3
Basic Overview on Gas Chromatography Columns

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3.1
Introduction

Gas chromatography (GC) is a separation technique used to isolate volatile components of a mixture depending on differences in the mode of partitioning between a flowing mobile phase and a stationary phase. Because of its simplicity, sensitivity, and effectiveness, GC has earned its place as one of the most important tools in chemistry.

Columns/stationary phases are considered the "heart" or "brain" of the chromatograph and are responsible for the separation process. In the GC system, a sample is vaporized and injected into the head of the separation column packed with a finely divided solid or coated with a film of a liquid. When a sample traverses the column by the flow of an inert gas employed as the mobile phase, its components are separated owing to differences in their interactions with the stationary phase. Upon elution from the column, the separated compounds pass over a detector that generates a signal corresponding to the concentration of the compound. The species present can be qualitatively identified based on the delay in the sample passing through the column. Extensive research has led to improved columns for achieving better separation and resolution. Since the initial development of packed columns, many technological advancements have been made. The capillary column was the first advancement in which stationary phases fabricated by using the latest technology was employed.

3.2
Main GC Modes

GC is the only form of chromatography that does not utilize a mobile phase for interacting with the analyte. When the stationary phase is a solid adsorbent, the process is termed gas–solid chromatography (GSC), and when it is a liquid on an

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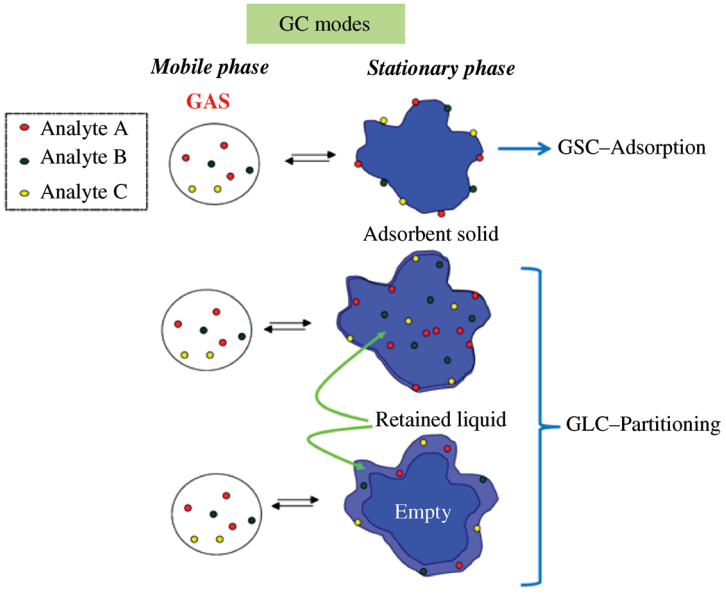

Figure 3.1 GC modes showing interaction between the mobile phase and the stationary phases.

inert support, the process is termed gas–liquid chromatography (GLC). A schematic diagram explaining each GC mode is presented in Figure 3.1.

3.3 Main GC Columns

In GLC, the liquid stationary phase is adsorbed onto a solid inert packing or immobilized on the capillary tubing walls. The column is considered packed if the glass or metal column tubing is filled with small spherical inert supports. The liquid phase is adsorbed onto the surface of these beads in a thin layer. In a capillary column, the tubing walls are coated with the stationary phase or an adsorbent layer that is able to support the liquid phase. However, GSC has a limited application in the laboratory and is rarely used due to severe peak tailing and semipermanent retention of polar compounds within the column. Therefore, the term "gas–liquid chromatography" is simply shortened to "gas chromatography." Having established the distinctions between the main GC modes, a classification of GC columns is presented in Scheme 3.1.

3.3.1 Packed GC columns

Because the first commercial instruments accepted only packed columns, all initial studies of GC were performed on packed columns. Packed columns

Columns

Packed columns	Capillary columns
Stationary phase is coated directly in the column	Stationary phase is coated with the inner wall of the column
Applicable for both GSC and GLC	Applicable only for GLC
Liquid phase is adsorbed onto the surface of the beads in a thin layer or onto the solid inert packing	Liquid stationary phase is immobilized on the capillary tubing walls

Scheme 3.1 Types of columns used in GC: packed columns and capillary columns.

are typically made of stainless steel and have an outer diameter of 0.64 or 0.32 cm and lengths of 0.61–3.05 m. Alternative inert materials have also been used, including glass, nickel, fluorocarbon polymer (Teflon), and steel covered with glass or Teflon. The packing is an inert support impregnated with 5–20% stationary phase. The solid support holds the liquid stationary phase and should have a large surface area (0.5–5 m^2/g), be chemically inert, have low sorptive activity toward common analytes, and have good mechanical strength to prevent the fracture of the coated particles during loading and handling. Diatomaceous earth, composed of hydrous silica with impurities, has been used as a solid support under the brand name Chromosorb® [1,2].

The surfaces of the diatomaceous earth support have many active sites generated from free hydroxyl groups that form undesirable hydrogen bonds with polar solute molecules and cause peak tailing. Even the most inert material (white Chromosorb) must be washed with acid and silanized to make it more inert. Some typical deactivated white supports are Supelcoport®, Chromosorb W-HP®, Gas Chrom Q II®, and Anachrom Q®. The disadvantage of deactivation is that these supports become hydrophobic, and coating them with a polar stationary liquid can be difficult [3].

GC liquid phases are primarily silicone-based oils with high temperature stability. These liquid phases are available in a range of polarities, extending from methyl silicone (OV-1, OV-101, SE-30, and DC-200), methyl phenyl silicone (OV-17 and SE-52), and methyl trifluoropropyl silicone (OV-210 and QF-1) to methyl cyanoethyl silicone (OV-225 and AN-600). The use of a higher liquid phase load (~10%) both decreases the adsorptive interactions between the solute and the solid support and increases the column capacity to prevent overloading from dirty samples, but requires the use of a higher column temperature for elution [4,5].

3.3.2 Capillary GC Columns

Although capillary columns were introduced in 1959, they did not gain popularity until 1980. At present, it is estimated that more than 80% of all applications are run on capillary columns due to the fast and efficient separation the afford.

Capillary chromatographic columns are not filled with packing material; instead, a thin film of liquid phase coats the inner wall. Because the tube is open, its resistance to flow is very low, and it is thus referred to as an open tubular column.

Open tubular columns can be divided into three groups and are described in the next sections.

3.3.2.1 Porous Layer Open Tubular Column

Porous layer open tubular (PLOT) columns, first suggested by Golay in the late 1950s, have been successfully developed and commercialized [6]. PLOT columns contain a porous layer of a solid adsorbent such as alumina, molecular sieves, or Porapak. PLOT columns are well suited for the analysis of light, fixed gases, and other volatile compounds. The typical structure of a porous layer open tubular column is shown in Figure 3.2.

3.3.2.2 Wall-Coated Open Tubular Column

In 1957, Golay demonstrated the superiority of wall-coated open tubular (WCOT) columns (a 100-fold or higher increase in efficiency) relative to packed columns; yet, it took a quarter century before this efficiency was realized in practice [7]. In WCOT columns, the wall is directly coated with the stationary-phase layer at a film thickness of 0.05–3 μm. A typical wall-coated open tubular column is shown in Figure 3.3.

3.3.2.3 Support-Coated Open Tubular Column

Support-coated open tubular (SCOT) columns were introduced in 1963 by Halász and Horváth [8]. These columns contain an adsorbed layer of a very fine solid support (such as Celite) coated with the liquid phase. SCOT columns can

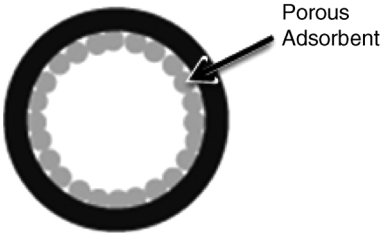

Figure 3.2 Porous layer open tubular column (http://community.asdlib.org/imageandvideoexchangeforum/2011/06/21/gc-columns/).

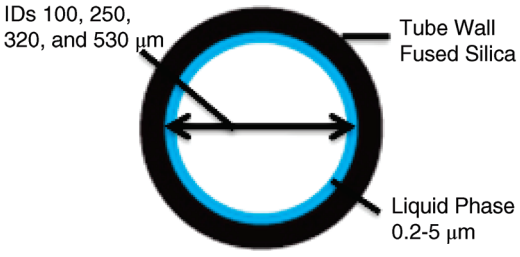

Figure 3.3 Wall-coated open tubular (WCOT) column (http://community.asdlib.org/imageandvideoexchangeforum/2011/06/21/gc-columns/).

hold more liquid phase and have a higher sample capacity than the thin films of early wall-coated open tubular (WCOT) columns had. With the introduction of cross-linking techniques, the use of stable, thick films in WCOT columns has become possible, thereby making SCOT columns redundant. A typical support-coated open tubular column is shown in Figure 3.4.

3.3.2.4 **Fused Silica Open Tubular Column**

Stainless steel was utilized early as a material for capillary GC. However, due to the lack of efficiency and high reactivity with compounds, including steroids, amines, and free acids, the steel capillary has been outdated. Glass columns suffer from the drawback of being fragile. Thus, fused silica was introduced in 1979, and almost all capillary columns are made of fused silica [9–13]. The cross-section of a fused silica open tubular (FSOT) column is depicted in Figure 3.5.

The fused silica tubes have much thinner walls than glass capillary columns, and are strengthened by the polyimide coating. These columns are flexible and can be wound into coils. They offer the advantages of physical strength, flexibility, and low reactivity.

Capillary columns offer certain advantages relative to packed columns. Capillary columns are coated with a thin, uniform liquid phase. Because of the smooth, inert surface of fused silica, high efficiency can be achieved, typically 3000–5000 theoretical plates per meter. In contrast, packed columns have

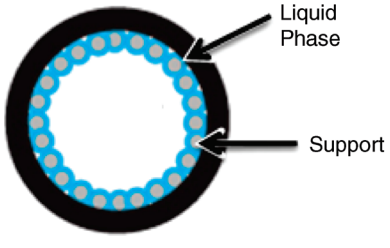

Figure 3.4 Support-coated open tubular column (http://community.asdlib.org/imageandvideoexchangeforum/2011/06/21/gc-columns/).

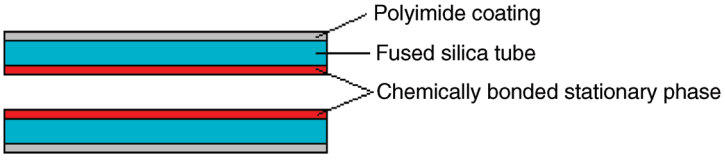

Figure 3.5 Cross-section of a fused silica open tubular column (http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm).

thicker, often nonuniform films, and generate only 2000 plates per meter. Thus, the total plates available in long capillary columns range from 180 000 to 300 000, whereas packed columns typically generate only 4000 plates and have much lower resolution. Due to the small pressure drop associated with open tube capillary columns, long columns of up to 60 m can easily be used. However, packed columns are tightly filled with solid support and suffer from greater pressure drops; thus, it is impossible to use packed columns much longer than 2 m [1].

Optimizing GC separation requires fine-tuning of a number of variables and their interactions. Both physical (internal diameter, length, and stationary phase) and parametric (temperature and flow velocity) column variables affect the separation process [14]. To illustrate the wide range of combinations to be considered when selecting a GC capillary column, an overview of available internal diameters is presented in Table 3.1.

Many capillary columns have internal diameters (IDs) of 250–320 µm. These IDs represent the best compromise between resolution, speed, sample capacity, and ease of operation [1]. Various capillary column IDs and their characteristics are shown in Table 3.2.

The longer the column, the more theoretical plates and the better the separation. Resolution is proportional only to the square root of the column length, that is, if the column length is doubled, the resolution increases only by the square root of two or 41%.

Table 3.1 Classification of capillary columns with respect to column diameter.

Types	Column diameter range (mm)	Standard commercial column diameters (mm)	Maximum flow rate (ml/min)[a)]
Megabore	≥0.5	0.53	≥660
Wide bore	≥0.3 to <0.5	0.32 and 0.45	≥85 to <660
Narrow bore	≥0.2 to <0.3	0.20, 0.25, and 0.28	≥17 to <86
Microbore	≥0.1 to <0.2	0.10, 0.15, and 0.18	≥1 to <17
Submicrobore	<0.1	Various	<1

Source: Table is reproduced with permission from Ref. [15].

a) Flow rate calculation: Helium carrier gas at 690 kPa, 200 °C oven, vacuum outlet conditions, and 10 m column length [15].

Table 3.2 Effects of internal diameter [1].

Internal diameter (ID)	Resolution	Speed	Capacity	Outcome
0.1 mm	Excellent	Excellent	Good	Good
0.25 mm	Better	Better	Better	Better
0.32 mm				
0.53 mm	Good	Better	Excellent	Excellent

Table 3.3 Column length recommendation [1].

Column length	Resolution	Speed
Long (60–100 m)	High	Slow
Medium (25–30 m)	Good compromise between resolution and speed	
Short (5–10 m)	Moderate	Fast

Short columns of 10 m should be used for fast analysis of simple samples. Only moderate resolution is possible, but the speed of the analysis can be impressive [1]. Table 3.3 indicates the recommended column length.

Figure 3.6 presents a basic classification of GC stationary phases based on polarity. There are other novel ways to classify stationary phases, particularly when trying to address the polarity of columns based on ionic liquids (ILs, commercialized by Supelco). Luigi Mondello (University of Messina, Italy) suggested a procedure for evaluating the polarity of GC columns in which each column

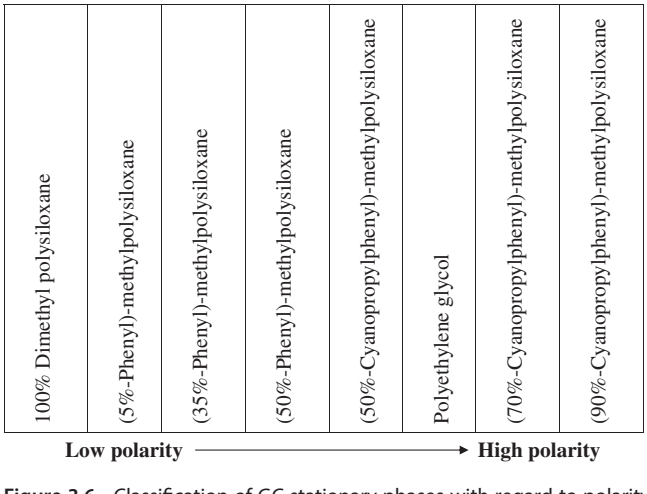

Figure 3.6 Classification of GC stationary phases with regard to polarity. (Reproduced with permission from Ref. [14].)

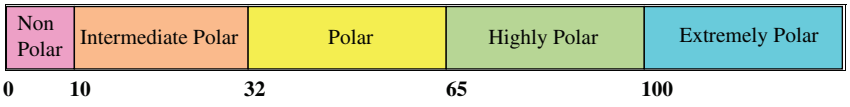

Figure 3.7 Polarity region based on ionic liquid.

is characterized with a series of five probes plus several *n*-alkane markers to determine the retention index for each probe. McReynolds constants are then calculated using the retention index data of the column relative to the retention index data for the same five probes on squalane, the most nonpolar GC stationary phase. The five McReynolds constants are summed to obtain polarity (*P*) values, which are then normalized to SLB®-IL100, anIL GC column (set at $P = 100$) to obtain polarity number (PN) values. Once the PN values are calculated, the relationship between the polarity and the numbers can be depicted in the visual representation in Figure 3.7.

The scale is divided into five regions. The first four regions (nonpolar, intermediate polar, polar, and highly polar) are generally accepted and used by several GC column manufacturers. The fifth region (extremely polar) was required with the introduction of the SLB-IL111 column in 2010, prior to which there was no column classified in this region.

3.4 Trends and Novelties in GC Columns

3.4.1 Novel Materials as GC Stationary Phases

Polysiloxane polymers, traditional phases, were introduced in the early 1950s and several improvements were achieved over the years. Common commercial columns were found as −1, −5, −20, −1701, −35, −50, −2330, −2380, and −2560. Polyethylene glycols (PEGs) are another traditional phase introduced in the mid-1950s; however, very few improvements have been achieved over the years in these phases. Common commercial columns were found as "wax" or "PEG." Although some improvements have been achieved, these phase platforms have remained virtually unchanged since the initial introduction of GC. These traditional phases have certain limitations such as (i) active hydroxyl (−OH) groups at the polymer termini that make these phases susceptible to a backbiting reaction if exposed to moisture and oxygen, leading to phase degradation and contributing to column bleed; (ii) the limited ability to modify the phase restricts the ability to alter the selectivity of the column; and (iii) a major limitation of PEG phases is their thermal limit (around 280 °C).

Recent research has paved the way for the prospective application of unique, newly developed substances in GC column technology. These substances include

ILs, a new phase commercially introduced in 2008. Organic ILs currently used as the stationary phases for gas chromatography were first described by Gordon, Selwyn, and Torne in 1966 [16]. The first systematic study of the separation properties of an IL stationary phase was performed in 1982 by employing the room-temperature IL (RTIL) ethyl ammonium nitrate. A wide range of volatile organic compounds were successfully separated at temperatures below 120 °C [17]. However, practical application of this salt was limited due to poor efficiency. Ethylpyridinium bromide was the first IL that was demonstrated to have acceptable chromatographic properties and useful separation selectivity [18] with a liquid temperature range of 110–160 °C and it exhibited chromatographic efficiencies similar to those of conventional stationary phases.

ILs have many properties that make them exceptional stationary phases. For example, their viscosity can be varied over a broad range, they exhibit high thermal stability, they can be coated on fused silica capillaries with high efficiency, they have unique solvent properties, and they can be immobilized and cross-linked. Indeed, IL stationary phases exhibit dual properties in that they separate nonpolar analytes (as if they were nonpolar stationary phases) and simultaneously separate polar analytes (as if they were polar stationary phases) [19–24].

Another very important aspect of IL stationary phases is that their physicochemical properties are almost infinitely tunable. Tunability is a characteristic that is unavailable with all other classes of GC stationary phases. By means of relatively simple synthetic modifications or changes to the cation, anion (or substituents thereon), and the linkage chains of ILs, the desired solvent and selectivity characteristics can be altered and controlled [25–29].

As a new family of mesoporous and microporous materials, metal-organic frameworks (MOFs) are considered versatile materials for widespread technical applications. MOFs are a new class of crystalline porous materials. They are composed of inorganic subunits, which act as joints, connected to multidirectional organic linkers, possessing chelating groups with strong ion covalent or dative bonds [30]. Consequently, MOFs possess extended periodic one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) hybrid networks. The application of MOFs as novel stationary phases in chromatography in place of conventional materials has led to notable improvements in the performance of GC.

The high thermal stability and easy-to-engineer characteristics of MOFs make them attractive as new stationary phases for the fabrication of MOF-coated capillaries for high-resolution GC [31]. MOFs have thus been employed in the design of tandem molecular sieves as a dual platform for selective solid-phase microextraction (SPME) and high-resolution GC separation of target analytes in complex matrices. The highly ordered, nano- to micro-sized pores, and large surface area also make MOFs appealing candidates for use as stationary phases in conventional GC [32,33]. The first example of an MOF-coated capillary column for GC separation was reported by Gu and Yan [34]. MIL-101, a chromium terephthalate MOF with coordinatively unsaturated sites (CUSs), was selected as

the stationary phase because of its large surface area (5900 m^2/g), large pores (2.9–3.4 nm), accessible CUSs, and excellent chemical and thermal stability (stable over months under air atmosphere and unaltered when treated with various organic solvents at room temperature or under solvothermal conditions) [33].

Carbon-based materials, especially carbon nanotubes (CNTs), have received extensive attention due to their unique electrical, mechanical, and chemical properties [35]. The exceptional features of CNTs combined with the large number of active sites and the ability to undergo π–π stacking with volatile aromatic or unsaturated organic compounds make them a preferred choice as a stationary phase in GC [36–40]. As a newly developed carbon-based material, graphene oxide (GO) possesses most of the advantages of CNTs [41]. GO is a single-layered nanosheet prepared via chemical exfoliation of graphite. GO has a high surface area, high adsorption ability, and is stable at high temperature. It is strongly hydrophilic and water soluble due to the presence of epoxy, hydroxy, and carboxyl groups on its graphitic backbone.

3.4.2 Columns for Micro-GC

For converting table-top instruments to in-field use, microelectromechanical systems (MEMS) technology has been introduced for the replacement of bulky components (heaters; temperature, pressure, and humidity sensors; flow sensors; valves; pumps; and wireless transceivers) with low-cost, low-volume, low-power microfabricated alternatives. In conventional GC, the separation column is one of the bulky components. Tremendous efforts have been made to miniaturize such columns (along with the rest of the instrument) [42,43]. The development of microfabricated columns faces formidable challenges in terms of minimizing power and implementing the complex temperature and pressure control required to enhance the performance. However, in 2005, Agah *et al.* [44] reported a ground-breaking development of high-performance, silicon glass microgas chromatography (μGC) columns equipped with integrated heaters and temperature sensors for temperature programming and integrated pressure sensors for flow control. These 3 m long, 150 μm wide, and 250 μm deep columns, integrated with a 3.3 cm square die, were fabricated using a silicon-on-glass dissolved wafer process. By analyzing the contributions to heat dissipation from conduction, convection, and radiation with and without packaging, it was demonstrated that using a 7.5 mm high atmospheric pressure package reduces the power consumption to about 650 mW at 100 °C, whereas vacuum packaging reduces the steady-state power requirements to less than 100 mW. Under vacuum conditions, 600 mW is needed for a temperature-programming rate of 40 °C/min. The TCR (2300 ppm/°C) of the temperature sensors and the sensitivity (50 fF/kPa) of the pressure sensors satisfy the requirements to achieve reproducible separation in a μGC system. Using these columns, highly resolved 20-component separations were obtained with analysis times that were faster by a factor of two relative to isothermal responses.

References

1 McNAIR, H.M. and Miller, J.M. (1997) *Basic Gas Chromatography*, John Wiley & Sons, Inc. New York.

2 O'Keeffe, M. (ed.) (2000) *Residue Analysis in Food, Principles and Applications*, Harwood Academic Publishers, Amsterdam, The Netherlands.

3 Ottenstein, D.M. (1973) The chromatographic support in gas chromatography. *J. Chromatogr. Sci.*, **11**, 136–144.

4 Zweig, G. and Sherma, J. (1972) *Analytical Methods for Pesticides and Plant Growth Regulators, Vol. VI, Gas Chromatographic Analysis*, Academic Press, New York.

5 George Fong, W., Anson Moye, H., Seiber James, N., and Toth John, P. (1999) *Pesticide Residues in Foods, Methods, Techniques, and Regulation*, 1st edn, Wiley-Interscience.

6 Golay, M.J.E. (1958) *Gas Chromatography (Amsterdam Symposium)* (ed. D.H. Desty), Butterworths, London, pp. 36–55 and 62–68.

7 Ettre, L.S. (1987) M.J.E. Golay and the invention of open-tubular (capillary) columns. *J. High Resolut. Chromatogr.*, **10**, 221–230.

8 Halász, T. and Horváth, C. (1963) Thin-layer graphited carbon black as the stationary phase for capillary columns in gas chromatography. *Nature*, **5** (197), 71–72.

9 Inczedy, J., Lengyel, T., and Ure, A.M. (1997) *Compendium of Analytical Nomenclature*, 3rd edn, Blackwell Science, Malden, MA.

10 Falwell, S.O. (1997) Modern gas chromatographic instrumentation, in *Analytical Instrumentation Handbook* (ed. G.W. Ewing), Marcel Dekker, New York, Chapter 23.

11 Poole, C.F. and Poole, S.K. (1991) *Chromatography Today*, Elsevier, Amsterdam, The Netherlands, Chapter 8.

12 Jennings, W. (1980) Evolution and application of the fused silica column. *J. High Resolut. Chromatogr.*, **3**, 601–608.

13 Russo, M.V. (2002) Chiral separation of methoxamine and lobeline in capillary zone electrophoresis using ethylbenzene-deactivated fused-silica capillary columns and cyclodextrins as buffer additive. *J. Pharm. Biomed. Anal.*, **29** (6), 999–1003.

14 Hajslova, J. and Cazka, T. (2007) *Food Toxicants Analysis* (ed. Y. Pico), Elsevier, Amsterdam, Chapter 12.

15 Maštovska, K. and Lehotay, S.J. (2003) Practical approaches to fast gas chromatography–mass spectrometry. *J. Chromatogr. A*, **1000**, 153–180.

16 Gordon, J.E., Selwyn, J.E., and Torne, R.L. (1966) Molten quaternary ammonium salts as stationary liquid phases for gas–liquid partition chromatography. *J. Org. Chem.*, **31**, 1925–1930.

17 Pacholec, F., Butler, H.T., and Poole, C.F. (1982) Molten organic salt phase for gas–liquid chromatography. *Anal. Chem.*, **54**, 1938–1941.

18 Pacholec, F. and Poole, C.F. (1983) Stationary phase properties of the organic molten salt ethylpyridinium bromide in gas chromatography. *Chromatographia*, **17**, 370–374.

19 Han, X. and Armstrong, D.W. (2007) Ionic Liquids in Separations. *Acc. Chem. Res.*, **40**, 1079–1086.

20 Anderson, J.L. and Armstrong, D.W. (2005) Immobilized ionic liquids as high-selectivity/high-temperature/high-stability gas chromatography stationary phases. *Anal. Chem.*, **77**, 6453–6462.

21 Huang, K., Han, X., Zhang, X., and Armstrong, D.W. (2007) PEG-linked geminal dicationic ionic liquids as selective, high-stability gas chromatographic stationary phases. *Anal. Bioanal. Chem.*, **389**, 2265–2275.

22 Bretibach, Z.S. and Armstrong, D.W. (2008) Characterization of phosphonium ionic liquids through a linear solvation energy relationship and their use as GLC stationary phases. *Anal. Bioanal. Chem.*, **390**, 1605–1617.

23 Payagala, T., Zhang, Y., Wanigasekara, E., Huang, K., Breitbach, Z.S., Sharma, P.S., Sidisky, L.M., and Armstrong, D.W. (2009) Trigonal tricationic ionic liquids: a generation of gas chromatographic stationary phases. *Anal. Chem.*, **81**, 160–173.

24 Anderson, J.L., Armstrong, D.W., and Wei, G.T. (2006) Ionic liquids in analytical chemistry. *Anal. Chem.*, **78**, 2893–2903.

25 Soukup-Hein, R.J., Warnke, M.M., and Armstrong, D.W. (2009) Ionic liquids in analytical chemistry. *Annu. Rev. Anal. Chem. (Palo Alto Calif.)*, **2**, 145–168.

26 Armstrong, D.W., He, L.F., and Liu, Y.S. (1999) Examination of ionic liquids and their interaction with molecules, when used as stationary phases in gas chromatography. *Anal. Chem.*, **71**, 3873–3876.

27 Payagala, T., Huang, J., Breitbach, Z.S., Sharma, P.S., and Armstrong, D.W. (2007) Unsymmetrical dicationic ionic liquids: manipulation of physicochemical properties using specific structural architectures. *Chem. Mater.*, **19**, 5848–5850.

28 Anderson, J.L., Ding, J., Welton, T., and Armstrong, D.W. (2002) Characterizing ionic liquids on the basis of multiple solvation interactions. *J. Am. Chem. Soc.*, **124**, 14247–14254.

29 Anderson, J.L., Ding, R., Ellern, A., and Armstrong, D.W. (2005) Structure and properties of high stability geminal dicationic ionic liquids. *J. Am. Chem. Soc.*, **127**, 593–604.

30 Devic, T. and Serre, S. (2009) *Ordered Porous Solids: Recent Advances and Prospects* (eds V. Valtchev, S. Mintova, and M. Tsapatsis), Elsevier, Amsterdam.

31 Chang, N., Gu, Z.Y., Wang, H.F., and Yan, X.P. (2011) Metal-organic-framework-based tandem molecular sieves as a dual platform for selective microextraction and high-resolution gas chromatographic separation of *n*-alkanes in complex matrixes. *Anal. Chem.*, **83**, 7094–7101.

32 Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., and Yaghi, O.M. (2002) Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science*, **295**, 469–472.

33 Ferey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surble, S., and Margiolaki, I. (2005) A chromium terephthalate-based solid with unusually large pore volumes and surface area. *Science*, **309**, 2040–2042.

34 Gu, Z.Y. and Yan, X.P. (2010) Metal-organic framework MIL-101 for high-resolution gas chromatographic separation of xylene isomers and ethyl benzene. *Angew. Chem. Int. Ed.*, **49**, 1477–1480.

35 Valcarcel, M., Cardenas, S., and Simonet, B.M. (2007) Role of carbon nanotubes in analytical science. *Anal. Chem.*, **79**, 4788–4797.

36 Herrera-Herrera, A.V., Gonzalez-Curbelo, M.A., Hernandez-Borges, J., and Rodriguez-Delgado, M.A. (2012) Carbon nanotubes applications in separation science: a review. *Anal. Chim. Acta*, **734**, 1–30.

37 Karwa, M. and Mitra, S. (2006) Gas chromatography on self-assembled, single-walled carbon nanotubes. *Anal. Chem.*, **78**, 2064–2070.

38 Yuan, L.M., Ren, C.X., Li, L., Ai, P., Yan, Z.H., Zi, M., and Li, Z.Y. (2006) Single-walled carbon nanotubes used as stationary phase in GC. *Anal. Chem.*, **78**, 6384–6390.

39 Stadermann, M., McBrady, A.D., Dick, B., Reid, V.R., Noy, A., Synovec, R.E., and Bakajin, O. (2006) Ultrafast gas chromatography on single-wall carbon nanotube stationary phases in microfabricated channels. *Anal. Chem.*, **78**, 5639–5644.

40 Hussain, C.M., Saridara, C., and Mitra, S. (2010) Self-assembly of carbon nanotubes via ethanol chemical vapor deposition for the synthesis of gas chromatography columns. *Anal. Chem.*, **82**, 5184–5188.

41 Geim, A.K. (2009) Graphene: status and prospects. *Science*, **324**, 1530–1534.

42 Kolsear, E.S. and Reston, R.R. (1998) Review and summary of a silicon micromachined gas chromatography system. *IEEE Trans. Comp. Packag. Manufact. Technol.*, **66**, 481–486.

43 de Boer, M.J., Tjerkstra, R.W., Berenschot, J.W., Jansen, H.V., Burger, G.J., Gardeniers, J.G.E., Elwenspoek, M., and van den Berg, A. (2000) Micromachining of buried micro channels in silicon. *J. Microelectromech. Syst.*, **9**, 94–103.

44 Agah, M., Potkay, J.A., Lambertus, G., Sacks, R., and Kensall, D. (2005) High-performance temperature-programmed microfabricated gas chromatography columns. *J. Microelectromech. Syst.*, **14** (5), 1039–1049.