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MEMS Devices for Miniaturized Gas Chromatography

Imadeddine Azzouz and Khaldoun Bachari

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Abstract

In the era of the Internet of Things, the need for mobile devices able to analyze accurately real samples with sometimes very small volumes is a must. Gas chromatography (GC) is a common laboratory technique widely used for analyzing semi-volatile and volatile compounds. However, this technique is not suitable to be used outside labs. The development of micro-machined processes encouraged the development of miniaturized gas chromatographs. This chapter focuses on the recent development in the field of miniaturized gas chromatography and its component up to the present in various fields of analyses.

Keywords: gas chromatography, MEMS, micro-detector micro-column, microinjector, miniaturization

1. Introduction

Gas chromatography (GC) is a common and a complex analytical technique involving the separation of different types of gas or molecules easily vaporized without decomposition. The gas molecules are carried through the column using a carrier gas, typically nitrogen or helium. Based on their affinity for the coating material inside the column which is called the “stationary phase,” molecules are separated based on certain molecular characteristics such as their molecular weight, polarity, and presence of certain functional groups. At the end of the column, molecules are separated and detected by a detector.

Commercially available GC analyzers use conventionally manufactured components (~30 kg) and need power and gas sources that often limit their portability and suitability of “outside-laboratory” use. Miniaturization of GC is based on theoretical and practical considerations. This chapter describes the miniaturization of analytical system, in order to give a complete view of miniaturized chromatographic separations.

2. Need for portable analytical systems

Conventional GCs provide accurate analysis of complex mixtures but at the cost of using large, power-hungry, and relatively expensive table-top instruments. Usually, samples are collected and brought back to the laboratory for analysis. On-site analysis is becoming increasingly important, especially in the area of environmental monitoring. It reduces the risk of contamination, sample loss, and sample decomposition during transport. Furthermore, on-site monitoring also results in much shorter analysis turnaround times and thus allows for faster response to the analytical results. Lightweight devices with low maintenance are needed. In order to achieve these features, the miniaturization of the main components of GCs is performed.

Miniaturization of GC is based both on theoretical and practical considerations [1]. Theory predicts that reducing the dimensions of flow channels enhances the analytical performances. In practice, miniaturization also enhances analysis of small-volume samples and increases analysis speed. A microfabricated GC system requires a number of components to function properly: preconcentrator, micro-valves for injecting the sample into the carrier gas, micro-fabricated columns well-functionalized for the specific use, heaters and temperature sensors for controlling column temperature, and detector(s) for detecting the arrival of different types of molecules. Temperature stability is also critical for GC operation, as the adsorption/desorption processes responsible for molecular separation in the column are very sensitive to temperature. The issues of microfluidic integration are therefore critical in GC microsystems.

Despite the fact that the first work on microchip-based chromatographic system was a miniaturized gas chromatograph in 1979 [2] using microelectromechanical systems (MEMS), this development was hardly pursued afterward, probably because the analytical community was not yet ready to embrace this new technology.

3. Injectors-preconcentrators

The injector is a device used for introducing liquid or gas samples into the gas chromatograph. The sample is introduced directly into the carrier gas stream via a temperature-controlled chamber temporarily isolated from the system by gas sampling valves. Among all reported studies, several research teams have used commercial injectors (part of a convention GC) in split mode or gas sample valves to introduce samples into the micro-columns. Some other teams designed and fabricated a chip-based preconcentrator instead of an injector to increase sensitivity and selectivity when solute concentration is below detection limit of the detector [3, 4]. In both cases, the device must be capable of generating sharp injection plugs.

A six-valve MEMS-based injector with constant 250 nL of sample volume and suitable for harsh environment was introduced in 2010 emulating Valvo® six-valve injector. Each valve is made from sandwiching polyether ether ketone (PEEK) membranes between silicon substrate and glass. The six valves opened and closed by changing the pressure through their actuation holes. In sampling mode, valves A, D, and E are closed, while for injecting samples onto

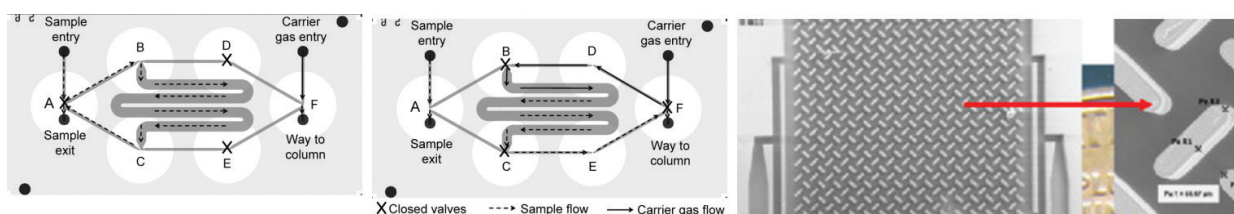


Figure 1. Left: Illustration of the MEMS injector in loading and injecting modes, adapted from [6], right: Optical image of a 3D preconcentrator with embedded pillars, adapted from [8].

separation channels, valves B, C, and F are closed (**Figure 1**) [5, 6]. Moreover, a customized volume injector (0.5–15 μL) was designed by Holland et al. [7].

As a general definition, the preconcentrator relies on an adsorbing material deposited on the active area adjacent to the heating element [8]. Ideally, the sorptive material must adsorb selectively one or more chemical species of interest over a time period necessary to concentrate the chemical compound in the adsorptive material. Then, the sorptive layer must be heated with a pulse of temperature for providing narrow desorption peaks with relatively high concentration to the connecting sensor or detector. This process must allow the analytes present in a large air volume to be purified and concentrated, so increasing the efficiency of detection. Since the first micro-machined preconcentrator designed by the ChemLab at Sandia National Laboratories in 1999 [9], many works have been carried out. In literature, different preconcentrating microstructures are now available in different designs and are combined with a wide range of adsorbents [10–12].

The optimization of the device performance (adsorption and desorption duration and flow rates, heating rates) is rather important for achieving a high preconcentration factor. A compromise must be then established between a suitable adsorbent, low power consumption, and simple fabrication technology.

4. Columns

The gas chromatographic column is considered the “heart” in a gas chromatograph. Over the last three decades, the nature and design of the column have changed considerably. Conventional GCs are equipped with conventional columns: a silica or stainless steel tube containing an immobilized or a cross-linked stationary phase bound to the inner surface. Terry et al. [2] were the first group to introduce “miniaturized GC” and “planar column” concepts by etching channels into a substrate rather by using capillaries of conventional GC technology (**Figure 1**). However, this groundbreaking work had not led to further developments of related skills or technology until the early 1990s.

4.1. Technology fabrication

Silicon is a very common substrate for microelectronics. The material is relatively inexpensive, is abundant in nature, and can be ordered with well-controlled crystal orientation, thickness, and

surface roughness. A large number of processes have been developed over the past 50 years, giving the microsystem designer a wide range of options from which to choose.

Glass, via its optical and mechanical properties, is very interesting to be included in MEMS devices. Additionally, glass can be customized by adding additives to improve some properties, boron oxides, to produce Pyrex well known to its low thermal expansion or sodium to easily to bond with silicon.

The combination of glass and silicon provides the most versatile fabrication technique for producing GC columns (**Figure 2**). However, silicon and glass fabrication requires the use of a clean room, making this technology relatively expensive and not within the reach of every academic laboratory. Fabrication processes for both glass and silicon can be divided into three main steps: patterning, etching, and bonding.

Many processes involve the deposition and patterning of thin films (e.g., for heating or as a stationary phase) [13, 14]. There is a wide variety of methods for performing such depositions, from nano- to microscale, such as physical vapor deposition (PVD), sputtering [15, 16], and atomic layer deposition (ALD).

4.2. Performance of MEMS columns

Theoretical plate number N defines the efficiency of the column or sharpness of peaks. The concept of plate theory was originally proposed for the performance of distillation columns. It is proportional to the square root of the retention time and inversed proportional to the peak width following the normal distribution law. The theory assumes that the column is divided into a number of zones called “theoretical plates.” Moreover, the zone thickness is considered as height equivalent to a theoretical plate (H or HEPT):

$$N = 16 \frac{(t_r)^2}{w} \quad (1)$$

where t_r is the retention time of a compound, w is the width of the peak at the base.

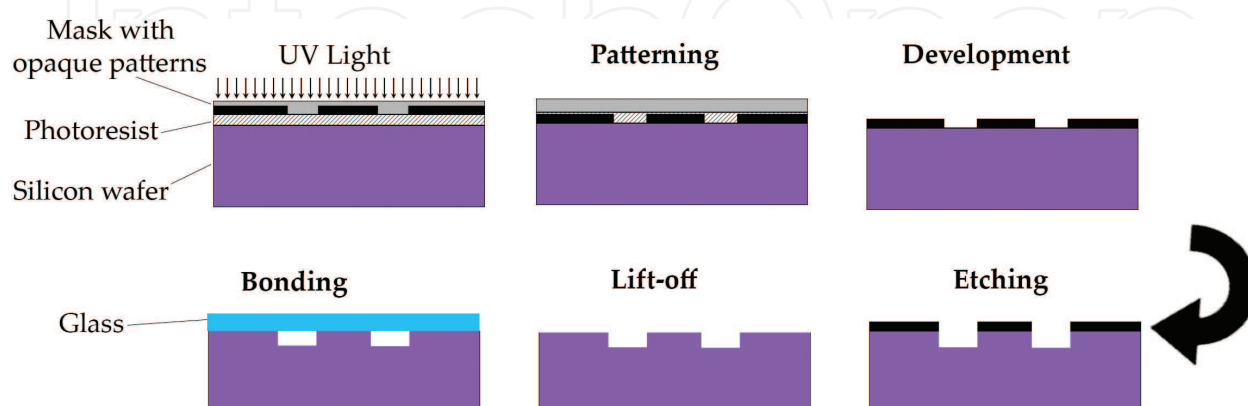


Figure 2. Illustrating steps to obtain a MEMS column.

The fundamental equation underlying the performance of a gas chromatographic column is the Van Deemter equation expressed as

$$H = A + \frac{B}{u} + C\bar{u} \quad (2)$$

where H is the height equivalent to a theoretical plate, A is the eddy diffusion or multiple path term, B is the longitudinal diffusion contribution, C is the resistance to mass transfer term, \bar{u} is the average linear velocity of the carrier gas.

Thus, equation is simplified in case of open columns. The A term is equal to zero because there is no packing. This abbreviated expression is often referred to as the *Golay Eq.* [17].

The profile of “H” versus “u” graphic goes through a minimum value of “H” where the efficiency is greatest. This minimum is reached at different carrier gas velocities depending on the nature of the carrier gas. For example, speed of analysis must be sacrificed when nitrogen is used as a carrier gas. On the other hand, if one is willing to save time with slight loss of the efficiency, helium or hydrogen can be used. Additionally, efficiency varies slightly for hydrogen than helium as velocity increases. Finally, the use of hydrogen for any application in the laboratory always requires safety precautions in the event of leak:

- The flow rate, and consequently the linear velocity, through smaller columns is difficult to measure accurately and reproducibly by conventional apparatus. Linear velocity may be calculated, through a column of length L, by injecting a volatile, non-retained solute and noting its retention time t_M using this equation:

$$u \text{ (cm/s)} = \frac{L}{t_M} \quad (3)$$

- In gas chromatography, when the temperature increases, linear velocity decreases because of increased viscosity of the carrier gas.
- Van Deemter curve is fitted under isothermal conditions.

4.3. Functionalization

It is quite straightforward to etch channels into silicon or glass chip. However, finding a comprehensive and reproducible method of fabrication enabling incorporation of a stationary phase inside the channel under conditions of extreme miniaturization, and production under clean room conditions, was a major challenge. This part covers various functionalization methods from classic coating to unusual MEMS-based techniques.

4.3.1. Polymer coating

In the beginning of the MEMS-based column era, researchers tried to adjust expertise gained from the preparation of conventional columns. Usually, columns are made by etching silica

substrate followed by capping with Pyrex. Stationary phase application after sealing the channel was usually performed by liquid coating using static or dynamic method. These methods led to wall-coated open tubular MEMS (WCOT-MEMS) columns commonly named “open columns.” The goal in coating is the uniform deposition of a thin film, typically ranging from 0.1 to 10 μm in thickness. To reach this, two varieties of coating exists: static and dynamic.

Polysiloxanes are the most widely used as stationary phases for both conventional and MEMS columns. They offer high solute diffusivities coupled with excellent chemical and thermal stabilities. Additionally, because a variety of functional groups can be incorporated into their structures, polysiloxanes exhibit a wide range of polarities. Since many polysiloxanes are viscous gums and, as such, coat well on MEMS columns. Polysiloxanes are easily cross-linked to be used as stationary phases. The basic structure of 100% dimethylpolysiloxane (PDMS) is depicted in **Figure 3**.

Lambertus et al. [18] reported a 3-m-long square-spiral MEMS column dynamically coated with PDMS achieving 8200 plates (**Figure 4**). Moreover, non-treated surface gave 1500 plates more than treated (CVD oxidation prior to bonding).

Nishino et al. [19] developed circular, 8.5–17.0-m-long MEMS columns to separate a mixture of 13 compounds which included polar and nonpolar compounds. Before coating with the liquid phase, deactivation treatment to reduce adsorption sites causing peak tailing or peak disappearance was completed. Stationary phase coating was performed by a static method with 5% phenyl 95% dimethylpolysiloxane to give a 0.25- μm -thick film.

Radadia et al. [20] improved separation of organophosphonate and organosulfur compounds by using a 3 m MEMS column coated with 0.25 μm OV-5 as stationary phase. To reduce Pyrex’s active sites, they were deactivated by the use of a variety of agents. Organosilicon hydride deactivation reduced micro-column adsorption activity more than silazane and silane treatment, enabling baseline separation of nine compounds as peaks with very low asymmetry in 2 min and providing 5500 theoretical plates/m (**Figure 5**).

The most widely used non-silicon-containing stationary phases are the polyethylene glycols. They are commercially available in a wide range of molecular weights under several designations, such as Carbowax 20M and Superox-4. Unfortunately, their operational temperature is reduced compared to siloxane-based polymers. In addition, trace levels of oxygen and water from the sample or the carrier gas have adverse effects especially with Carbowax 20M leading to their fast degradation. An example of a MEMS-based column coated with Carbowax 20M was reporter by Lee et al. [21].

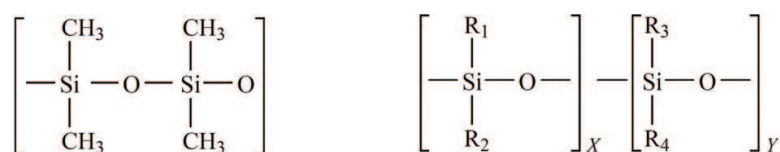


Figure 3. Chemical structure of basic dimethylpolysiloxane PDMS (left), and substituted polysiloxane.

4.3.2. Solid packing

A packed column refers to a column packed with either a solid adsorbent or solid support coated with a liquid phase. However, stable and reproducible performances depend mainly on the quality of packing. In conventional GC, this kind of column began to decline since 1979 by the apparition of capillary fused-silica columns. A packed column consists of three basic components: tubing in which packing material is placed (**Table 1**), packing retainers (such as glass wool plugs), and the packing material itself. In MEMS-based columns, tubes are replaced by MEMS channels and glass wool plugs by grids or meshes (**Figure 6**) [22].

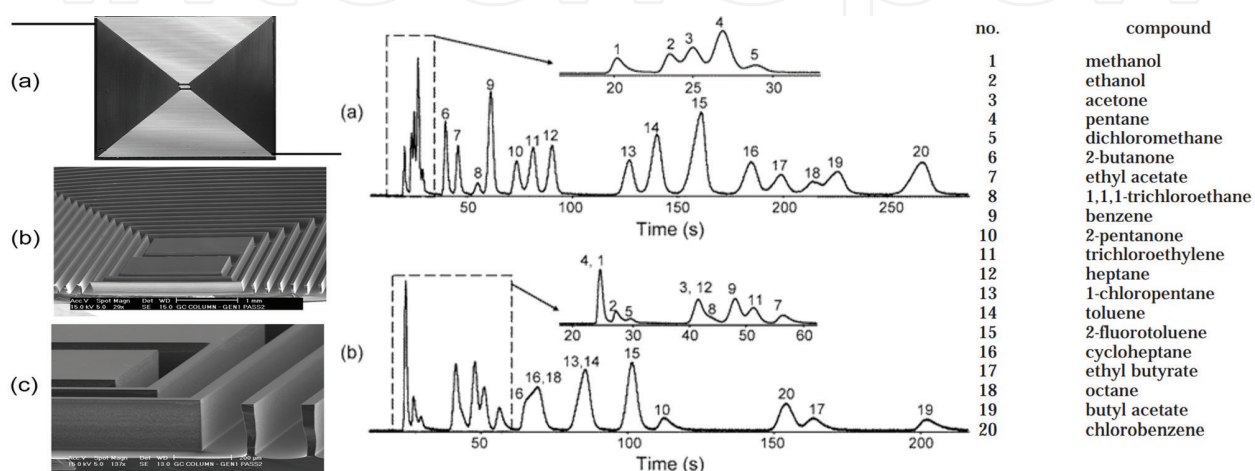


Figure 4. Left: (a) entire chip; (b) SEM image detail of gas flow (c) detail of etched-channel, right: Isothermal chromatograms at 22°C of the 20-component using channels coated with the nonpolar (a) and the moderately polar (b) stationary phases, reprinted with permission from [19].

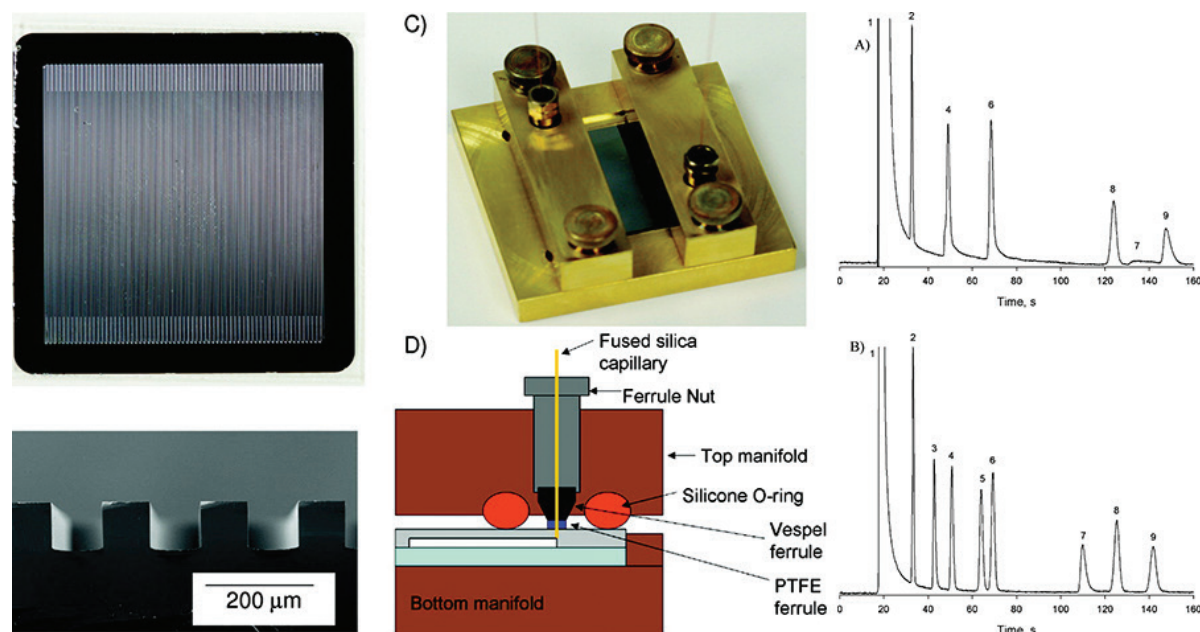


Figure 5. Left: (A) photograph of the MEMS column, (B) SEM of channels, (C) manifold packaging, and (D) connection to the micro-column. Right: Separation of test, reprinted with permission from [21].

Stationary phase	Usual applications
Alumina	Alkanes, alkenes, alkynes, aromatic hydrocarbons (C1-C10)
Silica gel	Hydrocarbons (C1-C4), inorganic gases, volatile ethers
Carbon	Inorganic gases, hydrocarbons (C1-C5)
Carbon molecular sieves	Oxygenated compounds (C1-C6)
Molecular sieves (5X, 13 X)	Hydrogen, oxygen, methane, permanent gas, halocarbons

Table 1. Illustrative examples of some adsorbents and usual applications.

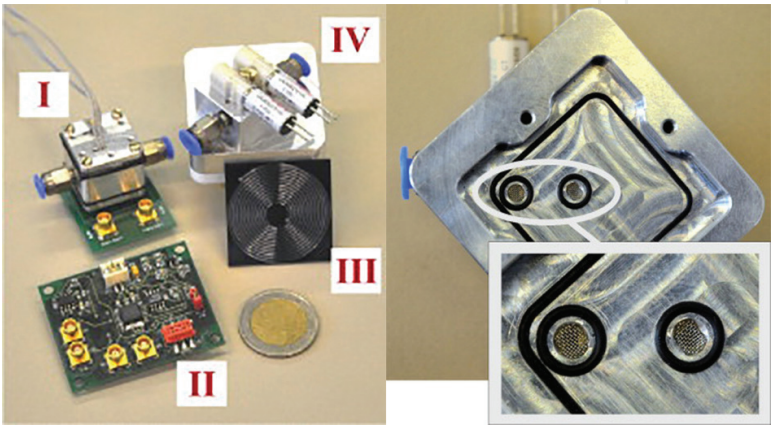


Figure 6. Left: Photograph of different components of miniaturized GC, right: Stainless steel meshes to keep the stationary phase particles in the column, adapted from [23].

Some separations require the use of packed columns: permanent gases, unsaturated isomers of light hydrocarbons, and standardized methods (ASTM E260, NF ISO 17494, etc.) [23]. Although these columns remain effective, their implementation in reduced sizes, low efficiency, and the pressure generated in the column are the main obstacles to their use.

4.3.3. Carbon nanotubes

Soon after their discovery in 1991 [24], carbon nanotubes (CNTs) received much attention because of their unique geometry, chemical stability, and high surface-to-volume ratio. Stadermann et al. [25] successfully used single-wall carbon nanotubes (SWCNTs) as a stationary phase by means of CVD in a microfabricated GC column (**Figure 7**). Following on from their study, the team developed a new process to produce a highly uniform mat of CNT stationary phase [26].

SWCNTs demonstrate a good ability to be used as stationary phase in gas chromatography to separate alkanes and other analytes. It can be used as is, and no functionalization is required. However, their performance is limited by the fabrication difficulty. CNTs are deposited only on three sides of the column’s channel (silicon) leading to peaks broadening. Additionally, columns with CNTs suffer from poor separation of high-boiling compounds, which is often attributed to the thickness of the CNT layer.

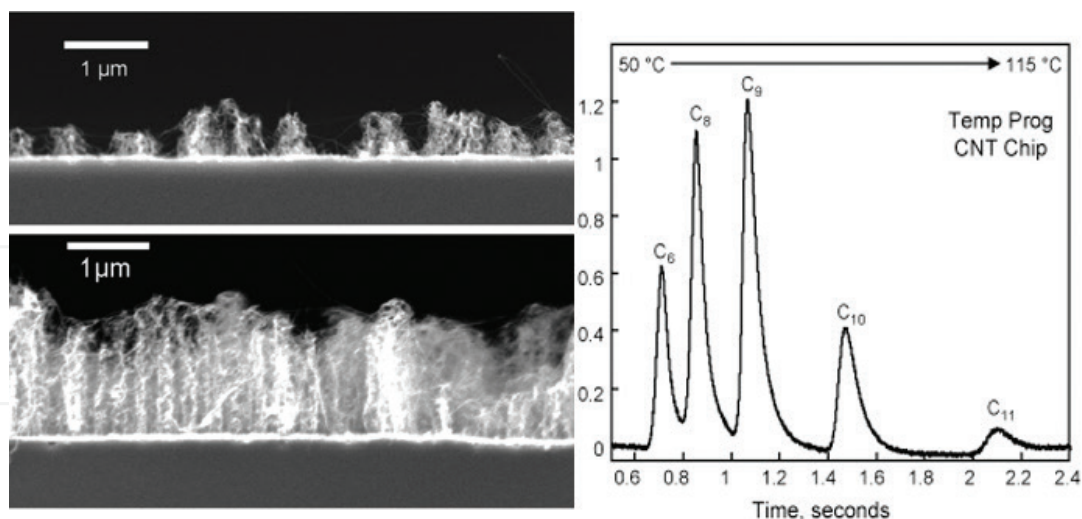


Figure 7. Left up: SEM image of the old CVD process to produce SWCNTs, left down: SEM image of the new CVD process lead to obtain a “mat” of SWCNTs, right: Separation chromatogram of n-alkanes with SWCNTs, reprinted with permission from [26, 27].

4.3.4. Sputtering

Sputtering is widely used in electronics for deposition of metals and dielectrics. Vial et al. [15] use this technique to provide solid and porous stationary phase. By varying the duration of the sputtering process, sputtered silica layers of different thicknesses were produced. For example, silica layer having 0.75 μm thickness produced 2500 theoretical plates for hydrocarbon separation (**Figure 8**). At the opposite, producing a thicker layer leads to loss separation efficiency (number of plates). To overcome this, the same group used a semi-packed column with high aspect-to-ratio pillars [13].

In that case separations were greatly improved because retention increased and efficiency was close to 5000 theoretical plates m⁻¹. The same group tested various targets such as graphite and alumina to separate light hydrocarbons [13, 16]. However, alumina requires a tedious activation step before using.

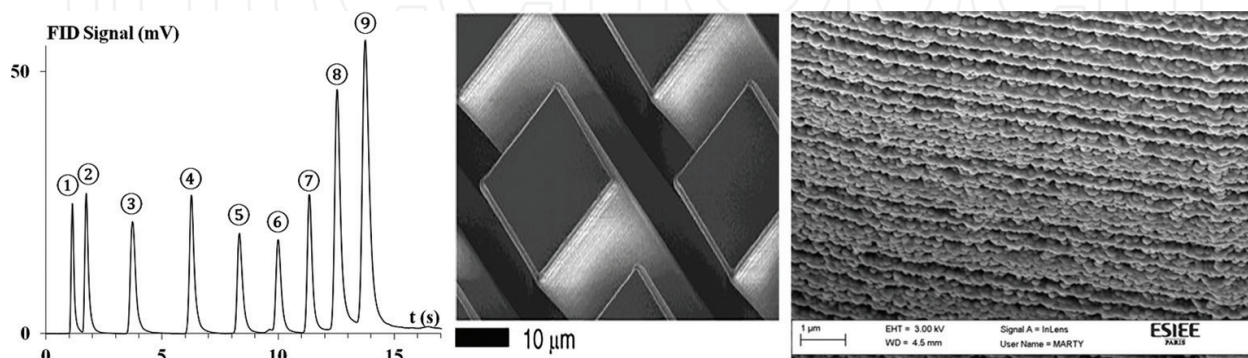


Figure 8. Left: Fast separation of linear hydrocarbons with a silica sputtered MEMS column, middle: Micro-pillars covered with sputtered silica, right: SEM picture of graphite-sputtered layer deposited on the inner wall of a micromachied column, reprinted with permission from [14, 17].

4.3.5. Gold layers

In the separation sciences, nanoparticles have been used as stationary phases to provide high separation efficiency for a variety of analytes. Because the nanoparticles are too small to be packed into the column, they are usually used as pseudo-stationary phase to enhance separation [27, 28]. Gold nanoparticles have become increasingly popular because of their long-term stability, high surface-to-volume ratio, and ease of chemical modification. The use of gold enables a variety of functional groups to be incorporated into the monolayer [29].

Agah's group introduced in 2010 a new stationary phase based on depositing gold by electroplating followed by its functionalization [30, 31]. The thickness and the regularity of the layer are customized by varying the current density. Additionally, they used a multi-capillary microfabricated 25 cm column to separate hydrocarbons yielding 20,000 plates m^{-1} (Figure 9).

Although such results were promising, a disadvantage is that nonselective deposition meant that the fabrication process required "mechanical" removal of gold from the upper surface. This step could damage the very thin fluidic channels. To resolve this problem, Shakeel et al. [32] proposed two different ways, highly reproducible, for the deposition of gold:

- Self-patterning gold on the vertical sidewalls only (varying electroplating conditions)
- Double-doped self-patterning to cover the interior surfaces of the channel (three silicon sides)

The use of gold stationary phases has furnished interesting results. However, uniformity and quality of deposition depend on the deposition conditions. Additionally, this stationary phase is not suitable for light hydrocarbons separation.

4.3.6. Ionic liquids

Ionic liquids constitute a group of organic salts with a particulate specification. They are liquid below 100°C and consequently liquids at room temperature. Ionic liquids are polar, nonflammable, chemically inert, thermally stable, easy to synthesize, and already used in conventional gas chromatography [33, 34]. Additionally, their selectivity can be tuned by altering the constituent cation or anion, and hence there is more than 300 commercially varieties.

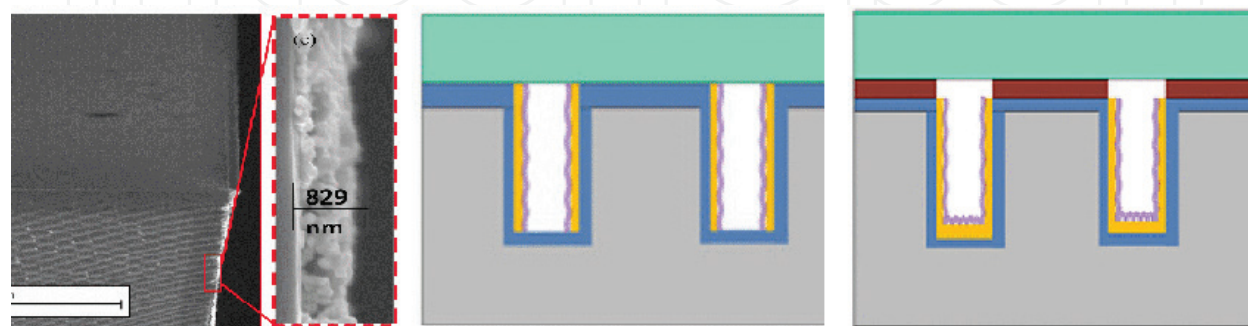


Figure 9. Left: Cross-section of a single side-wall with zoom (thickness of the gold layer, middle and right: Thiol deposition using single and double doping methods respectively, adapted from [33].

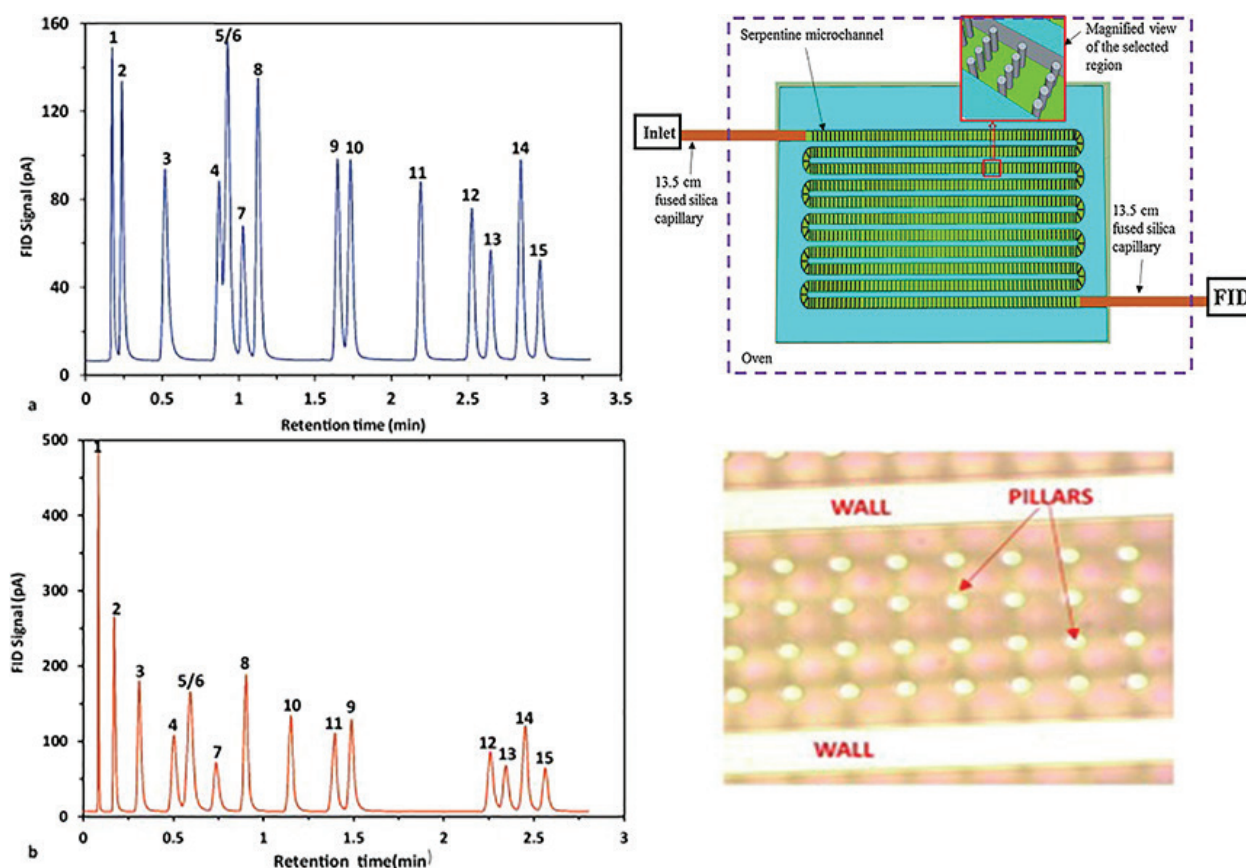


Figure 10. Left: Separation of a 15-compound mixture using (a) [P66614][NTf2]- and (b) [BPyr][NTf2]-coated columns, right: Up schematic diagram of the measurement setup, right down optical micrographs of the uncoated micro-column.

Zellers' group [35] was the first team to use ionic liquids in miniaturized gas chromatography by coating a rectangular column as a second dimension in a GC \times GC system. Two years after, Agah's group [36] successes integration of ionic liquids for high-performance separation of complex chemical mixtures (**Figure 10**).

Ionic liquids can be easily statically or dynamically coated (immobilized). However, two points should be highlighted:

- Due to the vast number of ionic liquids, no correlation between the stationary phase and the group of analytes to be separated is known.
- Like normal polymer coating, homogeneity of the coating is not systematically reported. Moreover, no one can be sure that the coating thickness is homogeny along the column.

4.4. Geometry

In conventional gas chromatography, used columns are tubes functionalized by a stationary phase having length ranging from 10 to 100 m. To obtain an excellent column, few parameters can be optimized: length, inner diameter, film thickness, and the coiling radius [37]. Theory of chromatography predicts an increase of efficiency, while the diameter of a capillary column decreases. However, with the emerging of "planar columns," other parameters appear (**Figure 11**).

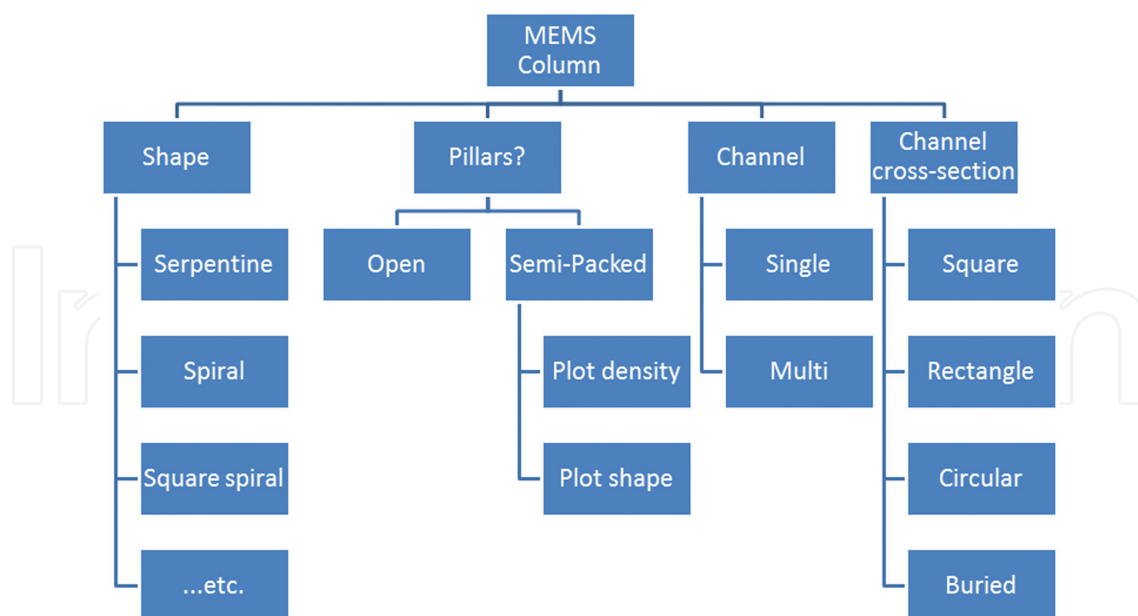


Figure 11. Illustration of some geometrical parameters related to MEMS columns.

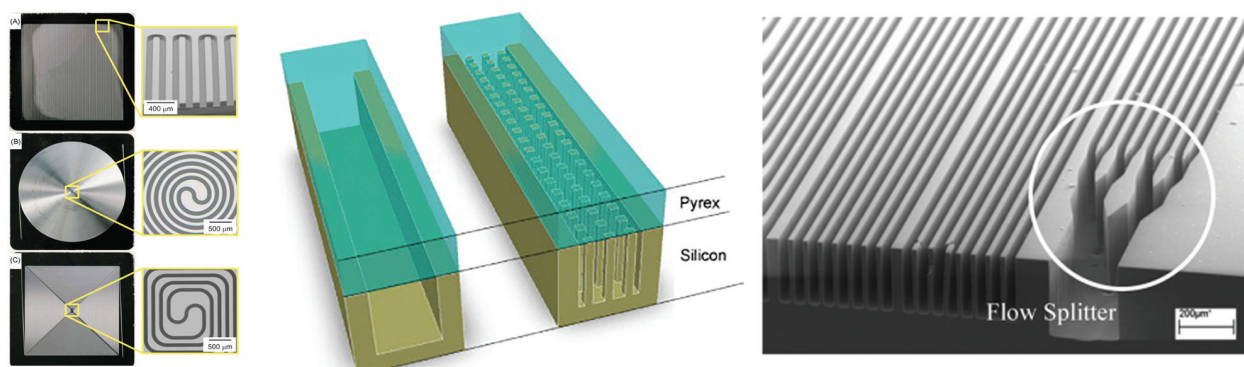


Figure 12. Left: Photograph showing three different micro-column (a) serpentine, (B) circular-spiral, and (C) square-spiral. Adapted from [39], middle: Section of an open and a semi-packed columns, adapted from [40], right: Multi-capillary MEMS column, adapted from [41].

The effect of microfabricated columns' geometries on separation performance was compared by Radadia et al. [38]. In fact, three configurations were tested under isothermal and temperature-programmed mode: serpentine, circular-spiral, and square-spiral (**Figure 12**). Although all the geometries have similar gas permeability, it is shown that the serpentine columns show higher separation plate numbers (lower band broadening) for retained solutes in isothermal mode of operation compared to circular- or square-spiral configurations. Additionally, in temperature-programmed mode of operation, the serpentine design yields higher separation numbers (peak-to-peak resolution) compared to spiral configurations. These performances were attributed to the more favorable hydrodynamic flow.

To increase the efficiency and the surface-to-volume and the loadability without scarifying inlet pressure, a new class of gas chromatographic column was introduced in 2009 by Agah's

group [39]. This “semi-packed” column contains embedded $20\text{ }\mu\text{m}$ square posts along the length of the channel paced at $30\text{ }\mu\text{m}$ (**Figure 12**).” This novel configuration enhances both the sample capacity and the separation efficiency compared to the open rectangular columns. Furthermore, due to the uniform spacing and distribution of the posts, these columns have lower-pressure drops and eddy diffusion as compared to conventional packed columns.

Among the shape of the column and implemented pillars or none, some researchers tried different layouts including width modulation [40], multi-capillary [41], and partially buried channel [42].

4.5. Resistive heating

The major goal of GC method development is to minimize the analysis time with desired resolution for accurate qualitative and quantitative analysis. Additionally, fast analysis time means also bring the system back to its initial state (for another cycle). For conventional GC, the column is placed inside an oven and heated using a bare resistive metal wire positioned at the back of the oven. Heating rate for the entire GC analysis is between 30 and $60^\circ\text{C}/\text{min}$ when cooling down after running a sample takes approximately 5 minutes. Slow heating and cooling are due mainly to the large total thermal mass of the oven making it unsuitable for separations in fast GC.

Microfabricated columns hold a promise for field applications, as they feature fast analysis time, low power consumption, and easy portability. Although the conventional oven has often been used to evaluate to MEMS column performance, heating element is directly incorporated on this plan columns. Because of the high thermal conductivity of silicon, localized heaters are usually deposited on that side to achieve reasonably uniform temperatures across the silicon chip (**Figure 13**).

Patterned resistive metal layers can be deposited on the surfaces of column substrates to form robust micro-heaters with good thermal conduction, wide temperature range, and extremely low thermal mass. Deposition is performed by various methods such as sputtering or CVD. The resistance temperature detector (RTD) is one of the most accurate temperature sensors. Not only does it provide good accuracy, but it also provides excellent stability and repeatability. Platinum (Pt) is often used in RTDs, and the thin metal film can also function as the heater and temperature sensor simultaneously, which is advantageous for system integration compared to external heaters [13, 43].

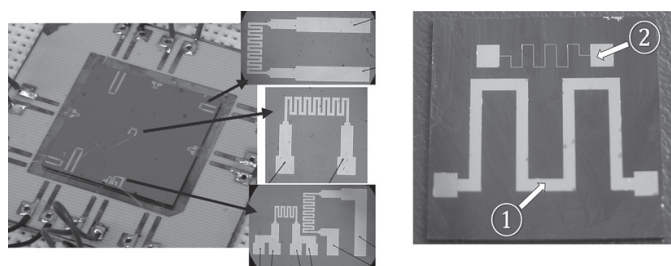


Figure 13. Examples of various deposited platinum resistance for sensing and heating the column, adapted from [14, 44].

Instead of using only platinum as metallic resistance, deposition of various metals was reported: chromium/gold film (Cr/Au) or titanium/platinum (Ti/Pt). Intimate contact between the heater and the column allows extremely high heating rates (1500°C/s) [44]. Depending on the thickness and size of the chip, a heating power consumption can be as low as 4 W/m.

In gas chromatography, separations are performed by temperature programming starting from lower to upper. For continuous monitoring or on-site analysis, GC system should be cooled to the initial state to start a new cycle. Peltier coolers are widely used in miniaturized GC. Also, the column can be set at sub-ambient temperature to retain volatile compounds, for example. This is an advantage compared to conventional GC systems which require liquid carbon dioxide or nitrogen.

5. Detectors

After separating the compounds, a detector is used to monitor the outlet stream from the column. Detection in analytical microsystems is a subject of paramount importance. Indeed, detection has been one of the main challenges for analytical microsystems, since very sensitive techniques are needed as a consequence of the ultrasmall sample volumes used in micron-sized environments.

The flame ionization detector (FID) is the most popular and widely used detector for the analysis of trace levels of organic compounds. Its success is based on outstanding properties, such as a very low minimum detectable limit, a high sensitivity, and a broad linear measurement range. Kuper's team works on miniaturized planar FID since 2000 where the oxygen-hydrogen flame burns inside a glass-silicon chip (**Figure 14**) [45].

At the opposite of FID, thermal conductivity detector (TCD) is a nondestructive system. It measures the difference in thermal conductivity between pure carrier gas and the carrier gas

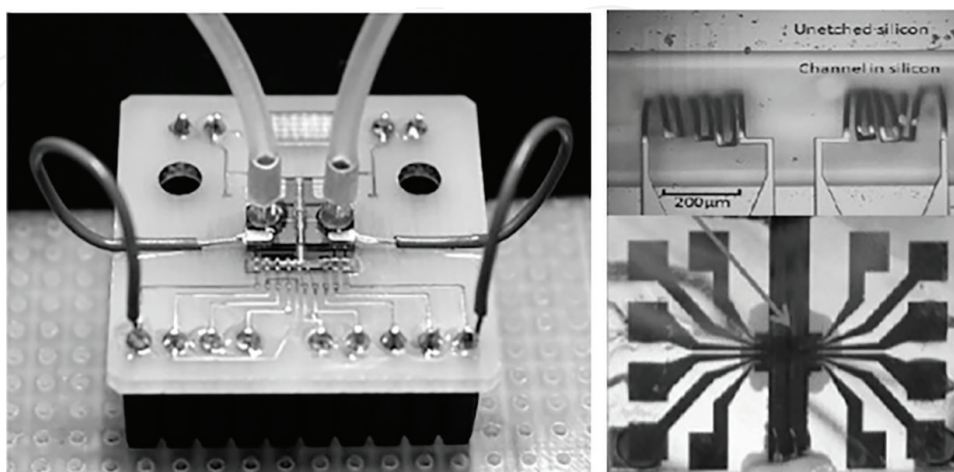


Figure 14. Left: Photography of a micro-FID on a PCB adapted from [47], right: A suspended micro-TCD, adapted from [48].

contaminated with the sample components. Miniaturization of TCD started with the first micro-GC in 1979, and since then several studies have been published in this area [46, 47].

Many sensors such as chemiresistor array and metal oxide (MOX) sensors have been reported for chip-based GC. The response mechanism of these sensors mainly relies on the impedance changes. Typically, a chemiresistor consists of a conductive or semiconductive polymer or emulsion and organometallic compounds [48, 49].

6. Integrated analytical systems

The development of MEMS gas chromatographic components is in progress at several laboratories and universities. Some characteristics of miniaturized GCs are listed in **Table 2**.

At this stage, microfabrication is an attractive option for the development of greatly improved instruments, and many investigations have been reported. However, there are no portable devices able to work anywhere, making accurate, automatic, and continuous analyses of gas samples.

Features→↓reference	Sampling and injection	Separation	Detection	Products to be separated
Sandia National Laboratories [51] (2004–2010)	MEMS cavities	MEMS spiral columns coated with PDMS, WAX, etc.	Chemiresistor, surface acoustic wave	C5–C12 polar and nonpolar compounds (hydrogen*)
μGC system CNR-IMM [52] (2009)	MEMS cavity filled with quinoxaline	0.5 m square-spiral column, packed with Carbograph	Metal-oxide semiconductor	Benzene, toluene, ethylbenzene, xylenes (ambient air*)
μGC system Arizona State University [53] (2013)	Stainless steel tube packed with Carbo-pack	2–19 m commercial columns	Quartz crystal fork detector with imprinted polymer (MIP)	Benzene, toluene, ethylbenzene, xylenes (ambient air*)
Intrepid GC University of Michigan WIMS [54] (2013)	Combination of stainless steel tube and MEMS elements	1 m MEMS column (PDMS coating)	Chemiresistor array	Explosives vapors (ambient air*)
Zebra GC system Virginia Tech [55] (2015)	MES cavity with embedded pillars (Tenax TA coating)	2 m MEMS column (PDMS coating)	μTCD embedded in the column	Benzene, toluene, tetrachloroethylene, chlorobenzene (helium*)
μGC system University of Michigan WIMS [56] (2016)	MEMS cavity filled with Carbo-pack	10 m commercial column	Homemade PID	26 VOCs (helium cartridge*)
* carrier gas.				

Table 2. Comparison of some portable GC systems.

C2V Company released its first commercial micro-GC product (model C2V-200) in 2010. The platform, based on cartridges, allows hybrid integration of components such as sensors and valves to be assembled together with reduced dead volume. Integrated microchip technology combined with narrow bore capillary GC columns results in a higher performance for lower costs. The C2V-200 micro-GC is designed for ease of use, reduced maintenance, and low gas consumption. Exchangeable column cartridges, with integrated heating zones, can be easily installed (up to 4) with a different column and detection method. This modular setup allows the ability to monitor a wider spectrum of gas components in the same timeframe of 10 to 60 seconds [50].

7. Conclusion

The concept of micro-gas chromatographs demonstrates the potential of mobile devices in various fields related to analytical chemistry such as oil and gas, air analyses, defense, food processing industry, etc. New instrument designs and component manufacturing methods are coming on line that will result in the development of a new generation of high-performance, moveable, and miniaturized instruments for high-performance gas chromatography (HP-GC). The use of microelectromechanical system technologies for the manufacturing of microfabricated gas chromatographic components results in very small, autonomous, and low-cost instruments. Completely autonomous GC instruments require no daily maintenance and can be placed in remote locations for long-term service. This requires battery operation, wireless communications, and freedom from tanks of compressed gases. To this end, work is in progress to develop a high-performance micro-GC that will have acceptable volume. To achieve complete autonomy, vacuum outlet GC should be used with ambient air as carrier gas. In addition, remote battery charging with radiofrequency transmission will be feasible. The use of ambient air as a carrier gas poses several challenges. First, some stationary phases rapidly decompose in air. Poly(ethylene glycol) is a good example. In addition, particulate material and water vapor may need to be removed. Sensor array detection also is needed because these devices can be microfabricated with very low dead volumes; they require no support gases for their operation, and they can be fabricated with a variety of selectivities, which can be used for vapor recognition and for the deconvolution of overlapping peaks. This can reduce the resolution requirements for the column. Sensors and detectors usually have lower sensitivity than detectors incorporated in laboratory gas chromatographic instruments. Low detector sensitivity, coupled with the very low concentrations often associated with air monitoring, requires the use of a preconcentrator for sample enrichment prior to separation and detection. More energy is then needed to heat the preconcentrator to release the adsorbed sample. It seems that one way to solve these problems is a future integration of the instrument on a single chip, focusing each device to one field of application instead to make universal apparatus emulating conventional gas chromatographs.

Conflict of interest

The authors declare no conflict of interest.

Author details

Imadeddine Azzouz^{1,2*} and Khaldoun Bachari¹

*Address all correspondence to: imadeddine.azzouz@esiee.fr

1 Research Center in Analytical Chemistry and Physics (CRAPC), Algiers, Algeria

2 ESYCOM/ESIEE Paris, University of Paris-Est, Noisy-le-Grand, France

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