CHROMATOGRAPHY, GAS

1. Introduction

Gas chromatography (GC) is a physical method of separation in which compounds are separated using a moving gaseous phase (mobile phase) passing over or through a non-moving liquid or solid phase (stationary phase) (1). GC was first proposed in the Nobel Prize winning work of A.J.P Martin in 1941 (2) and was first developed as an instrument by Martin and James in 1952 (3). GC may be described as a form of column chromatography in that both the mobile and stationary phases are contained within a tube (column) and that the mobile phase is driven through the tube by a pressure drop between the two ends of the tube. Initially, GC was performed using packed columns, with the stationary phase consisting of solid particles packed into the column. In 1956, Golay (4) developed capillary columns, in which the stationary phase consists of a coating on the walls of a capillary tube. In this article, the technology of gas chromatography is briefly described, with reference to the original developments and to additional details that may be found in the chemical literature.

Much of the theoretical development in GC that forms the basis of current ideas on the development of GC analytical methods occurred in the 1950s and 1960s. Many current "hot topics" in GC were, in fact, proposed by researchers in these early days, including temperature programming (5), rapid separations (6), and novel stationary phases (7). The 1970s saw improvements in instrumentation, including pneumatic systems and electronic data systems. The 1970s culminated with the introduction of fused silica capillary columns in 1979 (8), which revolutionized GC analysis by making high resolution capillary columns accessible to routine users. In the 1980s, stationary phases, pneumatics, inlets and detectors were optimized for capillary columns, as the demand for these increased with increasing sales of capillary column systems. Capillary columns began to supplant packed columns for many routine applications and data systems evolved form simple chart recorders to computer-based data and instrument control systems. The 1990s saw the introduction of electronic control of the pneumatics, which provided microprocessor-controlled pneumatics and again revolutionized GC by allowing extremely precise control of gas flows, a critical parameter in GC analysis. Improvements in column, inlet and detector technologies have followed, with renewed interest in the development of rapid GC, improvements in analytical sensitivity, novel and specialty stationary phases and data systems.

In 2001, GC is a high resolution, sensitive and relatively easy to use separation technique. Samples for GC must be volatile under conditions readily achieved in GC instruments, typically temperatures $<350^{\circ}C$. They also are typically gases, solutes dissolved in an organic solvent, or sampled from head-space and must provide a signal from a GC detector. This article describes the technology of GC, with a focus on instrumentation, stationary phases, applications, and theory, as needed to describe the technological developments in a small space. For further details, this article is heavily referenced, plus there are numerous texts and journals dedicated or focused on GC. References (9–18) include a few of the more important resources. Additional resources, especially on the most

current state of the art, may be found in the annual Fundamental and Applications Reviews issues of the journal *Analytical Chemistry*, published by the American Chemical Society. Further, several research journals, including the *Journal of Chromatography A and B* (Elsevier), *Journal of Separation Science, Journal of Microcolumn Separations and Journal of High Resolution Chromatography* (Wiley), *Journal of Chromatographic Science* (Preston Publications), *Chromatographia* (Vieweg), and *LC-GC* (Advanstar) have strong emphasis in GC. A thorough discussion of GC instrumentation, including an overview and descriptions of modern inlet systems, columns, detectors and data systems is included, along with discussion of environmental, industrial, pharmaceutical, clinical, and forensic applications.

The data provided by an experiment in GC are called a chromatogram. A typical chromatogram is shown in Figure 1 (19). This figure shows the separation of a homologous series of *n*-alcohols at a temperature of 90°C. There are a number of important pieces of information that are generated by analysis of every chromatogram. First, the retention time, indicated by the time elapsed from the point of injection to the maximum of a peak, is a physical property of the compound under the conditions of the experiment. Retention times, although not unique (many compounds may have the same retention time), are used for

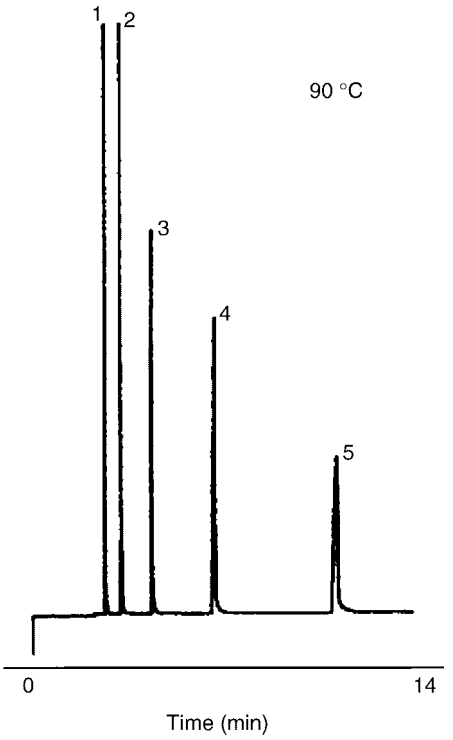

Fig. 1. Typical chromatogram of alcohols obtained from a GC analysis. 1 = *n*-Butanol, 2 = *n*-pentanol, 3 = *n*-hexanol, 4 = *n*-heptanol, 5 = *n*-octanol. [Reprinted from (19). Used with permission from the *Journal of Chemical Education*. © 1996, Division of Chemical Education, Inc.]

qualitative analysis by the matching of retention times of unknowns with those of known standards. The peak height, or peak area is related to the mass or concentration of the analyte present and is used for quantitative analysis. The gas hold-up time, defined as the retention time of a nonretained substance, is another important piece of information. The gas hold-up time is typically measured by injecting a small molecule gas, such as methane and recording the retention time.

There are several additional quantities that are commonly calculated from chromatograms. These provide the basic connection between the results generated from chromatographic data and terms familiar to most chemists. First, the retention time (t_R) for a compound, defined as the time elapsed from the point of injection to the maximum signal generated during peak elution can be divided into the time that the analyte spends sorbed in the stationary phase (t_R') and the time the analyte spends moving through the mobile phase (t_m).

$$t_R = t'_R + t_M$$

t_R', the time spent sorbed (not moving) in the stationary phase is termed the adjusted retention time and t_M, the time spent moving in the mobile phase is termed the gas hold up time. In order to relate retention times to the chemical equilibrium expressions that generate separation, the retention factor is defined as

$$k = \frac{t'_R}{t_m}$$

The retention factor, k, has an important context other than being the simple ratio of the adjusted retention time and the gas hold-up time. It also represents the ratio of mass of analyte sorbed in the stationary phase to the mass of analyte vapor in the mobile phase, at any moment that the analyte is in the column. This allows connection to a classical equilibrium constant for the phase transition between the stationary phase and the mobile phase.

$$K = k\beta$$

K is the equilibrium constant for the phase transition, k is the retention factor, defined above, and β is the ratio of mobile phase volume-to-stationary phase volume, termed the phase ratio.

If this analysis is viewed in reverse, it is seen that the retention time in GC is determined by the chemistry of the analyte-stationary phase interactions, the analyte vapor pressure, and the flow rate of the carrier gas. Temperature, carrier gas flow rate, and stationary phase composition are therefore the main variables that affect retention times. Note that while retention time is a physical property of a compound, it is not a unique property; many compounds may have the same retention time on a given column under a given set of conditions. A more thorough review of the basic theory behind retention times may be found in the texts already referenced (9–18) and in the paper by Snow (19).

In GC, column temperature is either maintained constant (isothermal GC) or the temperature is ramped (usually linearly) from a low value to a high value during the run (temperature programmed GC). Isothermal GC is much simpler, both instrumentally and conceptually, so it is often used in teaching and in process control environments, when method simplicity outweighs the need for high resolution. Due to the high thermal mass of the column and ovens used in packed column GC, isothermal conditions are often used in packed column methods. Temperature programming is most often employed with capillary columns, as they have low thermal mass and therefore, reach temperature equilibrium quickly. Also, temperature programming provides an excellent combination of improved resolution and analysis of compounds with a wide range of vapor pressures. A comparison of isothermal and temperature programmed chromatograms for a normal alkane standard is shown in Figure 2. Not only are the peaks much sharper in the temperature-programmed analysis, but there are more of them, indicating a much higher resolution separation for a wider range of analytes. The theory of temperature programming is discussed in detail in the classical text by Harris and Habgood (20) and is reviewed in the texts already referenced.

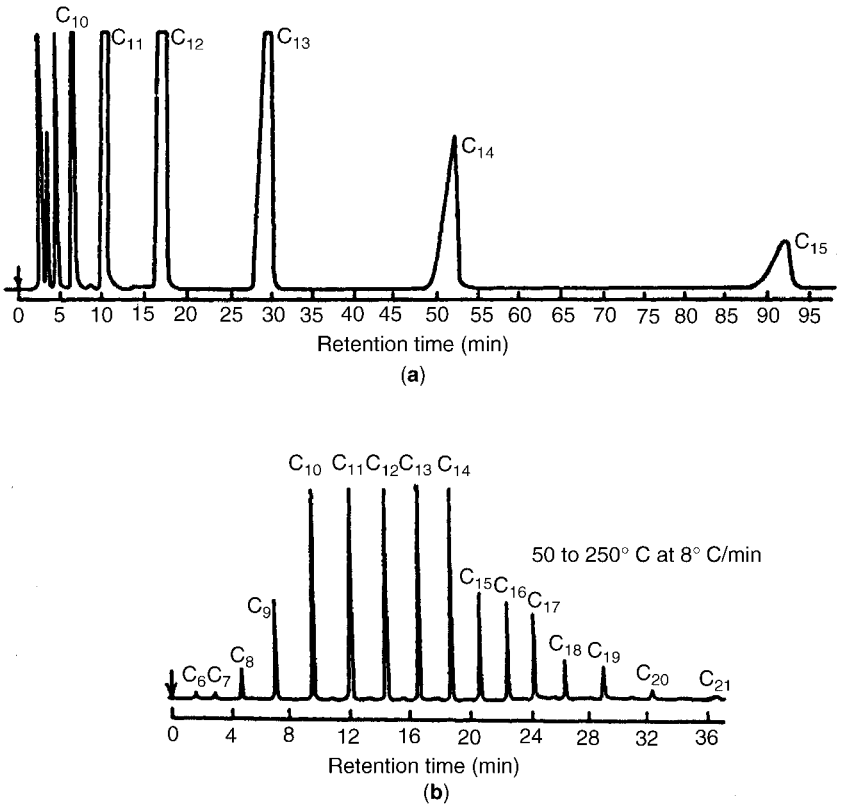

Fig. 2. Comparison of isothermal and temperature programmed chromatograms for a sample of normal alkanes. (**a**) Isothermal analysis. (**b**) Temperature programmed analysis. [Reprinted from Ref. 12, p. 145].

The peak widths are the other feature of note in the chromatogram shown in Figure 1. If it is assumed that all chromatographic peaks begin moving through the column as very sharp square bands and that they emerge as the Gaussian-appearing bands shown in the chromatogram, then random spreading mechanisms must be affecting the distribution of analyte molecules in the column. Numerous investigators have studied band broadening since the inception of GC, with the classical work being done by Van Deemter for packed columns (22) and Golay (4) for capillary columns. Their basic theories are still in use today as the most commonly applied explanations for band broadening in GC. The Van Deemter equation describes the rate of band broadening in a packed GC column. Its general form is given by

$$H = A + \frac{B}{\mu} + C\mu$$

and the Golay equation, for capillary column GC is given by

$$H = \frac{B}{\mu} + (C_S + C_M)\mu$$

In both equations, H represents the height equivalent to a theoretical plate, which roughly measures the length of column required to generate a single phase transition between the stationary phase and mobile phase, and idea drawn from the theoretical place concept used in fractional distillation. The parameter H is also a measure of the rate of band broadening; a larger value for H indicates more rapid band broadening, leading to wider peaks. Thus, minimizing H is a very important aspect of chromatographic method development. Also, in both equations, μ represents the average linear carrier gas velocity in the column, a measure of the carrier gas flow rate.

The "A term" represents band broadening due to multipath effects in packed columns. It arises from the fact that every molecule traveling through a packed bed will take a slightly different path through the particles. Thus, some analyte molecules will require more time than others to reach the column outlet. The multipath effect is most affected by the particle diameter and the quality of the packing process in a packed column. It is noted that, since a capillary column is an open tube, with no obstructions, that this term is not considered in capillary GC.

The "B term" in both equations represents molecular diffusion in the mobile phase. Given time, all populations of molecules will diffuse in the mobile phase. To minimize this term, molecules should be passed as quickly as possible through the column, using a high flow rate, along with a relatively high molecular weight carrier gas, such as nitrogen.

The "C terms" shown in both equations relate to mass transfer that occurs between the individual molecules in both the mobile phase (C_M) and the stationary phase (C_S). In the packed column equation, there is a single C term, as there is a far larger mass of stationary phase in a packed column, so the mobile phase term is neglected. The main considerations in the stationary phase term include the analyte retention factor, diffusion coefficient of the analyte in the stationary

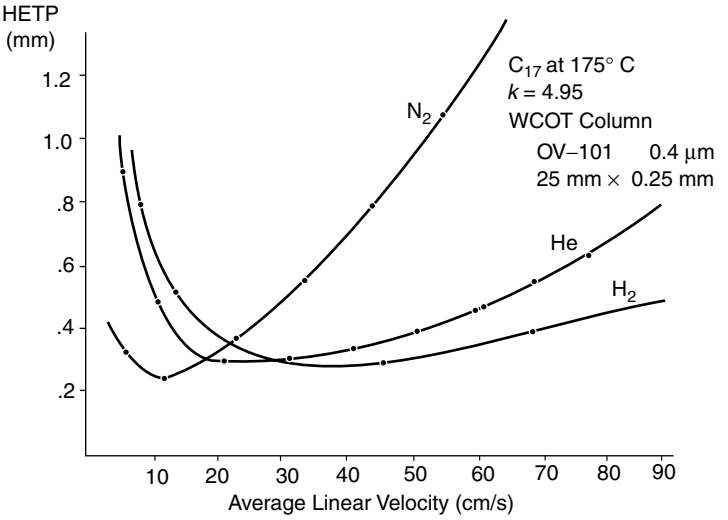

Fig. 3. Van Deemter plot showing height equivalent to a theoretical plate versus average linear carrier gas velocity. [Reprinted with permission from Ref. 24.]

phase, and stationary phase coating thickness for packed columns, plus, column inside diameter, carrier gas viscosity, and diffusion coefficient of the analyte in the carrier gas for capillary columns. Generally, low viscosity liquids, coated in thin films on the particles or capillary wall are used to minimize band broadening. For capillary columns, low molecular weigh carrier gases, such as hydrogen or helium are preferred.

Figure 3 shows a "Van Deemter plot" of height equivalent to a theoretical plate versus average linear carrier gas velocity for the three common carrier gases on a capillary column (24). It is seen that, for capillary columns, at practical linear gas velocities, the mass transfer terms dominate the rate of band broadening. Thus, for capillary columns, at practical carrier gas flow rates, hydrogen provides the best efficiency, followed by helium, then nitrogen. In the United States, helium is used most often, due to the potential safety concerns with hydrogen, while hydrogen or nitrogen are often used elsewhere. Each curve shows a minimum, which gives the optimum average linear carrier gas velocity. In practice, GC work is generally performed at higher velocities than optimum, for practical reasons. The curve shape shows the combination of the three terms, with molecular diffusion dominating at low carrier gas velocities and with mass transfer dominating at high velocities.

2. Overview of Instrumentation

A schematic diagram of a modern instrument for GC is shown in Figure 4. A GC system consists of a carrier gas supply, pneumatics, and gas scrubbers, an instrument consisting of three separately controlled heated zones: inlet, column oven and detector, and a data collection and processing system. All of these can be

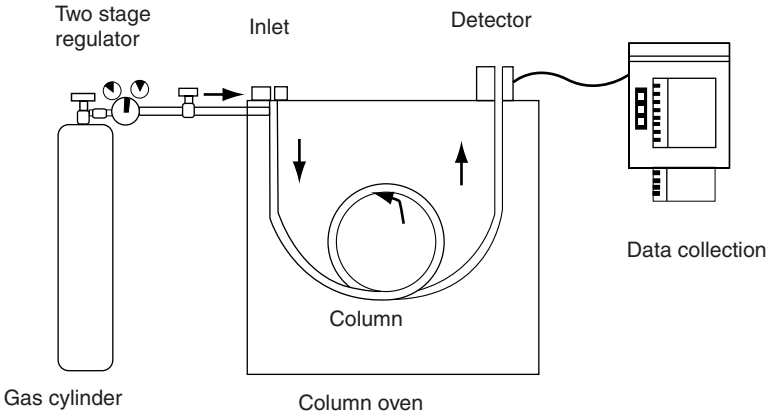

Fig. 4. Schematic diagram of a GC. (Courtesy of Professor Harold McNair.)

microprocessor controlled and generally use solid-state pneumatics and controls. Older GC's built prior to ~1995, employ a combination of digital and analog controls, while the oldest systems are mostly manually controlled. Modern GC, performed with capillary columns, requires that all ancillary equipment, such as gas supplies and equipment, syringes and devices for delivering samples and the samples be as free from contaminants as possible. This article will not address sample preparation and "cleaning-up" directly, but information on sample preparation techniques can be found in the textbooks and journals already referenced (9–18).

In capillary GC, helium is the most commonly employed carrier gas, with hydrogen used in cases where higher resolution is needed, or when the cost of helium is prohibitive. With packed columns, nitrogen is also used. The main requirements for the carrier gas are that it be of high purity and free of impurities such as water, hydrocarbons, and oxygen.

3. Inlet Systems

The ability to transfer the analyte sample into a moving gas stream at elevated pressure, without causing the system to leak is an important consideration in instrument design. Furthermore, the analyte must be transferred quantitatively, without losses or contamination and without decomposition. These requirements make the inlet and sampling system perhaps the most difficult part of the system to use and to understand for the average user. The common techniques for injecting samples into both packed and capillary GC are described there. These include simple flash vaporizers and direct inlets used with packed columns and splitters, splitless techniques, on column and programmed temperature inlets for capillary columns. Also, there are myriad on-line sampling techniques for both liquid and nonliquid samples. Some of these will be described briefly here, but the basic techniques are the focus of this chapter. For the basic techniques, there are two especially informative texts, both authored by K. Grob (25–26).

Most commonly, the injection device used in GC and with the inlets described here, is a small-volume analytical syringe. These syringes are generally composed of glass, with stainless steel plungers, and deliver volumes ranging from 0.1 to 10 μL of liquid sample, or 1 to 100 μL of gas. If gaseous samples are injected, a gas-tight syringe (1–5 mL) is generally used. Syringes should be checked often for leaks and for poor plunger performance. They generally are accurate to +/− 5% and precise to +/− 0.1% when using an autoinjector. There are several needle configurations used for specific applications, including pointed tips for manual injections, blunt tips for autoinjections and side hole tips for injection of especially labile analytes.

In order to prevent leaks during injection, the syringe must be passed through a polymeric septum or through a sampling valve. Septa come in a variety of materials and the choice of a proper septum can be critical in trace analysis. Septa are specially designed for specific inlets and it is important to use the proper septum for the inlet vendor and type. Also, especially for capillary GC work low bleed, high temperature septa should be used to prevent contamination and "ghost peaks" on chromatograms. Septa should be replaced frequently; they typically last for 30–50 injections and will leak if not replaced frequently.

3.1. Direct Inlet. Packed column systems generally employ a simple inlet called a direct inlet or a flash vaporizer. This inlet is heated to enhance rapid vaporization of the injected sample and is pressurized to enhance rapid transfer of the sample to the stationary phase. A typical packed column inlet is shown in Figure 5. The major advantage of this inlet is that a syringe needle will easily fit within a $\frac{1}{4}$- or $\frac{1}{8}$-in. outside-diameter packed column. In this system, the column is loosely fitted into a sleeve and is sealed with a compression fitting. Carrier gas flows into the inlet, around the outside of the column and into the column end, so that its temperature is equilibrated. When a sample is injected, the syringe needle pierces the septum and the sample is ejected directly onto the

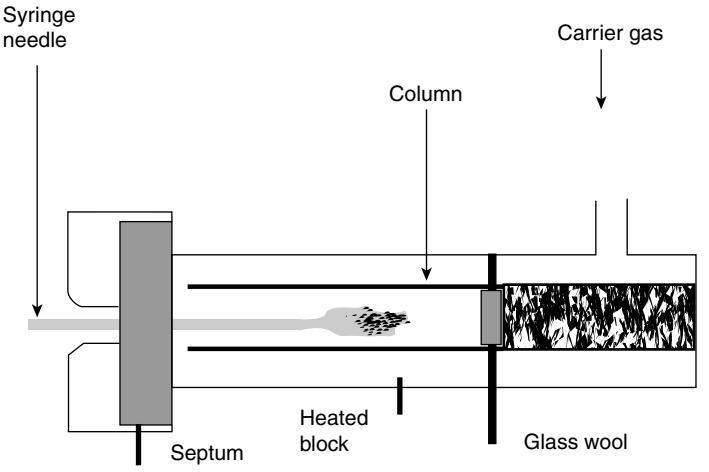

Fig. 5. Diagram of a direct injection onto a packed column (21). (Courtesy of Professor Harold McNair.)

stationary phase. The main advantage of this inlet is that all of the sample material ejected from the syringe reaches the column (see Fig. 5).

3.2. Split Inlet. In capillary GC, there are two fundamental problems with sample injection. First, the inside diameter of most capillary columns is too small to accommodate a typical syringe. Second, the small mass of stationary phase present in a capillary column can be very easily overloaded by a 1-μL liquid sample. Thus, along with the development of the capillary column in the late 1950s, a new inlet system, the inlet splitter, was conceived. In this inlet, the sample is injected by syringe into a pressurized, heated glass sleeve. The sample vaporizes and mixes homogeneously with the carrier gas stream. Finally, the mixture is passed to two possible exits: the capillary column and a larger diameter purge vent. The purge vent exit is controlled by a needle valve that controls the split ratio, which is the ratio of the amount of the vapor mixture transferred to the vent (waste) and the amount transferred to the column. Typical split ratios range from 10:1–100:1. For example, a split ratio of 50 indicates that, for the injected sample, 50 parts is ejected out the purge vent to waste and 1 part is transferred to the capillary column. A split inlet also includes a septum purge valve that provides a small (3–5 mL/min) flow of carrier gas underneath the septum to reduce contamination. A diagram of a split inlet is shown in Figure 6.

Although first developed in the 1950s, split inlets are in very common use today. The main advantage of split injection lies in simplicity; there are three main variables: inlet pressure, inlet temperature, and split ratio. Split injection is also a very rapid technique, requiring only a few hundred milliseconds for the entire injection process to complete. This results in very sharp chromatographic peaks, necessary for high resolution separations and for good detector sensitivity. The main disadvantages of split injection are in the low final mass of sample

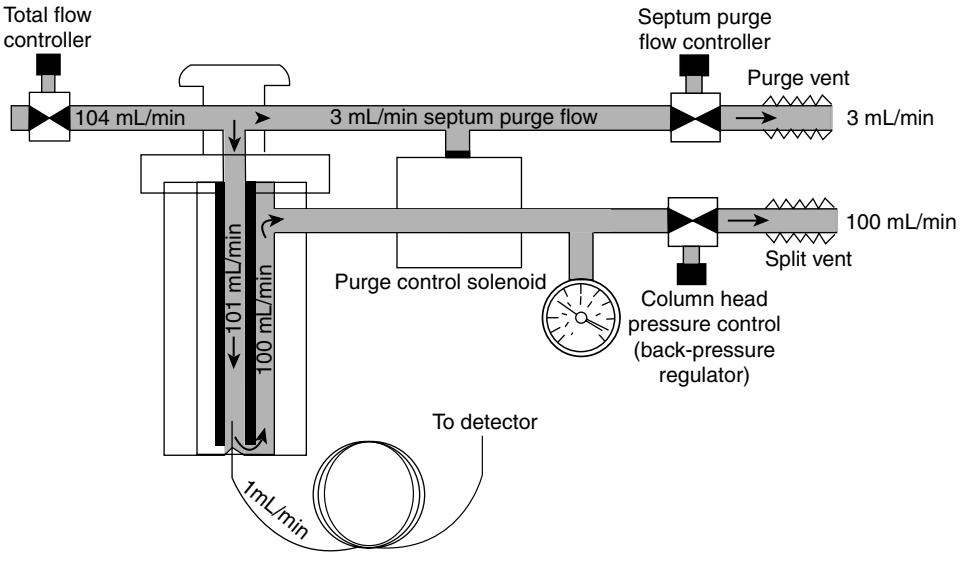

Fig. 6. Schematic of a split inlet for capillary GC. [Reprinted from Ref. 11, p. 485].

reaching the column and in the potential for contamination or reaction of the sample components in the inlet. GC analytical sensitivity and detection limits are relatively poor (concentration detection limits ~1 ppm) when split injection is used, since most of the injected sample is transferred to the split purge, rather than to the column. Split injection also suffers from the potential reaction of analytes with the inlet components themselves. Glass sleeves should be checked for contamination and replaced often, depending upon the type and level of contaminants in the samples. Further, there are hot metal components within most split inlets that may react with organic analytes. A more complete description of the issues involved with split injection is found in the text by K. Grob (27) and in the chapter by Klee (28).

3.3. Splitless Inlets. In 1968, K. Grob, Sr., when working on routine analysis using GC with split injection, began an analysis with the purge valve fully closed. Closing the purge valve when the instrument was not being used was common practice for reducing carrier gas usage. When the mistake was realized, shortly after beginning the analysis, the valve was opened, forcing a large flow of carrier gas through the inlet and mostly out through the purge vent. The expected result was a contaminated column and a ruined analysis. The observed result, shown in Figure 7 (29), was a chromatogram showing all analytes with very strong responses. Since this injection was performed without splitting of the injected sample vapor, it was termed "splitless" injection and has become the most commonly employed injection technique for trace analysis by GC over the past 30 years.

A schematic diagram of a modern splitless inlet is shown in Figure 8, with the "purge" shown both closed, for splitless operation and open for splitting. Note the similarity between the split and splitless inlets. In fact, on most GCs, they use the same hardware, with the difference between the configurations being the position of an electronic solenoid valve on the purge vent line. A splitless injection is begun with the purge vent closed. The electronic pneumatic controller will maintain a constant head pressure, and therefore a constant column flow. Following injection of the sample, the only outlet from the glass sleeve is the column. After allowing most of the sample to enter the column has elapsed (typically 30–45 s), the electronic solenoid valve is moved, opening the split purge. The electronic pneumatic controller will then send a large flow of carrier gas through the inlet in order to maintain the pressure with this additional outlet. This large flow, the bulk of which exits through the split purge vent, has the effect of cleaning residual solvent and sample from the inlet, causing the solvent peak to be very sharp. Unlike split injection, in which the bulk of the injected sample is lost out the split purge vent, 90–95% of the injected sample is passed to the column.

There are a large number of processes that are involved in a splitless injection, many of which are not readily obvious. Note that while the injection process may require up to 1 min to complete, the chromatographic peaks are generally very sharp, so some type of band focusing must occur. There are several processes that contribute to this focusing. These include cold trapping, solvent effects, and the use of a retention gap. Splitless injections are always associated with temperature programmed analysis, so while the inlet is heated, the column is usually relatively cool. First, high molecular weight compounds will be

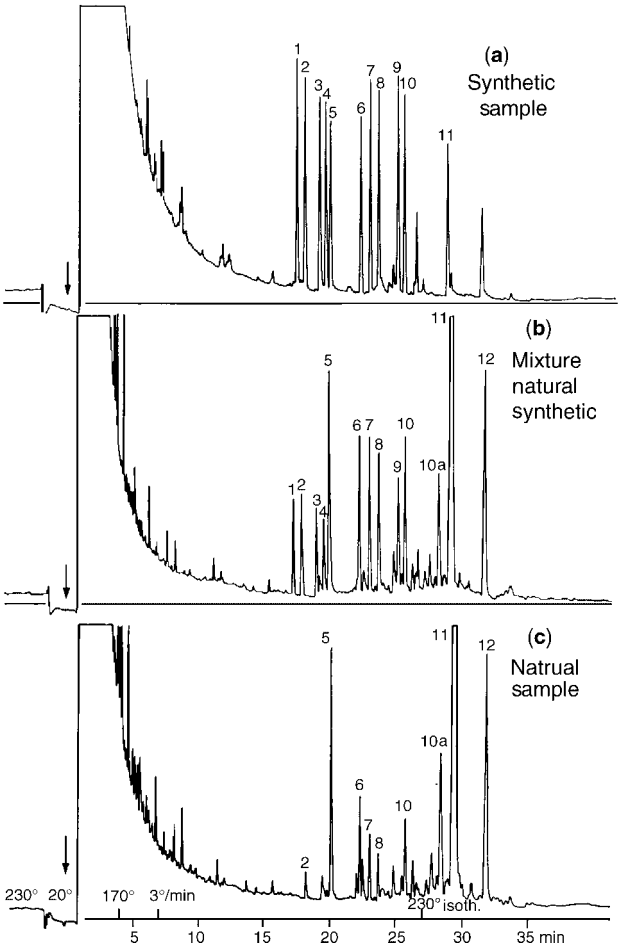

Fig. 7. First application of splitless injection for the analysis of steroids. (**a**) synthetic sample. (**b**) Mixture of natural and synthetic samples. (**c**) Natural sample. Experimental details may be found in (29). [Reprinted From the *Journal of Chrometographic Science* (29) by permission of Preston Publications. A Division of Preston Industries, Inc.].

transferred through the hot inlet, but will immediately condense as they are sorbed on the cool stationary phase. As the first molecules that reach the stationary phase stop, the remaining molecules "catch up" generating a sharp peak by concentrating the entire population of molecules into a small sharp band.

Second, solvent effects play a strong role, especially sharpening peaks representing compounds that are more volatile and are not effectively cold trapped. Solvent effects are shown schematically in Figure 9. First, the injected sample spreads out over a significant length (>1 m) of the capillary column immediately following the injection. The large amount of solvent acts like a thick stationary phase coating that dissolves the analyte components and spreads them throughout the length of the plug. If this broad band of analyte molecules is not focused further, it will be very broad, resulting in broad,

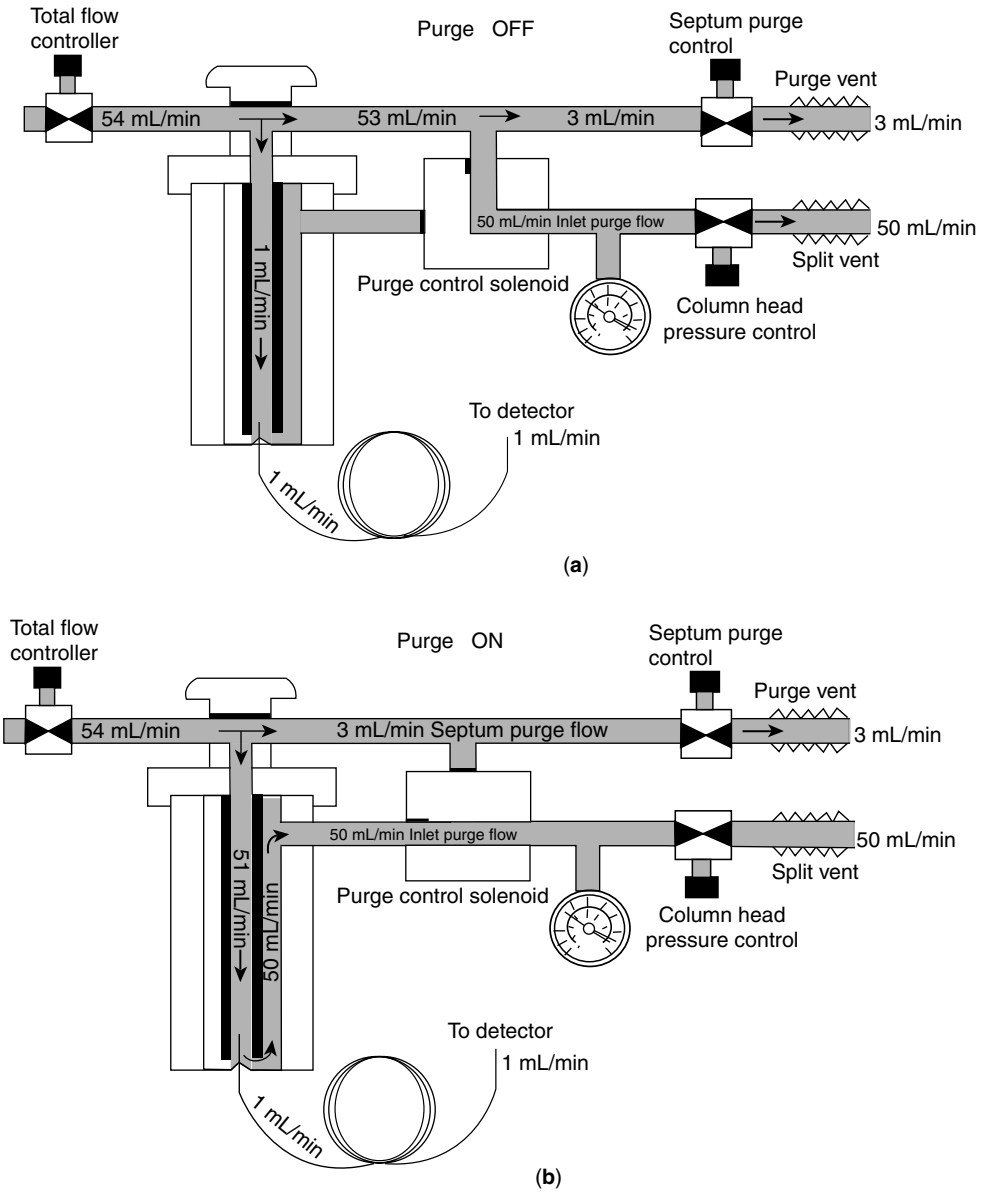

Fig. 8. Schematic diagrams of a splitless inlet for capillary GC with the inlet shown in the "Purge OFF" and "Purge ON" positions. Note the configuration of the solenoid valve. [Reprinted from Ref. 11, p. 489].

misshapen peaks. This phenomenon is termed "band broadening in space". Solvent effect focusing occurs when the flow of carrier gas causes this solvent plug to evaporate. Eventually, the solvent evaporates away, leaving the analyte behind, focused into a very sharp band. As the column temperature is increased, the focused analyte bands begin to migrate along the column and to separate.

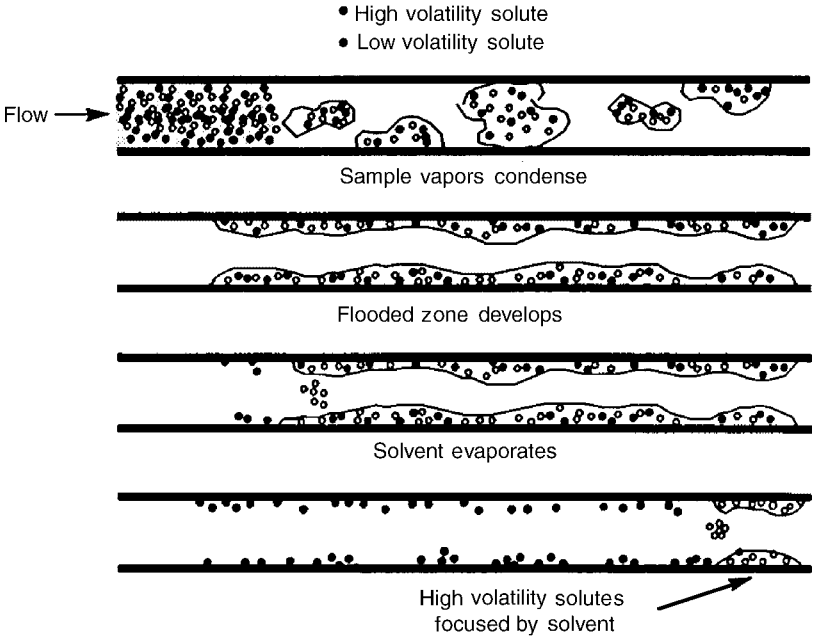

Fig. 9. Diagrammatic representation of solvent effects in splitless injection. [Reprinted with permission from Ref. 11, p. 478].

Thorough descriptions of splitless injection and its many principles are found in the chapter by Klee (30) and the text by Grob (31).

3.4. On-Column Inlet. On-column injection is receiving increased attention recently, as syringes and autoinjectors have been improved to accommodate the delicate handling required. A schematic of an on-column inlet is shown in Figure 10. Note that the column extends all the way into the inlet and that the syringe must be guided into the column by the inlet fittings. Also note the low thermal mass, so that the inlet may be temperature programmed along with the column, to ensure that the analytes elute. A syringe with a specially tapered needle is used to inject liquid sample directly into the column. During injection, the column oven and inlet are maintained below the boiling point of the sample solvent; the inlet temperature is usually increased to follow the column oven during a temperature-programmed analysis. The main advantage of on-column injection is that the entire injected sample reaches the column without the potential degradation that comes from the other hot injection techniques. The main disadvantage of on-column injection is also that the entire sample reaches the column, including any and all matrix and nonvolatile components that may be present. Column fouling and maintenance are often increased dramatically when using on-column injection techniques. Grob provides an excellent review of on-column injection (26).

A modified on-column inlet has been used for large volume injections, sometimes of up to hundreds of microliters (remember that $\sim$1 μL is typically injected), which allows an analogous increase in analytical sensitivity and low-

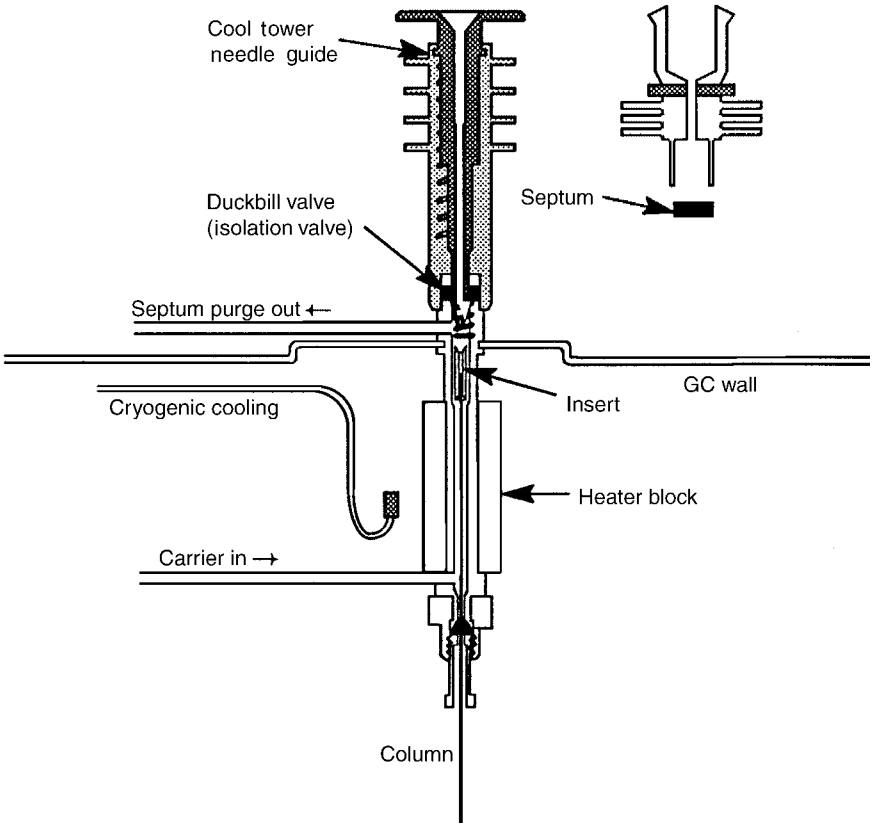

Fig. 10. Diagram of a cool-on-column inlet. [Reprinted from (11), p. 494].

ering of detection limits. The configuration of this system is shown in Figure 11. Note the addition of the retention gap, which allows physical space for the injected sample, the retaining precolumn, which helps to retain the more volatile analytes and the solvent vapor exit valve. The sample is injected with the vapor exit valve open to allow escape of the solvent vapors. When ~95% of the solvent vapor has escaped (the timing can be calculated using the vapor pressure of the solvent and the instrumental conditions) the valve is closed, directing the remaining material to the column. In both types of on-column injection presented here, the inlet is maintained at a temperature below the boiling point of the sample solvent, as the liquid must be injected onto the column without rapid evaporation, in contrast to split and splitless injections. A representative sampling of applications of large volume injection using the solvent vapor exit device is given in (32–34).

3.5. Programmed Temperature Vaporization. Temperature programmed injection has also been used in combination with the classical split and splitless injections described above. Developed in 1979 and promoted by Schomburg, the programmed temperature vaporization (PTV) inlet allows for the at-once injection of sample volumes up to 100 μL (35). The PTV inlet design is based on the classical splitless inlet, except that it has a low thermal mass to

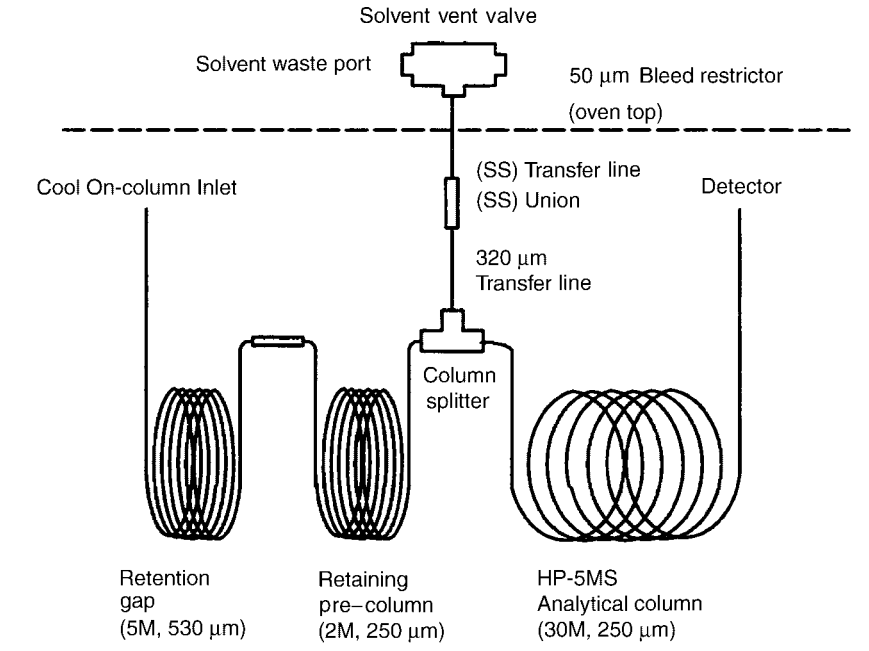

Fig. 11. Diagram of a cool-on-column inlet configured for solvent vapor exit large volume injection. Courtesy of Agilent Technologies.

allow for rapid heating and cooling. There are a number of modes in which it can operate, including hot split and splitless, which are the same as the classical split and splitless techniques, and cold split and splitless, which involve a cool inlet during injection, which is temperature programmed to pass the injected material into the column. In a cold splitless large volume injection, the glass liner is packed with an inert, high surface area material to accommodate a large volume of injected liquid. During the injection, the inlet is cooled with the purge vent open to allow solvent vapor to escape, while analytes are trapped on the liner packing. After ~95% of the solvent vapor has evaporated, the purge vent is closed, the inlet is temperature programmed and the analytes are transferred to the column in splitless mode. Following transfer, the purge vent is opened again to clean any residual material out of the inlet. The PTV large volume injection is seeing increased attention, especially in environmental analysis, in situations where increased sensitivity is needed. Representative applications include analysis of very low levels of pesticide residues (36), constituents of landfill gases (37), and petrochemicals (38). A schematic of a PTV inlet is shown in Figure 12, which is very similar to a classical splitless inlet, except that it has low thermal mass and the capability for rapid heating and cooling.

4. Columns and Liquid Phases

In GC, the separation occurs in the column, in which the gaseous mobile phase passes over a solid or liquid stationary phase consisting of solid particles, or solid

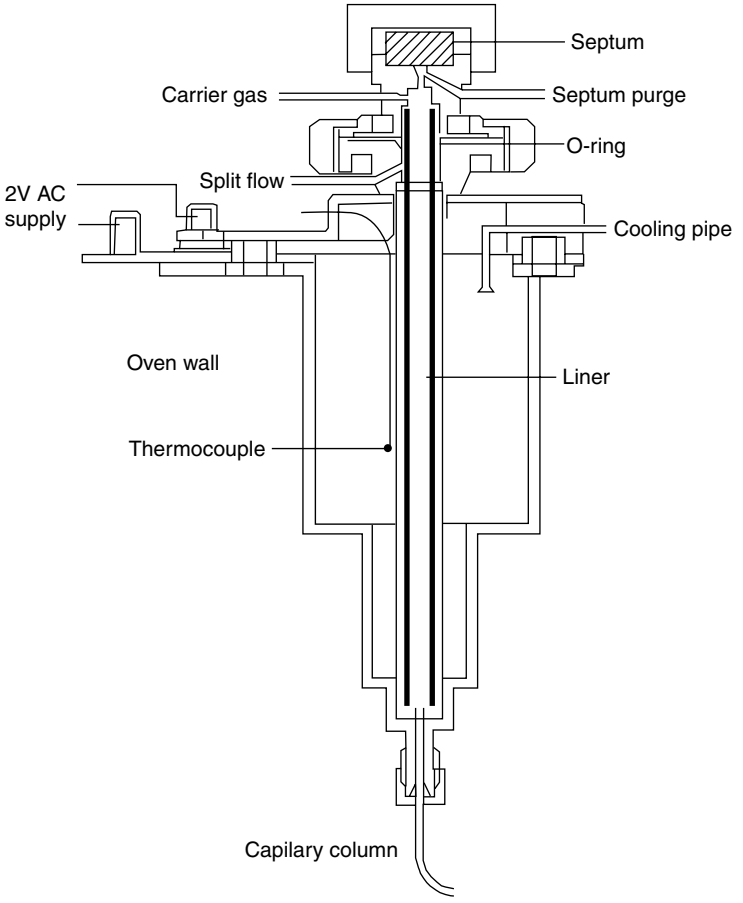

Fig. 12. Schematic of a programmed temperature vaporization inlet. (Courtesy, ATAS GL International.)

particles coated with a liquid, or consisting of a liquid or solid material coated onto the walls of a capillary tube. There is a huge variety of materials that have been employed as stationary phases over the years. With packed columns, separation efficiency is relatively low, so there are a huge number of stationary phases available, to take advantage of the myriad available surface chemistries. Inherently, capillary columns have much higher separation power than packed columns, so there is less need for a wide variety of stationary phase chemistries. Traditionally, there have been fewer capillary GC stationary phases available, although recently, specialty phases, for specific applications, have become available. In this section, the technology involved in using packed and capillary columns will be described, along with a summary of common stationary phases.

4.1. Packed Column Instrumentation. The original GC's were outfitted with packed columns. A packed column typically consists of a $\frac{1}{4}$- or 1/8-in. outside-diameter stainless steel or glass tube with length of 3–12 ft. The diameters of packed columns are generally determined by the availability

of tubing and fittings from the suppliers of such equipment. The pressure drop that can be accommodated by a gas chromatograph limits the length of a packed column. Tubing materials commonly include glass, which is least reactive, but often more difficult to work with, stainless steel, which is robust but potentially reactive with organic analytes and copper, which is easy to work and install into the small ovens used in GC, but is very reactive toward organic compounds. When purchased from vendors, packed columns are generally custom configured to fit properly into the major manufacturers' GCs. Some laboratories also readily make packed columns in-house. Packed columns have a relatively large thermal mass, so temperature equilibration is a major factor in the development of methods. Commonly, to avoid this problem, packed column GCs are operated isothermally, so that temperature equilibrium and reproducibility is maintained. These constraints, taken together, leave a great deal of emphasis on the choice of stationary phase in packed column methods, which is the reason that there are a huge number (hundreds) of these available.

4.2. Capillary Column Instrumentation. In contrast to packed columns, capillary columns, also called "wall coated open tubular" columns, are available in a huge variety of lengths and inside diameters, with relatively few (dozens, rather than hundreds) stationary phases available. Generally, capillary columns vary in length from 10 to 100 m, inside diameters of 0.10 to 0.53 mm, and liquid phase coating thickness 0.1 to 5.0 μm. Since they are open tubes, capillary columns do not share the pressure drop limitations with packed columns, allowing for very long lengths. However, the relatively small inside diameter places limitations on the carrier gas flow rate, injection system and sample capacity. Capillary column instrumentation is therefore more complex and expensive (a factor of 2–5) than packed column instrumentation, with the main differences being in the inlet systems, described earlier in this article. There are also minor differences in the operation of the common detectors flame ionization detector (FID), thermal conductivity detector (TCD), electron capture detector (ECD), mass selective (MS), between capillary and packed column instruments. Capillary columns themselves are generally manufactured from polyimide coated fused silica tubing, which imparts flexibility and ease of handling. The long length necessitates coiling in to a cage for easy handling, so the user should beware that the coils may uncoil rapidly and should wear eye protection at all times when handling capillary columns. For many years, glass was the most common material used for capillary columns, but was not flexible and required expensive drawing machines to obtain the necessary inside diameters. Stainless steel and aluminum clad fused silica have been used for special high temperature applications.

4.3. Stationary Phases. In both packed and capillary GC, the stationary phase may be either a liquid or solid. In a capillary column, the stationary phase is coated or chemically bound onto the capillary wall; in a packed column, the stationary phase consists of either solid particles or liquid coated solid particles. As discussed previously, there are myriad stationary phases available for GC, as a perusal of manufacturers' literature (several WWW sites for larger manufacturers are provided here; these also include extensive application notes and educational brochures and publications) shows (39–42). Snow (43) recently reviewed recent trends and developments in liquid phases for GC. The most

Table 1. **Commonly Used Stationary Phase Materials and Applications**[a]

Stationary phase temperature range	Application
100% methyl polysiloxane – 60–350°C.	alkaloids, amines, drugs, FAME, hydrocarbons, petroleum products, phenols, solvents, waxes, general purposes
5% phenyl–95% dimethyl polysiloxane –60–350°C	alcohols, alkaloids, aromatic hydrocarbons, flavors, fuels, halogenates, herbicides, pesticides, petroleum products, solvents, waxes, general purposes
50% phenyl–50% methyl polysiloxane –60–350°C	alcohols, drugs, herbicides, pesticides, phenols, steroids, sugars
14% cyanopropylmethyl–86% dimethyl polysiloxane 0–250°C	alcohols, aroclors, alcohol acetates, drugs fragrances, pesticides
50% cyanopropylmethyl–50% phenyl polysiloxane 0–250°C	carbohydrates, FAME
trifluoropropyl polysiloxane 0–275°C	drugs, environmental samples, ketones, nitro-aromatics
polyethylene glycol 60–225°C	alcohols, flavors, fragrances, FAME, amines, acids

[a] Reprinted with permission from Ref. 43.

commonly used stationary phases and their applications are summarized below in Table 1.

A potentially confusing problem in working with stationary phases for GC is that each manufacturer uses a different name or designation to describe materials that are, for most purposes equivalent. Table 2 provides a summary of these designations for the common stationary phases and several major manufacturers.

As evidenced in the manufacturers' literature, there are also numerous variations on these common chemistries. An emphasis today is on the manufacture of specialty stationary phases, tailored to specific applications or compendial methods. A summary of some of these specialty applications is shown in Table 3.

Finally, there are numerous recent developments in the use of cyclodextrins for chiral separations (44,45), liquid crystals (46,47), crown ethers (48,49) and sol-gels (50,51) as new stationary phase materials with specific, beneficial properties for difficult separations.

5. Detectors

The purpose of the detector is to sense analytes as they elute from the column and record that information in the form of a chromatogram. The signals generated by the detector are received and recorded by a data collection device, such as a chart recorder, electronic integrator, computer data station, or central data collection system. The collected data is plotted as intensity versus time, as described previously in Figure 1 and the accompanying discussion. A summary of the capabilities of the three most common GC detectors, FID, TCD, and ECD is provided in Table 4.

Table 2. **Cross-Reference of Manufacturers' Designations for Common Stationary Phases**[a]

Stationary phase	Restek	J + W	Supeclo	HP	SGE	Chrompack	Quadrex
100% polydimethyl siloxane	Rtx-1	DB-1	SPB-1, SP-2100	HP-1, Ultra-1	BP-1	CP-Sil 5 CB	007-1
95% dimethyl–5% phenyl polysiloxane	Rtx-5, XTI-5	DB-5	SPB-5	HP-5, Ultra-2	BP-5	CP Sil 8 CB	007-2
80% dimethyl–20% phenyl polysiloxane	Rtx-20		SPB-20				007-7
65% dimethyl–35% phenyl polysiloxane	Rtx-35						007-11
14% cyanopropyl phenyl–86% dimethyl polysiloxane	Rtx-1701	DB-1701			BP-10	CP Sil 19 CB	007-1701
50% methyl-50% phenyl polysiloxane	Rtx-50	DB-17	SP-2250	HP-17		CP Sil 43 CB	007-17
trifluoropropyl-methyl polysiloxane	Rtx-200	DB-210					
50% cyanopropyl phenyl–50% dimethyl polyslioxane	Rtx-225	DB-225	SP-2300	HP-225	BP-225		007-225
carbowax PEG	STABILWAX	DB-WAX	SUPELCOWAX-10	HP-20M	BP-20	CP Wax 52 CB	007-CW
carbowax PEG for amines	STABILWAX-DB	CAM					
carbowax PEG for acids	STABILWAX-DA	DB-FFAP	NUKOL, SP-1000	HP-FFAP	BP-21	CP Wax 58 CB	FFAP

[a] Reprinted with permission from Ref. 43.

Table 3. **Specialty Applications for Capillary GC Columns**[a]

Application	Description
thermally stable modified form of common phases; low bleed; highly inert	for GC/MS, ECD, other highly sensitive analyses
35% phenyl polysiloxane	conformational analysis
bonded poly(ethylene glycol)	fatty acid methyl esters
bis(cyanopropyl) polysiloxane	positional and geometric isomers of polysiloxanes
base modified polysiloxanes	amines; basic analytes
carbowax amine	primary, secondary, tertiary amines
6% cyanopropyl phenyl, 94% polydimethyl siloxane	USP and EP volatile organic contaminants methods

[a] Reprinted with permission from Ref. 43.

The ideal detector would be both universal, meaning that it is able to detect all compounds that elute from the column, and sensitive. However, in reality detectors are often either universal or selective. A selective detector is capable of only detecting certain types of compounds, and this selectivity is often why the detector has a high sensitivity. Analysts frequently trade selectivity for sensitivity. For these reasons, over 60 detectors have been developed and described in literature. Currently a handful of detectors are most commonly used FID, TC, MSD, ECD (52).

5.1. Flame Ionization Detector. The FID employs an ionization detection method invented specifically for GC. It was first introduced in 1958 (53,54) and has since become the most widely used detector. This detector has good

Table 4. **Summary of Characteristics—Flame Ionization, Thermal Conductivity, and Electron Capture Detectors**

	FID	TCD	ECD
limit of detection	10^{-11} g (50 ppb)	10^{-9} g (10 ppm)	10^{-14} g/s for sulfur hexafluoride, an ideal compound for ECD, the LOD is unique per compound
applications	nearly universal for organics, no fixed gases	universal	halogenated material, especially pesticide residues
linear range	10^6	10^4	10^2 in direct current (dc) mode
temperature limits	~400°C	~400°C	limited by radioactive source used: 400°C (^{63}Ni)
other	highly stable, easy to operate, conventional amplifier required	requires good temperature control otherwise stable, easy to operate, no amplification needed He carrier gas used for optimum performance	radioactive source needed one of the most easily contaminated detectors, needs ultrapure dry gases (must be free from O_2, H_2O) and clean samples

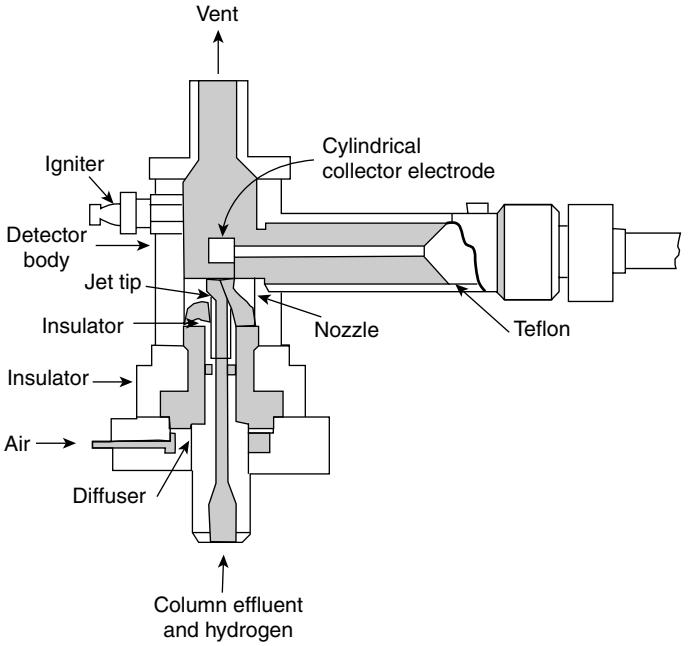

Fig. 13. Schematic of FID. [Reprinted with permission from Ref. 12, p. 115.]

sensitivity with a minimum detectable quantity (MDQ) of ~50 ppb and wide linear range (10^6). The main advantages are its simple design, affordability and reliability. Occasionally this detector is classed as a universal detector, but in fact the FID is only able to detect organic analytes, and will not detect compounds such as water, hydrogen, helium, nitrogen, carbon monoxide, and carbon dioxide. The inability to detect these compounds is rarely an issue and when these compounds are to be detected, another method of detection, such as thermal conductivity, must be used.

A schematic for a typical FID is shown in Figure 13. A diffusion flame is used in the FID, which is to say that the detector uses two gases, hydrogen and air, and it is the rate of diffusion of the two gases that controls the burn rate of the flame. The analytes are then introduced from the column into the flame jet, where they are ionized. A voltage (300 V) is applied across the flame to produce a current that is amplified by an electrometer to pick up the signals from the analytes. This signal generates the chromatogram.

5.2. Thermal Conductivity. Thermal conductivity detection is another commonly used detection method. This detector is a universal detector and is frequently used with packed columns and for inorganic analytes that are not detected by FID. The general characteristics of the TCD are as follows: MDQ of detection ~10 ppm, universal detection, linear for four orders of magnitude, good stability, and an upper temperature limit of 400°C.

The TCD operates on the principle that a hot body (the filament) will lose heat at a rate that is proportional to the surrounding gas and this heat loss can be used to detect the elution of analytes from the column. Since any analyte,

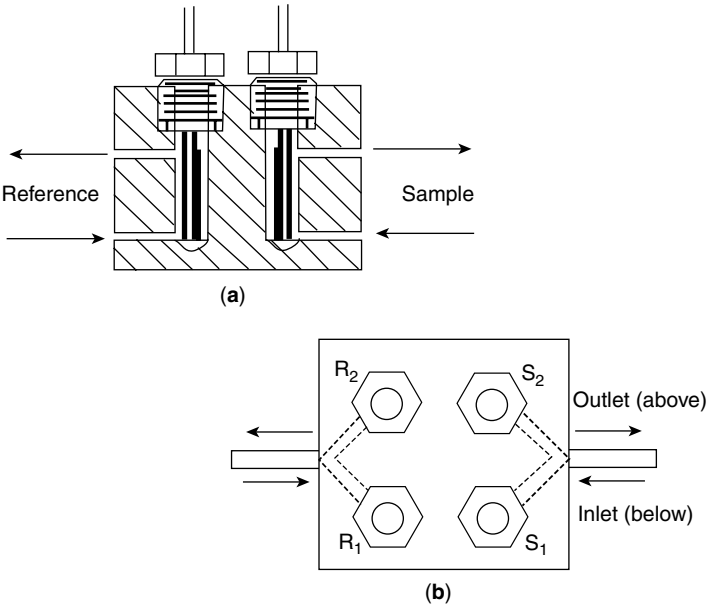

Fig. 14. Schematic of thermal conductivity detector typical four-filament tcd cell. (**a**) Side view. (**b**) Top view. [Reprinted from Ref. 12, p. 117].

except for the carrier gas itself, that passes through the detector will change the rate of heat loss this detector is truly universal. A schematic of a conventional four-filament TCD cell that is commonly used with packed columns is presented in Figure 14. Since resistance is a function of filament temperature any changes in the thermal conductivity of the gas that passes by the filament changes the resistance. The difference in resistance between a reference filament (R_1 and R_2), which is in pure carrier gas, and the sample filament (S_1 and S_2), which is in carrier gas and analyte, is used to detect the presence of the analyte as it elutes from the column. The detectors use a Wheatstone bridge circuit, which generates a signal when there is a difference between the output signals of the reference and sample filaments. For a TCD to be effective the thermal conductivity of the carrier gas must be significantly different than that of the analytes, which is not difficult to achieve since hydrogen and helium, which have the highest TC values, are commonly used as the carrier gas (55).

An important advantage of the TCD is the ability to detect air, which is not retained by most GC columns. The detection of air is useful in determining the void volume of a column. Traditionally the TCD was considerably less sensitive than the FID. However, recently the TCD has been adapted to capillary columns. The cell volume has been reduced to be more compatible with capillary GC columns and the use of a reference cell has been eliminated in some designs. Since a single cell is used, the gas flow to the detector is rapidly oscillated between the carrier gas and a reference gas. The capillary design of the TCD is reported to have sensitivities that approach that of the FID. Recently, TCD performance has improved, through the development of smaller flow cells.

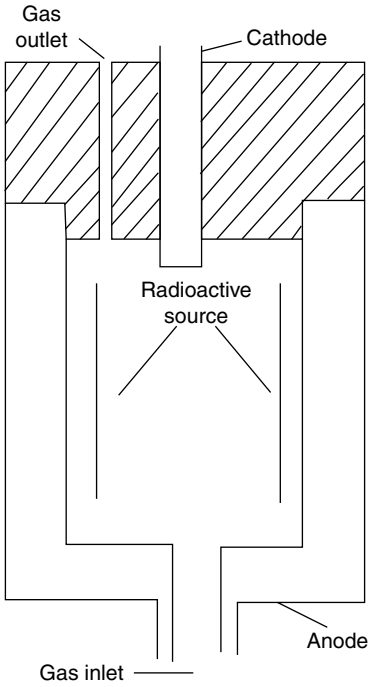

Fig. 15. Pin-cup ECD. [Reprinted from Ref. 11, p. 293.]

5.3. Electron Capture. The invention of ECD is attributed to Lovelock (56), who first published on the device in 1961. This selective detector is very sensitive toward compounds that can capture electrons. These are typically halogenated or nitrogen containing compounds. Its primary use is in pesticide analysis. For standard capillary column ECD the MDQ is 10 pg, the response is very selective, the linear range is three or four orders of magnitude and the detector is stable, although it is sensitive to contamination from traces of oxygen or water and requires extreme care in use and maintenance for optimal results.

A schematic of an ECD is presented in Figure 15. This detector uses a radioactive source, usually ^{63}Ni, to ionize the carrier gas (helium with nitrogen make up gas, or nitrogen, or a mixture of argon and methane), causing a high standing current. Electronegative analytes such as halogen-containing compounds, entering the detector cause a decrease in standing current as the analytes capture the free electrons. The standing current is kept constant by pumping electrons into the detector system. The decrease in electrons is measured as the analyte signal.

This is a quantitative detector, as the extent of electron capture is proportional to the analyte concentration. The ECDs are straightforward to use, but do require extra care in maintaining a clean system. Only very high quality nitrogen or argon/methane gas should be used as the makeup gas. If the detector is well maintained, conventional ECDs can easily detect picograms of analyte and micro ECD can detect as little as 4 fg of material (57). The detection limit is very dependent on the analyte's ability to capture electrons and thus the sensi-

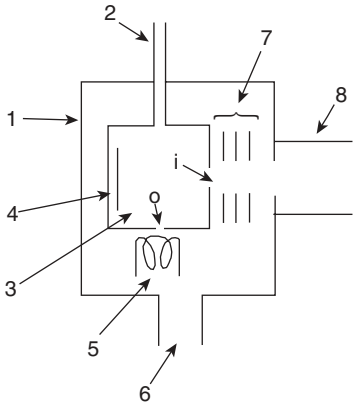

Fig. 16. Mass spectrometer ionization chamber (1) housing for ionization chamber; (2) sample inlet; (3) ionization chamber; (4) ion repeller; (5) cathode-e- emitter; (6) high vacuum system; (7) ion-beam collimator; (8) analyzer tube. Represented with permission from Ref. 59.

tivity of an ECD can drastically different from one analyte to another. For example, perflourobutene, C_4F_8, has a relative response of 1.3×10^5:1 with reference to perfluoropropane, C_3F_8 (58).

5.4. Mass Spectrometer. Perhaps the most useful detector for GC is mass spectrometry (MS). This detector provides both quantitative and qualitative analysis. State of the art bench-top GC MS systems are capable of unit mass resolution. The GC/MS system uses a narrow-bore GC capillary column; and by using a low flowrate and a vacuum pump, the column can be inserted directly into the MS.

The ionization chamber for a typical bench top mass spectrometer is diagrammed in Figure 16. The mass spectrometer ionizes the incoming sample and presents either the total ion chromatogram (TIC), or it will scan for only certain specified ions in selected ion monitoring (SIM) mode. The TIC of a sample contains all data necessary for compound identification and can be used to compare the mass spectrum of each individual peak in the chromatogram with reference spectra in a computer-based library. The SIM only monitors for one or a few ions in a sample, and so SIM data can be used to identify compounds with previously determined reference spectra.

Complete details on mass spectral interpretation and how this is applied to structure elucidation and chemical analysis may be found in the classical text by McLafferty (60) and in the more recent text edited by Busch (61).

5.5. Other Selective Detectors. Many more types of detectors exist than what has been discussed above. This section will discuss two detectors used for specific atoms, as well as infrared (ir) and ultraviolet (uv) detection.

The nitrogen-phosphorous detector (NPD) is another ionization detector that was invented for use with GC. As the name suggests, this detector is selective for nitrogen- and phosphorous-containing compounds. The detector has no flame; the NPD uses a rubidium silicate bead heated by a platinum resistance wire, and combustion is not supported because the hydrogen flow is very low.

The NPD is used in pharmaceutical labs for nitrogen-containing drugs, as it is the most sensitive detector available for nitrogen and phosphorous. Other applications of NPD are for the analysis of nitrogen- or phosphorous-containing pesticide residues, carcinogens, and amines.

The flame photometric detector (FPD), invented by Brody and Chaney in 1966 (62), is primarily used for detection of sulfur and phosphorous. A hydrogen-rich flame is used to burn the samples, which form chemiluminescent species that emit light at 394 nm for sulfur and 526 nm for phosphorous. Applications for FPD include pesticide residue analysis, air pollution studies, and petroleum analysis. Infrared spectrophotometers have been successfully attached to a GC and used as a specific detector. Discussions of these and many other selective detectors can be found in the previously referenced textbooks (9–17) and in the chapter by Henrich (63).

6. Data Collection and Handling

The purpose of a chromatographic data system is to collect analogue data from an analytical instrument and convert it to digital data. This is accomplished by an analogue-to-digital converter (ADC). The important characteristics of ADCs are speed and accuracy of conversion. Since capillary columns generate sharp peaks that elute in seconds, the major requirement of a data system is a rapid sampling rate which is easily accomplished by computer technology. The three basic types of data collection currently used in GC are integrators, dedicated computer based instrument(s) data systems and multi user server networked systems. The function of all of theses systems is to collect data from the instrument and provide the analysts with a means of interpreting the data generated by the instrument. In the distant past, chart recorders were used, but today they are rare and typically found on some educational chromatographic systems.

6.1. Integrators and Recorders. Until the early 1980s, most data was collected and stored using classical strip chart recorders and plotters, when digital computers and integrators supplanted them. The key advantage of a strip chart recorder was simplicity, however, the myriad disadvantages, especially the difficulties in postprocessing of quantitative data, led to their demise. In the 1980s, the primary data systems were digital electronic integrators, which combined strip chart recording with rudimentary computing capability. Chromatograms could be stored electronically and reprocessed, and the instrument could be controlled through the data system, although procedures for these operations tended to be tedious. Integrators are still in existence however they have been mostly replaced by dedicated and server based computer systems.

6.2. Computer-Based Data Systems. In the 1990s, stand-alone and networked computers, usually built around PC platforms, replaced many of the older integrators. These computer-based systems including servers are also capable of instrument control, data collection, and archiving, generating detailed reports and documents, generating system suitability results and interfacing with laboratory information management systems (LIMS). In many industries, strict data security is also a requirement.

Stand-alone computer based systems are typically found in smaller laboratories where only a few instrument reside. The disadvantage of these systems is the need for the user to maintain backups of the data systems and the advantage is they are generally more flexible with regards to updating the software systems which control them. Server based systems are typically used in large well-regulated corporations where the data from all the instruments is collected and stored in one location. These systems can support hundreds of instruments simultaneously. While the details of computer-based data collection are beyond the scope of this article, an excellent introduction can be found in the chapter by McDowall (64).

6.3. Regulatory Issues. In many industries, especially pharmaceutical, forensic, environmental and clinical analysis, data systems and instruments must be validated to assure that they are operating within established norms and procedures. Typically, instrument and data system vendors provide assistance with validation, although it is wise for laboratories to have internal standard operating procedures in place. Validation requirements may also go beyond instrumental and scientific concerns, to include data storage, retrieval, and security. The validation process is often lengthy and labor intensive.

For example, when using many of these data systems, the analyst must set the operating parameters for data collection and analysis and, in general data manipulation can be done after data collection. Suppose that the analyst can set the data collection rate or peak width. This determines the number of data points collected per unit time. If too few points are collected, the apex of the peak can be missed, which leads to inaccurate quantitation. If too many points are collected the analyst can data bunch or average the data collected. The problem with collecting too many data points is rapid filling of data storage space. If there is no standard operating procedure or validation in place, then two analysts, who may be running the same nominal procedure on the same samples may obtain dramatically different analytical results. A useful introduction to validation and method transfer issues in the pharmaceutical industry is found in the chapter by Crowther and co-workers (65).

7. Multidimensional GC

In order to dramatically increase separation power, multidimensional GC, employing two columns, has been developed. In multidimensional GC, the column effluent from the first column, as it elutes, is transferred to a second column, typically with another stationary phase chemistry, for further separation. This affords tremendous separation power, as, with two dimensions, chromatograms have space for thousands of peaks. Multidimensional GC is most often employed in the petroleum industry, and sometimes for toxicology and environmental problems. There are two common instrument configurations: traditional multidimensional GC, in which the effluents represented by single peaks from the first column are collected, trapped, then transferred to the second column, and comprehensive two dimensional GC, in which the column effluent is trapped continuously and transferred to the second column at regular intervals, using a trap combined with a switching valve. Due to the complexity of the valve

and switching systems involved, multidimensional GC is not used by many routine analysis laboratories, but is used for specialized applications requiring especially strong separation power.

7.1. Traditional Multi-dimensional GC. In traditional multidimensional GC, column effluent representing one or more peaks in a separation is trapped and transferred to a second column, which is generally termed "heart-cutting" to represent the interesting portion of the chromatogram being further analyzed. Two-dimensional GC systems often consist of two ovens so that the two columns can be temperature programmed independently. They are often much more complex than traditional one-dimensional GCs, and are generally not in routine use. As an example, a two-dimensional separation of fire debris, in which several heart cuts were sampled and analyzed is shown in Figure 17 (66). The ability to analyze very complex mixtures, which is the main advantage of two-dimensional GC, is easily seen. Other typical applications of two-dimensional GC include chiral separations (67,68) urinary acids and (69) bornane congeners (70). Bertsch (71) provided an especially thorough description of theory and application of multidimensional GC.

7.2. Comprehensive Two-Dimensional GC. Comprehensive two-dimensional GC, in which the effluent from a traditional column is continuously sampled into a short, narrow bore, thin film second column, was originally proposed by Schomburg (72) and was developed and promoted by Phillips and coworker (73,74). The continuous use of the second dimension column generates tremendously high peak capacity. Notable applications of comprehensive two-dimensional GC include complex petroleum analysis (75,76) and pesticides from biological samples (77). A typical two-dimensional chromatogram showing the separation of pesticides extracted from serum is shown in Figure 18. In this two-dimensional chromatogram, viewed "from above" as a contour plot, the x-axis represents separation an the traditional column and the y-axis represents separation on the short second column. It is seen that several compounds (shown as peaks lined up in the y direction) that would have coeluted if separated just on the traditional column, are well resolved on the second column. The tremendous peak capacity is evidenced by the large amount of "blank space" seen in the two-dimensional space.

8. Fast and Micro-GC

Obtaining faster separations has been an interest of chromatographers since the pioneering work in the 1950s (6). Separations in a matter of seconds were first shown in the early 1960s, although the routine use of fast separations was not seen until the 1990s. The instrumental requirements for obtaining fast separations are more stringent than for traditional GC, as the columns are very short, the gas flows are high and require very precise control and the chromatographic peaks elute very quickly, requiring careful detector choices and optimization. Along with the drive toward faster separations in traditional bench-top systems, there has been a move toward smaller systems that are field portable. Systems for both applications have become commercially available in the late 1990s (78).

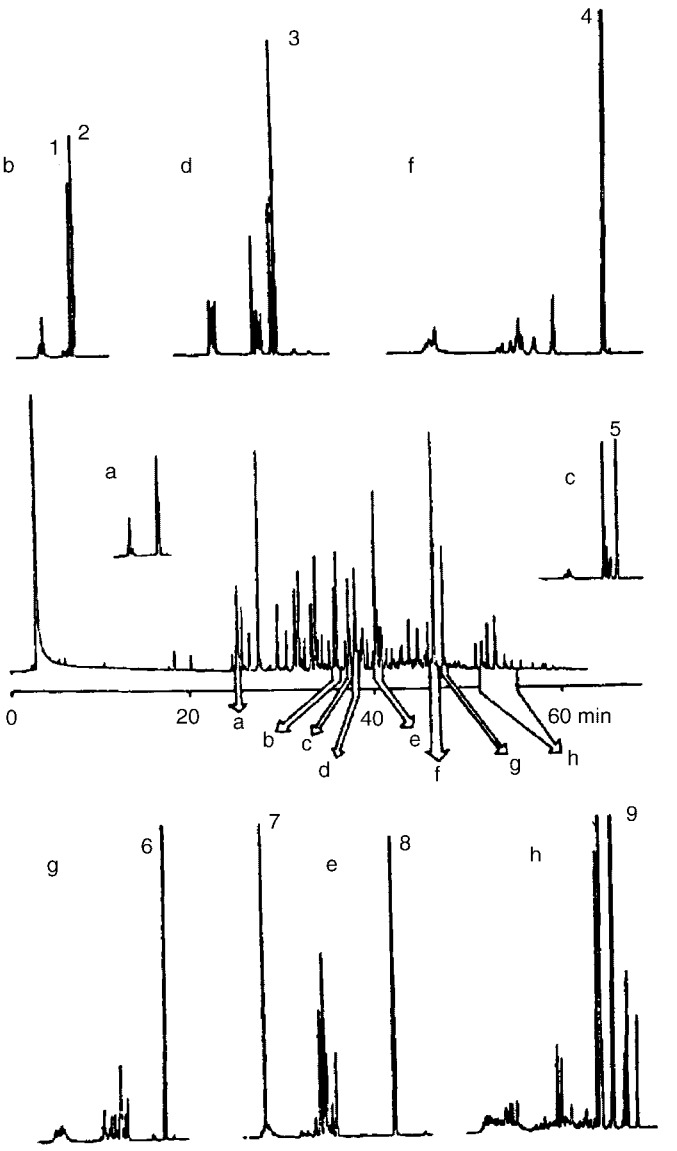

Fig. 17. Use of heart-cutting for the identification of target compounds in 90% evaporated gasoline. 1 = 1,2,4,5-Tetramethylbenzene, 2 = 1,2,3,5-tetramethylbenzene, 3 = 4-methylindane, 4 = 2-methylnaphthalene, 5 = 5-methylindane, 6 = 1-methylnaphthalene, 7 = dodecane, 8 = naphthalene, 9 = 1,3-dimethylnaphthalene. [Reprinted with permission from (65).]

The main limiting factor in developing both faster and smaller systems is the bulk of the column, column oven, inlet, detector, and fittings that accompany them. As miniaturized electronics and microprocessor-controlled pneumatics have become available, this problem has been significantly reduced. While most of these systems employ traditional inlets and detectors for ease of sample

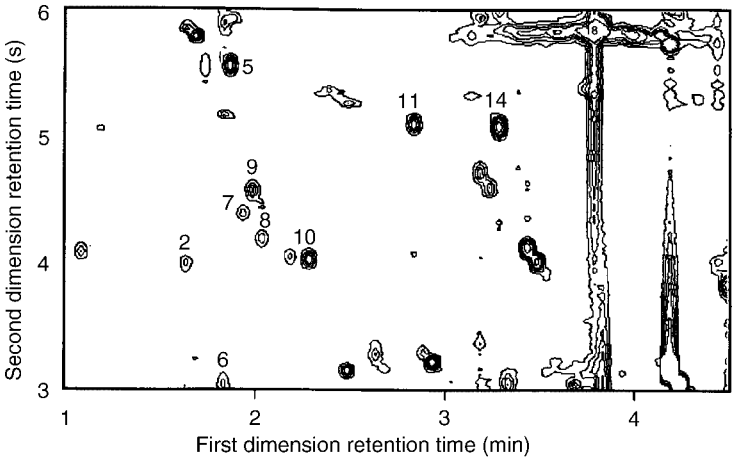

Fig. 18. Comprehensive two-dimensional GC chromatogram of supercritical fluid extract of spiked human serum. 1 = dicamba, 2 = trifluralin, 3 = dichloran, 4 = phorate, 5 = pentachlorophenol, 6 = atrazine, 7 = fonofos, 8 = diazinon, 9 = chlorothalonil, 10 = terbufos, 11 = alachlor, 12 = matalaxyl, 13 = malathion, 14 = metalochlor, 15 = DCPA, 16 = captan, 17 = folpet, 18 = heptadecanoic acid. [Reprinted with permission from Ref. 77. Copyright 1994 America Chemical Society.].

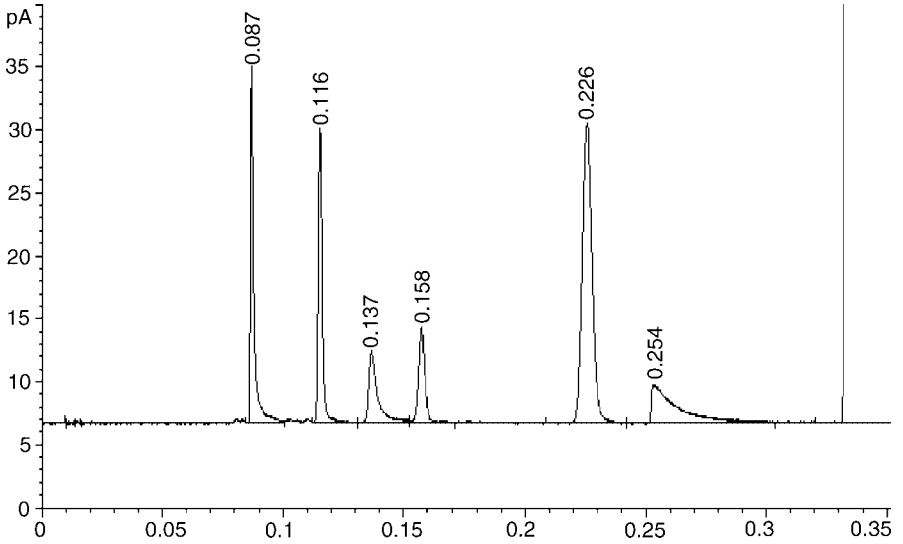

Fig. 19. Fast GC separation of residual solvents from a pharmaceutical analysis. inlet: split 100:1, 10 psi, 300°c; Column: HP-5MS, 5 m × 0.25 mm × 0.25 μm; TP: 40°C/1 min, 200°C/min to 80°C. Detector: FID, 300°C, 100 Hz. 1. Ethanol, 2. ethyl acetate 3. 1-butanol 4. Heptane 5. Toluene 6. Dimethylformide (DMF) 7. Dilution: dimethyl sulfoxide (DMSO) (80).

handling, the main modifications have been to the column and oven configuration. For fast GC, metal sheathed, resistively heated columns have been used to provide very rapid (up to 1200°C/min) temperature programming of a 5 m column. The specially sheathed column and an external controller can be added to many commercial GCs. A representative fast separation of several solvents is shown in Figure 19. An additional approach to faster and shorter columns involves wrapping a column around a heated metal rod, which allows a very small oven (79).

9. Sample Preparation

Almost all GC-based analytical methods in use today also involve some form of sample pretreatment prior to the injection and analysis. While it is beyond the scope of this article to describe sample preparation in detail, the reader is directed to a number of references for more information. Many of the standard referenced texts (9–18) and journals described above include sections or research papers dealing with sample preparation. Some of the newer techniques for which texts are available, that are often employed on-line with analysis include pyrolysys (81), static and dynamic head-space, (82) supercritical fluid extraction (83), solid-phase extraction (84), and solid-phase microextraction (85,86).

10. Conclusions

Gas chromatography is considered by many researchers to be a mature technique. Developed 50 years ago, it remains one of the most widely used instrumental techniques in analytical chemistry today. Recent advances in inlet, column, detector and data system technology have made GC straightforward and cost effective to use for myriad routine applications. Recent attention in the field has focused on novel column technologies, fast separations, selective detectors, especially MS, and sampling techniques.

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