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ADVANCEMENT OF GAS CHROMATOGRAPHY IN QUANTITATIVE ANALYSIS

Gas chromatography (GC) is a versatile analytical technique with a rich history of advancements in quantitative analysis. This review explores the enduring relevance of GC, focusing on principles and instrumentation. GC's ability to separate and quantify volatile compounds has solidified its place in environmental analysis, pharmaceuticals, food chemistry, and forensic science. With advanced instrumentation, sample preparation techniques, and quality control, GC continues to meet the demands of modern research. Recent innovations, including miniaturization, hyphenated techniques, and automation, enhance its precision and accessibility. This review highlights the challenges and prospects for GC in a changing analytical landscape, emphasizing sustainability and efficiency. Gas chromatography remains an indispensable tool for researchers, offering continued innovation and steadfast performance in quantitative analysis.

Keywords: Sensitivity, Selectivity, Stationary Phase, Carrier Gas, Injector, Detectors, Column, Sample Introduction.

Introduction

Gas chromatography (GC) has long been a mainstay in the field of analytical chemistry, serving as an indispensable tool for qualitative and quantitative analysis [1]. Over the decades, it has continuously evolved, benefiting from remarkable advances and adaptations to meet the growing needs of modern science. This review begins a comprehensive journey to explore the enduring importance and recent innovations of quantitative gas chromatography analysis and explain simply the instrumentation and working process [2]. The creation of GC, generally attributed to Martin and James in 1952, was nothing short of a revolutionary advance in the field of chemical analysis [1]. Its basic principle,

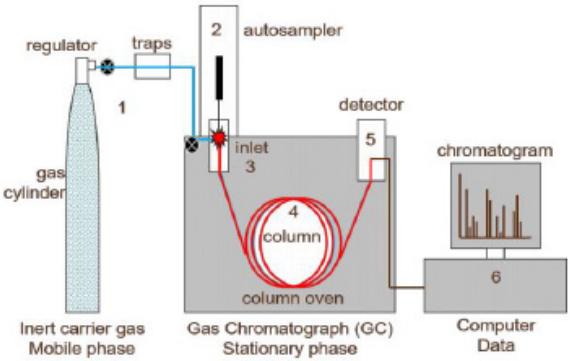
the differential distribution of analytes between a stationary phase, typically a coated capillary column, and a mobile phase, typically an inert carrier gas, offers a method capable of separating and quantify complex mixtures with excellent precision [3]–[5]. This fundamental separation technique plays a pivotal role in both qualitative and quantitative analyses [6]. As the years have passed, gas chromatography has transcended its rudimentary origins to become a highly sophisticated and versatile method. With a remarkable capacity to accurately quantify volatile compounds, distinguished by its exceptional sensitivity, precision, and speed, GC has solidified its role in an array of scientific disciplines [2]. From environmental analysis to pharmaceutical research, food chemistry, and forensic science, it continues to be the go-to analytical tool for researchers and analysts [7]. In this exploration of GC's advancements, this review will delve into its core principles, instrumentation, methodology, and recent developments. From modern gas chromatograph instrumentation to evolving methodologies, it underscores GC's undying relevance in the ever-advancing landscape of analytical science. While navigating the intricate facets of this powerful analytical technique.

Material and method

In this review article, which has been written about the advancements of gas chromatography in quantitative analysis, new books and articles have been used, as well as reliable websites. In this review, the important components of gas chromatography in the form of a comparison have been discussed and the crucial features of each have been highlighted.

Principles of Gas Chromatography

Gas chromatography is a fundamental analytical technique that relies on two key components: a carrier gas, typically inert like helium, argon, or nitrogen, and a column, often a small capillary column coated with a liquid [8]. The separation of compounds occurs based on how they interact with the stationary phase, with stronger interactions leading to longer retention times and slower movement through the column [9].



Scheme 1 – A simplified diagram of a gas chromatograph showing:
(1) carrier gas, (2) auto sampler, (3) inlet, (4) analytical column,
(5) detector and (6) PC [10]

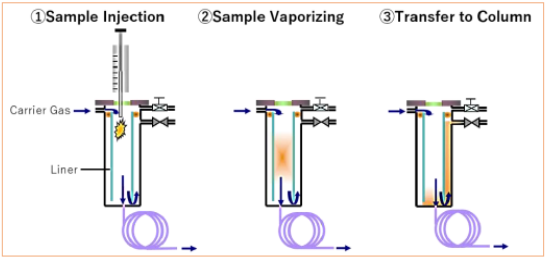
This method capitalizes on the principle that «similar dissolves similar». Compounds that strongly interact with the column material remain in the column longer, while those with weaker interactions move through more swiftly, resulting in distinct retention times [11]. Gas chromatography leverages these differences in compound-stationary phase interactions to effectively separate and identify chemical components in a sample, making it a versatile and invaluable tool in analytical chemistry [1].

Results and discussion

Instrumentation

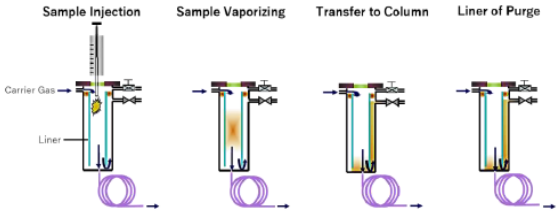
Modern gas chromatographs are equipped with highly advanced instrumentation to enhance quantitative analysis [1]. Key components include:

Injector Systems: There are different sample introduction methods such as split, splitless, on column and direct injections that the principle of each one discussed as bellow. Split Injection employs a turbulent liner design, vaporizing and mixing the sample with the carrier gas before splitting. It restricts the sample reaching the column to avoid overloading. The split ratio is crucial and varies depending on column characteristics [12].



Scheme 2 – Steps for introduction of sample through the column in split injection.

Splitless Injection, Split Injection, Direct Injection, and On-Column Injection are distinct techniques in gas chromatography. in Split less Injection, the sample evaporates in a heated liner, with the split valve initially closed. Once most of the sample moves to the column, the valve opens. Timing is crucial for peak quality. Too short splitless time leads to sample loss, while too long can cause solvent traces and tailing peaks. Deactivated liners are advisable to prevent sample adsorption [12].



Scheme 3 – Steps for introduction of sample through the column in splitless injection

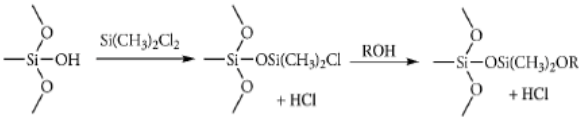
Direct Injection offers high sensitivity for gas phase samples. It's used in headspace, purge and trap, and solid phase micro-extraction. No solvent means no volume increase, and narrow bore liners maintain peak quality [2]. n-Column Injection is ideal for samples with different boiling points. It directly introduces the liquid sample into a wide bore column with a tapered liner design, minimizing sample loss. It's advantageous for trace analysis [12].

Columns: Two types of columns are widely used in gas chromatography; packed column and capillary column. packed columns are constructed from glass,

stainless steel, copper, or aluminum, and typically are 2–6 m in length with internal diameters of 2–4 mm. The column is filled with a particulate solid support, with particle diameters ranging from 37–44 μm to 250–354 μm. Figure (1) shows a typical example of a packed column[14].

Figure 1 – Packed column [10]

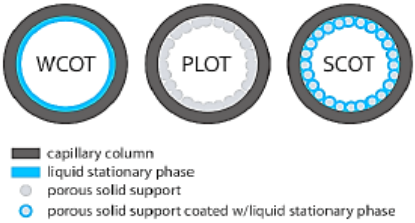
Constructed from the silica skeletons of diatoms, diatomaceous earth is the most commonly used particulate support. These particles offer plenty of contact between the stationary phase and the mobile phase (carrier gas) due to their high porosity, with surface areas ranging from 0.5 to 7.5 m^2/g. Gas-solid chromatography (GSC) uses the silanol groups (–SiOH) that are produced when a diatomaceous earth hydrolyzes to act as active sites for absorbing solute molecules [15]. In gas-liquid chromatography (GLC), we coat the packing material with a liquid mobile phase. To prevent uncoated packing material from adsorbing solutes, which degrades the quality of the separation, surface silanols are deactivated by reacting them with dimethyldichlorosilane and rinsing with an alcohol (equation 1) typically methanol before coating the particles with stationary phase [16].



A capillary, or open tubular column is constructed from fused silica and is coated with a protective polymer coating. Columns range from 15–100 m in length with an internal diameter of 150–300 μm. Figure (2) shows an example of a typical capillary column [14].

Figure 2 – Capillary column [10]

Capillary columns are of three basic types. In a wall-coated open tubular column (WCOT) a thin layer of stationary phase, typically 0.25 nm thick, is coated on the capillary's inner wall. In a porous-layer open tubular column (PLOT), a porous solid support—alumina, silica gel, and molecular sieves are typical examples is attached to the capillary's inner wall. A support-coated open tubular column (SCOT) is a PLOT column that includes a liquid stationary phase. Scheme (4) shows the differences between these types of capillary columns [7].



Scheme 4 – Shows the differences between
these types of capillary columns [5]

A capillary column provides a significant improvement in separation efficiency because it has more theoretical plates per meter and is longer than a packed column.

Detectors: Different detectors in gas chromatography, such as FID, TCD, and MS, offer varying levels of sensitivity and selectivity, with MS providing compound-specific identification and quantification. Detectors convert solute interactions into electronic signals for chromatogram generation [17]. Selective

detectors respond to solutes with specific structures, functional groups, or atoms, enhancing their applicability in targeted analyses. Proper gas usage, including combustion, reagent, auxiliary, and makeup gases, is crucial for detector function, with gas types being universal among GC manufacturers. Following recommended flow rates is essential to optimize sensitivity, selectivity, and the linear range for each detector [18].

Table (1): show the characteristics of different types of GC detectors [16].

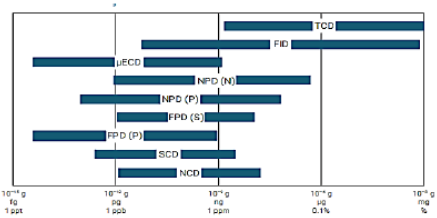
Detectors	**Descriptions**	**Linear dynamic range**	**Destructive**	**Analytes**
Flame Ionization Detector (FID)	The Flame Ionization Detector (FID) is widely employed in GC due to its versatility. It combusts samples in a hydrogen/air flame, measuring ionized particles as an electrical current for sensitive detection.	>107 (±10%)	Yes	Most organic compounds
Sulfur Chemiluminescence Detector (SCD)	The Agilent SCD uses ozone and sulfur monoxide to produce light, enabling sensitive detection of sulfur compounds in gas chromatography. Its signal can be displayed or transmitted to a data system, enhancing its utility for sulfur compound analysis.	>104	Yes	Sulfur-containing compounds are ubiquitous, present in fuels, industrial emissions, food, and natural sources, highlighting the significance of their analysis in both industry and environmental monitoring.

Nitrogen Chemiluminescence Detector (NCD)	The Agilent NCD's light-producing reaction with nitric oxide enables precise detection of nitrogen compounds in gas chromatography, with the emitted light directly linked to nitrogen content and output for analysis, making it a valuable tool for nitrogen compound analysis.	>104	Yes	Nitrogen-containing compounds (e.g., chemicals, environmental pollutants, foods and beverages, fuels, gases, pesticides and herbicides, petrochemicals, polymers, nitrosamines in pharmaceuticals)
Flame Photometric Detector (FPD)	The Flame Photometric Detector (FPD) is employed for sulfur and phosphorus compound detection, with samples burned to produce light. Sulfur detection is quadratic to sulfur atom concentration, while phosphorus response is more linear, allowing for versatile compound analysis.	>103S, 104 P	Yes	Sulfur and phosphorus-containing organic compounds (e.g., pesticides, petroleum streams)

Micro-Electron Capture Detector (micro-ECD)	The micro-Electron Capture Detector (ECD) is highly sensitive and selective for halogenated compounds, utilizing a low-level radioactive source to generate free electrons for electron-capture analysis. Analyte concentration is proportional to the extent of electron capture, making it a valuable tool for detecting halogen-containing compounds.	>5 × 104 >104 for 8860 GC	No	Halogenated organic compounds, aromatic compounds, other analytes with high electron affinity (e.g., organometallics, nitriles, or nitro compounds)
Nitrogen-Phosphorus Detector (NPD)	The Agilent 8890/8860 NPD's heated glass bead plasma offers outstanding selectivity, with impressive selectivity ratios for nitrogen and phosphorus compounds, making it a valuable detector in gas chromatography for specific compound analysis.	>105N, >105 P >104N, >104P for 8860 GCY	Yes	Phosphorous containing compounds (e.g., pesticides) Nitrogen-containing compounds (e.g., drugs)

Thermal Conductivity Detector (TCD)	The Thermal Conductivity Detector (TCD) is a versatile and universal detector in gas chromatography, capable of measuring any sample component with different thermal conductivity from the carrier gas. It operates with a single filament and requires only the carrier gas, which can be helium, argon, nitrogen, or hydrogen, simplifying analysis.	>105(±5%) 105(±10%) for 8860 GC	No	Permanent gases, light hydrocarbon gases, fatty acids, flavors, and fragrances

But for every type of detector sensitivity is a key criterion because it directly impacts the detector's ability to detect, quantify, and provide accurate results for analytes in a wide range of concentrations, making it essential for various analytical applications [19].



Scheme 5 – Relative sensitivity of GC detectors [4]

Conclusion

Gas chromatography (GC) has evolved from a groundbreaking technique into an essential and versatile tool for quantitative analysis across scientific disciplines. Its enduring utility is evident in applications ranging from environmental monitoring to forensic investigations, consistently delivering precise and sensitive results. Advancements in GC instrumentation, including injectors, columns, and detectors, have improved precision and expanded its applications. These innovations, coupled with advanced data systems, enhance accuracy and reduce

errors. methodology remains critical, with calibration, sample preparation, and quality control essential for accurate quantification. Calibration curves, method validation, and assessing precision and accuracy are integral aspects of GC analysis. recent developments, like miniaturization, hyphenated techniques, and automation, have broadened GC's accessibility and sustainability in analytical chemistry. However, challenges persist, such as analyzing non-volatile compounds and reducing analysis times, which require ongoing attention. in conclusion, GC's journey from innovation to state-of-the-art analytical technique ensures its enduring role in analytical chemistry. Its commitment to precision, sensitivity, and adaptability positions it to meet evolving scientific needs, solidifying its place as a cornerstone of quantitative analysis.

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ГАЗ ХРОМАТОГРАФИЯСЫНЫҢ САНДЫҚ ТАЛДАУДА ЖЕТІЛУІ

Газ хроматографиясы (ГХ) – сандық талдаудағы жетістіктердің бай тарихы бар жан-жақты аналитикалық әдіс. Бұл шолу принциптерге, құралдарға, әдіснамаға және соңғы әзірлемелерге назар аудара отырып, МК-ның өзектілігін зерттейді. МК-ның ұшпа қосылыстарды бөлу және сандық анықтау қабілеті қоршаған ортаны талдауда, фармацевтикада, тамақ химиясында және сот сараптамасында өз орнын нығайтты. Жетілдірілген жабдықтың арқасында, МК үлгілерін дайындау және сапаны бақылау әдістері қазіргі заманғы зерттеулердің талаптарын қанағаттандыруды жалғастыруда. Соңғы инновациялар, соның ішінде миниатюризация, тасымалдау әдістері және автоматтандыру дәлдік пен қолжетімділікті арттырады. Бұл шолу тұрақтылық пен тиімділікке баса назар аудара отырып, өзгермелі аналитикалық ортадағы МК қиындықтары мен перспективаларын көрсетеді. Газ хроматографиясы үздіксіз инновациялар мен тұрақты сандық өнімділікті ұсынатын зерттеушілер үшін таптырмас құрал болып қала береді.

Кілтті сөздер: Сезімталдық, таңдамалылық, стационарлық фаза, тасымалдаушы газ, инжектор, детекторлар, баған, үлгіні енгізу.

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РАЗВИТИЕ ГАЗОВОЙ ХРОМАТОГРАФИИ В КОЛИЧЕСТВЕННОМ АНАЛИЗЕ

Газовая хроматография (ГХ) — универсальный аналитический метод с богатой историей достижений в количественном анализе. В этом обзоре исследуется непреходящая актуальность GC,

уделяя особое внимание принципам, инструментам, методологии и последним разработкам. Способность ГХ разделять и количественно определять летучие соединения укрепила его место в анализе окружающей среды, фармацевтике, пищевой химии и судебной медицине. Благодаря передовому оборудованию, методам подготовки проб и контролю качества ГХ продолжает отвечать требованиям современных исследований. Последние инновации, в том числе миниатюризация, методы переноса и автоматизация, повышают точность и доступность. В этом обзоре освещаются проблемы и перспективы GC в меняющейся аналитической среде, уделяя особое внимание устойчивости и эффективности. Газовая хроматография остается незаменимым инструментом для исследователей, предлагая постоянные инновации и стабильную эффективность количественного анализа.

Ключевые слова: Чувствительность, селективность, стационарная фаза, газ-носитель, инжектор, детекторы, колонка, введение пробы

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