# GC-MS AND ITS APPLICATIONS


Presented by – *ANAMIKA BANERJEE* (RESEARCH

Gas chromatography coupled to mass spectrometry is a versatile tool to separate, quantify and identify unknown (volatile) organic compounds and permanent gases. By combining sensitivity and a high resolving power, complex mixtures can be analyzed. The information obtained can be used for detection of impurities, contamination control and improvement of for example semiconductor manu
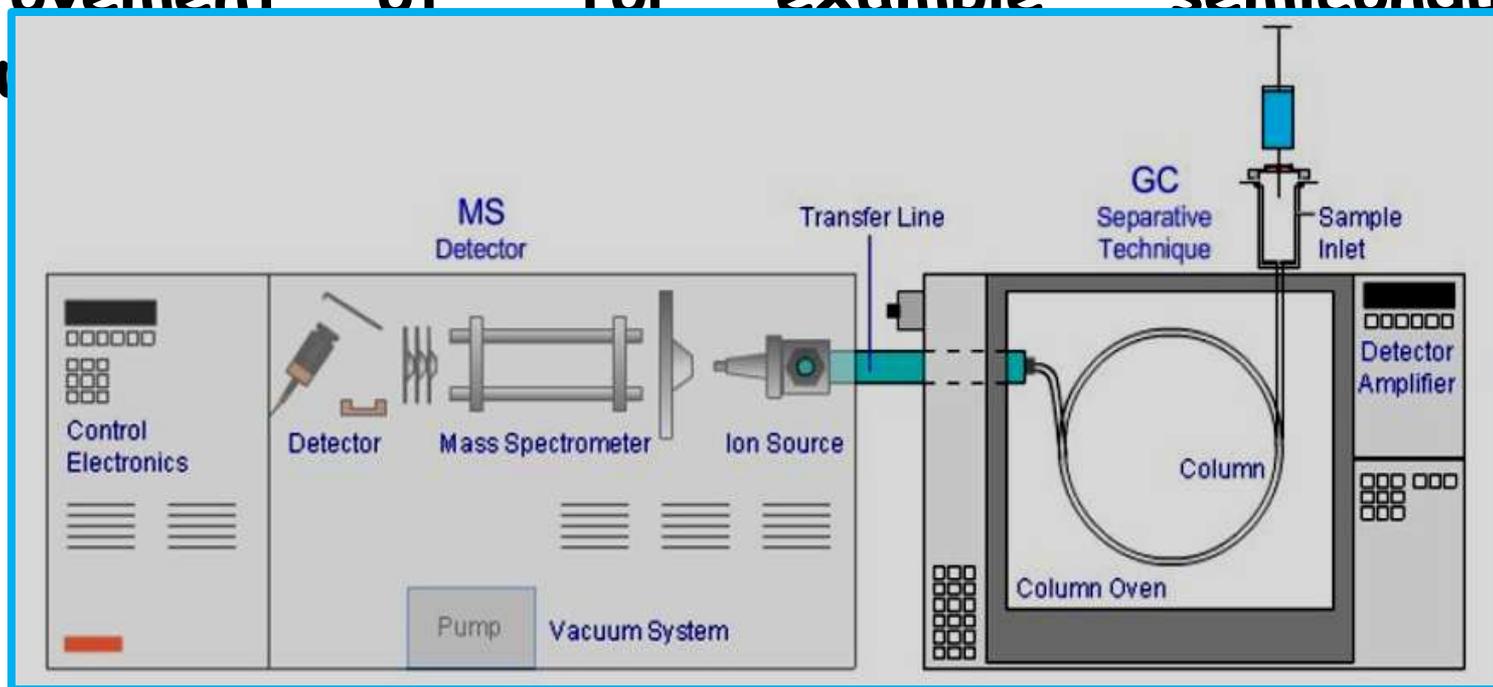
FUNDAMENTAL OF GC
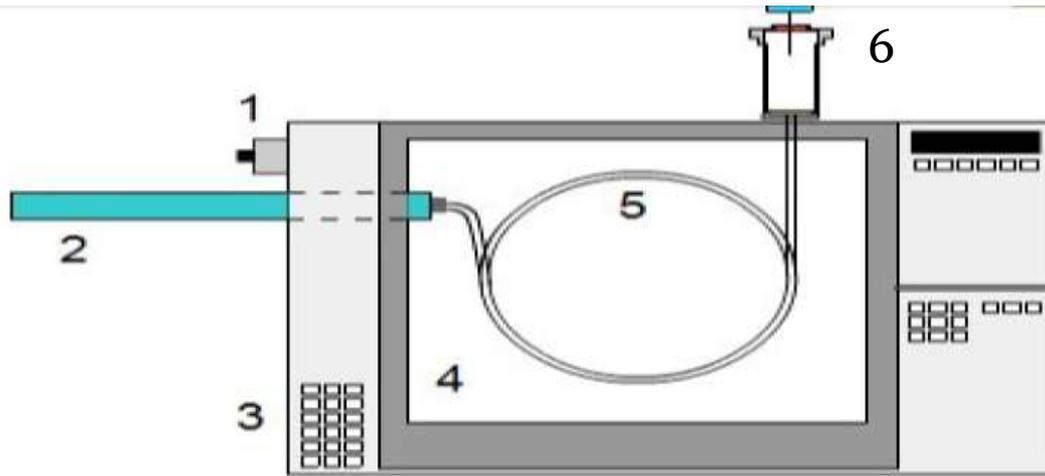
Gas Chromatography (GC) uses a carrier gas to transport sample components through either packed columns or hollow capillary columns containing the stationary phase. In most cases, GC columns have smaller internal diameter and are longer than HPLC columns.

In Gas Chromatography, the mobile phase is a gas and the stationary phase is either:

- A solid, commonly termed "Gas solid chromatography (GSC)".
- An immobilised polymeric liquid, referred as "Gas Liquid Chromatography (GLC)".

1. Gas Supply: Gas is fed from cylinders through regulators and tubing to the instrument. It is usual to filter gases to ensure high gas purity and the gas supply pressure. Required gases might include:

- Carrier – (H_2, He, N_2 – helium is most usual with MS detection)

- Make-up gas– (H_2, He, N_2 - if using an FID detector in parallel to the MS detector)

- Detector gas – (H_2 & Air – if using an FID detector in parallel to the MS detector)

2. Interface: After separation in the GC system, analyte species have to be transported to the mass spectrometer to be ionised, mass filtered and detected. The interface in modern instruments is heated to prevent analyte condensation and in some instruments will contain a device to remove carrier gas molecules to allow analyte pre-

3. Pneumatic controls: The gas supply is regulated to the correct pressure (or flow) and then fed to the required part of the instrument. Modern GC instruments have ElectronicPneumatic pressure controllers –older instruments may have manual pressure control via regulators.

4. Oven: Gas chromatography have ovens that are temperature programmable, the temperature of the gas chromatographic ovens typically range from 5oC to 400oC but can go as low as -25oC with cryogenic cooling.

5. Column: Gas Chromatography uses a gaseous mobile phase to transport sample components through columns either packed with coated silica particles or hollow capillary columns containing the stationary phase coated onto the inner wall. Capillary GC columns

are usually several meters long (10 – 120m is typical) with an internal diameter of 0.10 – 0.50mm, whilst packed GC columns tend be 1 – 5 meters in length with either 2 or 4mm internal diameter.

**6. Injector**: Here the sample is volatilised and the resulting

Weaknesses of GC:

• Requires the analyte to have significant vapour pressure between about 30atm and 300°C.

• Presents a lack of definitive proof of the nature of detected compounds. The identification process is based on retention time matching, which may be inaccurate or at worst misleading.

INSTRUMENT FUNDAMENTALS –MS

The mass spectrometer is an instrument designed to separate gas phase ions according to their mass to charge ratio (m/z) value.

mass to charge ratio (m/z):
This represents the mass of a given particle (Da) to the number (z) of electrostatic charges (e) that the particle carries. The term m/z is measured in Da/e.
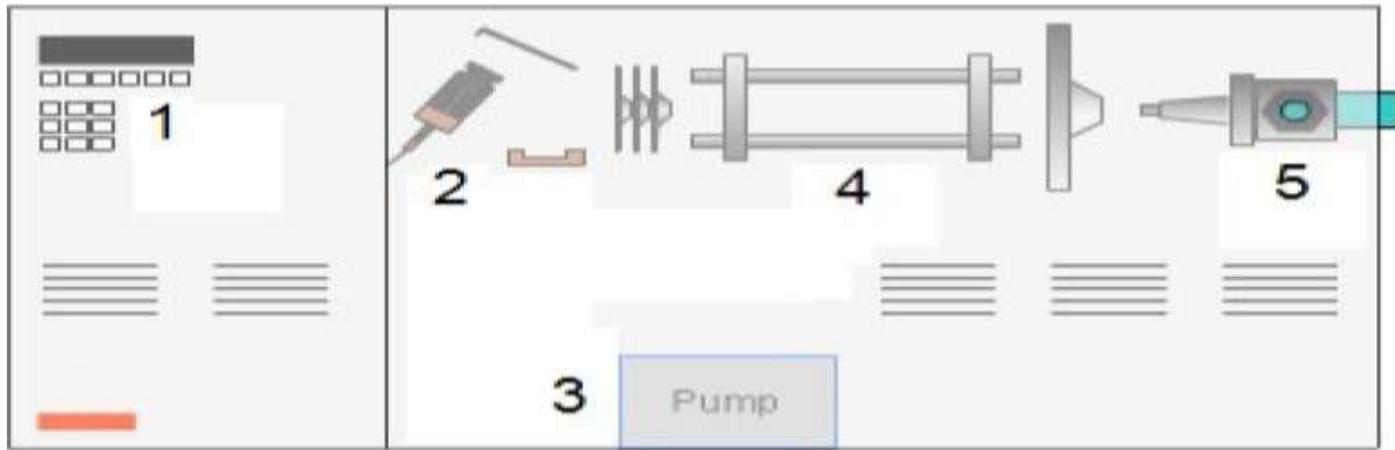
1. **Control Electronics:** The MS parameters can be selected and controlled from this panel. Modern instruments will also allow to control MS parameters from a computer by using specially designed software.

2. **Detector:** The ion beam that emerges from the mass analyzer, have to be detected and transformed into a usable signal.

   The detector is an important element of the mass spectrometer that generates a signal from incident ions by either generating secondary electrons, which are further amplified, or by inducing a current (generated by moving

3. Vacuum System: Mass analysers require high levels of vacuum in order to operate in a predictable and efficient way.

The vacuum systems of most modern GC-MS systems consist of a differentially pumped system, usually with a foreline pump establishing a 'rough' vacuum and a high vacuum pump or pumps situated on the analyser body to establish the high levels of vacuum required for effective mass to charge ratio measurement.

4. Mass Analyser: There are several very popular types of mass analyser associated with routine GC-MS analysis and all differ in the fundamental way in which they separate species on a mass-to-charge basis.

5. Ion Source: In the ion source, the products are ionized prior to analysis in the mass spectrometer.

The Coupling of GC/MS

GC-MS has the advantages of higher chromatographic resolution and higher peak capacity, a single mobile phase (helium), fewer issues with solubility and separations can be adjusted by electronic controls such as temperature and flow programming.

Today with the advent of capillary columns using relatively low carrier gas flow rates, the need for vapour concentrator devices has been eliminated. The mass spectrometer pumping system can easily deal with gas flows for direct injection into the mass spectrometer.

GC-MS Coupling
• Bieman concentrator
• Direct Introduction
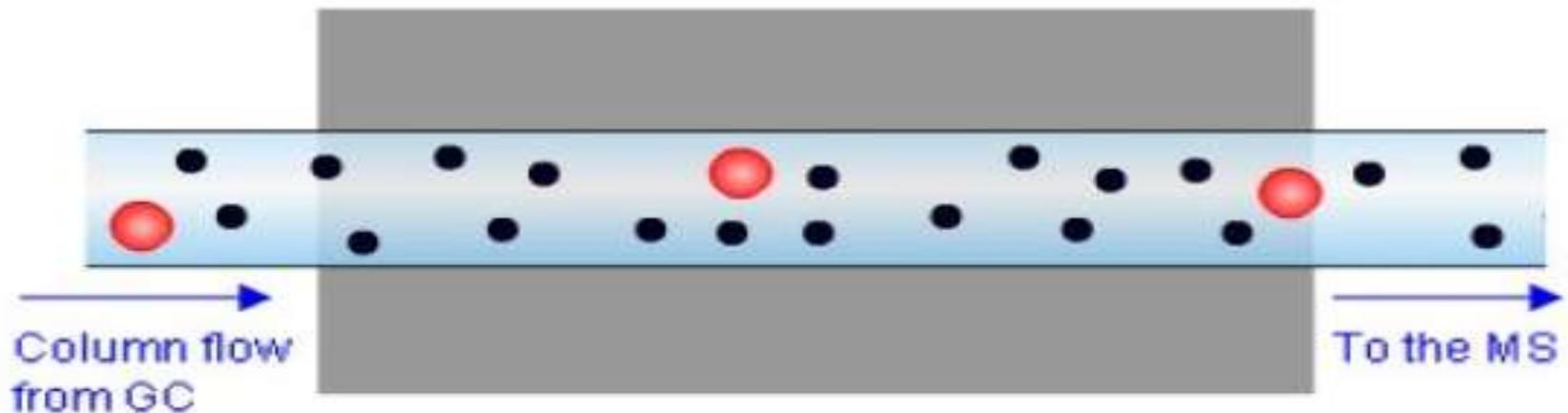
Pump
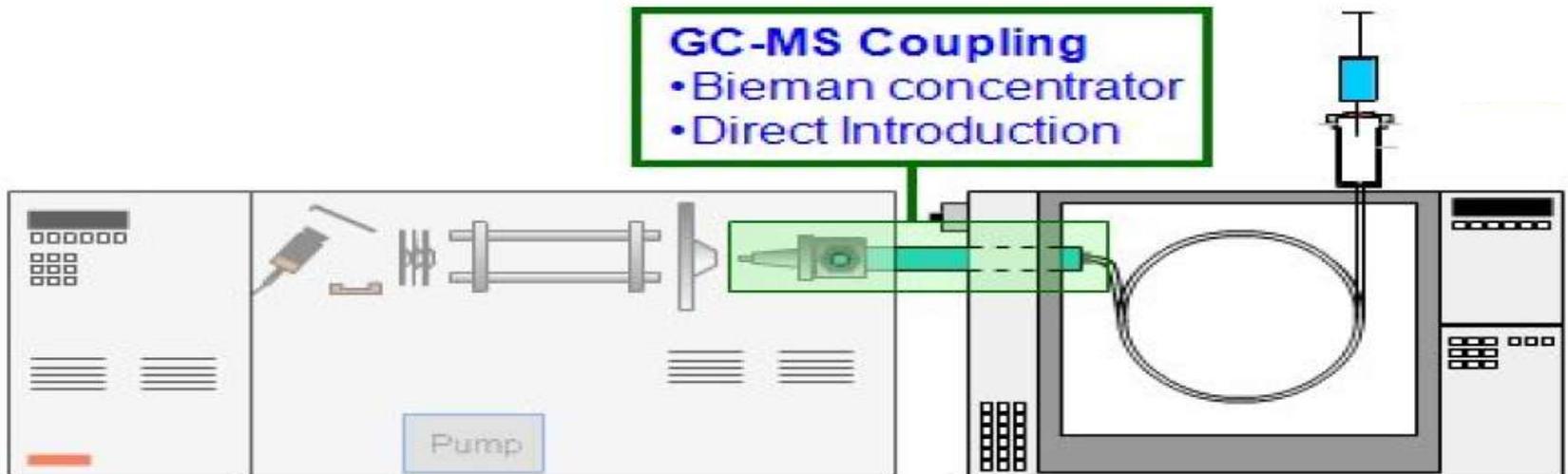
The Bieman Concentrator

The Bieman concentrator device is used with packed columns or with wide bore capillary columns at higher flow rates. In this device the carrier gas is removed in preference to the analyte and hence analyte enrichment occurs.
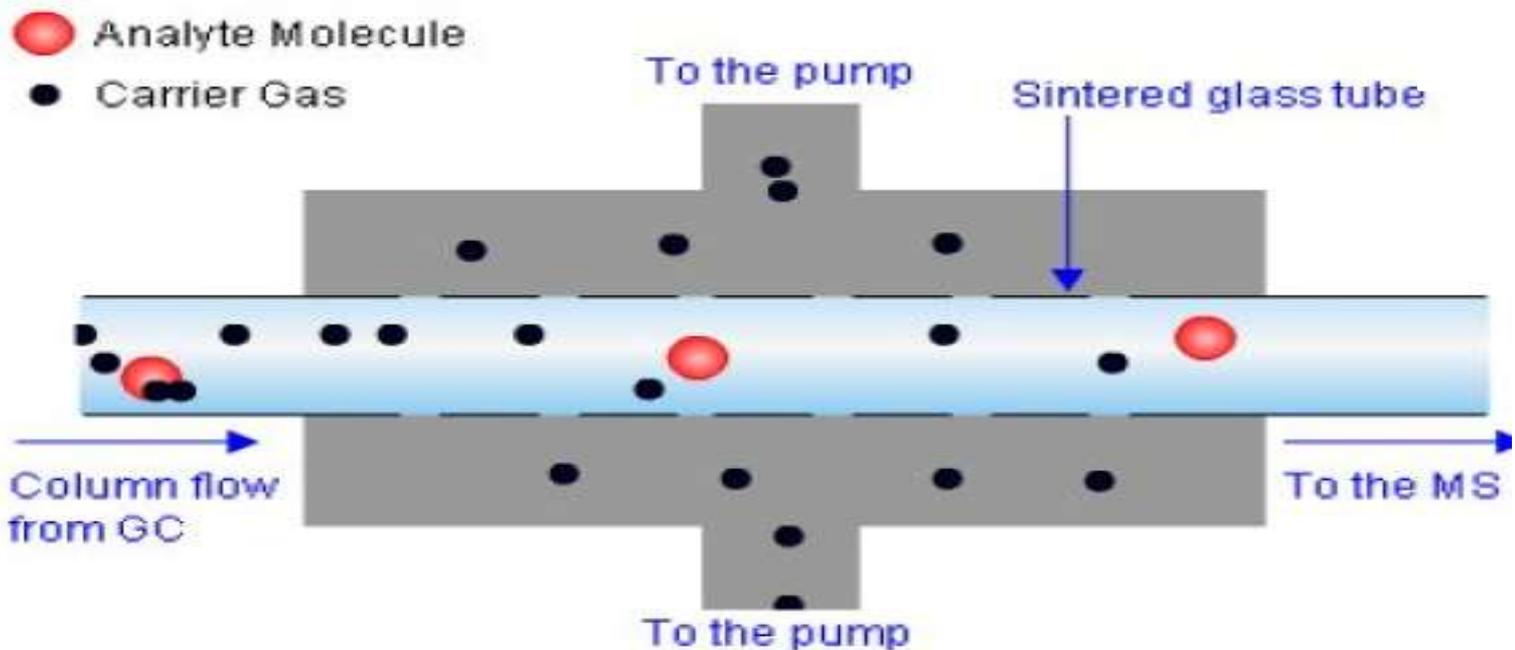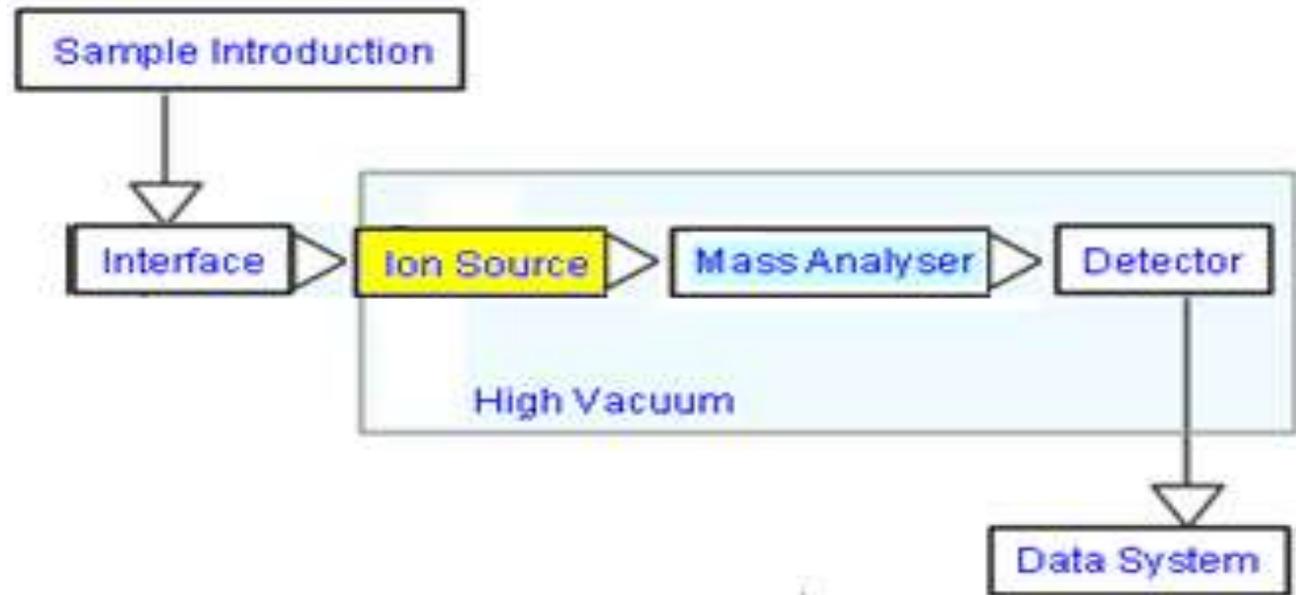
Direct Introduction

Direct introduction is typically used with capillary GC columns and most modern instruments can easily cope with flow rates up to 2 mL/min

Ionisation

Sample Introduction → Interface → **Ion Source** → Mass Analyser → Detector → Data System
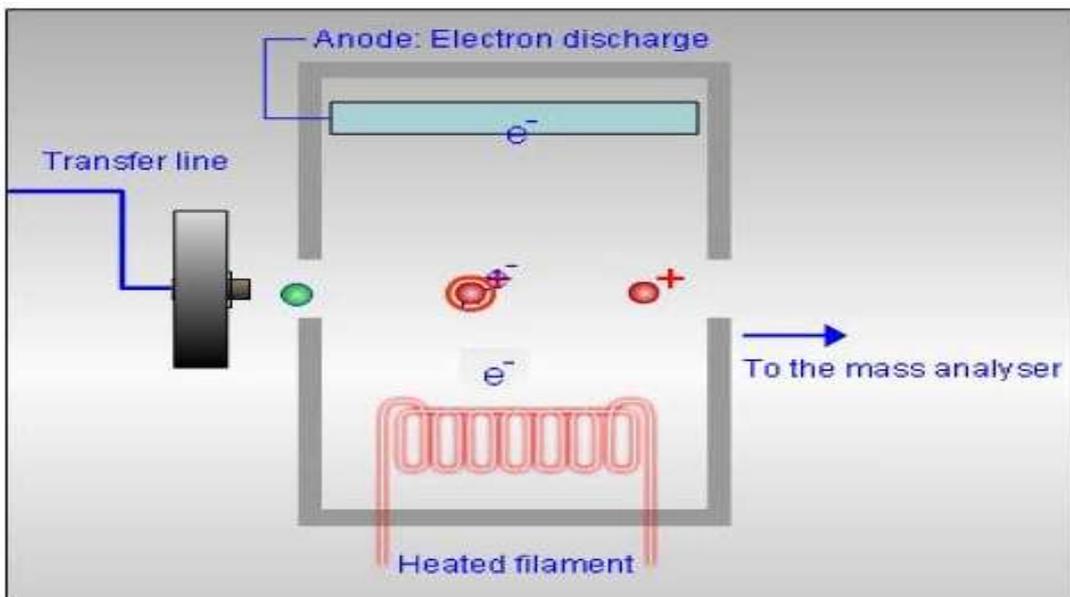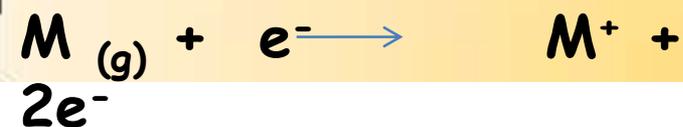
High Vacuum

Mass spectrometry involves the separation of charged species which are produced by a variety of ionisation methods in GC-MS. These include:

• **Electron impact Ionisation (EI)** - where analyte molecules are directly ionised through collision with a bombarding electron stream resulting in the removal of an electron to form a radical cation species.

• **Chemical Ionisation (CI)** - where analyte molecules are charged through reaction processes with a charged reagent gas

Electron Impact (EI)

In the Electron Impact (EI) process, electrons are emitted from a heated filament (usually made of tungsten or rhenium) and are accelerated across the source by using an appropriate potential (5-100V) to achieve the required electron energy (sufficient to ionize the molecule).

$$M_{(g)} + e^- \longrightarrow M^+ + 2e^-$$

Anode: Electron discharge

Transfer line

e^-

e^-

To the mass analyser

Heated filament

Key:	Analyte
Non Ionised	🟢
Ionised	🔴+

Chemical Ionisation (CI)

Chemical ionisation involves the ionisation of a reagent gas, such as methane at relatively high pressure (~1 mbar) in a simple electron impact source. Once produced, the reagent gas ions collide with the analyte molecules producing ions through gas phase reaction processes such as proton transfer.

$$nNH_3 + e^- \longrightarrow NH_4+ + 2e^-$$

$$NH_4^+ + M \longrightarrow NH_3 + [M+H]^+$$

$$NH_4^+ + M \longrightarrow [M+ NH_4]^+$$
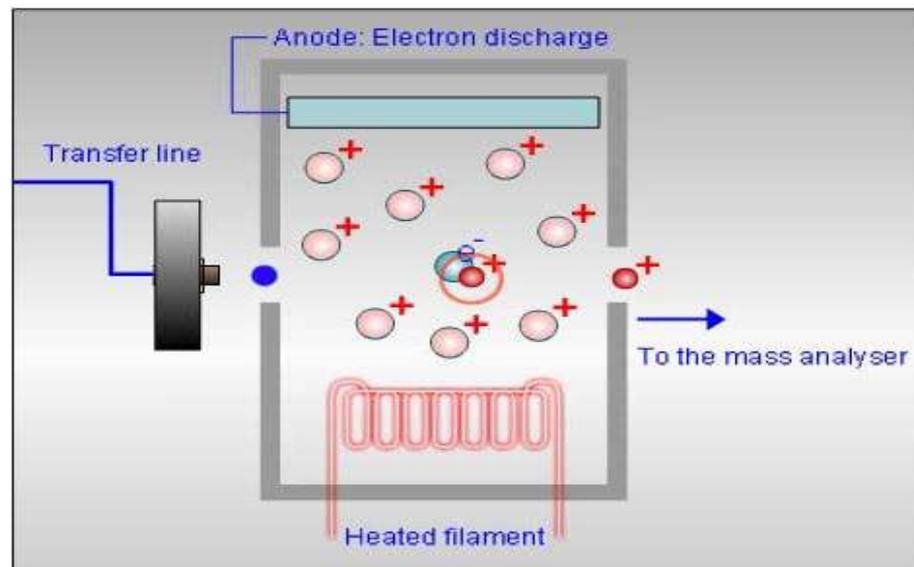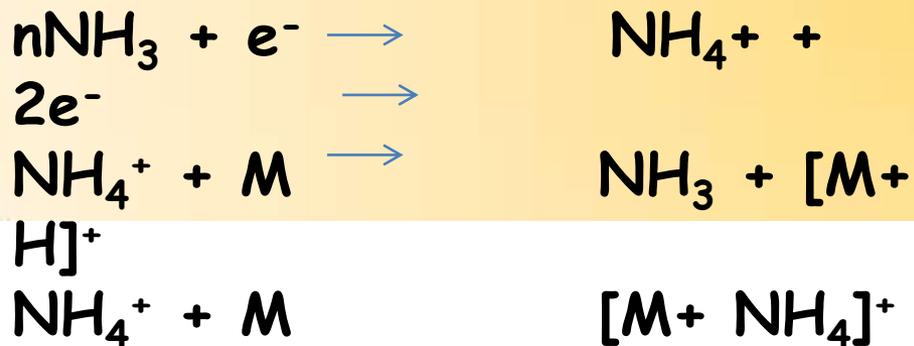
GC-MS Process

To achieve the identification of different compounds, three steps can be distinguished in a GC-MS system:

- **Sample injection**

- **Separation.**

- **Detection**

INJECTION

Depending on the sample (gas, liquid or solid), compounds in a mixture need to be volatilized or

INJECTION TECHNIQUE	USED FOR
Split	High concentration samples (liquid/gas)
	Only small amounts of sample required
Split-less (liquid/gas)	Trace analysis
Thermal Desorption and solid samples	Trace analysis (gases)
	Desorption of volatile compounds in a solid matrix
Headspace in difficult matrices	Volatile compounds
	For collection of vapors above dirty samples

SEPARATION

After injection of a mixture, separation is achieved in the capillary column. This column is coated with a fluid or a solid support, the stationary phase. An inert gas, also called the mobile phase, is flowing through the column. Depending on the phase equilibrium between the stationary and mobile phase, compounds travel with different velocities through the column. The mixture becomes separated, and as a result, individual compounds reach the detector with a different retention time. By choosing a column, which separates on boiling point, polarity, size or stereochemistry, a wide range of compounds can be separated.

DETECTION

Many different detectors can be used for detection of the separated compounds. The mass spectrometer combines a high sensitivity with the unique property of being able to determine the molecular composition.

DETECTOR	USED F OR
Flame Ionization Detector (FID)	Compounds containing Carbon
Thermal Conductivity Detector (TCD)	Universal detection for gases without C
Nitrogen Phosphorous Detector (NPD)	Selective detection of N and P containing organic compounds
Electron Capture Detector (ECD)	Selective detection of halogen containing compounds
Atomic Emission Detector (AED)	Selective detection of elemental composition

The use of GC-MS in many application areas within analytical science continues to grow almost exponentially. Listed below are some pointers as to the applicability of both GC as a separative technique and MS as a means of detecting analyte species
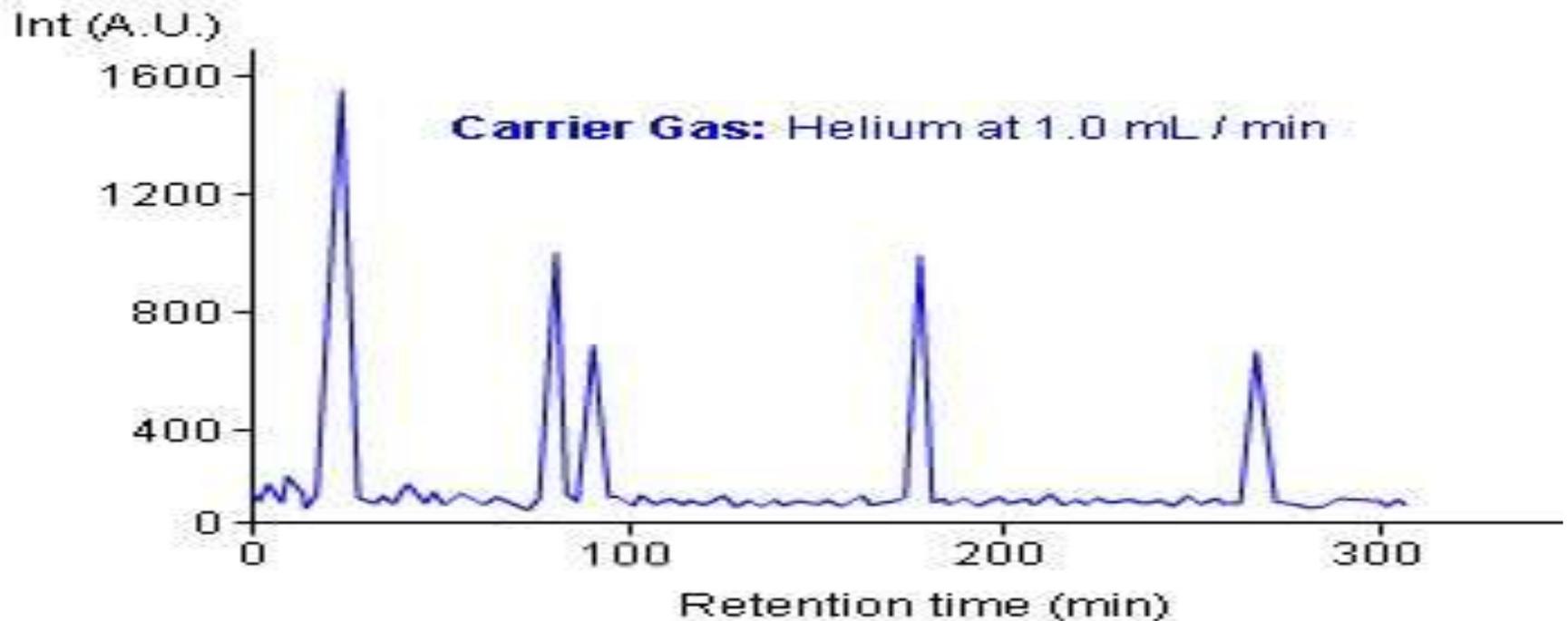
GC analysis of urine sample know to contain cocaine
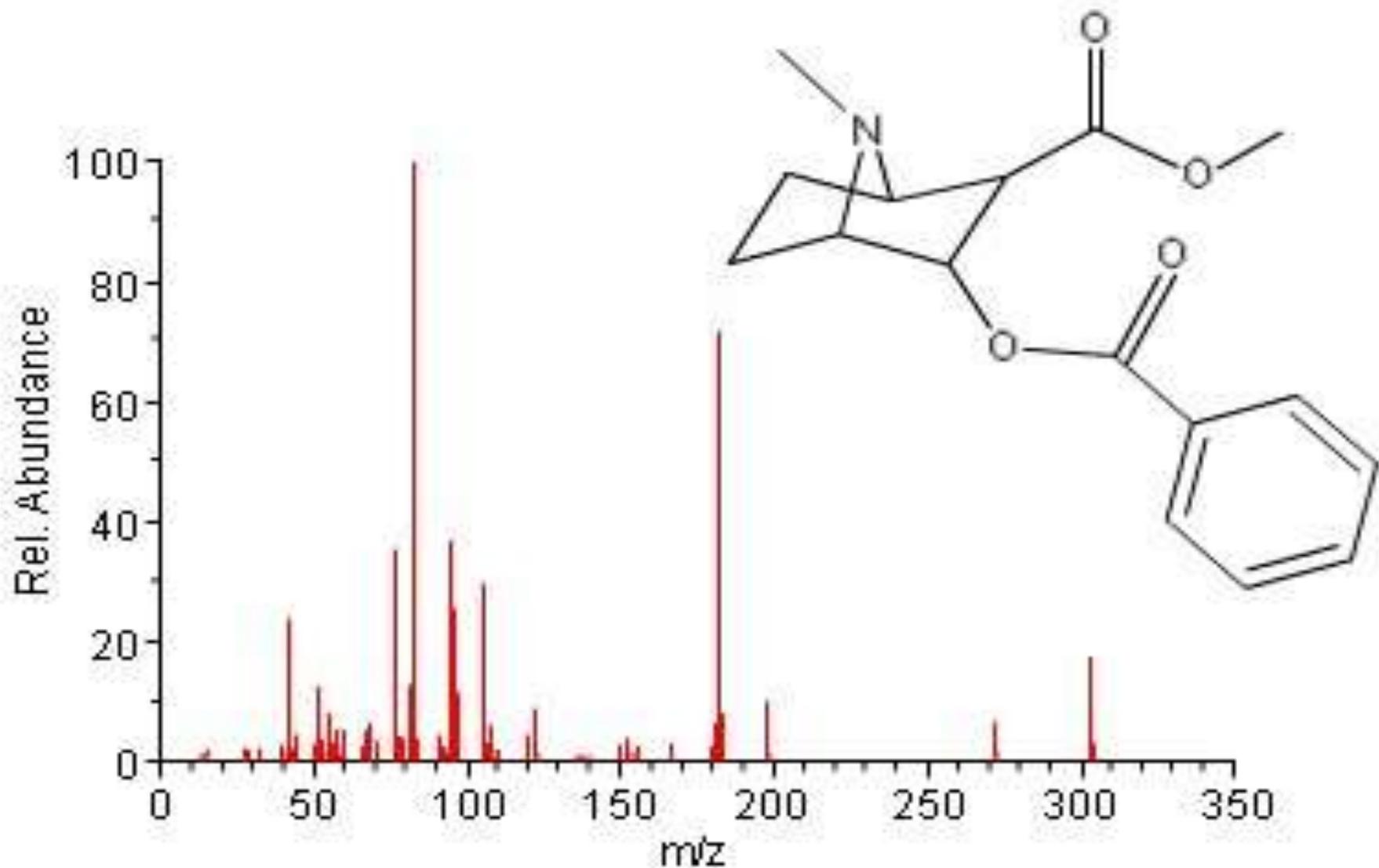
MS spectrum of cocaine

GC Separations

• Produce fast analyses because of the highly efficient nature of the separations achieved

• By using a combination of oven temperature and stationary phase very difficult separations may also be undertaken

• Excellent for quantitative analysis with a range of sensitive and linear detectors to choose from (including the MS detector)

• A practical upper temperature limit for conventional GC columns is around 350-380°C.

In GC analysis, analyte boiling points rarely exceed 400°C and the upper molecular weight is usually around 500 Da

MS Detection

•   Allows specific compound identification. Structural elucidation via spectral interpretation combined with elemental composition from accurate mass analysers is possible.

•   Allows high sensitivity detection - femto-gram amounts have been detected by certain mass analyzer types.

•   Is highly selective, certain analyzer and experiment combinations can lead to highly selective and sensitive analysis of a wide range of

Cleanroom air

The presence of airborne molecular contamination (AMC) in cleanroom air can have a negative effect on the health. To assess the level of AMC in a cleanroom several samples are taken using adsorption tubes and sent to the laboratory for analysis. At the laboratory, the adsorption tubes are desorbed at elevated temperature and the organic contamination present is analyzed using GC-MS. Typically, over 100 different compounds are detected, including compounds like cleanroom solvents (acetone, ethyl acetate etc.) and large hydrocarbons. Quantification of the

Chromatogram of cleanroom air.
Some of the characteristic peaks are indicated:
1= ethanol
2= acetone
3= ethylacetate
 4= cyclohexanone
5= dodecane
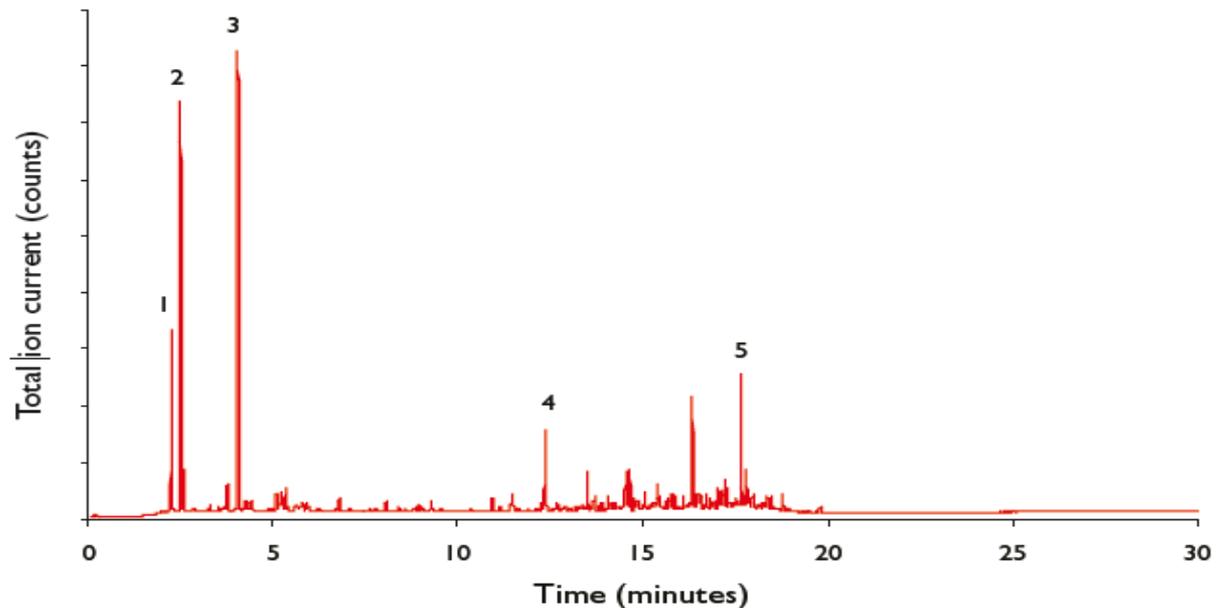
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