

# Exploration of Volatile Organic Compounds through Gas Chromatography: Analytical Insights

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**Abstract:** *This research focuses on the analysis of volatile organic compounds (VOCs) using gas chromatography (GC) in the food, taste and fragrance, medicinal, and environmental domains. Recent advances in sample injection, separation, and detection—such as multi-dimensional and high-speed GC—are discussed. It is shown that there is growing interest in quality assessment*

**Keywords:** Gas chromatography (GC); Volatile organic compounds (VOCs)

## I. INTRODUCTION

VOCs are of interest to many academic disciplines, such as the culinary, forensic, and medical sciences. Environmental chemistry may be the main discipline investigating volatile organic compounds (VOCs) because of its connections to deleterious and carcinogenic effects on human health, stratospheric ozone depletion, tropospheric ozone formation, and other difficulties.

Specifically, there is debate about the definition of a volatile organic compound (VOC). In spoken language, vocabulary and organic solvents are often used interchangeably. Any organic compounds that help produce photochemical ozone are considered volatile organic compounds (VOCs), according to an effect-oriented definition that is commonly used in the United States. More general definitions are based on the physical and chemical properties of the compounds, including their composition, vapour pressure, boiling point, and air/water partitioning.

Vapour pressure-based definitions are often used. In the US, organic compounds having a vapour pressure greater than 13.3 Pa at 25 °C are categorized as volatile organic compounds (VOCs) in accordance with ASTM test method D3960–90. The term "VOC" is often used in the EU to refer to organic compounds with a vapour pressure more than 10 Pa at 20 °C, as per the European VOC Solvents Directive 1999/13/EC. Any chemical molecule with a carbon chain or ring foundation (including hydrogen content) and a vapour pressure of greater than 2 mm of mercury (0.27kPa) at 25 °C, except methane, is classified as a volatile organic compound (VOC) by the Australian National Pollutant Inventory.

Whatever the criteria, it is evident that every area of research on volatile organic chemicals has progressed because of GC's analysis. Other techniques of VOC analysis are not widely used. Using DOAS (differential optical absorption spectroscopy) for formaldehyde and gaseous BTEX (benzene, toluene, ethylbenzene, and xylenes) as well as MIMS (membrane introduction mass spectrometry) for gaseous and liquid samples are a few of these techniques.

The primary objective of this study is to focus on the analytical methods used in GC's VOC determination. The initial stage in VOC analysis is often pre-concentration of VOCs, whether in a gaseous, liquid, or solid matrix. Many recent review papers cover a variety of topics, including pre-concentration using solid sorbents, cryogenic pre-concentration, membrane devices, solvent extraction, static and dynamic headspace, solid phase micro-extraction (SPME), stir-bar sorptive extraction (SBSE), supercritical fluid extraction (SFE), distillation, and sublimation techniques. General reviews are given by Majors [1], while papers with an emphasis on the environment are provided by Clement et al. [2,3], Fox [4], Richardson [5], Dewulf and Van Langenhove [6–8], and Helmig [9].

In particular, sorbent-based pre-concentration methods need to take the target analytes' polarity into account. Water interference is a distinct issue that requires attention. Recent papers [3, 6, 8, 13] have discussed ways to water removal. These include the use of hygroscopic salts, water-sorbing polymers (Nafion), dry purge phases, and the selection of hydrophobic sorbents.

This study will primarily concentrate on the GC-analysis itself, including sample injection, separation, detection, and analytical quality assurance and control. Most emphasis will be paid to developments that have occurred within the last two to three years. The following are the three pillars of the work:

Using a 979-article internal database on ambient VOC analysis that has been gathered over the last ten years; a thorough scan of Analytical Abstracts (Silver Platter International) for the months of January 1999 through August 2001; an analysis of the Analytical Chemistry review issues for the same time [2-5,19-24].

### Sample Injection

Target volatile organic molecules in a range of physical states are obtained by pre-treatment and sampling. Because VOCs are gaseous, dissolved in liquid, cryogenically contained, or adsorbed on solid materials, they must be added to the GC column. A few recent research address the problem of VOCs sample injection [6-9,12-18,25].

For the on-column, split, and split less injection of liquid or gaseous samples, syringes and sample loops are often used. For solvents, large volume injection has been developed to improve detection limits. One major obstacle to large-volume liquid injections of volatile organic compounds (VOCs) is the modest volatility difference between the solvent and analytes. Recent methods to circumvent this issue have been reported [26-29]. By placing restrictions between the uncoated precolumn and the vapour outflow, Boselli et al. [26] avoided the accumulation of solutes at the front of the flooded zone. The accumulation at the front was generated by a considerable pressure decrease throughout the flooded region as a result of the formation of a liquid plug. According to Hankemeier et al. [27] and Adahchour et al. [28], extending the injection length while maintaining a constant injection temperature, speed, and head pressure is one way to calculate the evaporation rate. Measuring the flow rate in the carrier-gas supply line to the on-column injector allowed for a speedy optimization; it turned out that around five injections were required. A different strategy called "inverse large-volume injection" entails eluting a semi-volatile solvent after the target compounds have been added [29].

Pocurull et al. [30] developed a novel swing injection approach to introduce significant volumes of water-containing materials. Sample evaporation and solvent-solute separation were carried out separately using a system made up of two PTV (planned temperature vaporization) injectors filled with different sorbent materials and maintained at different temperatures. The design allows for the analysis of target compounds with a wide range of volatilities present in liquid samples, including water. VOCs (volatile organic compounds) that have been cryogenically pre-concentrated may release in a narrow band.

The result of targets being thermally desorbable from a solid sorbent is band widening. Cryogenic focusing, which is carried out in front of the injector after thermal desorption, is often used to resolve this problem. This method raises variances and error risks by complicating the analytical procedure and equipment. There have been recent studies that aim to provide online analytical capabilities, speed up pre-concentration, and simplify the solid-sorbent desorption process. In the first arrangement, refocusing takes place within the GC injector on a cold column head. A second technique is the thermal desorption of small traps. Typical examples of this include the use of PTV injectors [31-34], narrow-bore capillaries [35, 36], and SPME fibers [13, 15-18]. The last two are filled with absorbent substance.

### Separation

Volatile organic compounds (VOCs) were formerly separated primarily using silicone-type Wall Coated Open Tubular (WCOT) and aluminum-based Porous Layer Open Tubular (PLOT) columns for very volatile chemicals. In more recent times, separation technology has seen a number of noteworthy advancements.

### Recent column developments

Silicone-based columns containing 100% poly dimethylsiloxane are marketed under a number of names, including AT-1, EC-1, CP-Sil5CB, DB-1, BP-1, HP-1, OV-1, RSL-150, RTX-1, SPB-1, and MXT-1. Manufacturers provide columns designed exclusively for EPA-recommended VOCs analysis, such as VOCOL, RTX-VMS, RTX-VGC, RTX-VRX, and DB-VRX, in addition to these multifunctional columns. The design, which makes use of computer modeling [37], seeks to shorten analysis times by increasing peak capacities; analysis of 66 targets in 30 minutes on a WCOT column [38] and 15 targets in 16 minutes on a PLOT column [39] have been documented. Ji et al.'s study from [40] looked at the creation, applications, and future of PLOT capillary columns; [41] discussed how PLOT applications might grow as a result of the column's improved mechanical, chemical, and thermal stability. There have been reports of PLOT column applications for airborne oxygenated compounds [42]. By applying a sol-gel coating to the inner wall of a fused silica capillary, Zeng

et al. [43] were able to generate a capillary column with crown-ether-based saturation phases. The columns showed good selectivity when it comes to the separation of positional isomers of aromatic compounds. Mangani et al.'s BTEX investigation recently employed graphite-lined open tubular (GLOT) [44].

Published reviews [45,46] discuss the use of chiral cyclodextrin-based stationary phases in the quantification of biogenic volatile organic compounds (VOCs), such as terpenoids, taste, and fragrances.

The separation of volatile organic compounds (VOCs) is often based primarily on the interaction with the stationary phase since interactions with mobile phases, such as He, N<sub>2</sub>, or H<sub>2</sub>, are negligible. Certain gases or vapours are used as the mobile phase in a technique that has been reported by Berezkin et al. [47, 48]. Volatile organic compounds (VOCs) in the stationary liquid phase of a "acidic-basic GC" (ABGC) exhibit apparent dissociation to varying degrees depending on the gases or vapours employed to separate carboxylic acids, such as ammonia and amines.

#### **Multi-dimensional separation**

Multi-dimensional, two-dimensional (2D) separation has been developed to prevent peak overlap in one-dimensional chromatograms of complex mixtures [49]. There is a current evaluation of the 2D concept available [50–52]. Two-dimensional volatile analysis has applications in petrochemicals [53], taste analysis [45], and air analysis [9]. With 2D GC, almost 550 different peaks of compounds in the C<sub>6</sub>–C<sub>14</sub> range may be separated in a single run, showcasing the method's exceptional capacity to separate volatiles [54]. An example of an urban air sample is shown in Figure 2. The massive number of species was subsequently classified using retention behavior, which revealed hundreds of aliphatic hydrocarbons together with around 100 multi-substituted aromatics and 50 carbonyls.

A polar second column with a second-order periodicity is often used to segregate components of a first, non-polar column [19]. Although thermal modulation is regarded to be the most extensive, valve modulation is also theoretically conceivable [55]. Thermal modulation may be achieved by either heating or cooling, as Fig. 3 roughly illustrates. The main element that moves wastewater in the form of sharp pulses suitable for high-speed chromatography from the first column to the second column is the modulator.

Because overlapping peaks may be allowed, 2D fast GC with time-of-flight mass spectrometry (TOFMS) may gather 500 spectra per minute, enabling very quick analysis times [56]. It has been claimed that two-dimensional comprehensive liquid chromatography-gas chromatography (2D-LC-GC) can separate volatiles using GC in the 1-2 second range and LC in the 5–10 minute range [57]. With 100% water mobile phase in the LC stage, this complete LC GC apparatus offers an alternative to the headspace analysis-based procedures that are currently in use. The compound separations using BTEX, methylene chloride, and chloroform are shown.

#### **High-speed GC**

Because GC analysis durations were being lowered, high-speed GC (HSGC), often referred to as fast, rapid, or ultra-fast GC, was developed in the late 1990s (for a report, see Sacks et al. [58], for reviews, see [22,59–62], and for theory on HSGC, see Blumberg [63–65]). Four capillary GC speed levels were determined by Hinshaw [62]. High-speed gas phase chromatography (HSGC) produces analytical times in the seconds range and is characterized by short columns, small column diameters, and quick temperature programming. The fast heat-up rates are based on resistive heating, which was first characterized in the 1960s [66]. Recent research has examined this technique's promise for fast-GC analysis [67, 68]. There are currently resistive heating systems available on the market that can heat up to 70 °C per minute [69].

Van Deursen et al. [70] looked at the use of wide-bore columns for fast GC with vacuum outlet, which allows a high sample volume. When combined with quick sample introduction methods, HSGC's employment in field monitoring devices is one of its distinctive features. In air and water analysis, portable devices like membrane-based sample pre-concentration or SPME are often used [71–74]. Time-of-flight mass spectrometry (TOFMS) integration seems to have a lot of promise in the future.

#### **Detection**

FID (flame-ionization detection), MSD (mass spectrometry detection), ECD (electron-capture detection), (D or H)ELCD ((dry or Hall) electrolytic conductivity detection), PID (photo-ionization detection), FPD (flame-photometry detection), and NPD (nitro-gen-phosphorus detection) are frequently used in capillary GC (continuous gas phase separation) analysis of volatile organic compounds (VOCs). Fox [5] and Eiceman et al. [22] have examined recent developments in detectors. But FID, MS, and ECD are still necessary for the majority of VOC detection.

Some new types have been documented, such as micro-ECD, HID (helium-ionization detection), which is more sensitive for oxygenates than FID, MIP-AES (microwave-induced plasma atomic-emission spectrometry) for halogenated volatile organic compounds, SCD (sulfur-chemiluminescence detection) [10], and RF-IMS (radio-frequency ion-mobility spectrometry).

Depending on their selectivity, sensitivity, and ability to provide structural information, detectors are connected in series or parallel at the GC column's output to get the maximum amount of information. For example, Koziel et al. reported on VOC analysis for environmental applications utilizing a portable GC equipped with PID, FID, and DELCD in series. For flavor analysis, which often makes use of GC-olfactometry, sniffing ports and FID have been developed concurrently. Flavor GC analyses have recently been compared to direct sensors that function without any separation, such as MS-based sensors and electronic noses built on semi-conducting polymer sensors. MS often offers structural data. Zhou et al. [11] state that FTIR and MS are used in sequence.

#### **Analytical quality**

Research papers mostly concentrate on novel improvements. However, statistical information on blank levels, limits of quantification (LOQ), limits of detection (LOD), accuracy, calibration, specificity, and range of application is seldom supplied in order to assess analytical performance. However, a number of recent articles [86–89] have addressed analytical performance. Huxham and have identified seven steps that lead to errors and ambiguity in the airborne VOC concentration estimate (Fig. 4).

The last performance test is the inter-laboratory comparison. Such exercises have included the analysis of terpenes in air, chlorinated volatile organic compounds (VOCs) in surface waters [88], VOCs by SPME, and volatiles in and spirits. Jurvelin et al. discussed common problems that arise in multi-center studies of gaseous VOC evaluations. This study highlights the need of carefully considered quality assurance and control (QC/QA) protocols in multi-center investigations that do not follow conventional methods for laboratory analysis or sampling.

To achieve outstanding quality in the measurement of airborne volatile organic compounds, a calibration mixture must be available [3,6,]. Usually, liquids or gaseous mixtures are started, and then mixtures are formed in the lab itself using either dynamic or static dilution. Dynamic dilution is often achieved via diffusion through a capillary or across a membrane (permeation). Gautrois and Koppmann have coupled diffusion via a capillary with a second dynamic dilution using pure air, lowering the concentration to pptv. This mixture showed a large linear dynamic range and included a broad spectrum of volatile organic chemicals. A study on the calibration of ethene, starting with the thermal breakdown of an appropriate surface compound, has been published].

McKinley and Majors cast doubt on the traceability of airborne volatile organic compound (VOC) analysis. Of the nearly 400 volatile organic compounds (VOCs) that may be evaluated for their impact on industry and the environment, only around thirty have trace-level standards available.

Calibration of VOCs analysis based on equilibrium-based pre-concentration techniques, such as static headspace or SPME, need information on the analyte partitioning between the matrix to be injected in the GC and the matrix to be analyzed [13,16]. Two approaches to calibrate SPME-GC were discussed by Namiesnik et al. [16]: creating reference mixtures or using distribution coefficient expertise. It has been recommended that SPME fibers be calibrated for air analysis using mathematical modeling. Examining the inconsistent calibration caused by competing sorption with higher molecular compounds that come from the matrix and differ across samples using SPME Murray.

## **II. CONCLUSIONS AND PERSPECTIVES**

The initial trend in contemporary GC studies of volatile organic compounds (VOCs) is the attempt to reduce analysis times. One example of this is the development of smaller pre-concentration stages that may be utilized online with the GC instrument, such as SPME and sorbent-filled PTV injectors. But because to high-speed GC, GC separation now only takes seconds as opposed to minutes.

Second, getting as much data as you can out of a sample is the aim of research. Innovative developments in this field include new column technologies like chiral separations and columns designed especially for the study of volatile organic molecules. Still, the development of 2D GC can be the primary source of improvements. It will enable important progress in the study of taste and fragrance, volatile organic compounds (VOCs) and their atmospheric fate, as well as biogenic VOCs.

In summary, published interlaboratory comparison results and recent research articles demonstrate a discernible rise in the attention paid to quality assessment.

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