, which involves the outer-most electron shells only. One exception to this rule involves low-Z elements with fewer electrons. The overall lack of chemical shifts allows the analyst to determine the elemental composition of the sample, whether the elements are present in their pure forms or as compounds.

Instrumentation

Most of the XRF instruments fall into two categories: energy-dispersive (ED) and wavelength-dispersive (WD) spectrometers. Within these two categories is a tremendous variety of differing

configurations, X-ray sources and optics, and detector technologies. A diagram of a WD system is shown in. The instrument operates based on the principle of Bragg diffraction of a collimated X-ray beam, in this case the beam emanating from the sample. A detector is angularly scanned relative to the analyzing crystal, registering the spectrum.

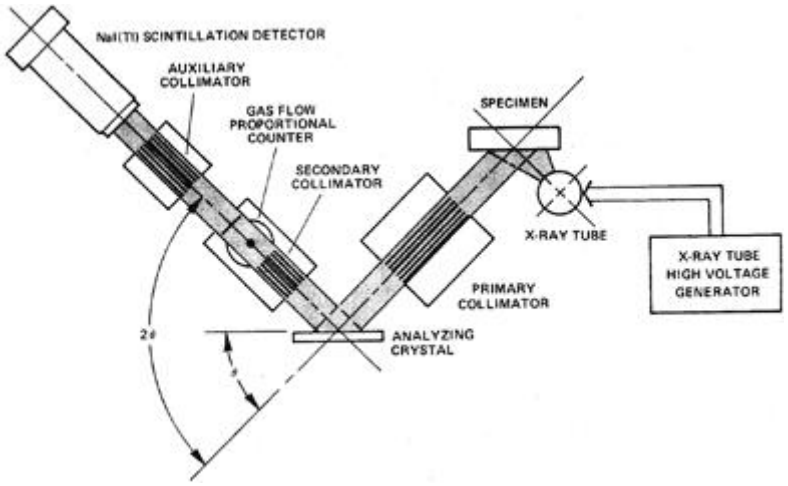


Figure No. 23: Schematic Diagram of Wavelength Dispersive Spectrometer

Here the entire polychromatic spectrum from the sample is incident upon a detector that is capable of registering the energy of each photon that strikes it. The detector electronics and data system then build the X-ray spectrum as a histogram, with number of counts versus energy.

X- Ray Source

The "front end" of both types of instruments is the X-ray source. The source consists of an evacuated chamber with a heated cathode, which is usually a tungsten wire, and an anode, which is held at a potential difference of several tens of kilovolts relative to the cathode. Thermal electrons are released from the cathode and accelerated toward the anode. When the electron beam impinges upon the anode, bremsstrahlung radiation as well as X-ray lines characteristic of the anode material are emitted. These photons escape through a beryllium window built into the side of the tube.There is no one-size-fits-all approach for source selection in XRF. X-ray tube powers may be set up at very different levels, from a fraction of a watt for EDXRF instruments with high detection efficiencies to several kilowatts for WDXRF instruments. In this latter case, the tube must be liquid-cooled since the majority of the power is dissipated as heat. The anode materials must be carefully chosen as well, since the wavelength of their characteristic lines is important for proper excitation of the sample. Some example single-element anode materials are aluminum, chromium, tungsten, palladium, or gold. For detection of light elements, a high intensity of low energy, i.e. 1-10 keV, radiation must be available, while heavy elements require excitation at higher energies up to 50 keV (Jenkins 1995: 43-47, Skoog 1998: 274). It is also important to keep in mind that the primary source of detector background will be the intense primary radiation from the tube, above which the secondary sample radiation must be detected. The use of secondary targets, or filters, can greatly reduce the background and improve sensitivity for specific portions of the spectrum.

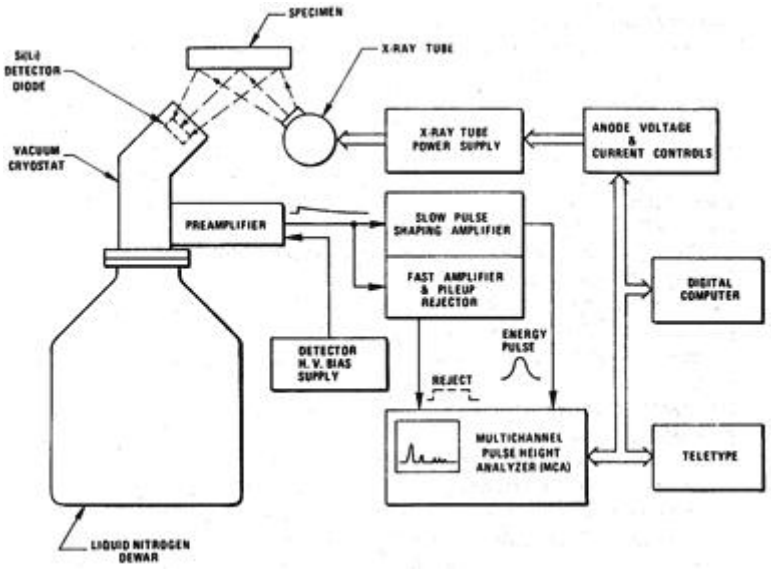


Figure No. 24:Block diagram of a typical EDXRF spectrometer

For instruments that are designed to acquire the entire spectrum with good sensitivity on light as well as heavy elements, a different approach is taken. A tube anode material is chosen to give a high bremsstrahlung or continuum output, which is used to excite a secondary fluorescer, or *target*, which gives off its own characteristic lines without the continuum. The sample is then excited by the emission from the target, which is chosen to efficiently excite elements in a certain Z range.

Sample Chamber

Up to this point, little has been said regarding what kinds of samples may be analyzed by XRF. The development of portable XRF (PXRF) instruments has greatly expanded the range of samples suitable for analysis. There is no longer a need to fit a sample into a small chamber. In the case of PXRF, it is possible to analyze the samples with the instrument in a stand or the instrument can be moved to the sample, as in the case of analyzing a exposed rock outcrop or a large painting.

Detector Systems

The two main types of XRF spectrometers (WD and ED) differ completely in their detection systems. EDXRF systems depend on semiconductor-type detectors which receive the entire emitted spectrum from the sample and decode it into a histogram of number of counts versus photon energy. WDXRF spectrometers, however, use an analyzing crystal to disperse the emitted photons based on their wavelength and place the detector in the correct physical location to receive X-rays of a given energy.

Applications of XR Spectrometry

Currently XRF spectrometry is very widely applied in many industries and scientific fields. The steel and cement industries routinely utilize XRF devices for material development tasks and quality control.

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SCHOOL OF ELECTRICAL & ELECTRONICS ENGINEERING

DEPARTMENT OF ELECTRONICS & INSTRUMENTATION ENGINEERING

UNIT – V -Analytical Instrumentation – SIC1304

V.PRINCIPLE OF NUCLEAR MAGNETIC RESONANCE

NMR - basic principle - NMR spectrometers - Applications - Introduction to mass spectrophotometer - Nuclear radiation detectors - GM counter - proportional counter - solid state detectors

NUCLEAR MAGNETIC RESONANCE AND RADIATION TECHNIQUES

Nuclear magnetic resonance (NMR) is a physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation. This energy is at a specific resonance frequency which depends on the strength of the magnetic field and the magnetic properties of the isotope of the atoms

NMR results from resonant absorption of electromagnetic energy by a nucleus (mostly protons) changing its spin orientation

- The resonance frequency depends on the chemical environment of the nucleus giving a specific finger print of particular groups (NMR spectroscopy*)*
- NMR is nondestructive and contact free.
- NMR is an instrumental technique to determine the number, type, and relative positions of certain Nuclei in a molecule
- NMR is concerned with the magnetic properties of these nuclei
- Many Nuclei types can be studied by NMR, but the two most common nuclei that we will focus on are Protons ($^{1}H1$) and Carbon-13 ($^{13}C6$)

The magnetic properties of NMR suitable nuclei include the following

- Nuclear Magnetic Moments
- Spin Quantum Number (I)
- Nuclear Spin States
- Externally Applied Magnetic Field
- Frequency of Angular Precession
- Absorption of Radio Wave Radiation

Nuclear Magnetic Resonance Spectroscopy (NMR) depends on the following

- Nuclear Spin
- Nuclear Spin State
- Magnetic Moments
- Quantized Absorption of Radio Waves
- Resonance
- Chemical Shift
- Chemical Equivalence
- Integrals (Signal Areas)
- Chemical Shift - Electronegativity Effects
- Chemical Shift - Anisotropy (non-uniform) effects of pi bonds

Nuclear Spin States

Nuclei with spin (Magnetic Moment, Quantized Spin Angular Momentum, Magnetic Dipole) have a certain number of "Spin States."

The number of "Spin States" a nuclei can have is determined by its "Spin Quantum Number I," a physical constant, which is an intrinsic (inherent) property of a spinning charged particle.

The Spin Quantum Number (I) is a non-negative integer or half-integer (0, 1/2, 1, 3/2, 2, etc.).

The Spin Quantum Number value for a given nuclei is associated with the Mass Number and Atomic Number of the nuclei.

Odd Mass / Odd Atomic No - 1/2, 3/2, 5/2 Spin

Odd Mass / Even Atomic No - 1/2, 3/2, 5/2 Spin

Even Mass / Even Atomic No- Zero (0) Spin

Even Mass / Odd Atomic No - Integral (1, 2, 3) Spin

Spin

- the nuclei of some atoms spin: ^{1}H, ^{13}C, ^{19}F, …
- the nuclei of many atoms do not spin: ^{2}H, ^{12}C, ^{16}O, …
- moving charged particles generate a magnetic field ( )
- when placed between the poles of a powerful magnet, spinning nuclei will align with or against the applied field creating an energy difference. Using a fixed radio frequency, the magnetic field is changed until the $\Delta E = E_{EM}$. When the energies match, the nuclei can change spin states (resonate) and give off a magnetic signal.

NMR Spectrum.

The NMR spectrum is given below

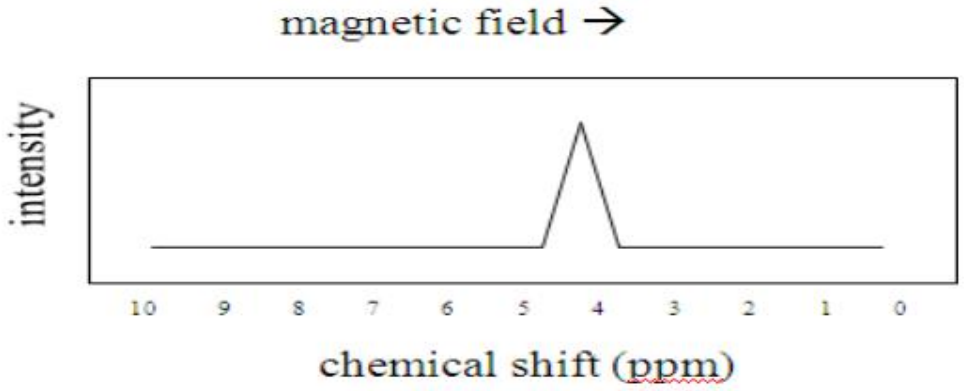

Figure No.1: NMR Spectrum

NMR Spectra – The Chemical Shift

- The differences in the applied Magnetic Field strength (Angular Frequency of Precession) at which the various proton configurations in a molecule Resonate are extremely small

- The differences amount to only a few Hz (parts per million) in a magnetic field strength of 60, 100, 300, MHz (megahertz)

- It is difficult to make direct precise measurements of resonance signals in the parts per million range

- A parameter, called the "Chemical Shift" ( ), is computed from the observed frequency shift difference (in Hz) of the sample and the "standard resonance signal" divided by the applied Magnetic Field rating of the NMR Spectrometer (in MHz)

$$\delta = \frac{\text{Difference between a resonance frequency and that of a reference substance}}{\text{Operating frequency of the spectrometer}}$$

Introduction to NMR Spectroscopy

- Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.
- Two common types of NMR spectroscopy are used to characterize organic structure: ^{1}H NMR is used to determine the type and number of H atoms in a molecule; ^{13}C NMR is used to determine the type of carbon atoms in the molecule.
- The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.
- When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including ^{1}H and ^{13}C.

NMR Spectrometers

NMR spectrometers are rated according to the frequency, in MHz, at whiproton processes - 60 MHz, 100 MHz, 300 MHz, 600 MHz, or even higher.Continuous Wave (CW) NMR instruments are set up so that the externally applied magnetic field strength is held constant while a RF oscillator subjects the sample to the full range of Radio Wave frequencies at which protons (or C-13 nuclei) resonate.In Fourier Transform (FT) NMR instruments, the RF oscillator frequency is held constant and the externally applied magnetic field strength is changed.Most NMR instruments today are of the Continuous Wave type

NMR is a technique of high specificity but relatively low sensitivity. The basic reason for the low sensitivity is the comparatively small difference in energy between the excited and the ground states (0.02 calories at 15 to 20 kilogauss field strength), which results in a population difference between the two levels of only a few parts per million. Another important aspect of the NMR phenomenon, with negative effects on the sensitivity, is the long lifetime of most nuclei in the excited state, which affects the design of the NMR analytical test, especially in pulsed repetitive experiments. Simultaneous acquisition of the entire spectrum instead of frequency-swept spectra can give sensitivity enhancement.

Equipment:

The distinctive components of an NMR spectrometer are a magnet and a source of radio frequency. The instruments are described by the approximate resonance frequency of the analytical nucleus, e.g., 1H NMR. More recently, instruments are being referred to by their field strengths. Some spectrometers are dedicated to the analysis of one type of nucleus; others are designed to obtain spectra of different nuclei.

There are two types of commercial NMR spectrometers: the classical continuous wave (CW) instruments and the more modern pulse Fourier-transform (FT) instruments. The CW spectrometers use a technique similar to that of classical optical spectrometers: a slow scan of radio frequency (at fixed magnetic field) or of the magnetic field (at fixed radio frequency) over a domain corresponding to the resonance of the nuclei being studied. The signal generated by the absorption of energy is detected, amplified, and recorded.

Various instrument configurations are possible. The arrangement of a typical double-coil spectrometer, as one might see in the lower resolution 60-MHz and 100-MHz CW instruments, is illustrated in Figure.

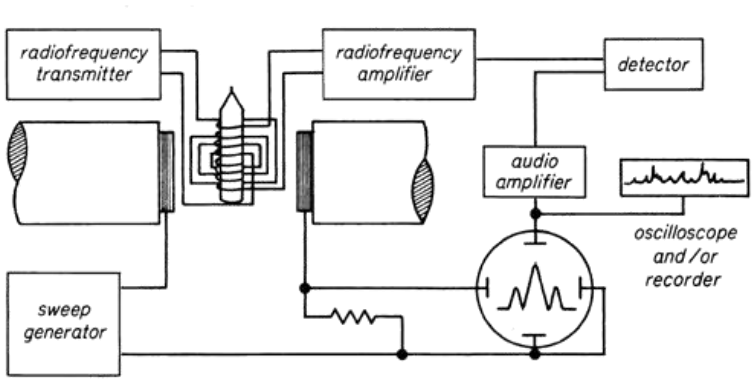

Figure No.2:Schematic of NMR Spectrometer

The limitations of the CW spectrometers are low sensitivity and long analysis time. In pulsed NMR spectrometers, a single pulse of radio frequency energy is used to simultaneously activate all nuclei. The excited nuclei returning to the lower energy level generate a free induction decay (FID) signal that contains in a time domain all the information obtained in a frequency domain with a CW spectrometer. The time domain and the frequency domain responses form a pair of FTs; the mathematical operation is performed by a computer after analog-to-digital conversion. After a delay allowing for relaxation of the excited nuclei, the pulse experiment (transient) may be repeated and the response coherently added in the

computer memory, with random noise being averaged out. (A similar signal-to-noise increase can be obtained by combining CW spectrometers with computers that average transients.)

Detectors:

A Geiger counter (Geiger-Muller tube) is a device used for the detection and measurement of all types of radiation: alpha, beta and gamma radiation. Basically it consists of a pair of electrodes surrounded by a gas. The electrodes have a high voltage across them. The gas used is usually Helium or Argon. When radiation enters the tube it can ionize the gas. The ions (and electrons) are attracted to the electrodes and an electric current is produced. A scaler counts the current pulses, and one obtains a "count" whenever radiation ionizes the gas. The Geiger-Mueller tube is usually cylindrical, with a wire down the center. When ionizing radiation such as an alpha, beta or gamma particle enters the tube, it can ionize some of the gas molecules in the tube. From these ionized atoms, an electron is knocked out of the atom, and the remaining atom is positively charged. The high voltage in the tube produces an electric held inside the tube. The electrons that were knocked out of the atom are attracted to the positive electrode, and the positively charged ions are attracted to the negative electrode. This produces a pulse of current in the wires connecting the electrodes, and this pulse is counted. After the pulse is counted, the charged ions become neutralized, and the Geiger counter is ready to record another pulse. In order for the Geiger counter tube to restore itself quickly to its original state after radiation has entered, a gas is added to the tube. For proper use of the Geiger counter, one must have the appropriate voltage across the electrodes. If the voltage is too low, the electric field in the tube is too weak to cause a current pulse. If the voltage is too high, the tube will undergo continuous discharge, and the tube can be damaged. First we will place a radioactive isotope in from of the Geiger-Mueller tube. When an ionizing particle enters the counter, collision with the filling gas produces ion pairs. The formed ion pairs move towards the appropriate electrode under the voltage gradient. The mobility of electron is high and under this potential gradient it acquires sufficient velocity to produce new ion pairs by collision with atoms of argon. Repeating of this process produces an avalanche of electron moving towards anode.

Proportional counter

When the electric field at the centre electrode of an ionization chamber is increased above the saturation level, but under that of the Geiger region, the size of the output pulse from the chamber starts to increase but remains proportional to the initial ionization. A device operated in this principle is called a proportional counter.

Mass Spectrometer

1. It measures mass better than any other technique.
2. It can give information about chemical structures.

The mass measurements are good for To identify, verify, and quantitate: metabolites, recombinant proteins, proteins isolated from natural sources, oligonucleotides, drug candidates, peptides, synthetic organic chemicals, polymers

Applications of Mass Spectrometry:

Pharmaceutical analysis

1.Bioavailability studies
2.Drug metabolism studies, pharmacokinetics
3.Characterization of potential drugs
4.Drug degradation product analysis
5.Screening of drug candidates
6.Identifying drug targets
7.Biomolecule characterization
8.Proteins and peptides
9.Oligonucleotides

Environmental analysis

1.Pesticides on foods
2.Soil and groundwater contamination

Forensic analysis/clinical

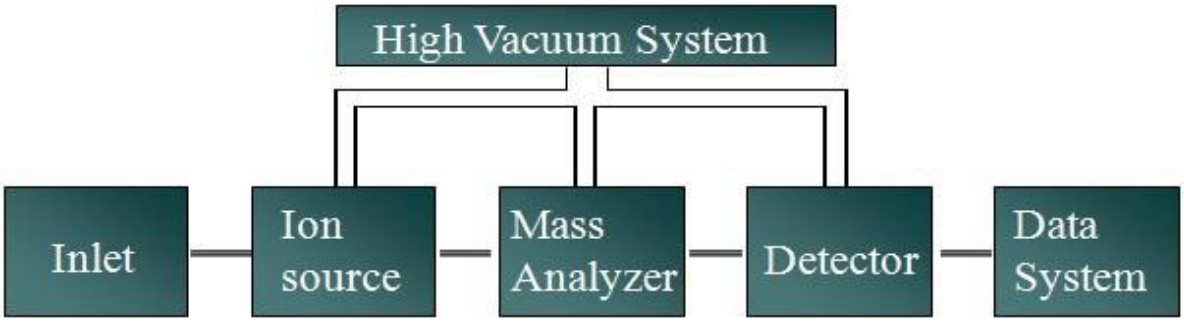

Figure No.2: Block diagram of Mass Spectrometer

- High Vacuum System uses Turbo molecular pumps
- Inlet is usually made of HPLC Flow injection Sample plate
- Mass analyzer may be of any of the following types.Time of flight (TOF) , Magnetic Sector FTMS and Quadrupole Ion Trap
- Detector- Microchannel Plate Electron Multiplier, Hybrid with photomultiplier

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