الشركة القابضة
لمياه الشرب والصرف الصحى

برنامج المسار الوظيفي للعاملين بقطاع مياه الشرب والصرف الصحي

دليل المتدرب

Basic Course in Organic Analyses Instrumentation

كيميائي مياه- الدرجة الثالثة

تم إعداد المادة بواسطة الشركة القابضة لمياه الشرب والصرف الصحي
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مقدمة الإصدار الثانى

تهدف مجموعة البرامج التدريبية المعدة من إدارة المسار الوظيفى بالشركة القابضة لمياه الشرب والصرف الصحى إلى رفع كفاءة الكيميائين العاملين بالشركة القابضة لمياه الشرب والصرف الصحى والشركات التابعة لها وتنمية مهاراتهم ومعارفهم بالشكل الذى يضمن الوصول إلى كوب مياه نظيف وبيئة آمنة يرضى متطلبات وإحتياجات العملاء الكرام.

ويعتبر الإصدار الثانى من برامج المسار الوظيفى لوظيفة كيميائى مياه الشرب هو ثمرة جهود الكيميائيين العاملين بمعامل الشركات التابعة والمعمل المرجعى لمياه الشرب بالشركة القابضة بما تحمله من مزيج متجانس من الخبرات والكفاءات الذين لم يدخروا جهدا حتى يخرج هذا العمل بالطريقة اللائقة.

وجدير بالذكر أن هذا الإصدار يعتبر مكتبة مرجعية وافية وشاملة لجميع الجدارات المتضمنة المهارات والمعارف التي تجعل الكيميائى كفؤا لوظيفته.

ومما تجدر الإشارة إليه بأنه تم الاعتماد على منهجية للمسار التدريبى بحيث يكون المتدرب قد تلقى الدورات الحقلية بداية من التعرف على مراحل التنقية والمعالجة ثم الانتقال إلى الدورات المعملية داخل معمله طبقا للإطار الزمنى المحدد للمدد البينية لكل درجة وظيفية.

ولقد اعتمدنا على وضع معايير لكل مرحلة فى إعداد هذا الاصدار وكان من أهم هذه المعايير:

- المشاركة الفعالة للخبرات والكفاءات التدريبية بالشركات التابعة فى وضع المناهج بما يناسب عموم الكيميائيين على مستوى الجمهورية.
- عقد ورشة عمل متخصصة لكل مادة تدريبية يشارك بها جميع المدربين ذوى التخصص والخبرات سواء من المعمل المرجعى أو معامل الشركات فضلا عن أن يكون المدرب قد قام بتدريس هذه المادة مرات عديدة.
- استخدام وسيلة اتصال غير تزامنى بين جميع المدربين المعتمدين لكل مادة على حدة من خلال انشاء جروب على الفيس بوك لكل مادة على حده (مذكور فى دليل المدرب).
- وضع حقيبة تدريبية كاملة لكل برنامج معدة طبقا لأحدث النظم والمعايير العالمية تحتوى على (دليل المتدرب- شرائح العرض- ملحقات مقروؤة ومرئية- دليل المدرب- بنك الأسئلة).
- بناء المحتوى لكل برنامج تدريبى طبقاً لأحدث المراجع العالمية ومن أهمها كتاب الطرق القياسية لتحليل مياه الشرب والصرف الصحى (الإصدار رقم 23) وبما يتوافق مع متطلبات آخر إصدارات الايزو(17025)، مع مراعاة التحديثات الخاصة بالتشريعات والقوانين ذات الصلة.

وجدير بالذكر أن الإصدار الثانى من البرامج التدريبية اعتمد فى تصميمه على عرض مبسط للمعلومات قدر الامكان طبقاً للأسس العلمية وطبقاً للجدارات المعتمدة على تحديد أهداف واضحة وصريحة لتدريب المتدربين، وتشتق تلك الجدارات من الفهم الواضح لدور المتدرب طبقا لبطاقة الوصف الوظيفى، وتتضمن معارف ومهارات وسلوك. مما يضمن إكساب المتدرب مهارات سلوكية بالإضافة إلى المواد التخصصية.

كما تم تصميم العديد من ورش العمل على أساس تسهيل و تسريع عمليتي التعلم و كسب المهارات بما يسمح بتعظيم الفائدة من العملية التدريبية.

كذلك تم استخدام أساليب التدريب الحديثة والاعتماد على التدريب التفاعلى والتركيز على الجوانب التطبيقية في استخدام الوسائل والأساليب المختلفة ، كما تم استخدام الطرق الحديثة للتعليم التفاعلي والغير تزامني كمصادر مساندة للتعلم من خلال انشاء جروب على الفيس بوك للمدربين المعتمدين **(HCWW Trainers)** .

وفى الختام نرجوا من الله أن يتقبل منا هذا العمل كما نأمل أن يكون هذا العمل علما نافعا للعاملين بقطاع المعامل بالشركة القابضة والشركات التابعة لما يشمله من معلومات فنية قيمة وأن يفيد العاملين الجدد بها ليصبحوا قادرين على تنفيذ مهامهم الوظيفية بالشكل الأمثل .

والله ولي التوفيق.

Chromatography

Introduction:

First classic liquid chromatography (LC) was carried out by Mikhail Tswett, a Russian botanist, in 1903. He used large diameter glass columns filled with solid powders to separate pigments extracted from plants (carotenoids and chlorophyll). To do so, he continuously added solvent to the column after introducing the pigment extract at the top of a vertical column. The pigments adsorbed differentially onto the solid and separated as they migrated down the column. As the pigments separated, colored rings appeared within the column, each ring being a different pigment extracted from the leaves. It is for this reason that the term chromatography (chroma =color and graphy =to write; i.e., writing in color) is used.

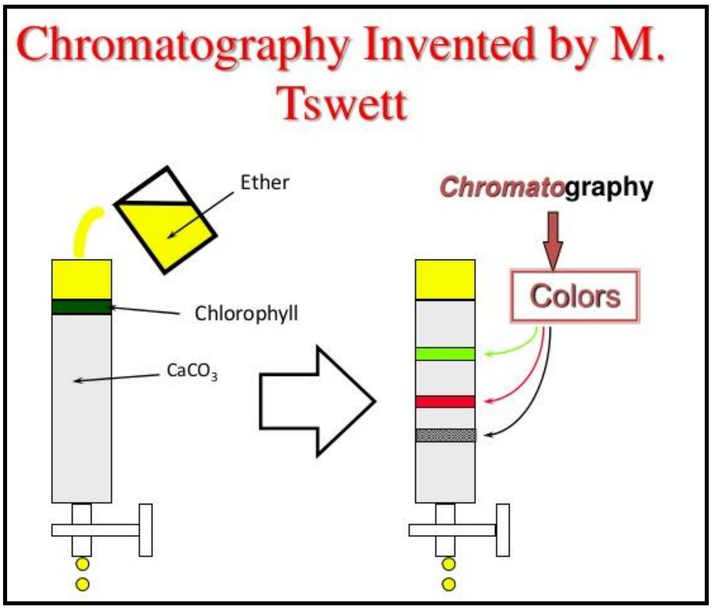


Figure 1: Column Separation Experiment

Chromatography can be defined as “a technique used for separation of a different compounds mixture using certain stationary phase (column) carrying by certain mobile phase”.

Or it is “the process (Adsorption) in which the mix. of components to be separated by distribution between two phase one called mobile phase and the other called stationary phase”.

Types of chromatography:

As mentioned above that the chromatography consists of two phases (stationary and mobile phases) the types of chromatography were divided into many types according to the mobile phase used.

A. Gas Chromatography (GC or GLC).

B. Liquid Chromatography (LC).

1. High Performance Liquid Chromatography (HPLC).
2. Ultra Performance Liquid Chromatography (UPLC).
3. Ion Chromatography (IC).
4. Thin layer Chromatography (TLC)

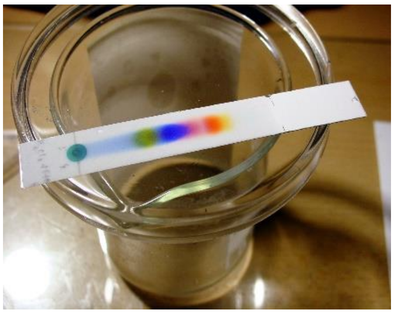


Figure 2: TLC Plate

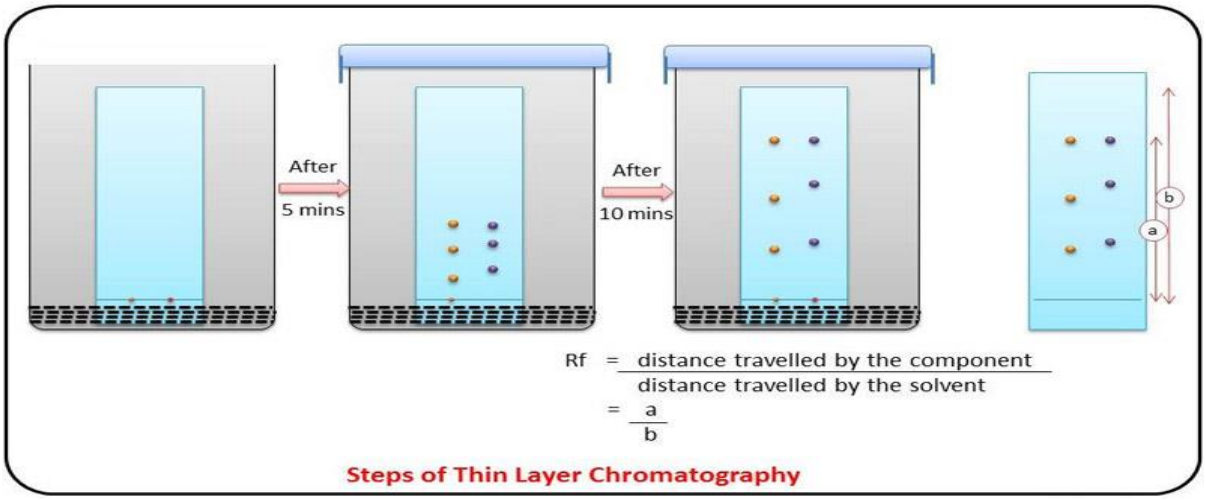


Figure 3: Steps of Thine Layer Chromatography

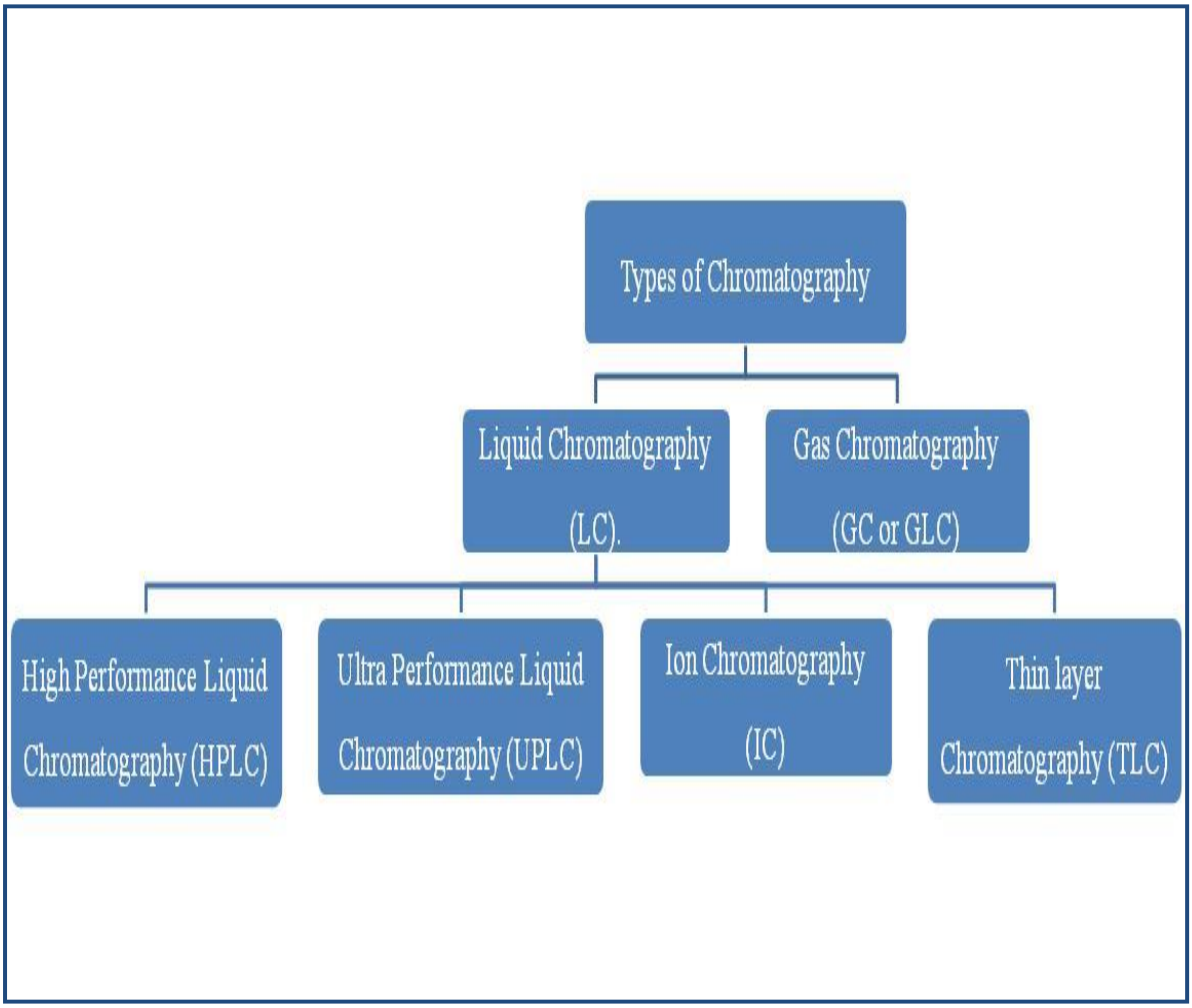


Figure 4: Types of chromatography

A. Gas Chromatography (GC or GLC):

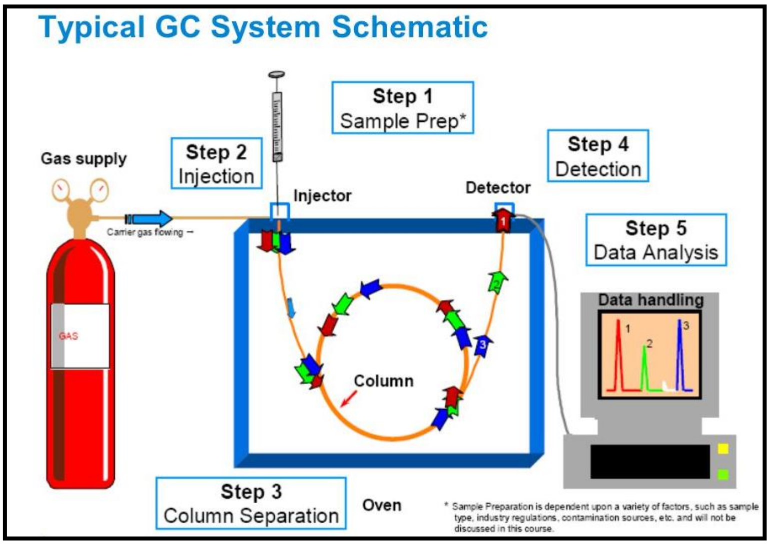


Figure 5: Schematic Diagram of GC System

- **<u>Sample inlet:</u>**

The sample introducing can be done either manually or via auto sampler. The auto sampler consists of a tray carrying the samples extracts (vials) and injection tower moves mechanically through software and contains the injection syringe.

The other part of the sample inlet system is the injection port which contains injection septum which is made from chemically inert and thermally stable silicon rubber to prevent the sample get out from the glass liner and maintain the desired pressure. The other part of the injection port system is the injection liner in which the sample is mixed with the mobile phase (carrier gas). The injection liner must be inert and highly resistant towards pressure and temperature. The injection liner is made from glass and coated to be inert and it had different shapes according to the application like (liner with goose nick, liner with two goose nick, straight liner and liner with or without glass wall). In gas chromatography the mobile phase (carrier gas) is usually an inert gas such as N_2, H_2 or He. He gas is the most commonly used as carrier gas in about 90% according test methods.

Also, there is a heater which is very important to evaporate the sample before going to the column. This evaporation is carried out inside the linear and the set up of the injection port temperature depends on the method of analysis.

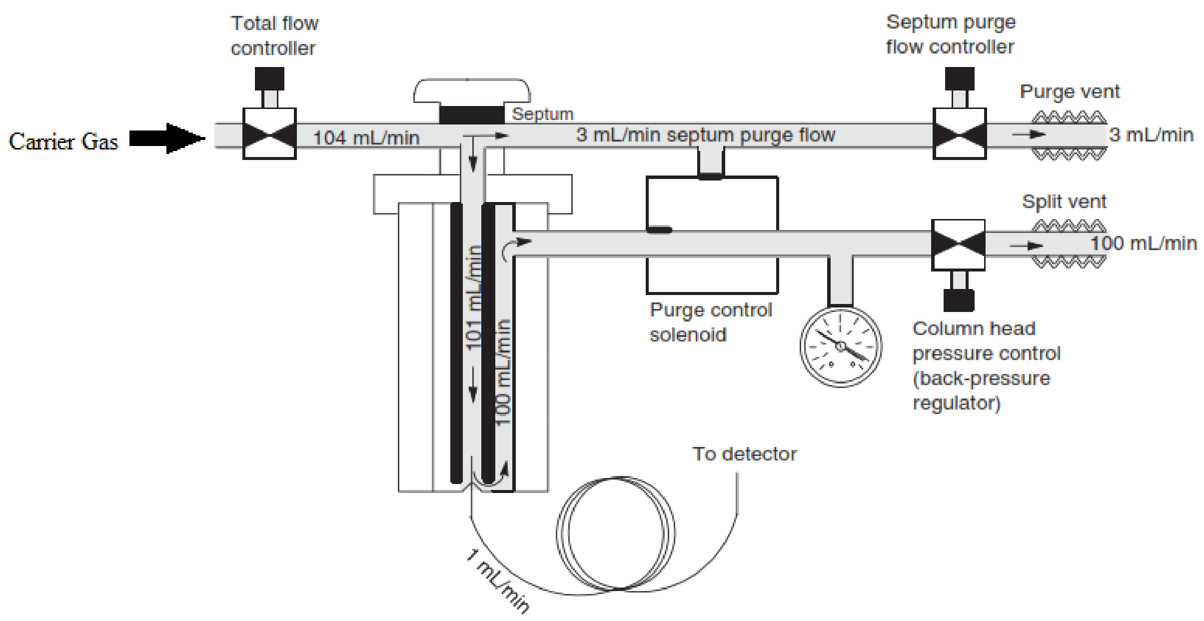


Figure 6: Schematic Diagram of Injection Port

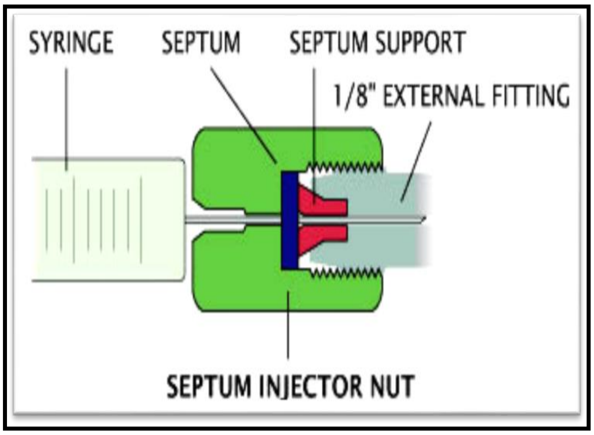


Figure 7: Septum injection nut

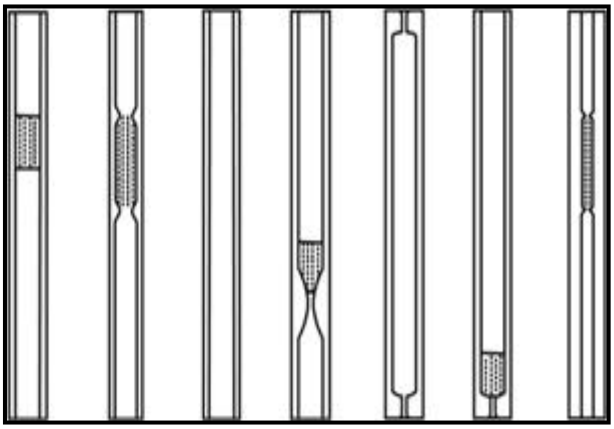


Figure 8: Types of glass linear

Oven and column:

The GC oven is the place that contains the separation column. The temperature of the oven is controlled by software (thermal program). This thermal program can be changed from application to another according to the test method.

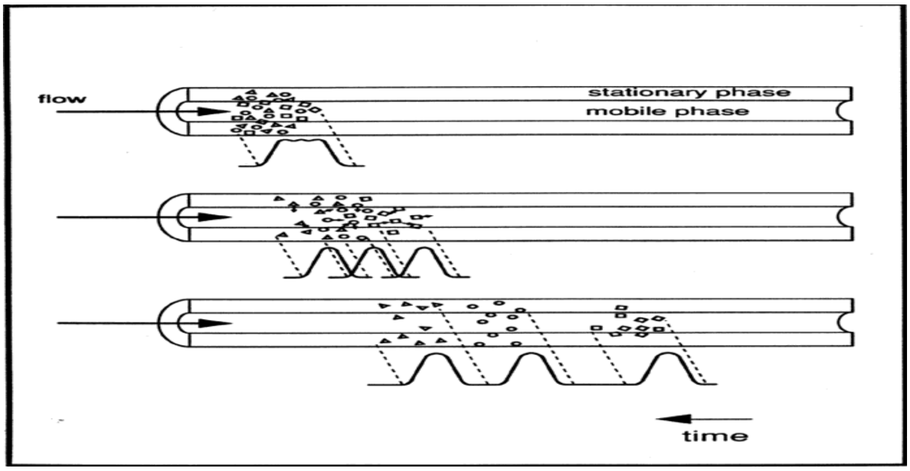


Figure 9: Separation Process

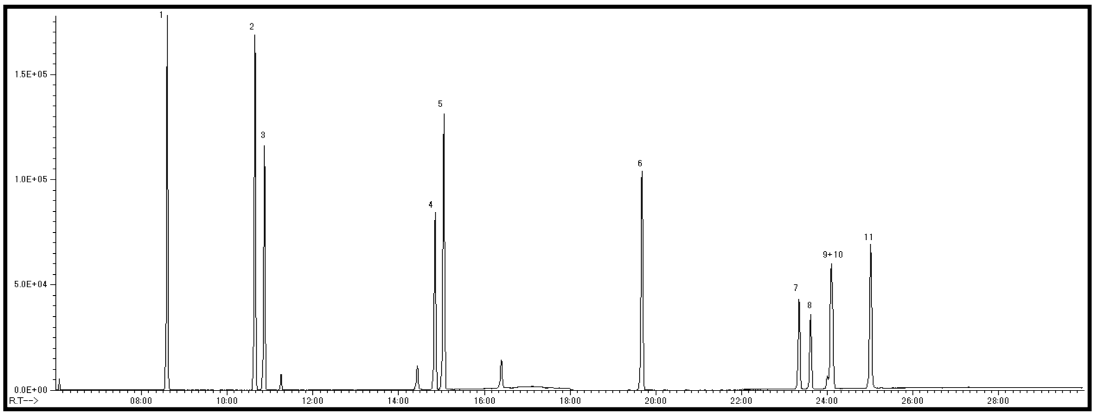


Figure 10: Chromatogram

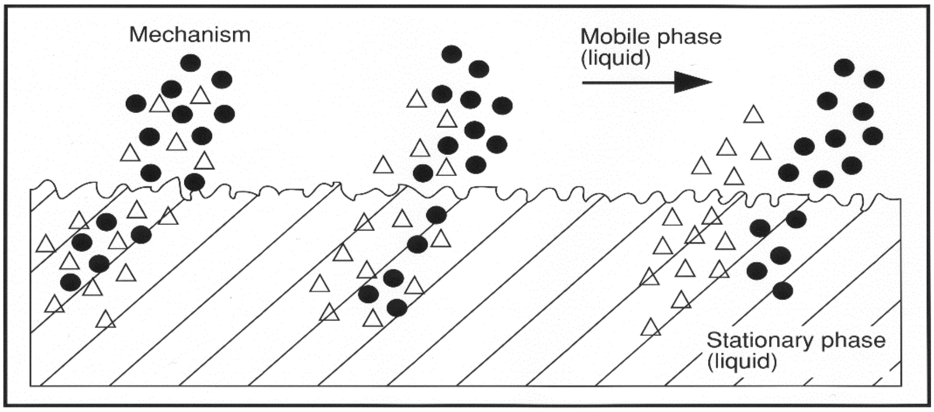


Figure 11: Separation Mechanism

There are two types of columns used in the GC applications. These two types are:

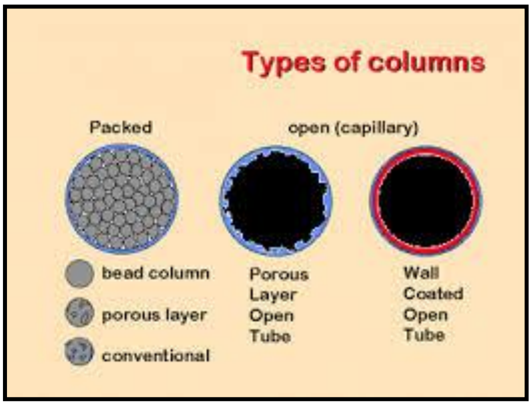


Figure 12: Types of GC Columns

- Conventional Packed column:

Packed columns are usually constructed from stainless steel or Pyrex glass. They are usually of 2 to 4 mm I.D. and 1 to 4 meters long and, packed with a suitable adsorbent, are mostly used for gas, essential oils, and flavors analyses.

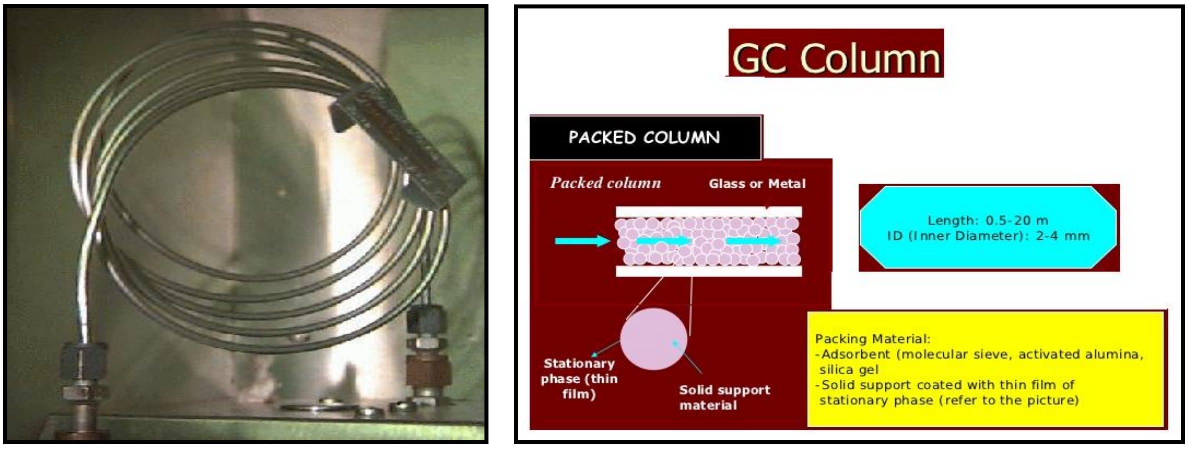


Figure 13: Conventional Packed column

- Capillary Column:

In capillary GC, the stationary phase is typically a polymer film that is 0.25–5 µm thick (see Figure 11). It is coated on the interior walls of a fused silica capillary column with an inner diameter of approximately 0.5 mm or smaller. The column is usually 10–60 m (30–180 ft) long.

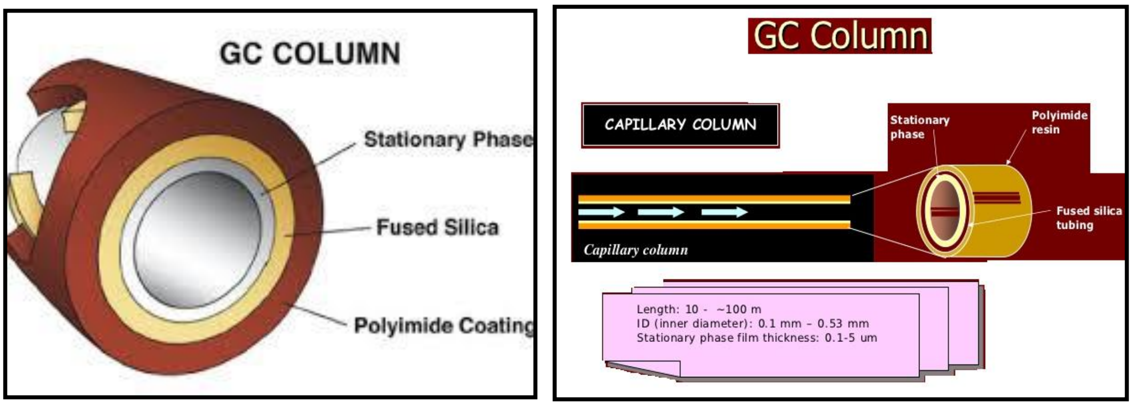


Figure 14: Schematic Diagram of the GC Capillary Column

Figure15: GC Capillary Column

Detector

The main task of the detector is to detect the eluted analytes from the column. There are a variety of detectors available for gas chromatographs, each with their own strengths and limitations. They all take advantage of particular characteristics or properties of the analyte molecules:

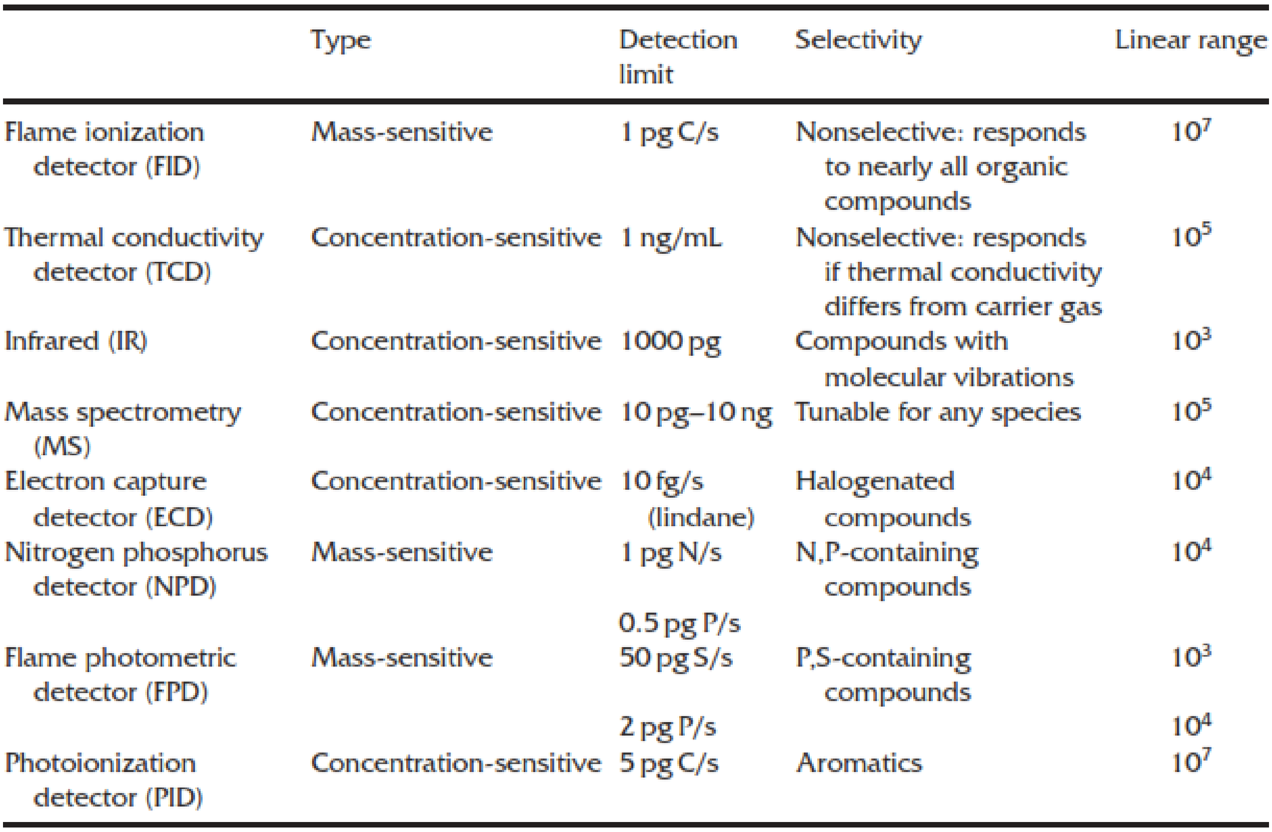
- Thermal conductivity.
- Ability to burn in a flame.
- Absorption of IR radiation.
- Absorption of electrons.

The best detector for a given application depends on the analytes, their expected concentrations, and the information about the sample that is desired.

> **"The ideal chromatographic detector gives very good S/N for only the compounds of interest at the concentration you are working at, has an acceptably wide linear range, and is insensitive to changes in operating variables"**
>
> (Prof./ Peter Carr, University of Minnesota)

Types of Detectors:

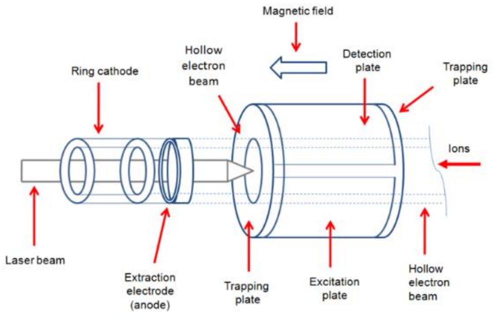
Table 1:Types of Detectors and their characteristics



	Type	Detection limit	Selectivity	Linear range
Flame ionization detector (FID)	Mass-sensitive	1 pg C/s	Nonselective: responds to nearly all organic compounds	10^7
Thermal conductivity detector (TCD)	Concentration-sensitive	1 ng/mL	Nonselective: responds if thermal conductivity differs from carrier gas	10^5
Infrared (IR)	Concentration-sensitive	1000 pg	Compounds with molecular vibrations	10^3
Mass spectrometry (MS)	Concentration-sensitive	10 pg–10 ng	Tunable for any species	10^5
Electron capture detector (ECD)	Concentration-sensitive	10 fg/s (lindane)	Halogenated compounds	10^4
Nitrogen phosphorus detector (NPD)	Mass-sensitive	1 pg N/s 0.5 pg P/s	N,P-containing compounds	10^4
Flame photometric detector (FPD)	Mass-sensitive	50 pg S/s 2 pg P/s	P,S-containing compounds	10^3 10^4
Photoionization detector (PID)	Concentration-sensitive	5 pg C/s	Aromatics	10^7

1. Electron Capture Detector

- The Electron Capture Detector (ECD) is selective to electronegative compounds, especially chlorinated, fluorinated, or brominated molecules. As examples of these compounds are the chlorinated pesticides, Trihalomethanes, Haloacetic acids, and Dalapon. It is sensitive to some of these compounds in the parts per trillion (ppt).
- The ECD detector requires nitrogen or argon / 5% methane to operate. The ECD detector consists of a stainless steel cylinder containing 5 millicuries of radioactive Ni^{63} in an oven enclosure that is thermostatically controllable from ambient temperature to 375°C. Since the detector contains only 5 millicuries of Ni^{63},the ECD is covered by a “General License”



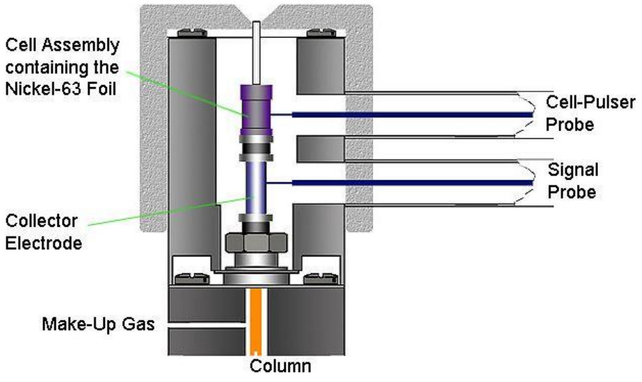


Figure 16: Schematic Diagram of (ECD)

- **Theory of Operation**

- The radioactive Ni^{63} sealed inside the ECD detector emits electrons (beta particles) which collide with and ionize the make-up gas molecules nitrogen.
- This reaction forms a stable cloud of free electrons in the ECD detector cell.

$N_2 \xrightarrow{\beta} N_2^+ + e^-$ ……..eq$^{\underline{n}}$ (1)

$AM + e^- \longrightarrow AM^-$ ……....eq$^{\underline{n}}$ (2)

$AM^- + N_2^+ \longrightarrow AM + N_2$ ……..eq$^{\underline{n}}$ (3)

- In an electron capture detector (ECD), column effluent is passed through a stream of electrons produced by a radioactive source (Ni^{63}). Analytes passing through the detector absorb these electrons.
- In the absence of analytes, a constant current between the radiation source and a collector anode is developed When analytes that absorb electrons are present, the measured current decreases. Thus, a. chromatogram is created by measuring the current versus time.

2. Thermionic Detector :

- This detector may be called Nitrogen-Phosphorus Detector (NPD) or Thermal Sensitive Detector (TSD) also.
- It has a linear response selective to organic compounds containing nitrogen and/or phosphorus (e.g. Triazine pesticides).
- The NPD also responds to normal hydrocarbons, but approximately 100,000 times less than nitrogen or phosphorus containing compounds.
- Due to its selectivity and sensitivity, the Thermionic Detector is often used to detect pesticides, herbicides, and other trace compounds containing nitrogen and/or phosphorus.

- Helium is the carrier gas of choice for the Thermionic Detector, especially when other detectors are installed on the same GC.
- The Thermionic Detector is similar in design to the FID, except it uses a thermionic bead to generate ions in hydrogen and air plasma.
- Thermionic Detector uses a stainless steel jet to deliver sample-laden carrier gas and hydrogen gas to the detector, and a positively charged collector electrode that also serves as the detector exhaust.
- The Thermionic bead is positioned between the jet and the collector electrode.

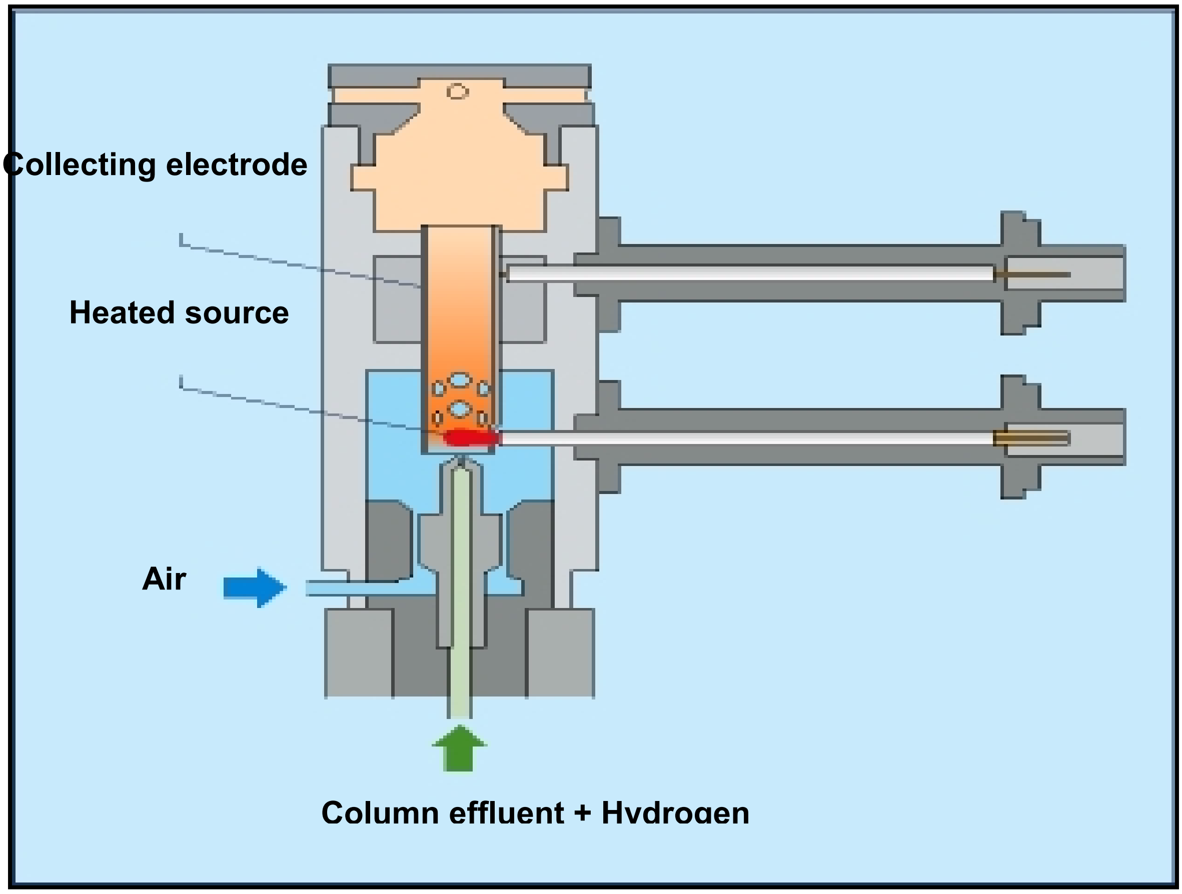


Figure 17: Schematic Diagram of Thermionic Detector

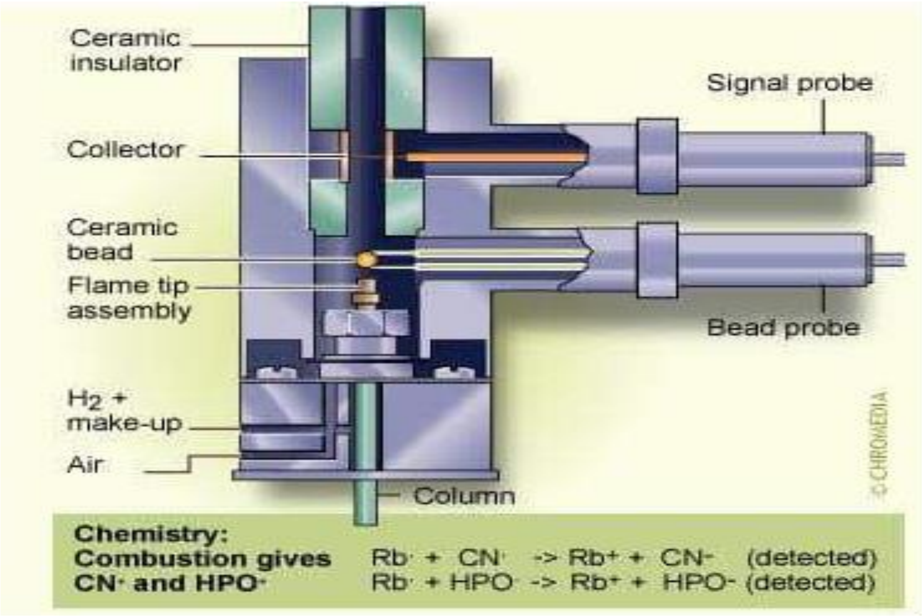


Figure 18: Schematic Diagram of Thermionic Detector

- **Theory of Operation**

- Inside the Thermionic detector body, an electrically heated thermionic bead is positioned between the jet orifice and the collector electrode.
- The bead is coated with an alkali metal which promotes the ionization of compounds that contain nitrogen or phosphorus.
- Hydrogen and air flows create hydrogen plasma around the hot Thermionic bead.
- When molecules containing nitrogen or phosphorus enter the plasma from the column and jet orifice, they undergo a catalytic surface chemistry reaction, producing thermionic electrons.
- The resulting ions are attracted to a positively charged collector electrode, then amplified and output to the data system.
- The hydrogen to air ratio is too lean to sustain a flame, therefore minimizing hydrocarbon ionization and contributing to the Thermionic detector’s selectivity.

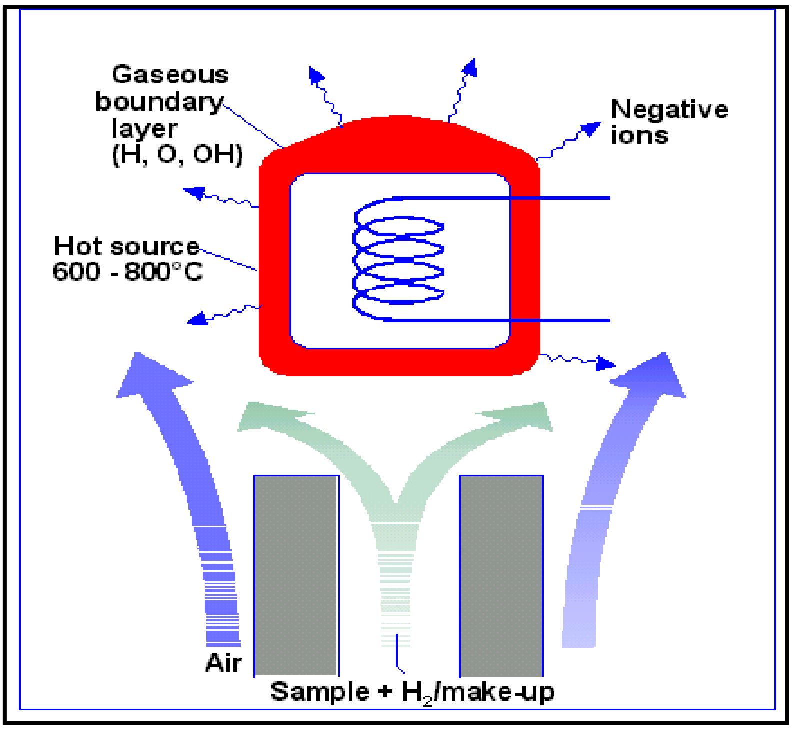


Figure 19: Thermionic detection mechanism

Sample Decomposition ⟶ Electronegative products (e.g. NO_2, CN, PO_2)

Electronegative species + Hot Source ⟶ Negative Ions

3. Mass Selective Detector (MSD)

Mass selective detector is a tunable detector for any species with a very low limit of detection (0.25 – 100 pg) and very high selectivity. It is used in case of qualitative analyses which give useful information about the molecular weight of unknown compounds using Mass spectra library. Also it is used in case of quantitative analyses.

- **Theory of Operation**

- It depends on the fact that when chemical compound is suffering from ionization it transform into fragments.
- These fragments are specific for their parents (i.e. original compound).

- These fragments have certain mass and charges.
- By classifying these fragments according to their mass and charge ratios (m/z) we can identify the unknown compound.

- The Vacuum System

The MSD unit must be operated under vacuum at least from (10^{-4} – 10^{-6} Torr). This vacuum gives an O_2, CO_2, H_2O, electric arc free path which maintains high sensitivity.

This vacuum is achieved by using two consecutive pumps. The first is rotary pump which serves as rough pump. It can produce a vacuum of (10^{-2} - 10^{-4} Torr). The second is the Turbo molecular or diffusion pump which is used to achieve vacuums in the (10^{-5} Torr) range.

- Components of (MSD):

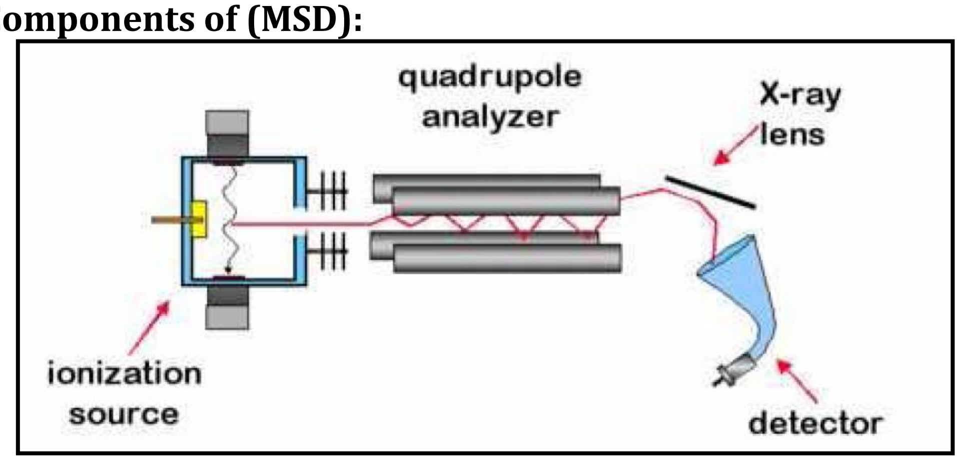


Figure 20: Schematic Diagram of MSD

Th mass selective detector consists of the following:

a) Ion source

There are many types of ion sources can be used for ionization and fragmentation. One of these ionization sources is the electron ionization (EI) in which the compound is bombarded by a beam of electrons causing ionization and then the compound is fragmented.

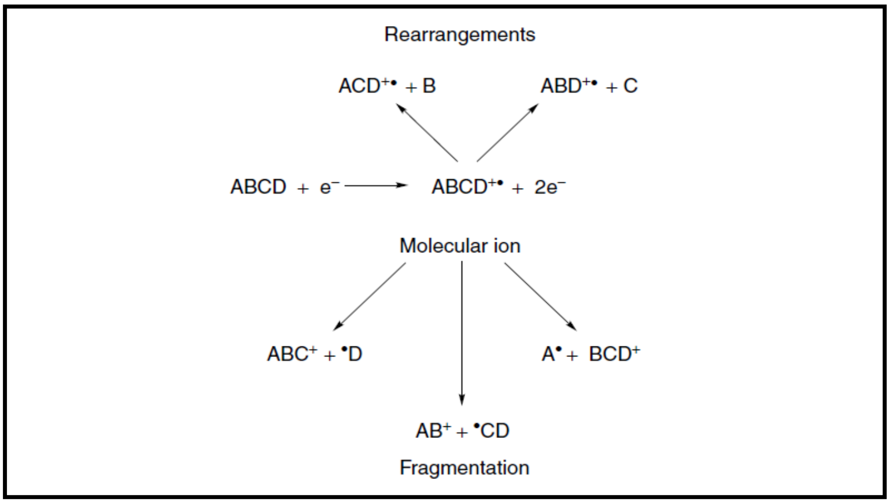


Figure 21: Electron Ionization Process

Another type is chemical ionization (CI) in which we use an atom instead of beam of electrons. There are another types like fast atom bombardment (FAB), electron sprays ionization (ESI) and atmospheric pressure chemical ionization (APCI). The selecting of the ion source depending on the technique which will be used and the type of compound which will be detected.

$$\begin{aligned}
CH_4 + e^- &\longrightarrow CH_4^{+\bullet} + 2e^- \\
CH_4^{+\bullet} &\longrightarrow CH_3^+ + H^\bullet \\
CH_4^{+\bullet} + CH_4 &\longrightarrow CH_5^+ + CH_3^\bullet \\
CH_3^+ + CH_4 &\longrightarrow C_2H_5^+ + H_2 \\
CH_5^+ + M &\longrightarrow MH^+ + CH_4
\end{aligned}$$

Figure 22: Chemical Ionization Process

b) <u>Analyzer (mass filter)</u>

The analyzer (mass filter) is an important part of the MSD due to its role. The analyzer is used to separate ions (fragments) within a selected range of mass-to-charge (m/z) ratios. There are three types of analyzers quadrupole, ion trap, and time of flight. Each type of these analyzers has advantages and disadvantages toward the selectivity and specificity. Also each of them is highly recommended for certain compounds and analytical ranges.

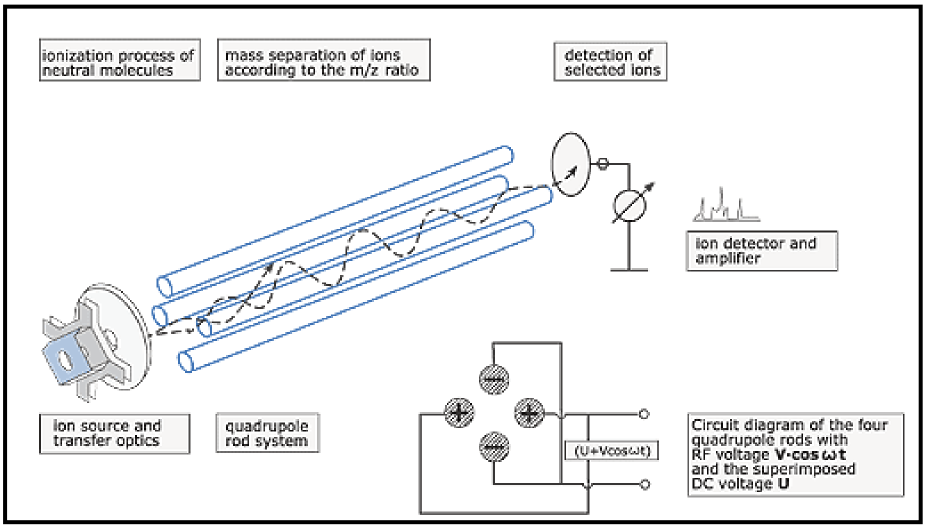


Figure 23: Schematic Diagram of Quadripole Analyzer

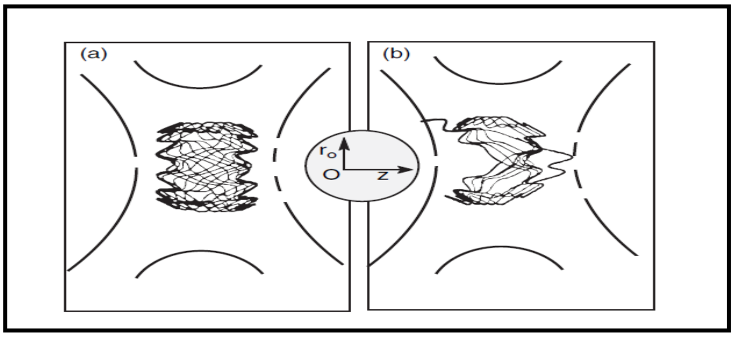


Figure 24: Schematic Diagram of Ion Trap Analyzer

c) Detector for analyte detection.

There are two types of detectors used in MS unit, electron multiplier and photomultiplier tube. Electron multiplier is more sensitive than photomultiplier but its life shorter than photomultiplier.

- **Electron Multiplier**

An electron multiplier is made up of a series of dynodes maintained at ever increasing potentials. Ions strike the dynode surface, resulting in the emission of electrons. These secondary electrons are then attracted to the next dynode where more secondary electrons are generated, ultimately resulting in a cascade of electrons.

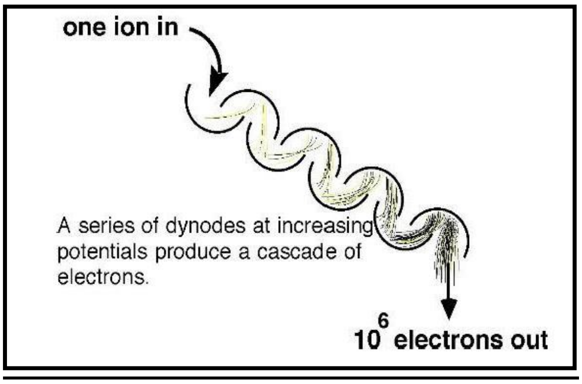


Figure 25: Schematic Diagram of Electron multiplier made up of discrete dynodes series

Electron multipliers can also be made from continuous dynode materials rather than discrete dynodes. This glassy material contains lead that provides conductivity comparable to the resistor chain in the discrete dynode electron multipliers.

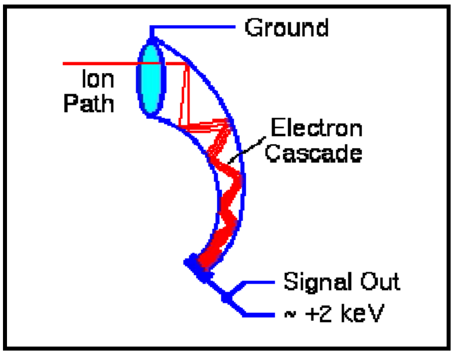


Figure 26: Schematic Diagram of Electron multiplier made up of continuous dynode

B. Liquid Chromatography

Liquid chromatography is a technique of separation depends on the polarity of the analytes (e.g. Carbamates Pesticides) and the polarity of the mobile phase which is a liquid.

High Performance Liquid Chromatography (HPLC)

One of the most famous liquid chromatographic instruments is the High Performance Liquid Chromatography (HPLC). A schematic diagram of (HPLC) system is shown in (Figure 23).

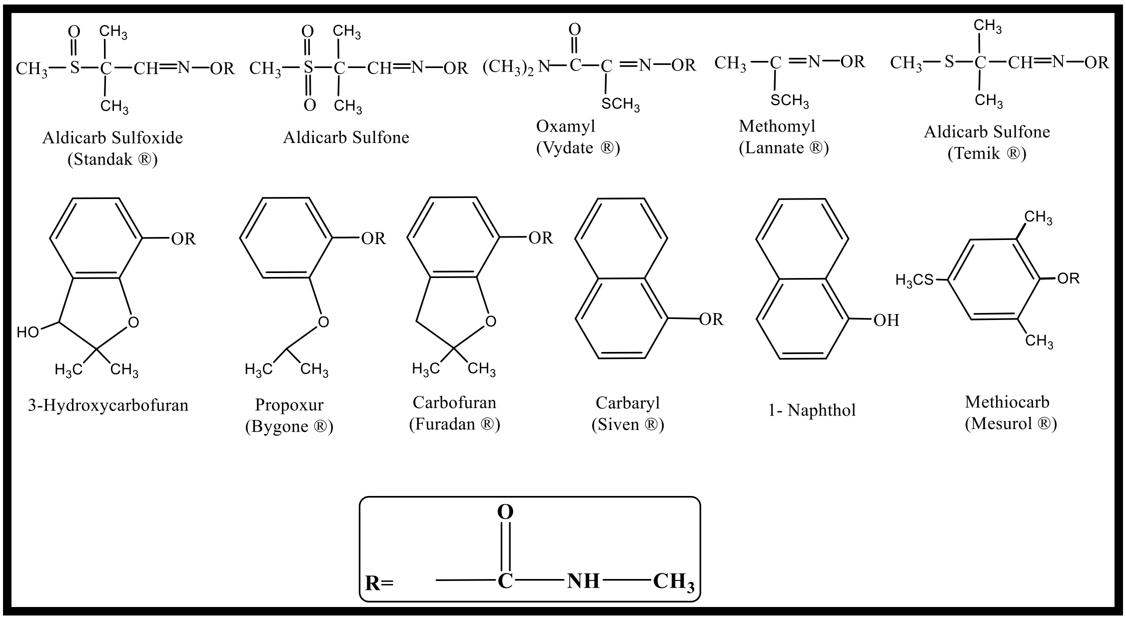


Figure 27:Carbamates Pesticides

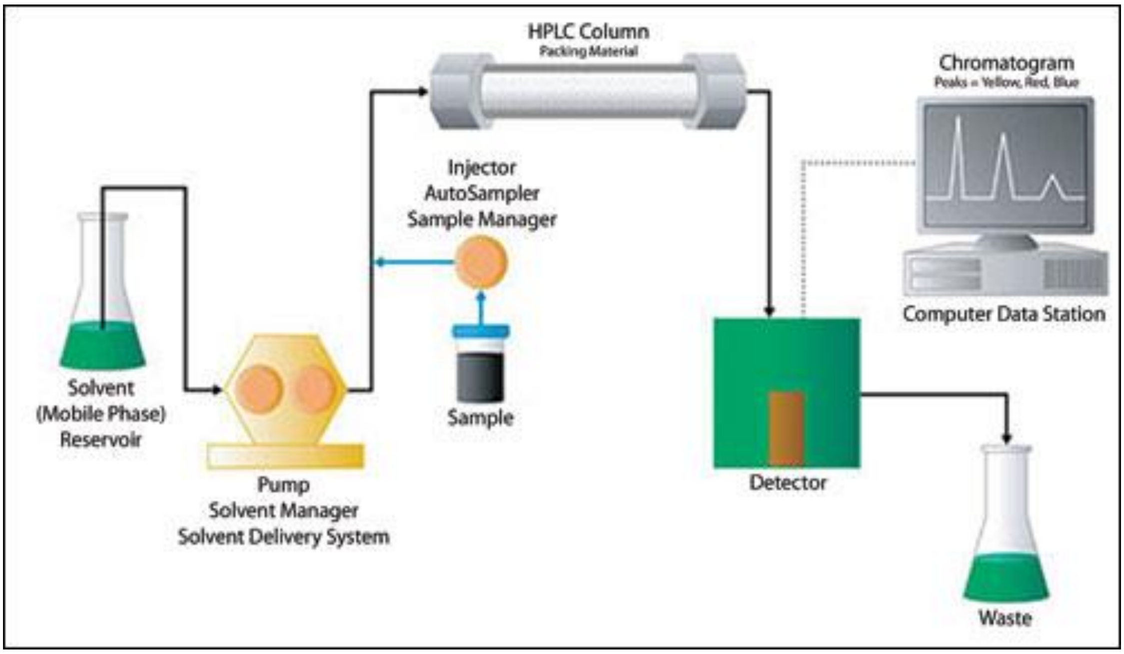


Figure 28: Schematic Diagram of HPLC System

- **Components of HPLC:**

- **Solvent Reservoir:**

Solvent reservoir is the place containing the mobile phase (e.g. methanol/water mix, ethyl ether/water mix, acetonitrile/water mix).

- **Pump:**

The Solvent Delivery System should fortify the following requirements:

- Stable flow with minimal pulsation
- Wide flow rate range
- High pressure capability
- Chemically inert
- High precision
- Low internal volume
- Resistant to corrosion by a variety of solvents.

- **Sample Manager**
- **Column (separation)**

There are many types of HPLC columns which are used in the separation of mixtures. Each column is specific in separation of certain compounds.

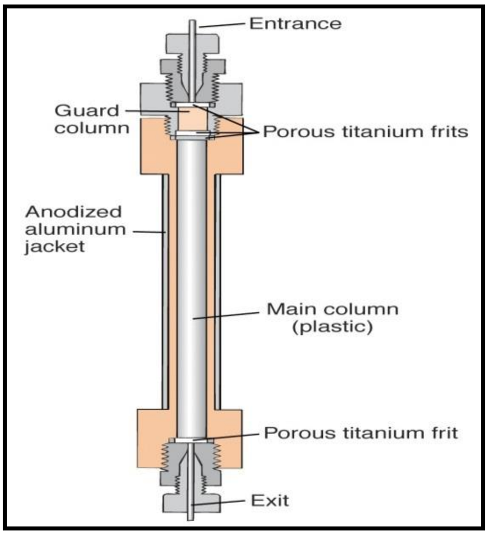


Figure 29: Schematic Diagram of HPLC column

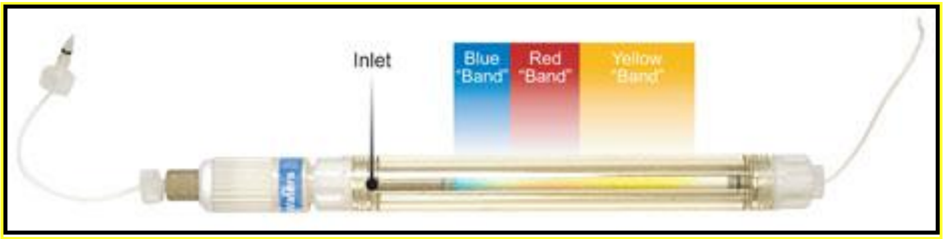


Figure 30: Glass column

Figure 31: Stainless steel

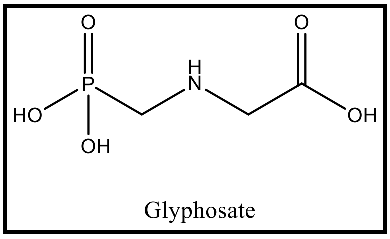
- **Detector (Identification & Quantitation):**

There are many types of detectors which are used in identification and quantitation of organic compounds separated by HPLC. Each of these detector depends on a change in certain properties (e.g. absorbance, refractive index, fluorescence, etc) to identify and quantitate each organic component.

Types of HPLC Detectors:

a) Fluorescence Detector:

This detector depends on the fluorescence character of the analytes to identify them. It converts the fluorescence of the analyzed compounds into electric current to quantify their concentrations e.g. polyaromatic hydrocarbons (PAH), glyphosate.



Glyphosate

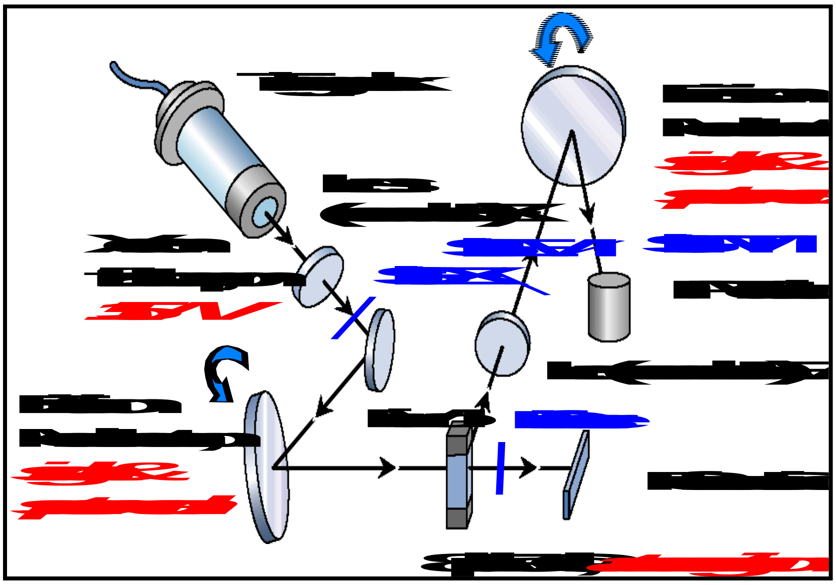


Figure 32: Schematic Diagram of Flourscence Detector

Also it could be used in identifying and quantifying non-fluorescent compounds e.g. Carbamates pesticides. This may be achieved via a side reaction carried out in post column after the separation column. In this reaction the analytes (Carbamates) are reacted with o-phethaldehyde in presence of mercaptoethanol to produce the iso-indol form of the Carbamates which has fluorescent characters.

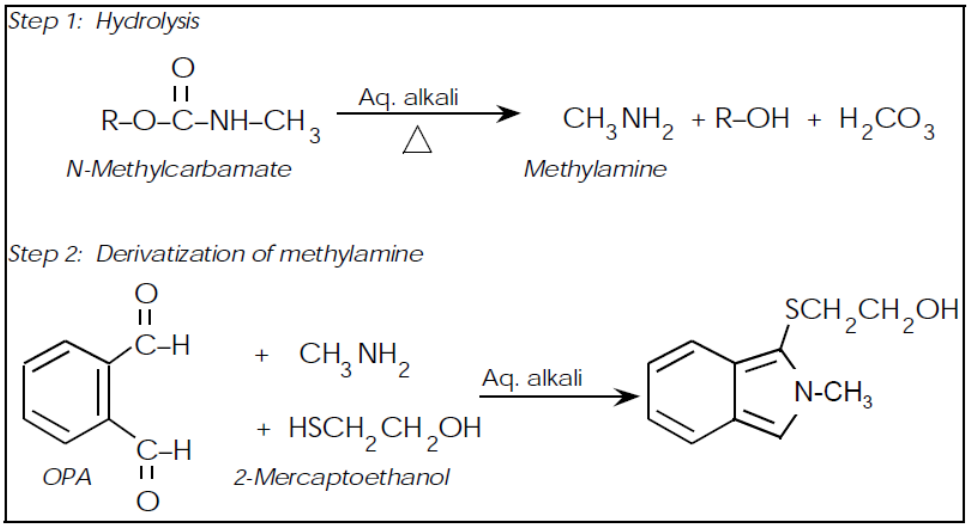
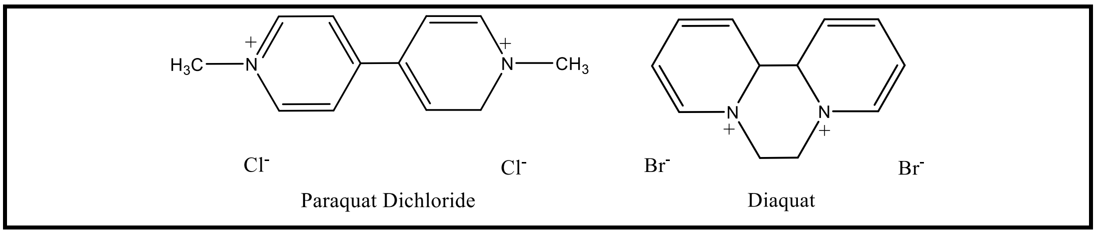


Figure 33: Scheme of Post Column Reaction

b) Diode Array Detector (DAD):

Another type of HPLC detectors is the Diode Array Detector (DAD) which is non-destructive and non-universal detector. DAD scans a range of wavelengths every second or few seconds. At each point in the chromatogram one gets a complete UV-VIS spectrum. It provides huge volumes of data and detailed spectra for each peak and each region of each peak. It considered as the most common tool for research-grade HPLC instruments. One of the most common application that carried out using Diode Array Detector is the determination of Paraquat dichloride and Diaquat.



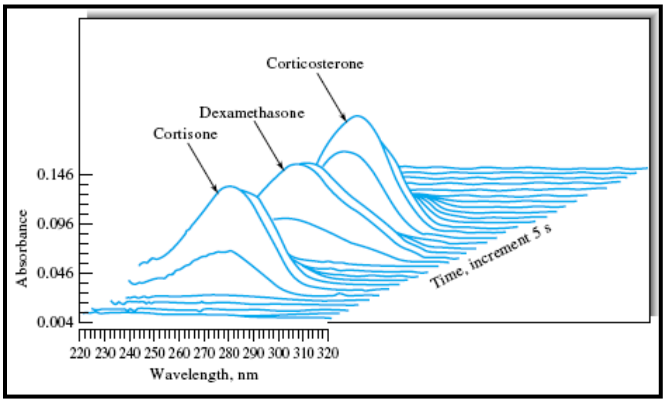


Figure 34: Absorption spectra of the Eluent from a mixture of three steroids taken at 5-seconds intervals

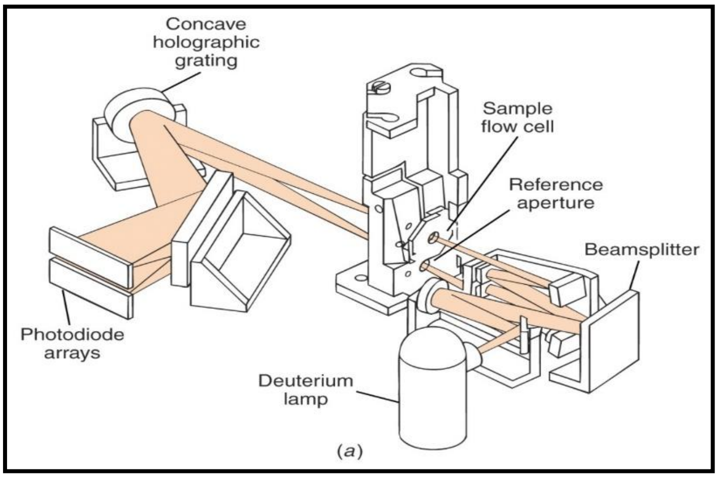


Figure 35: Schematic Diagram of Diode Array Detector

FT-IR (Fourier Transform – Infrared)

Introduction

Electromagnetic spectrum consists of a wide range of wavelengths. These wavelengths are divided into regions. These regions are ordered from the lowest wavelength to the highest as shown in figure (23). Infrared region lies between the visible and microwave regions. By convention, the infrared region is frequently divided into three sections :

- Near-infrared at frequency range (750 - 1300 nm).

- Mid-infrared at frequency range (1300 – 3000 nm).
- Far-infrared at frequency range (3000 – 10000 nm).

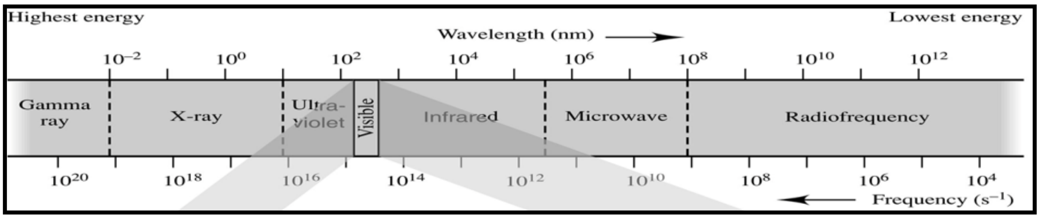


Figure 36: Electromagnetic Spectrum

The mid-infrared, or fundamental vibrational region, is the most useful area of the spectrum for analytical spectroscopy. One of its uses is the determination of total oils, grease, and total recoverable petroleum hydrocarbons in water samples.

Analytical Principle:

When a molecule absorbs infrared radiation of appropriate frequency it is excited and transport from one vibrational or rotational level to another. A graph of energy absorbed versus frequency is the absorption spectrum of the sample. This spectrum is characteristic of the particular molecule and its molecular motions .

For large molecules, the pattern of absorbance spectrum is characteristic for the functional groups in the molecule. The spectrum can be thought of as "fingerprint" of that chemical molecule, and therefore, infrared spectroscopy can be used to identify molecules (i.e., qualitative analysis). Spectroscopy can also be used for quantitative analysis because the intensity of absorption is proportional, beside other things, to the amount of the molecules present.

The main component of FT-IR spectrometer is the Michelson interferometer. The interferometer consists of a fixed mirror, a movable mirror, and a beam splitter. The beam splitter transmits half of the incident radiation to the moving mirror and reflects the other half to the fixed mirror.

The two beams are reflected by these mirrors back to the beam splitter, where they recombine. When the fixed mirror and moving mirror are equidistant from the beam splitter, the amplitudes of all frequencies are in phase and recombine constructively. This position of zero path difference (ZPD), or zero retardation, is where the interferogram center burst occurs.

As the moving mirror is moved away from the beam splitter (retarded), an optical path difference is generated. As the position of the moving mirror changes, the two beams travel different distances within the interferometer before recombining. A pattern of constructive and destructive interference is generated based on the position of the moving mirror and the frequency of the retardation.

The intensity of the radiation varies in a complicated pattern as a function of mirror movement, and the output beam is the result of modulation by the interferometer. This modulated output beam is then directed through the sample compartment to the detector. At the detector it generates a continuous electrical signal called an interferogram.

As an application of the FT-IR analyzer in the field of water analyses is the determination of oil and grease content in water samples.

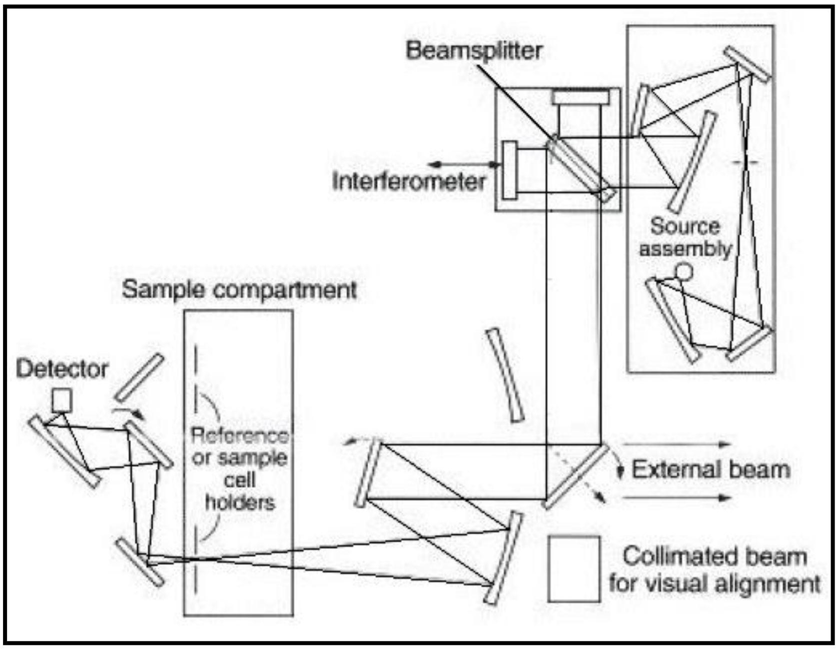


Figure 37: Schematic Diagram of FT- IR

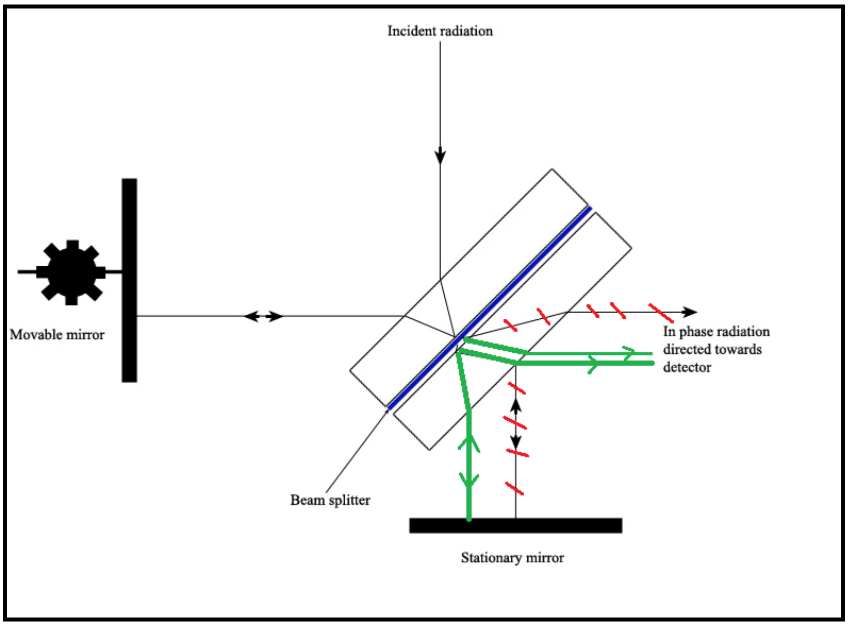


Figure 38: Schematic of the Michelson interferometer

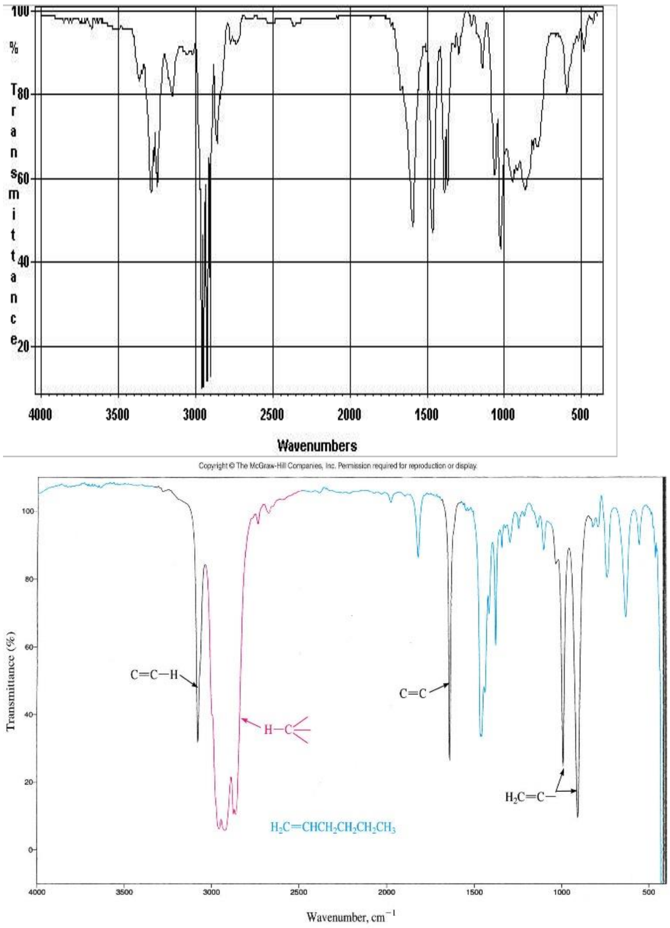


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Figure 39: Examples of FT-IR Spectra

Total Organic Carbon (TOC)

Introduction

The major component of the total organic carbon (TOC) in raw drinking water is the Natural organic matter (NOM). Natural organic matter (NOM) is found everywhere in aquatic environment. NOM is a broad term for the complex mixture of thousands of organic compounds found in water. These compounds are derived from decaying plant and animal matter. (NOM) is highly variable and relative concentrations of individual compounds can vary significantly from source to source.

The organic carbon in water and wastewater is composed of a variety of organic compounds. Total organic carbon (TOC) is a convenient and direct expression of total organic content in municipal water. Measurement of (TOC) is of vital importance to the operation of water and wastewater treatment plants. For drinking water in particular, organic compounds may react with disinfectants to produce disinfection by products.

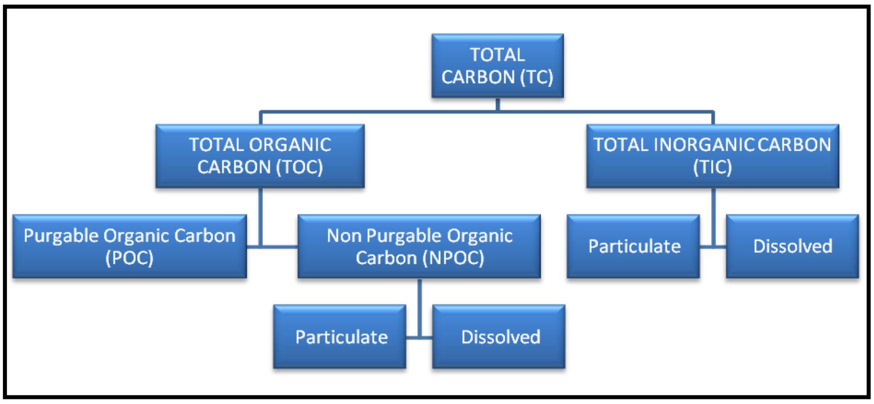

Figure 40: Components of Total Carbon in Aquatic

TOC Measurement Techniques:

The (TOC) measurements techniques depend on the conversion of the organic compound to pure carbon dioxide (CO_2) and then quantitate (TOC) by using non-dispersive infrared detector. To achieve this conversion one of the following techniques may be used:

- High temperature, catalysts, and oxygen (combustion).
- Lower temperatures (100 °C) with ultraviolet irradiation, chemical oxidants, or combinations of these oxidants (uv-persulphat oxidation).

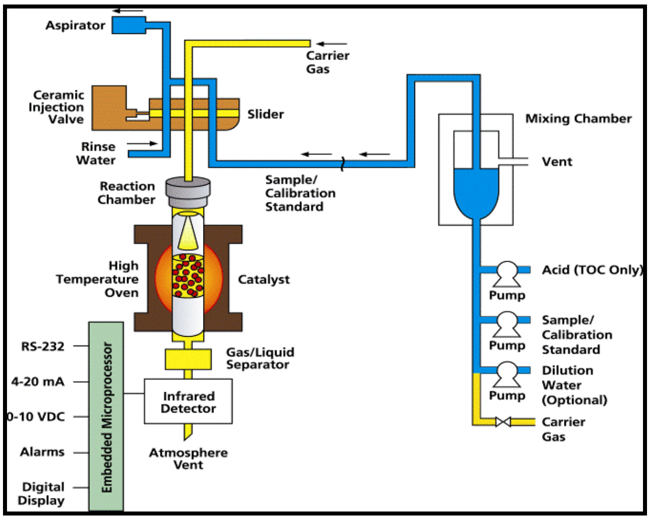

Figure 41: Schematic Diagram of Combussion TOC Analyzer

- The UV lamp emits wavelength of (185 nm) for photolysis of water.

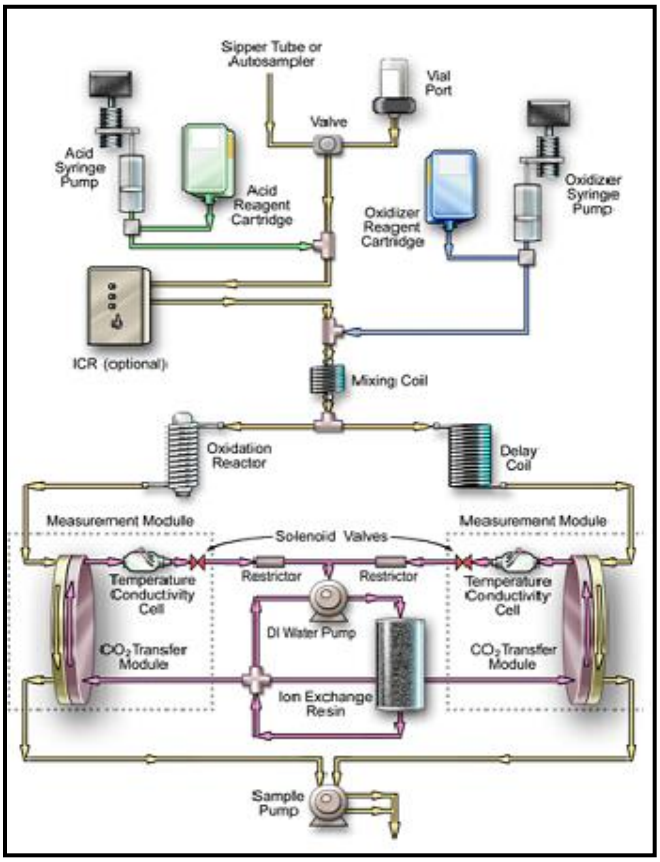

Figure 42: Schematic Diagram of uv-persulphat Oxidation TOC Analyzer

Analytical principles

The (TOC) Analyzer is based on the oxidation of organic compounds to convert the organic compounds into form carbon dioxide (CO_2) using UV radiation and a chemical oxidizing agent (ammonium per sulfate). Carbon dioxide is measured using a sensitive, selective membrane-based conductometric detection technique. For each TOC measurement, the concentration of inorganic carbon species (CO_2, HCO_3 and CO_3) is determined and, after oxidation of the organic compounds, the total carbon (TC) content of the sample is measured. The concentration of the organic compounds is then calculated from the difference between the concentrations of TC and total inorganic carbon (TIC), generally referred to simply as inorganic carbon.

$$\boxed{TOC = TC - IC}$$

Oxidation Reaction

H_2O + hע (185 nm) → $OH\bullet + H\bullet$ (1)

$S_2O_8^{-2}$ + hע (254 nm) → $2\ SO_4\bullet^{-}$ (2)

$SO_4\bullet- + H_2O$ → $HSO_4^{-} + OH\bullet$ (3)

Organic Compounds + $OH\bullet$ → $CO_2 + H_2O$ (4)

Total Organic Halogen Analyzer (TOX /AOX)

A. Introduction

the presence of the (NOM) in the surface water leads to form many halogenated organic compounds due to the use of chlorine as disinfectant during the process of water treatment.

Total organic halogen consists of three categories of organic halogen compounds. These three categories are adsorbable, extractable, and purgable organic halogens.

$$\boxed{TOX = AOX + POX + EOX}$$

Where:

TOX: Total organic halogen.

POX: Purgable organic halogen.

EOX: Extractable organic halogen.

AOX: Adsorbable organic halogen.

The major of the TOX is the adsorbable organic halogens (≈ 96%) so, in many cases the AOX refer to the TOX.

- **Analytical principles**

The determination of the total organic halogens (TOX) depends on the combustion of the organic halogen and converting them into the acidic form (HX). The acidic form determined by Argentometric-coulometric titration.

The silver anode generates silver ion (Ag^+) and one electron according to the following equation:

$$Ag^- \rightarrow Ag^+ + e^-$$

The generated silver ion (Ag^+) reacts with the halide ion (X^-) to give silver halide according to the following equation:

(Argentometry):

$$Ag^+ + X^- \dashrightarrow AgX$$

Where: X = Cl, Br, I

The generated electrons which are equal to the consumed silver ions are counted and then it transformed into concentration by the instrument software.

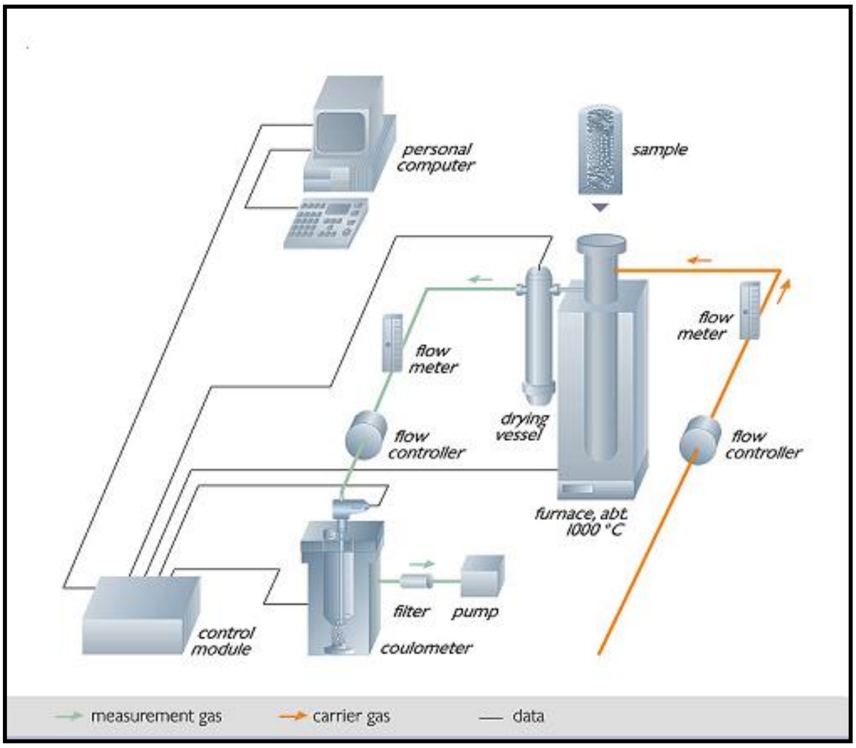

Figure 43: Schematic Diagram of TOX Analyzer

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