Review Article

2-Dimensional Gas Chromatography-Mass Spectroscopy: A Review

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ABSTRACT

Gas Chromatography separates components in time. Mass spectroscopy provides information that aids in the identification and structural elucidation of each component. Comprehensive 2-Dimensional gas chromatography (GC×GC) is a novel technique. The revolutionary aspect of GC x GC, with respect to classical multidimensional chromatography, is that the entire sample is subjected to two distinct analytical separations. The resulting enhanced separating capacity makes this approach a prime choice when GC analysts are challenged with highly complex mixtures. The combination of a third mass spectrometric dimension to a GC x GC system generates the most powerful analytical tool today for volatile and semi-volatile analytes. The present review is focused on the instrumentation of 2D GC-MS, the difference between GC and 2d GC, application of 2d GC-MS have been discussed.

Keywords: Gas chromatography, Interface, mass spectroscopy, detectors, mass analyzers.

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INTRODUCTION

Chromatography is derived from the Greek word Chroma meaning color. Chromatography provides a way to identify unknown compounds and separate mixtures. Chromatography is a laboratory technique for the separation of a mixture. The mixture is dissolved in a fluid (gas, solvent, water) called the mobile phase, which carries it through a system (a column, a capillary tube, a plate, or a sheet) on which is fixed a material called the stationary phase. The different constituents of the mixture have different affinities for the stationary phase. The different molecules stay longer or shorter on the stationary phase, depending on their interactions with their surface sites. So, they travel at different apparent velocities in the mobile fluid, causing them to separate. The separation is based on the differential partitioning between the mobile and stationary phases. Subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus affect the separation.[1]

Gas Chromatography/GC/1D GC

"It is a process of separating component(s) from the given crude drug by using a gaseous mobile phase." It involves a sample being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of the inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid.[2]

Two major types: 1) Gas-solid chromatography: Here, the mobile phase is a gas while the stationary phase is a solid. Used for separation of low molecular gases, e.g., air components, H2 S, CS2, CO2, rare gases, CO, and oxides of nitrogen. 2) Gas-liquid chromatography: The mobile phase is a gas while the stationary phase is a liquid retained on the surface as an inert solid by adsorption or chemical bonding.[3]

2D GC /GC×GC

Comprehensive two-dimensional gas chromatography or GC x GC is a multi-dimensional gas chromatography technique that are originally described in 1991 by Professor Phillips and his students. GC×GC chromatography employs a pair of GC columns (generally, nonpolar and polar columns) connected in series through a modulator. Effluent from the first column is trapped in the modulator for a fixed period (modulation time) before being focused and injected into the second column. The chromatograms obtained through repeated trapping and injection are rendered in two dimensions using specialized software. This result in a two-dimensional chromatogram with the first and second dimensions on respective axes.[4]

2D GC-MS

It is a hyphenated technique.MS is most often coupled to GC × GC allowing another dimension to classify compounds. MS ensures high selectivity throughout the chromatogram and provides structural information for unambiguous identification.

Comprehensive two-dimensional gas chromatography-mass spectrometry (GC×GC-MS) uses two GC columns,

usually connected via a thermal modulator. The second column is typically much shorter than the first (i.e., 1–2 m as opposed to 30–60 m for the first column) with a different stationary phase and is generally operated at a higher temperature. GC×GC-MS can provide superior chromatographic peak capacity, selectivity, and lower detection limit for the analysis of small molecules.[5]

INSTRUMENTATION

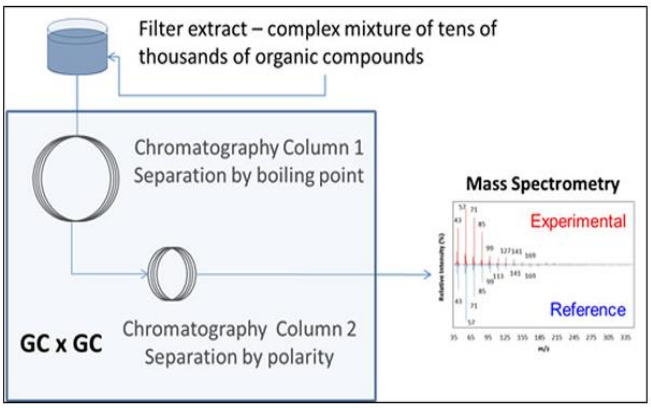


Figure 1: 2D GC-MS Instrument

1. **GC×GC/2D GC**

   Components of **2D** GC:

   1.1 Injector

   1.2 Column set

   1.3 Modulators

   1.4 Oven

   1.5 Detectors

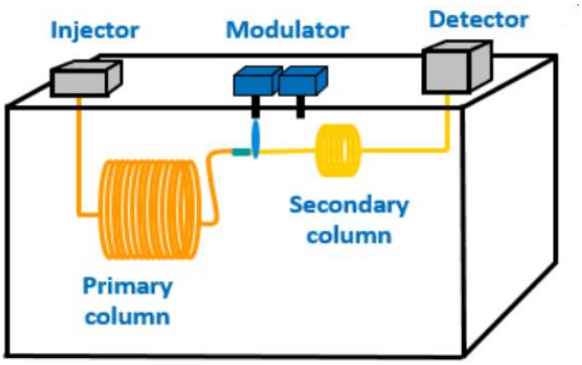


Figure 2: GC×GC Instrument

1. Injector

It is a component of the chromatographic system used to enter the sample into the chromatographic column. In the 2-D gas chromatography, the same dispenser types are used, as in GC. The sample must be of a suitable size and introduced instantaneously as a PLUG OF VAPOR. As Slow injection/oversize causes peak broadening and poor resolution The most common injection method is where a micro syringe is used to inject a sample through a rubber septum into a flash vaporizer port at the head of the column. The temperature of the sample port is usually about 50°C higher than the boiling point of the least volatile component of the sample. The injection port consists of a septum through which a syringe needle is inserted to inject the sample. A micro syringe injects the sample into a stream of inert gas usually at an elevated temperature. The vaporized sample is carried into a column packed with the stationary phase. To ensure rapid & complete solute volatilization temp of injector → 30-50 degrees Celsius>column temperature.

Injection techniques

1. Split
2. Splitless

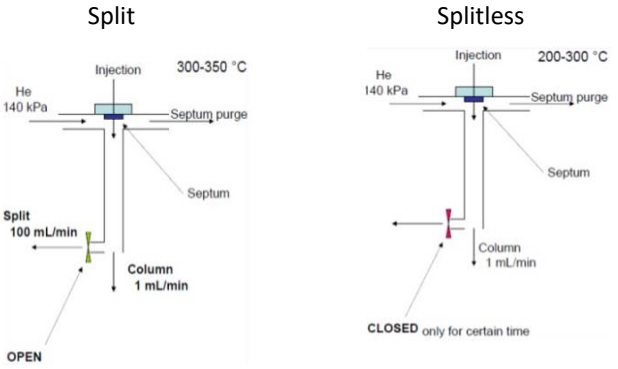


Figure 3: Split and Split less mode

Split less injection

The split-free injection is suitable for liquid samples, even if there is to be determined or substance to be separated only in traces. With the valve closed, the entire sample volume is first evaporated and then introduced into the separation column. The separation column must be able to accommodate the larger sample volume. Split less injection is not suitable for gaseous and solid samples.

Split injection

With the split injection, the sample enters the separation column while the injector valve is open. This increases the speed of the sample application and improves the resolution. This method is suitable for gaseous, solid, and liquid samples that can be vaporized and in which the substance to be determined or separated is not excessively diluted. The quotient of the volume of gas that enters the column from the injector and the total volume of the column is called the split ratio. The split ratios for older devices are between 1:10 and 1: 100, and for newer devices between 1: 200 and 1: 300.

2. Column

In GCxGC capillary types of columns are used. Generally, 2D-GC employs two columns of different sensitivity (such as boiling point versus polarity). Column sets are mainly poly (dimethyl siloxane) in the first dimension and poly (ethylene glycol) in the second dimension. The set of columns can be configured with various types.[6]

3. Column considerations

Phase selection

The "normal" combination for the column set appears to be a nonpolar column followed by a polar (more selective) phase. The rationale for this is that the first column separates according to dispersive forces (with solutes presented at the end of the first column according to their boiling points), thus co-eluting components may have a wide range of polarities. The second column then is chosen to enhance the separation of these when they are pulsed to column 2.

In the reverse geometry, a nonpolar second column may be less effective in resolving different polarity solutes, and dispersive forces alone may be insufficient to provide effective resolution. It is possible to use a more selective phase in the primary column, followed by the less selective.

Column dimensions

The GC×GC result can only be achieved if the analysis on column 2 is performed "fast". Thus, a complete elution on column 2 will be required in a few seconds. This puts certain demands on column 2, thus it will usually be a short column of narrower inner diameter and with a thin film thickness. Column 1 could be operated at a much lower flow than normal to allow column 2 to exhibit its best performance. As a starting position, a 1- to 1.5-m column of 0.1-mm internal diameter might be used in the second dimension, but work has also used columns as short as 30 cm. Again, this depends on the k values and carrier flow in this dimension. Column film thickness may be as low as 0.05–0.1 µm, and this has an impact on column activity if very polar or acidic/basic components are to be analyzed.[7]

Types of columns:

1. Packed column

2. Open tubular

Packed column

Columns are made up of glass or tubes of stainless steel, copper or aluminum Columns are available in a packed manner Packed columns contain a finely divided, inert, solid support material (commonly based on diatomaceous earth) which absorbs liquid used as stationary phase Most packed columns are 2 - 20m in length and have an internal diameter of 1- 8mm The ratio of the volume of the stationary phase to the mobile phase (Vs / Vm) for the column ranges from 10-20. The no. of theoretical plates per foot length of the column is 100-1000.

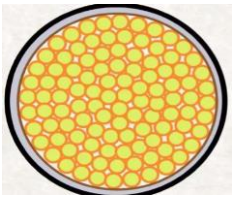


Figure 4: Packed column

Open tubular or capillary column or Golay column:

Long capillary tubing 10-100 M or more in length Internal diameter 0.3-0.5 Uniform & narrow d.m of 0.025 - 0.075 cm Inner layer of the capillary is coated with a very thin film (about 1µl) the liquid, which acts as stationary phase. The ratio of the volume of the stationary phase to the mobile phase (Vs / Vm) for the column ranges from 100-300 which is the main reason behind its high efficiency. The loading capacity <0. 01µ.Made of stainless steel and is in form of a coil.

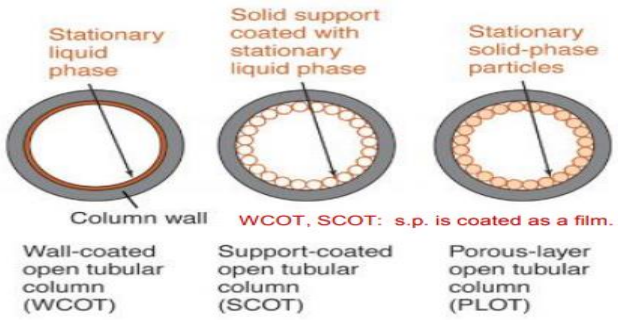


Figure 5: Types of open tubular column

Difference Between Capillary Column and Packed Column

Parameter	Capillary column	Packed column
Internal diameter	0.3- 0.5mm	1-8 mm
length	10-100m	2-20 m
Vs/ Vm	100-300	10-20
No. of theoretical plates	Several hundred thousand	Around 20,000
Sample loading capacity	lower	lower
Efficiency of separation	Higher	Comparatively lower
Efficiency (plates/m)	2000-400	500-1000
Sample size (mg)	10-75	10-100000
Relative pressure	Low	High
Relative speed	Fast	Slow
Chemical inertness	Best	Poorest
Flexible column	yes	No[8]

4. Modulator

In GC × GC two columns are connected sequentially, typically the first dimension is a conventional column and the second dimension is a short fast GC type, with a modulator positioned between them.

The function of the modulator can be divided into basically three processes:1) continuously collect small fractions of the effluent from 1D, ensuring that the separation is maintained in this dimension; 2) focus or refocus the effluent of a narrow band; 3) To quickly transfer the 2D fraction collected and focused as a narrow pulse. Taken together, these three steps are called the modulation

cycle, which is repeated throughout the chromatographic run.

Modulation period: The time required to complete a cycle is called the period of modulation (modulation time) and is actually the time in between two hot pulses, which typically lasts between 2 and 10 seconds is related to the time needed for the compounds to eluted in 2D.

Types of modulators:

1. Thermal modulator
2. Flow modulators

Thermal Modulator

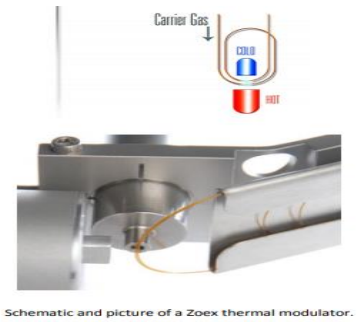


Figure 7: Thermal modulator

Thermal modulators are valve-less devices with minimized dead volume and active sites in the analytic path. The carrier gas is not affected while the analytes are trapped and rapidly re-injected based on temperature, usually by means of precisely controlled cold and hot gas jets. This produces very sharp modulated peaks and thus superior sensitivity and chromatographic resolution. Additional advantages are the possibility to tune freely column dimensions and the modulation time and the compatibility to all detectors. In the Loop Modulators, the column is configured in a loop so that only one cold and one hot jet are required for dual-step focusing. This minimizes the hardware necessary while granting excellent performance.

Liquid Nitrogen Cooled Loop Modulation System: This model uses a liquid nitrogen bath to cool the gas supplied to the cold jet, granting excellent trapping power.

Figure 8: Liquid Nitrogen Cooled Loop modulator

Closed Cycle Refrigerated Loop Modulation: This model does not require liquid nitrogen for the cold jet but uses a closed cycle refrigeration system, making GC×GC with thermal modulation more accessible and affordable.

Figure 9: Closed cycle Refrigerated Loop modulator

Flow Modulator:

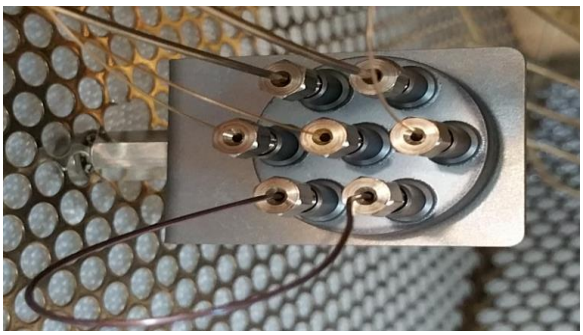


Figure 10: Flow modulator

Flow modulators provide accessible and affordable modulation without the need for cryogenic cooling. The carrier gas eluting from the primary column is separated in modulations which are periodically collected in a dedicated channel and transferred into the second dimension. This is achieved by means of a carefully optimized balance of flows/volumes/times. Thanks to this operational principle, flow modulators are not restricted in terms of analyte volatility.

Two types of flow modulators:

1. Differential Flow Modulator
2. Reverse Fill/Flush Differential Flow Modulator

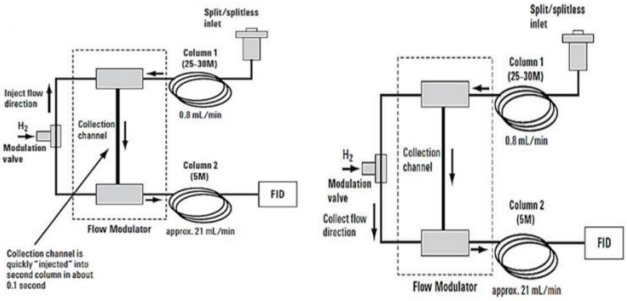


Figure 11: Differential Flow modulator

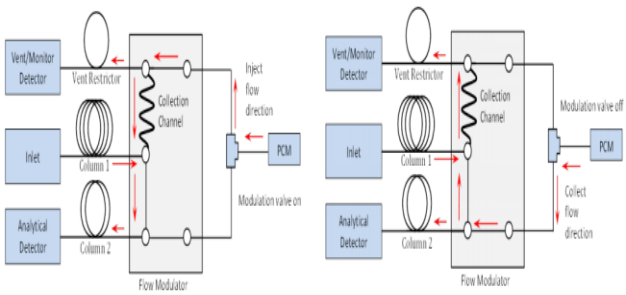


Figure 12: Reverse Fill/Flush Differential Flow modulator

5. Oven: A gas chromatographic element is responsible for maintaining the chromatographic system at a suitable temperature to ensure effective separation of the analyzed components of the mixture

The oven has three functions: **(i)** it keeps the column temperature constant. **(ii)**It allows operation at elevated temperature (faster; perhaps necessary to vaporize the sample). **(iii)** It allows "temperature programming", a controlled increase in column temperature during analysis to make the slow-moving components move faster, reducing the time needed for the analysis, and (iii) reducing the diffusion which makes peaks broader.[9]

6. Detectors

Several detectors are available for use in GC. Each detector has its own characteristics and features as well as drawbacks.

Flame ionization detector (FID):

The FID is the most common detector used in gas chromatography. The FID is sensitive to, and capable of detecting, compounds that contain carbon atoms (C), which accounts for almost all organic compounds. However, the FID is not sensitive to carbon atoms with a double bond to oxygen, such as in carbonyl groups and carboxyl groups (CO, CO2, HCHO, HCOOH, CS2, CCl4[9].

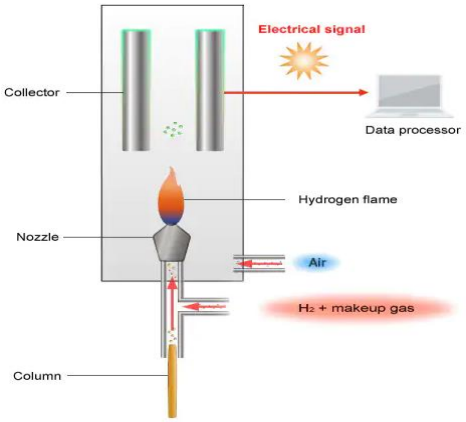
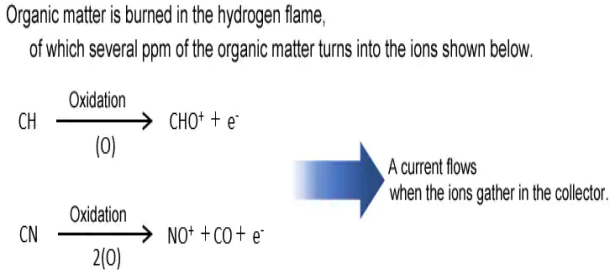


Figure 13: Flame ionization detector

It is a Mass sensitive detector. At normal temperature and pressure, gases are insulators. When electrically charged molecules are produced in gas, it becomes conductors. If proper voltage is applied to electrodes, all of the ions will be collected, so that final current will be proportional to the number of ions between the electrodes.



Advantages: Minute amount of solute can be detected, gives a linear response, as it responds to the number of Cations entering the detector per unit time, it is mass sensitive rather than concentration sensitive Insensitive towards the water, CO2, SO2, NO2

Disadvantages: More complicated and more expensive, Destructive of the sample, Functional groups like carbonyl, alcohol, halogen, and amine are not detected.

Electron-capture detectors (ECD)

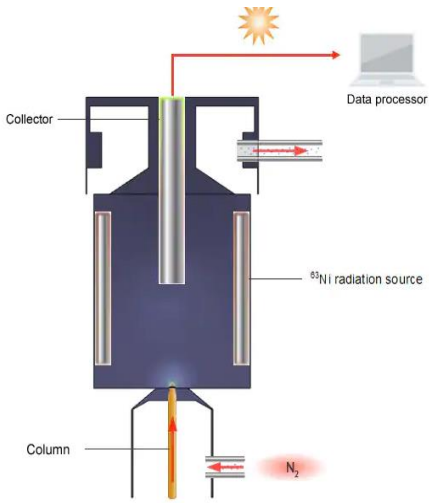


Figure 14: Electron-capture detectors (ECD)

The ECD is a selective, high-sensitivity detector for electrophilic compounds. The ECD is capable of detecting organic halogen compounds, organic metal compounds, diketone compounds, etc. Because the ECD is fitted with a radioactive isotope, installation requires a notice of use to be sent to the Japanese Ministry of Education, Culture, Sports, Science, and Technology. The ECD detects ions by reading the change in voltage value that maintains a constant ion current gathered at the collector.

N2, which is used as the carrier gas, is ionized by β waves emitted from the 63Ni radiation source.

N2 → N2+ + e-

A current flow when the ions gather in the collector.

When an electrophilic compound is placed in this equation,

PCB + e- → PCB-

PCB- is much larger and heavier than e- and so takes more time to reach the collector.
-A higher voltage is needed for a constant ion current to flow.

Advantages: Highly sensitive towards compounds containing electronegative functional groups such as halogens, peroxides, nitro, etc. Detection and determination of chlorinated insecticides, do not alter the sample

Disadvantages: Nonlinear response unless potential across the detector is pulsed.[10]

DIFFERENCE BETWEEN 1D GC AND 2D GC

Comprehensive two-dimensional gas chromatography (GC x GC) can reveal information on the composition of a sample in a way that cannot be done by one-dimensional GC (1D-GC).

GC x GC to have an order of magnitude larger peak capacity than 1D-GC.

The comparison of the performance of GC x GC to 1D-GC shows that the modulator is the key bottleneck limiting the performance of existing GC x GC.[11]

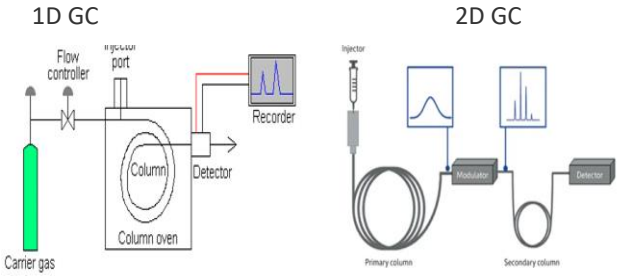


Figure 15: Schematic representation of 1D GC and 2D GC

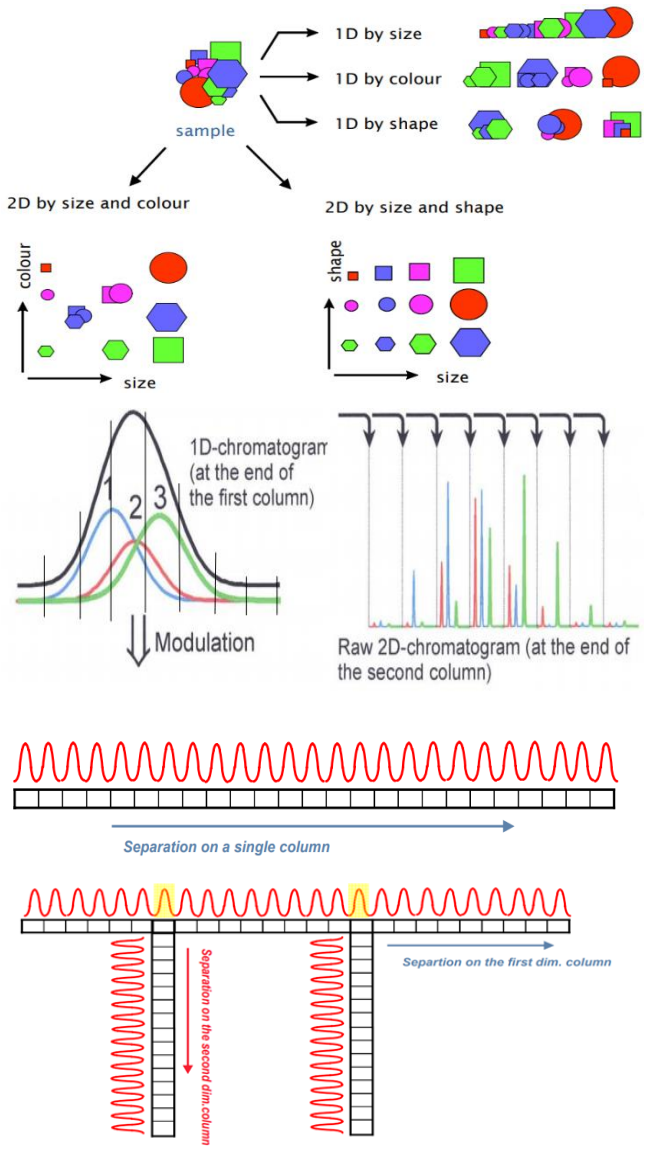


Figure 16: Difference between 1D GC and 2D GC

Advantages of 2D GC:

The main **advantages** of comprehensive **2D GC**, over conventional 1D **GC**, can be summed up in five points: I) increased separation power II) Enhanced selectivity III) Higher sensitivity IV) Speed, considering the number of peaks resolved per unit of time V) Formation of highly-organized patterns of compounds with the same functional groups (e.g., Alkenes, fatty acids, methyl ester, etc.).The chief advantage of two-dimensional techniques is that they offer a large increase in peak capacity, without requiring extremely efficient separations in either column.

APPLICATIONS OF 2D GC

Case studies 1:

Title: Comprehensive Two-Dimensional Gas Chromatography for Analysis of Volatile Compounds in Foods and Beverages

Journal: Journal of the Brazilian Chemical Society

Author name: Juliane Elisa Welke

Columns: column set consisted of a ^{1}D SE52 column coupled with a ^{2}D OV17 column (50% polydimethylsiloxane, 50% phenyl)

Sample: Foods and Beverages

Sample	Analyte	Extraction procedures
Wine	methoxypyrazines	headspace-solid phase micro extraction (HS-SPME)
Lemon juice and lemon-flavored beverage	Only 24 components were identified and a large number of components remained unassigned due to lack of further structural information.	
Liquor	Organic acids, alcohols, esters, ketones, aldehydes, acetyl's, lactones, nitrogen-containing and sulfur-containing compounds. These com	Distillation

Case studies 2:

Title: Recent Applications of Comprehensive Two-Dimensional Gas Chromatography to Environmental Matrices

Journal: CIRSEE (Centre International de Recherche Sur l'Eau et l'Environnement), France

Author: Cardinaël Pascal

Columns: ZB-5, HT-8, DB-17 and BP-10, as first dimension column and HT-8, BPX-50 and Carbowax as second dimension one

Recent Applications of Comprehensive Two-Dimensional Gas Chromatography to Environmental Matrices

Compounds	Samples	Extraction	Set of columns	References
Petroleum hydrocarbons	Soil	ASE	RTX-1×BPX50	Mao et al., 2001
Pesticides	Tap water	SPME	SLB-5ms×SLB-IL59	Purcaro et al., 2011
Halogenated compounds including PCBs, PCDDs, PCDFs…	Fly ash extract, Sediment, soil	Soxhlet	InertCap 5MS×BPX50	Hashimoto et al., 2011
4-Nonylphenols	Wastewater	Liquid-liquid extraction	DB-5 ms×Supelcowax 10	Eganhouse et al., 2009[12]

COUPLING UNIT

The interface b/w the GC&MS is an important role to play in the overall efficiency of the instrument. Pressure incompatibility problem between GC and MS was solved by inserting an interface. It must be capable of providing an inert pathway from the column to the ion source without loss of chromatographic resolution

Mainly three types of interfaces are there commercially available:

1. Jet/Orifice separator
2. Direct capillary infusion interface
3. Watson-Biemann effusion separator

Witson-Biemann Effusion Separator

The Witson-Biemann Effusion Separator consists of a sintered glass tube, the surrounded of which are evacuated. The carrier gas, usually helium, passes preferentially through the sintered glass and the effluent is concentrated by a factor of up to 100. Two stage separators may enrich the effluent by a factor of 400 and be capable of dealing with glass flow rates in order of 20-60 ml/min.

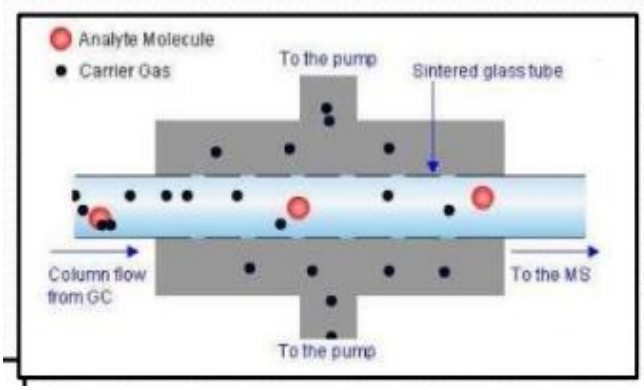


Figure 17: Witson-Biemann Effusion Separator

Ryhage Jet Separator

The Ryhage Jet Separator is based upon the differing rates of diffusion of different gases in an expanding supersonic jet stream. The heavier (sample) compound concentrates in the centre of the gas jet. The gases pass at high speed through an orifice aligned with a second orifice, and then on to the ion source, while the carrier gas is pumped away. Usually, a Ryhage separator is two stages, although all glass single stage units are used, particularly in combination with quadrupole mass spectrum.

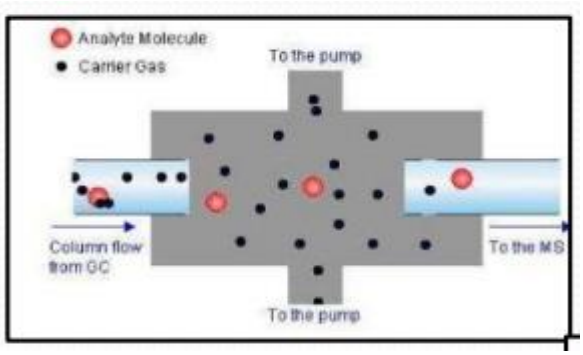


Figure 18: Ryhage Jet Separator

Llwellyn-Littlejohn Separator

In the Llwellyn-Littlejohn separator separation of organic molecules from carrier gas molecules is achieved by means of the selective permeability of an elastomer membrane. Permeability is a function the solubility of the gas molecules in the membrane and their ability to diffuse through it. Gases such as hydrogen, helium argon and nitrogen having a very low solubility and high diffusion rate, pass through the membrane much more slowly than organic vapours where the reverse is true. The vapour is therefore concentrated and the remaining carrier gas expelled into the atmosphere. The concentrated is further enriched by passes through a second semi-permeable membrane. Enrichment of the organic phase by a factor of greater than 10-5 has been achieved.

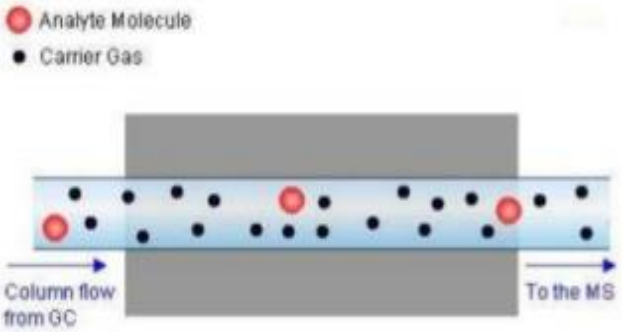


Figure 19: LLWELLYN-LITTLEJOHN Separator

MASS SPECTROSCOPY

Instrumentation:

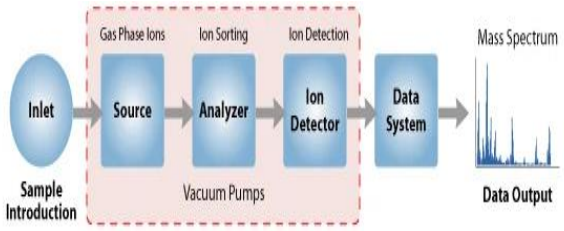
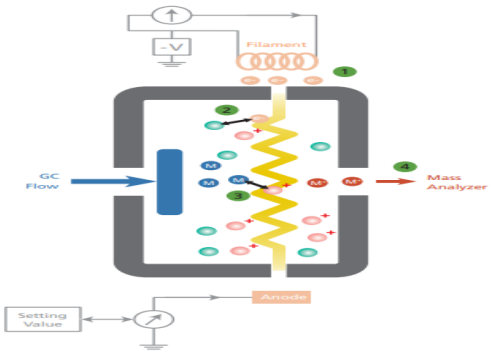


Figure 20: Schematic representation of mass spectroscopy

1. Ion Source

The ion source converts gaseous molecules into charged ions by means of electron bombardment or collision reaction with the reagent gas. Electron ionization (EI) and Chemical ionization (CI) are the main ionization methods used when gas chromatography coupled with mass spectroscopy.



Electron ionization (EI): Electron ionization (EI) is a typical ion source for GCMS.As its name implies, electrons collide with gaseous molecules to form ions.

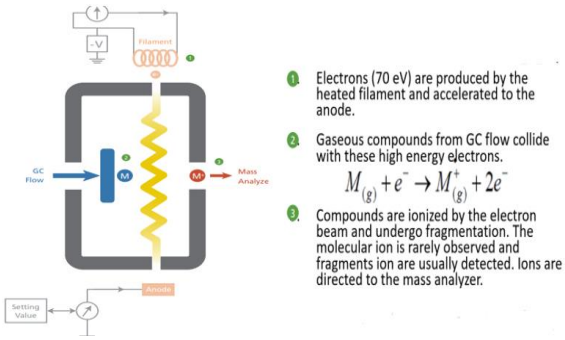


Figure 21: Electron ionization (EI)

Chemical ionization (CI): Chemical ionization a soft type of ionization, is often employed for the detection of molecular ions.

CI exits in 2 modes

1. Negative ionization
2. Positive ionization

Negative ionization:

Negative chemical ionization negative chemical ions are predominantly formed in negative chemical ionization (NCI). The processes are initiated by a heated filament which emits electrons these high energy electrons collide with the reagent gases and are decelerated to form low energy 'thermal electrons' these thermal electrons further collide with sample molecules (M) thus ionising and forming negatively- charged ions (M-).

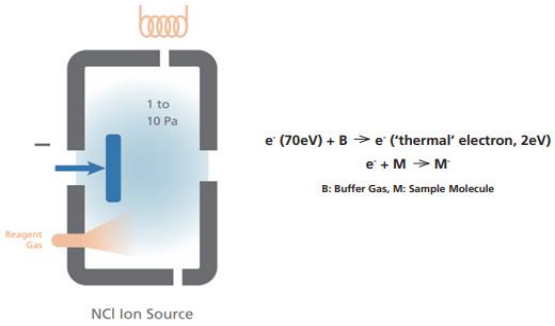


Figure 22: Negative ionization

Positive Chemical Ionization (PCI)

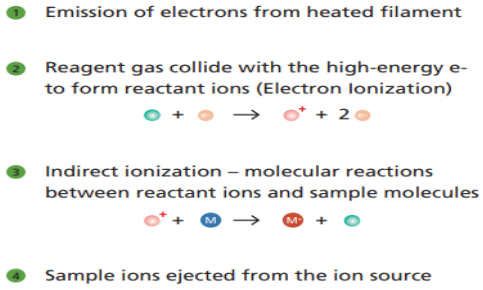


Figure 23: Negative ionization

Similar to EI, CI also requires electrons emitted from the filament. However, these high-energy electrons are released and accelerated into the chamber to collide with the reagent gases instead. PCI can be simply described in these three steps: (1) reagent gas molecules and these high-energy electrons collide and undergo electron ionization (EI), (2) reactant ions are formed from this ionization, and (3) sample molecules collide and react with these reactant ions to form ions.

2. Mass analyzer

A mass analyzer is the component of the mass spectrometer that takes ionized masses and separates them based on charge to mass ratios and outputs them to the detector where they are detected and later converted to a digital output.

Quadrupole mass analyzer

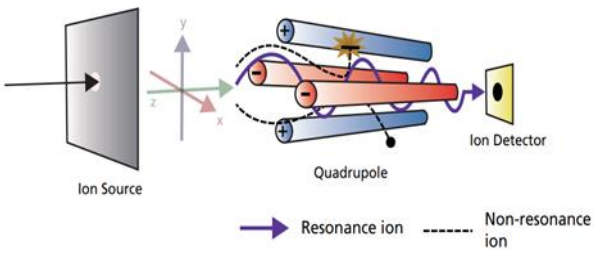


Figure 24: Quadrupole mass analyser

As the name implies, it consists of four cylindrical rods, set parallel to each other. The component of the instrument responsible for selecting sample ions based on their mass-to-charge ratio (*m/z*). Ions are separated in a quadrupole based on the stability of their trajectories in the oscillating electric fields that are applied to the rods.

The quadrupole consists of four parallel metal rods. Each opposing rod pair is connected together electrically, and a radio frequency (RF) voltage with a DC offset voltage is applied between one pair of rods and the other. Ions travel down the quadrupole between the rods. Only ions of a certain mass-to-charge ratio will reach the detector for a given ratio of voltages: other ions have unstable trajectories and will collide with the rods. This permits selection of an ion with a particular *m/z* or allows the operator to scan for a range of *m/z*-values by continuously varying the applied voltage.

Time of flight

Time of flight (TOF) is the measurement of the time taken by an object, particle or wave (be it acoustic, electromagnetic, etc.) to travel a distance through a medium.

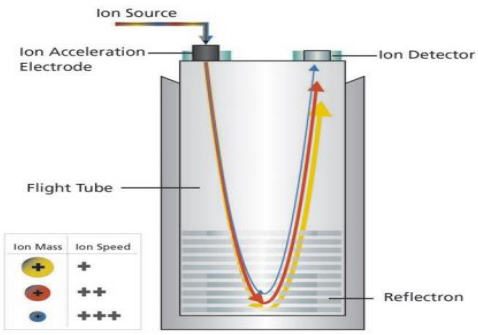


Figure 25: Time of flight

The time-of-flight principle can be applied for mass spectrometry. Ions are accelerated by an electric field of known strength. This acceleration results in an ion having the same kinetic energy as any other ion that has the same charge. The velocity of the ion depends on the mass-to-charge ratio. The time that it subsequently takes for the particle to reach a detector at a known distance is measured. This time will depend on the mass-to-charge ratio of the particle (heavier particles reach lower speeds). From this time and the known experimental parameters one can find the mass-to-charge ratio of the ion. The elapsed time from the instant a particle leaves a source to the instant it reaches a detector.[13]

3. Detector

A detector counts the number of ions with a specific mass. The mass spectrum is a graph of the number of ions with different masses that traveled through the mass analyzer.

Electron multiplier

For ion current less than 10-15 amp an electron multiplier detector (EMT) is used. An electron multiplier detector is used to detect the ion signals emerging from the mass analyser of a mass spectrometer.

Principle: The basic principle that allows an electron multiplier detector to operate is called secondary electron emission. When a charged ion (particle or electron) strikes on detector surface it causes secondary electrons which are released from atoms in the surface layer. The number of secondary electrons produced depends on the type of incident primary particle, its energy and characteristic of the incident surface.

Detector design: There are two basic design s of electron multipliers that are commonly used in mass spectrometry are:

1) The discrete -dynode electron multiplier

2) The continuous dynode Electron multiplier.

Faraday cup

A Faraday cup is a metal (conductive) cup designed to catch charged particles in vacuum. The resulting current can be measured and used to determine the number of ions or electrons hitting the cup. When a beam or packet of ions hits the metal, it gains a small net charge while the ions are neutralized. The metal can then be discharged to measure a small current proportional to the number of impinging ions. The Faraday cup is essentially part of a circuit where ions are the charge carriers in vacuum and it is the interface to the solid metal where electrons act as the charge carriers (as in most circuits). By measuring the electric current (the number of electrons flowing through the circuit per second) in the metal part of the circuit, the number of charges being carried by the ions in the vacuum part of the circuit can be determined. For a continuous beam of ions (each with a single charge), the total number of ions hitting the cup per unit time is N/t=I/e where N is the number of ions observed in a time t (in seconds), I is the measured current (in amperes) and e is the elementary charge (about 1.60×10^{-19} C). Thus, a measured current of one nanoamp (10^{-9} A) corresponds to about 6 billion ions striking the Faraday cup each second. Similarly, a Faraday cup can act as a collector for electrons in a vacuum (e.g. from an electron beam). In this case, electrons simply hit the metal plate/cup and a current is produced. Faraday cups are not as sensitive as electron multiplier detectors, but are highly regarded for accuracy because of the direct relation between the measured current and number of ions.[14]

Figure 27: Faraday cup

APPLICATIONS OF 2D GC-MS

Case Studies 1

Title: GC×GC-MSq: A New Tool in Arson Investigation

Journal: Labcompare

Author: Clifford M. Taylor

Injection: 1.0µl; Injection temperature:325°C; pressure: 70.1KPa;Split:10:1

First column: 30mx0.25mmx0.05µl, 50% phenyl polysilphynylene-siloxane

Modulator: Period: 4.0sec; const temp.330°C

Second Column: 2mx0.1mmx0.1µm, 100% polydimethylsiloxane

Oven programme: 40°C for 20 min, 40-325°cmin^{-1}, hold at 325°C for 30 min

Sample: Gasoline, kerosene and diesel samples

Conclusion: Hydrocarbon accelerants and a suspected arson sample were analyzed by comprehensive GC×GC-MSq, which has the advantage of using two orthogonal GC columns. Because the first column was polar and the second was nonpolar, the detector used was a fast scanning quadrupole mass spectrometer. Selective ion monitoring allowed 2-D separation of samples.

Case Studies 2

Title: Application of 2D-GCMS reveals many industrial chemicals in airborne particulate matter

Journal: Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

Author: Mohammed S. Alam

Extraction: Whole quartz fibre filters were extracted with two 30 ml aliquots of DCM (HPLC grade) and methanol (HPLC grade)

Columns: The first-dimension column was 50 mx0.25 mmx0.40 mm VF1-MS (Varian, Palo Alto, CA, USA). The second-dimension column was 2.5 m x0.15 mm x0.15 mm VF-17MS (Varian).

Sample: airborne particulate matter

Analyte: a large number of oxygenated VOC including linear and branched compounds, substituted aromatic compounds and alicyclic compounds, oxygenated polycyclic aromatic and alicyclic compounds, organic nitrogen compounds, branched chain VOC and substituted aromatic VOC, phthalates, organo-phosphates and organo-sulphate compounds.

Conclusion: Earlier GC-MS studies of semi-volatile compounds in atmosphere aerosol have focused on specific groups of compounds and have therefore not captured the remarkable range of compounds present.

Case Studies 3

Title: Analysis of Fresh and Aged Tea Tree Essential Oils by Using GC×GC–qMS

Journal: Journal of Chromatographic Science, Vol. 48, Apr 2010

Author: Peter Q. Tranchida1

Extraction: The first column was an SLB-5ms column (30 m × 0.25 mm i.d. × 0.25 µm df) [silphenylene polymer virtually equivalent in polarity to poly (5% diphenyl–95% methylsiloxane)], while the second was a Supelcowax 10 column (1 m × 0.1 mm i.d. × 0.1 µm df) [100% poly (ethylene glycol)].

Sample: oxidized tea tree oil, commercial Australian tea tree oil

Analyte: Many compounds have been identified some of them are 6-Methyl-3,5-heptadien-2-one, 3-Methyloctane, Nonane, Verbenene**.**

Conclusion: The results attained in the present research confirm the utility of GC×GC combined with rapid-scanning qMS for the qualitative analysis of complex matrices. The GC×GC–qMS method developed enabled high resolution separation and differentiation of the TTO samples, overcoming several shortfalls of conventional GC–qMS.

Case Studies 4

Title: Evaluation of the Performance of Cryogen-Free Thermal Modulation-Based Comprehensive Two-Dimensional Gas Chromatography-Time-of-Flight Mass Spectrometry (GC×GC-TOFMS) for the Qualitative Analysis of a Complex Bitumen Sample

Journal: Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1, Canada;

Author: Haleigh Boswell

Extraction: Solvent extraction

Sample: oil sand sample

Analyte: paraffins (orange), alkylated steranes (red), terpanes (green) and hopanes (purple)

Columns: 30 m × 0.25 mm i.d. × 0.25 µm Rxi-5MS from Restek Corporation (Bellefonte, PA, USA) as the first dimension (1D), 0.1x0.25 0.25 µm Rxi-5MS from Restek Corporation (Bellefonte, PA, USA) as the first dimension (1D), and a 1.0 m ×0.2mm I.d & 0.25 µm Rxi-17MS from Restek Corporation as the second dimension.

Conclusion: Overall, GC×GC-TOFMS with an SSM platform can be applied for the analysis of biomarkers in bitumen.

Case Studies 5

Title: Comprehensive two-dimensional gas chromatography–mass spectrometry combined with multivariate data analysis for pattern recognition in Ecuadorian spirits

Journal: Chemistry Central Journal

Author: Noroska Gabriela Salazar Mogollón

Columns: The column set consisted of a 25 m×0.25 mm×0.25 µm HP-5 MS (Agilent Technologies—Palo Alto, CA, USA) column (1D) fitted with a 1 m×0.10 mm×0.10 µm SupelcoWax 10 column (Sigma-Aldrich), as the second dimension (2D)

Sample: Spirit samples Six different samples of the beverage Puro, six of Pata de vaca and six of Pájaro azúl were taken for the analysis.

Analyte: citronellal, citronellol, geraniol, methyl anthranilate, (−)-trans-α-bergamotene, (−)-cis-α-bergamotene and d-limone

Conclusion: Comprehensive two-dimensional gas chromatography along with MPCA allowed the discrimination between three Ecuadorians artisan spirits, characterizing the volatile profiles of each them, in order to measure their qualities.[15]

CONCLUSION

MS is most often coupled to GC × GC allowing another dimension to classify compounds. MS ensures high selectivity throughout the chromatogram and provides structural information for unambiguous identification. Several compound classes demonstrate unique fragmentation patterns in the mass spectrum and thus give valuable information about compounds, which can be compared to spectral libraries in the literature

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