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A REVIEW OF CAPILLARY AND PACKED COLUMN GAS CHROMATOGRAPHS

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A REVIEW OF CAPILLARY AND PACKED COLUMN GAS CHROMATOGRAPHS

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ABSTRACT

In this review, the essential aspects of gas chromatography are discussed. The article begins with a very brief discussion of basic chromatographic theory, followed by an in-depth treatment of the instrumentation involved. This discussion starts a discussion of chromatographic columns, the distinctions among which are used to classify the different modes of gas chromatography. Following this is an in-depth discussion of instrumentation, the treatment of which follows the classification by column types. This discussion

Certain commercial instruments, materials or equipment are identified (*) in this article in order to specify adequately the experimental procedure or discussion. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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includes the operational principles and applications of injectors, detectors and data handling systems. In conclusion, a listing of suggested further reading is provided.

Keywords: Gas Chromatography, data systems, detectors, injectors.

INTRODUCTION

The term gas chromatography broadly covers several separation-analysis methods. All of these methods share the common characteristic of having a gaseous mobile phase or eluent that carries the solute or sample through the stationary phase, where separation occurs. While the eluent gas chosen is usually helium, nitrogen, or sometimes hydrogen[1], one may choose many other carrier gases (or gas mixtures) depending on the specific problem to be solved. The sample is transported to the stationary phase by the carrier gas, and, subject to both thermodynamic and kinetic considerations, some sample will enter the environment of the stationary phase. In this environment, intermolecular forces between the sample molecules and the stationary phase molecules will lead to an interaction (strong, moderate, or weak). In general, the stronger the interaction, the longer the interaction will persist. Strongly interacting species will be retained for relatively longer times in the environment of the stationary phase. The success of a gas chromatographic separation will depend largely upon the analyst's skill in using these intermolecular interactions as a tool for separating the various components of a mixture.

In gas-liquid chromatography (GLC), the solute interacts with a stationary phase that is either a supported liquid, or a phase that has a liquid-like structure. The solute is ***ab***sorbed into the liquid in much the same way as it would dissolve in a liquid. In gas-solid chromatography (GSC), the solute ***ad***sorbs on the surface of a solid, with little or no penetration into the bulk volume of the solid. In size exclusion gas chromatography, the solute penetrates a solid framework of relatively consistent size in which both adsorption and a "sieving" action occurs. Because of this combined mechanism of separation, size exclusion gas chromatography is usually treated as a subset of gas-solid chromatography.

Apart from this classification of chromatographic processes which is based on the nature of the sample-stationary phase interactions, we may further divide gas chromatography into two classes for practical instrumental reasons. These

[1] Hydrogen is a flammable gas which easily forms explosive mixtures with air and thus must be handled with extreme care, preferably in an explosion-proof laboratory.

classifications are: packed column gas chromatography and open tubular column (or capillary) gas chromatography. The terms "capillary column" and "open tubular column" are used interchangeably. Packed column gas chromatography usually employs a relatively large diameter tube containing a packed bed stationary phase, while open tubular column gas chromatography employs a relatively small diameter tube with the stationary phase placed only on the tube wall.

In most modern chromatographic work, open tubular columns are used for nearly all applications except the analysis of permanent gases and very volatile compounds. Thermodynamic measurements performed with chromatography usually require packed columns rather than open tubular columns, however. Packed columns are also used extensively for preparative and semi-preparative chromatographic separations.

BASIC CHROMATOGRAPHIC THEORY

We can better understand the separation process by examining characteristics common to all chromatographic processes (packed or open tubular columns). We will begin by referring to the hypothetical chromatogram shown in Figure 1. The chromatogram is presented as a graph of detector signal level (here represented as millivolts) as a function of time. Two peaks have emerged, one after the other, corresponding to two separated components, **a** and **b**. These two peaks serve to illustrate three important chromatographic parameters: efficiency, selectivity, and resolution.

The efficiency of a column is a kinetic (rate dependent) parameter which describes the column's ability to separate components sharply as a function of the

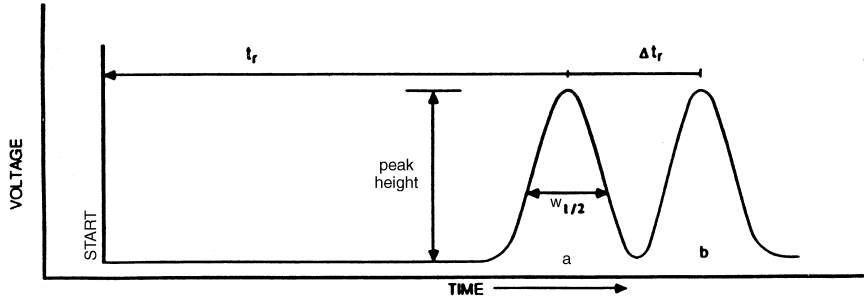

Figure 1. An idealized chromatogram illustrating the concepts of retention time (t_r), peak width ($w_{1/2}$) and resolution (shown by the displacement of the two chromatographic peaks from one another).

sample residence time in the column. The historical analogy between distillation and chromatography resulted in the common practice of expressing column efficiency using the chemical engineering concept of the theoretical plate. The concept of the theoretical plate, or more simply, the plate number, is a measure of solute zone spreading or dispersion. A theoretical plate can be thought of as an imaginary zone or volume element in which rapid equilibration of the solute between the mobile and stationary phases can take place. For the idealization of a Gaussian-shaped peak, the number of plates contained on a given column, n, is given by:

$$\mathbf{n = 5.545(t'_r/w_{1/2})^2,} \quad \textbf{(1)}$$

where $\mathbf{t'_r}$ is the retention time of the solute (adjusted for system hold up volume), and $\mathbf{w_{1/2}}$ is the peak width (at half the peak height) expressed in units of time. The larger the value for the dimensionless number, **n**, the higher is the column efficiency. An alternative expression for efficiency is the "height equivalent to a theoretical plate," h, which can be calculated from:

$$\mathbf{h = L/n,} \quad \textbf{(2)}$$

where **L** is the length of the column. The efficiency of the column increases as **h** decreases. It must be emphasized that these simplified equations are strictly applicable only to the Gaussian curve. For asymmetric peaks (such as those that tail or front) the equations become more complex, even when subject to many simplifying assumptions.

There are many factors that affect the efficiency of a column for the separation of a given solute. The major factors are the mobile phase velocity through the column, the nature and thickness of the stationary phase film (if any) on the support or capillary wall, the viscosity of the mobile phase, and column internal diameter. These factors, along with parameters such as solute-solvent diffusivity, can be controlled to some extent in order to optimize separations. The situation can become complex, however, since most of these factors are interdependent, many are also temperature dependent, and changing one parameter can cause a change in another.

The efficiency of a column can be predicted quantitatively using the Van Deemter equation:

$$\mathbf{h = A + B/u + C \cdot u.} \quad \textbf{(3)}$$

In this equation, which is a simplified version of the detailed mathematical treatment of the flow through capillaries, **A** is a geometrical constant which describes the multiple paths which carrier and solute can take in a packed column (we will discuss the different column types in more detail later). This is sometimes called the eddy current term because of the electronic analogy of current flow inhomogeneity. This term is minimized by keeping the particle size of the packing as

small as possible (approximately 200 μm) without causing an excessively high pressure drop across the column. As we will see later, the value of this term can be made negligible by using an open tubular column (or capillary column). The constant **B** describes the relative diffusion of the solute in the gas and stationary phase. It is most significant at low carrier gas velocity (**u** in the equation above). The **C** term represents the resistance to mass transfer of the solute at the solute/stationary phase interface. Slow mass transfer, of course, means longer analysis times. A plot of **h** against carrier gas velocity, **u**, shows a broad minimum which corresponds to the optimal carrier gas velocity. Typical values for practical operating linear velocities range from 8 to 12 cm/s, depending primarily on the relative molecular mass of the carrier gas used.

Selectivity is an essentially thermodynamic parameter which describes the ability of a column to isolate two (or more) solutes into distinct bands, such as the peaks a and b on Figure 1. The selectivity is a function of the relative magnitudes of the intermolecular forces between the solute(s) and the stationary and mobile phases. For example, a relatively polar stationary phase will interact more strongly with polar solutes than it will with simple alkanes. The choice of stationary phase is therefore a very important step in the design of a chromatographic analysis.

Several retention index systems have been developed to aid in the choice of stationary phase and provide adequate selectivity for an analysis. The scaling systems of Kovats, Rohrschneider, and McReynolds have all attempted to address this problem. The most extensive tabulation available is for the system developed by McReynolds, which provides an index of retention for a set of reference compounds on a given stationary phase as compared with the nonpolar hydrocarbon, squalene. The McReynolds constant system can provide a good starting point in the choice of stationary phase. The Kovats retention index is a logarithmic interpolation of retention times of solutes with respect to standards such as n-alkanes. The major usefulness of this system is in the qualitative identification of samples by gas chromatography. It is also very valuable in the selection of appropriate stationary phases.

The Ultimate Goal in a Chromatographic Measurement is to isolate a sample into successive bands corresponding to the individual components of the mixture. A measure of the isolation between components is the peak resolution, **R:**

$$\mathbf{R} = \frac{\Delta \mathbf{t_r}}{\frac{\mathbf{1}}{\mathbf{2}}\left(\mathbf{w^a_{1/2}} + \mathbf{w^b_{1/2}}\right)} \qquad \textbf{(4)}$$

where $\Delta \mathbf{t_r}$ is the difference in retention time of two successive peak maxima, and $\mathbf{w^a_{1/2}}$ and $\mathbf{w^b_{1/2}}$ are their corresponding peak widths (at the half height). Resolution is improved by increasing the peak separation (that is, improving selectivity) or by decreasing the peak widths (that is, improving column efficiency). It is important to realize that a given column may have good selectivity while having poor effi-

ciency, and vice versa. An optimized separation will produce both well-separated and sharp peaks on the chromatogram, and do so while minimizing the retention time, assuming the stationary phase had been properly chosen.

Resolution is adequate when the degree of separation allows the particular analytical problem being considered to be solved. It may not be necessary to obtain optimum "baseline resolved" peaks in every situation. Quite often, reasonable quantitative accuracy can be obtained with three percent overlap of two successive peaks. This corresponds to peak maxima separation of approximately $\mathbf{2w_{1/2}}$ for two adjoining Gaussian-like peaks of equal size.

CHROMATOGRAPHIC COLUMNS

Gas Liquid Chromatography Columns

Gas liquid chromatography (GLC) is characterized by a stationary phase consisting of a liquid which is coated or immobilized on an "inert" packed bed of supporting material, or coated on the inside wall of an open tubular (capillary) column. While the GLC separation processes are similar in packed and open tubular columns, we will discuss the process in open tubular columns separately because of their great importance, and because of their distinct instrumental requirements.

The liquid for GLC may be materials such as a heavy hydrocarbon (for example, squalene), a light polymeric liquid (such as a polyethylene glycol of specified molecular mass range), or a heavier silicone fluid (for example, polydimethylsiloxane). In all cases, the fluid must be of a low enough vapor pressure so that it will not evaporate (or bleed) appreciably from the support. The choice of stationary phase liquid, which we will discuss shortly, depends on the sample we wish to analyze. The inert bed of support material used for coated packed columns is usually a diatomaceous earth, although in some circumstances glass beads or Teflon particles may be chosen. Diatomaceous earth, which consists of the skeletal remains of small prehistoric algae called diatoms, is about 88 percent silica. The materials used for chromatographic supports are purified by acid washing, and the surface is deactivated by a process called silanization, in which active sites on the surface are capped synthetically. While this treatment cannot make the support surface perfectly inert, the deactivated surface is very suitable as a support for the analysis of all except the most polar materials, such as alcohols and organic acids. The liquid coating that is applied to the support is usually between 5 and 30 percent (mass/mass).

Even the most highly deactivated support surface will be affected by the phenomenon of adsorption. Adsorption, which we will discuss in more detail in the section on gas-solid chromatography, is a universal adhesion that occurs between the mobile phase (both the carrier and sample molecules) and the surface of

the stationary phase. A number of different supports may be chosen, differing mainly in density and available surface area and surface treatments. The choice depends upon the individual application, but the variety of supports provides a degree of flexibility.

The liquid phase is easily coated on the support by dissolving the liquid in a slight excess of a suitable solvent and adding the support to the mixture. The solvent is then removed in a rotary evaporator, leaving the support coated with the liquid. This may seem unusual, since the coated support will look and feel quite dry. What is meant, of course, is that there are layers of molecules of the liquid on the support, and these layers are liquid-like in their structure. The coated support is poured into a tube which will serve as the column. The tube can be made of copper, stainless steel, nickel, glass, Teflon or some more specialized material. The diameter of this tubing can range from 0.64 to 0.16 cm in diameter, and from 2 to 10 m in length. For preparative use, column diameters of 1 to 6 cm are used in lengths of up to 3 m.

Packed columns are relatively inexpensive when purchased from commercial sources, and are also quite simple to make up in the laboratory. The many possible choices of liquid coatings are both a blessing and a curse. It is possible to design a column to perform some very specific separations, but the sheer number of possible coatings can be bewildering.

The chemical nature of the coated liquid imposes a restriction on the operating temperature range. At lower temperatures, many liquids will become very viscous or even solidify. This phase change will be reflected in a deterioration of the chromatographic behavior. At higher temperatures, the liquid will "bleed" from the support as a result of the increased vapor pressure. This is clearly unfavorable, since not only does the separation power of the column decrease, but also the detector response will become noisy due to the continual passage of extraneous material. Detector fouling can also result from column bleed, which can cause significant instrument down-time. Some liquids will even decompose at higher temperatures, also leading to detector fouling. An understanding of the bulk and molecular properties of the sample will guide the analyst toward a good choice of stationary phase. Quite often, however, one or more "survey runs" with several columns at several temperatures may be needed to arrive at an optimal combination of liquid phase and operating conditions for a particular analysis.

An important characteristic of gas-liquid chromatography is the notion that the physical processes involved are actually solution processes, with the sample being absorbed or dissolved by the stationary liquid phase and later released through a "vaporization" step. All of the thermodynamic treatments applicable to solutions can be applied to gas-liquid chromatography, including considerations of enthalpy, entropy, equilibrium constants and activity coefficients. In fact, gas-liquid chromatography on packed columns has been used for many years as a tool for the study of solution thermodynamics. One can actually

measure thermodynamic properties of solution, such as enthalpies and entropies of solution and vaporization, activity coefficients, excess functions, and transport phenomena.

Gas Solid Chromatography Columns

Most of the instrumental requirements of gas-solid chromatography (GSC) are very similar to those of gas-liquid chromatography. The main difference is in the nature of the stationary phase, and the processes which occur in that phase. For clarity and convenience, we can divide the kinds of stationary phases available into three types: adsorption columns, size exclusion columns, and porous polymer columns. Naturally, many of the same physical processes occur in all of these stationary phases.

The first kind of column we will consider is the adsorption column. We stated earlier that adsorption was a universal adhesion process which will always occur at the boundary of any liquid or solid with another fluid medium such as a gas. The process is considered universal in that all solids, whether porous or nonporous, metal or nonmetal, hard or soft, will adsorb any gas, polar or nonpolar, on its surface. The attraction may be caused by physical interactions (such as van der Waals forces) or chemical interactions (such as those involving electron transfer). The second adsorption mechanism is called chemisorption, and only results in a monolayer of adsorbed material. It is not generally of interest in chromatographic processes.

Adsorption is an exothermic process; when a gas is adsorbed on a solid, heat is liberated. Elementary thermodynamic considerations therefore tell us that as the temperature of a given system is increased, the amount of gas adsorbed by the solid at a given pressure will decrease.

The most common packings used to prepare adsorption columns are silicas, aluminas, carbon blacks (especially the graphitized versions), and the synthetic zeolites (commonly called molecular sieves). This last class of material is usually associated with size exclusion chromatography, discussed below, but they are often used as adsorbents as well. The column diameters are typically the same as those that are used for the packings of gas-liquid chromatography, but the column length is often shorter. Also, it is possible to prepare open tubular columns that contain adsorbents such as silica and alumina.

All the adsorbent packings require heat activation prior to use, to drive off any material that may already be adsorbed. The length of time and the temperature at which activation is performed very often will affect the chromatographic behavior of the adsorbent. The adsorbents can be used successfully in the separation of lower relative molecular mass saturated, unsaturated, aromatic, and halogenated hydrocarbons, as well as for many permanent gas separations.

Adsorbent packings are very easy to prepare in the laboratory as packed columns, since the coating steps required for GLC columns are normally not required. Alternatively, as with the more common GLC columns, they can be purchased commercially prepared and ready to install in the chromatograph. The adsorbents can be used at higher temperatures than most other chromatographic stationary phases, since there is practically no danger of decomposition or bleeding of the phase. The absence of bleeding is very favorable from a detection standpoint, since the column will not contribute "impurity noise" to the signal baseline. Some adsorbents can become highly catalytic at higher temperatures, however, resulting in the decomposition of sensitive samples.

These phases can also be used in subambient temperature work, since there is no viscosity or solidification effect as there can be with coated liquid phases. With the one exception of the carbon black packings, the adsorption phases are much more resistant to degradation by trace amounts of oxygen in the carrier gas than other phases. Naturally, carbon is subject to attack by oxygen, especially at elevated temperatures.

The user must be aware of some pitfalls associated with the use of adsorbent columns. There may be significant nonuniformity between different lots of silica and alumina adsorbents. Many adsorbent columns will adsorb some samples so strongly that release will not occur without reactivation of the material at high temperature. An example is the nearly permanent adsorption of carbon dioxide by most of the zeolite molecular sieve materials. These phases will also adsorb trace quantities of water that may be present in the carrier and sample matrix, thus changing the retention characteristics of the packing during operation, sometimes during an analysis. Since the adsorption isotherms of these materials are, in general, nonlinear, changing the size of the sample will change the retention time on a given column. This will also cause peak asymmetry (such as tailing) and sometimes incomplete sample recovery from the column. Also, since the adsorptive surfaces are of high energy, many polar and moderately polar samples will show excessively long retention times on these columns.

Adsorption columns can be modified by coating the material with a small amount of a nonvolatile liquid or an inorganic salt. The most energetic sites on the surface of the adsorbent will preferentially bind to these modifiers. As a result, these sites will be unavailable to participate in retention, and solute retention will typically decrease. This technique is sometimes called gas-layer-adsorption chromatography.

The next type of column we shall consider is the size-exclusion column. The packing for this column is the same synthetic zeolite or molecular sieve that we discussed earlier as an adsorption column. The structures of these crystalline aluminosilicate materials are unique in that they contain cavities of a definite size, which can be controlled by the elemental composition of the zeolite. The cavities are roughly the same size as many smaller molecules such as water and the per-

manent gases. Solute molecules in this size range which can penetrate the internal pore structure will experience an increase in retention time due to entropically enhanced adsorption. The popularity of molecular sieve columns originally resulted from their ability to separate oxygen and nitrogen rapidly under reasonable chromatographic conditions. The most commonly used packings are the 5A (calcium alumino-silicate, having an average pore size of 0.5 nm), 13X (sodium alumino-silicate, with an average pore diameter of 1.0 nm), and the 3A (potassium alumino-silicate, having an average pore size of less than 0.5 nm). Molecular sieve 4A (another sodium alumino-silicate, with an average pore size of less than 0.5 nm) has also found chromatographic application.

Another type of molecular sieve is the carbon molecular sieve, which is prepared from the controlled pyrolysis of poly(vinylidene chloride). This material is very inert and nonpolar. The sieve structure results from the cross-linking of individual, small crystallites of carbon. This material has a high affinity for hydrocarbons; in fact, water will elute before methane under most chromatographic conditions. It is very useful for the separation of light inorganics, and has been particularly valuable with mixtures containing water solutions of formaldehyde.

The final solid that we will consider for application in GSC is the porous polymer phase. Most applications of porous polymer phases are with packed columns, but they are also available in capillary column dimensions as well. These packings are prepared using the method of suspension polymerization, in which monomers and cross-linking agents undergo reaction in an inert solvent. The more popular porous polymer phases are copolymers of styrene and divinylbenzene. The porous polymer phases are quite useful in the separation of polar compounds such as alcohols, carboxylic acids, amines and amides, aldehydes and ketones, and many organic and inorganic gases. The suspension polymerization technique produces a sponge-like structure having a uniform pore size which can be controlled by adjusting the reaction conditions. Externally, the packing resembles microscopic beads. The chromatographic behavior of the packings is a function of the chemical nature of the polymer, surface area and particle size in addition to the pore size. In general, however, retention times increase as the pore size is decreased.

Although we have chosen to discuss porous polymers under GSC, there is some doubt as to the mechanism of retention on these phases. At lower temperatures (say, below 100°C), adsorption appears to be the principle retention mechanism. At higher temperatures, the polymers behave more like a coated liquid phase (that is, the surface structure becomes liquid-like). Under these conditions, a partitioning of the sample in the polymer appears to occur.

As with the other GSC phases, activation or conditioning (at approximately 200°C) is required prior to use. This is done in order to drive off any residual monomer or solvent, and to remove any material which may be adsorbed on the surface. Most of the polymers have relatively high maximum operating tempera-

tures (at least 250°C), and introduce little impurity noise to the detector. A somewhat different porous polymer material is a linear polymer of p-2,6-diphenylphenylene oxide. This material has a maximum operating temperature of 375°C, but it can be run at 400°C for short periods. It is useful in the separation of high boiling, polar compounds such as diols, methyl esters of dicarboxylic acids, aldehydes and ketones, amines and amides, and phenols. Short cartridges of this material are also used as sampling sorbents for the collection of volatile or gaseous samples. These sorbent columns are especially useful in environmental analysis work, and play a role in many standard procedures set by regulatory agencies. One major disadvantage of the material is that it is very soluble in chlorinated solvents, and it may be degraded by the presence of chlorinated samples.

Some minor operational disadvantages may be experienced in the use of the polymeric phases. It is sometimes difficult to pack a porous polymer into a metal column due to the effects of static charge. This is especially pronounced in dry climates. It is therefore often necessary to purchase columns already prepared. Another problem occurs when some of the polymers are used over a large temperature range. The polymer beads tend to swell, thus changing the flow characteristics of a column. This can lead to less than optimum detector performance.

The typical packed column (for both gas-liquid and gas-solid chromatography) is operated with a volumetric flow rate of between 15 and 45 mL/min, measured at the column exit.

Open Tubular Columns

The final classification of gas chromatography we will consider is that involving capillary or open tubular columns. This technique centers around the use of columns consisting of long (30 to 60 m), coiled, small diameter (0.25 to 0.05 mm inside diameter) capillary tubes, usually made of fused silica coated with a protective layer of polyimide. In recent years, fused silica open tubes have been coated with a thin layer of aluminum in order to extend the operating temperature, since the polyimide will degrade at approximately 325°C. The stationary phase is coated as a film on the inside surface of the tube, rather than being packed in a bed of coated support particles. The flow heterogeneities associated with packed columns are thus eliminated, along with the "A" term (the multipath or eddy diffusion term) of the Van Deemter equation. Capillary columns are available with efficiencies as high as 500,000 plates, in contrast to the typical maximum of 10,000 plates obtainable for packed columns. Capillary column chromatography is useful for all types of separations except permanent gas analysis and the analysis of very volatile materials. Of course, preparative scale separations are also not suited to capillary columns due to the very low solute capacity. Open tubular

columns are especially suited for the separation of complex mixtures containing upwards of a hundred individual components. In general, separations on capillary columns can be performed at temperatures averaging 30°C lower than would be required using a liquid phase coated on a solid support.

The extremely high efficiencies of capillary columns make stationary phase selectivity a less important consideration in the design of an analysis. The most common liquid phases used with open tubular columns are the methyl silicones and their derivatives. An open tubular column coated with cross-linked polydimethyl siloxane is essentially a boiling point separation column (using primarily London dispersion forces as the separation mechanism), while phenyl- and cyano-substituted polymers provide for more specific polar interactions. These liquids are coated to the desired thickness (typically 0.3 to 1 °m, although even thicker films are possible) and immobilized by cross-linking the fluid to form a nonextractable polymer network. The silicone-based phases have high thermal stability, and can be operated at temperatures in excess of 275°C for short periods of time.

The capillary column length is a relatively unimportant parameter in the design of effective analyses. Column length is far more important to packed columns. The parameter of film thickness is very important to capillary columns, however. An increase of 0.3 μm in film thickness can produce the same increase in resolution as quadrupling the column length, without the fourfold increase in analysis time that the longer column would entail. Significantly increasing the film thickness beyond 1 μm will cause unfavorable mass transfer effects caused by the time needed for solute diffusion into the stationary phase. While the percent loading characterizes the amount of liquid on a GLC packed column, the phase ratio, β, characterizes this for the open tubular column:

$$\beta = \mathbf{r}/2\mathbf{d_f}, \tag{5}$$

where **r** is the radius of the capillary and $\mathbf{d_f}$ is the film thickness. A typical open tubular column will have a phase ratio of approximately 250. The typical volumetric flow rate through an open tubular column is between 0.5 and 3 mL/min, measured at the column exit.

There are a number of disadvantages in the use of open tubular columns that must be addressed. The manufacture of these columns is a nontrivial process which cannot usually be duplicated successfully in the laboratory. The commercially available columns tend to be very expensive relative to packed columns. Since the columns are so small in size, their sample capacities are also quite small. To prevent column overload, a flow splitter (to be discussed in more detail in the next section) on the injection port is almost always necessary. The splitter discards most (90 to 99 percent) of the sample injected from the syringe. For trace analysis work, an injector capable of operating in "splitless mode" during injection is usually used. These injectors are more complex and more expensive than the sim-

pler devices used with packed columns, and require a bit more skill and effort to use properly. An additional consequence of the low sample capacity is the requirement for the use of the most sensitive detectors available. These are usually limited to the flame ionization, thermionic, electron capture and mass selective detectors. The small diameter of the open tubular column also requires a higher degree of stability in the oven temperature than is required for a packed column. The stationary phase films in the columns are prone to oxidative damage, and therefore require a constant flow of oxygen-free carrier at temperatures very much above ambient.

INSTRUMENTATION OF GAS CHROMATOGRAPHY

While the instrumental details of packed column and open tubular column gas chromatography are unique and must be understood in detail to properly use the methods, many of the features are common to both classifications. Figure 2 shows a "generic" schematic of instrumental features common to all gas chromatographs. The carrier gas is usually supplied from a high pressure (approximately 15 to 16 MPa, or 2200 to 2400 psi) cylinder equipped with a two-stage pressure regulating valve. The pressure of this high purity gas (most often 99.995 percent purity or better) is usually regulated down to between 0.4 and 0.7 MPa (that is, 60 and 100 psi). A set of traps to remove trace quantities of water and oxy-

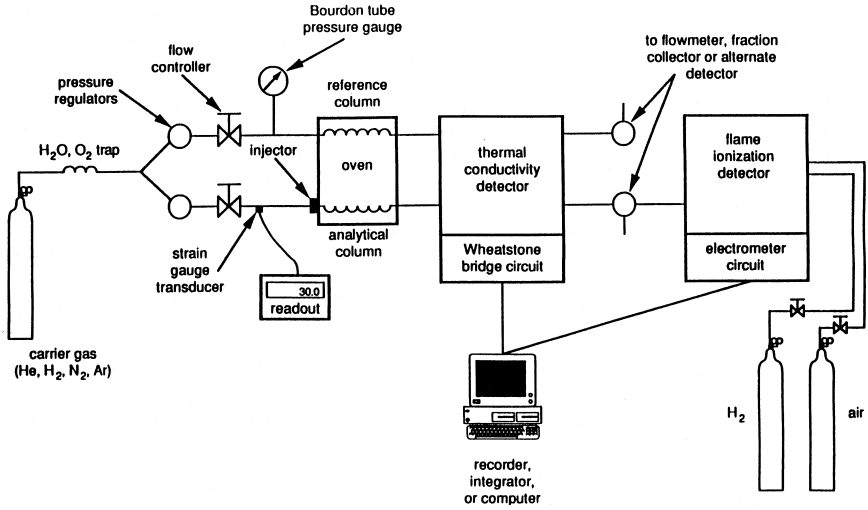

Figure 2. A schematic diagram showing the essential components of a typical gas chromatograph.

gen are installed after the regulator, which are themselves followed by particulate filters. Trace water is effectively removed with a short length of tube filled with 5A molecular sieve, which is a synthetic zeolite (calcium alumino silicate). Commercial traps are available which contain redox resins to remove oxygen. These traps can also remove traces of carbon dioxide and carbon monoxide. The filters which follow the traps are usually sintered metal fitted disks having a 3 μm pore size.

The carrier gas stream is usually split at this point because many common detectors require two streams, one for the sample and one with pure carrier as a reference for property comparison. We will discuss the more common detectors in detail later on. After the division of flow, the carrier gas is passed through another stage of regulation. This is done using precision pressure controllers followed by needle valves (flow controllers), or by using a set of mass flow controllers. For work requiring the highest accuracy, these valves are maintained at constant temperature in a separate oven. Pressure measurement is usually provided by precision gauges or sometimes strain gauge transducers having an electronic readout. The most advanced instruments are equipped with electronically-controlled pressure regulation and measurement. The flow rate of the carrier gas through the column is an important parameter which we have under our control. Flow rate is often measured at the column exit using a soap-film flowmeter, or *in situ* using a rotameter or anemometer. Flow rate can also be determined hydrodynamically with a system of equations that describe the flow of gas.

The sample line contains an injection device which introduces sample into the carrier stream while causing minimal flow disturbance or pressure pulsation downstream. Following the injector in the flow stream is the column oven area. This temperature-controlled region is usually a forced-air oven (only rarely is a liquid bath used, most often for physicochemical measurement work). The oven should be large enough to hold several chromatographic columns, but not so large that it has an inconveniently long thermal lag time. This optimal size allows the oven to respond quickly to temperature adjustments. The temperature should be stable to ±0.5°C for analytical work, and should ideally be programmable. Temperature programming allows the oven temperature to vary during an analysis to control solute retention, according to some preselected pattern. For example, we may wish to program the column oven temperature to begin at, say, 100°C, but to increase to 150°C at the rate of 2°C per minute.

Not all gas chromatography is done at elevated temperatures; occasionally one must resort to low temperatures (-100 to 0°C) to separate some stubborn mixtures, especially those involving gases and volatile organics. This can be done by pumping a cryogenic liquid (such as liquid nitrogen) into the oven, or by permanently mounting a Ranque-Hilsch vortex tube on the oven. A vortex tube is a unique refrigeration device which can produce temperatures as low as -40°C simply using a source of compressed air.

Following the column oven are the detection devices. The generic gas chromatograph presented in the figure has two detectors: a thermal conductivity detector and a flame ionization detector, the responses of which may be logged on a computer or on an electronic recorder/integrator. Most modern gas chromatographs are equipped with multiple detectors, in order to make the instrument more versatile. We will discuss all of the more common detectors in detail later, including some of the more useful optimization strategies.

Sample Introduction

Chromatographic Syringes

A major consideration in the design of effective GC analyses is the method used to introduce sample into the carrier stream. This involves the appropriate choice of chromatographic injector, and the optimal operation of the device. If this initial step is not handled properly, the outcome can be excessive experimental error (reaching order of magnitude levels), incorrectly assigned peaks, unexpected "ghost" peaks, or even no peaks at all. We actually have a two-step process for sample introduction, and we will discuss both steps separately. The first step is to get the sample into the appropriate injector, and the second is to properly use that injector to apply the sample to the column.

The delivery of liquid samples to the injector is conveniently performed using a graduated glass-barrel syringe that usually has a total capacity of 5–10 μL. When packed columns are used, injection volumes may be as high as 5 μL, while the lower capacity of open tubular columns dictates volumes of between 0.5 and 2 μL. For the handling of volatile liquids and solvents, it is possible to cool the syringe to −40°C using a vortex tube, which supplies cold air to a glass jacket surrounding the syringe. This approach can also aid in the analysis of thermally sensitive mixtures. There are a number of pitfalls to be aware of concerning the use of chromatographic syringes. The influence of the needle volume (which is typically 0.8 μL) on sample size must be considered. It is therefore desirable to "bracket" the sample solution between two plugs of air or pure solvent in the syringe in order to achieve the best reproducibility. Some solutes can be adsorbed on the ground glass parts of the interior of the syringe and thereby lost from the sample. In addition, catalysis by this glass surface is not unknown. Another difficulty, called sample discrimination, occurs with all heated injectors such as flash vaporizers. This refers to the selective evaporation of the more volatile solutes from a mixture. Discrimination will also occur within a syringe, and especially within the syringe needle. This will be discussed in more detail in the next section. We will also postpone for separate discussion the use of automatic samplers for sample delivery to the injector.

The application of solids directly into an injector presents many problems. Fortunately, many solid samples can be dissolved in a suitable solvent and handled the same way as a liquid sample. When this is impossible, the best choice is usually an encapsulation method. The sample is placed in a capsule which can be opened inside of the injector. Capsules made of Wood's metal (which is melted at 60.5°C), glass (which is mechanically crushed), or gold (which is pierced by a hollow "thorn") have been used with varying degrees of success. Another technique that has been used involves a syringe that contains a fine wire projecting from the plunger through the syringe needle, extending approximately 2 mm beyond the end of the needle. The solid is deposited on this wire (usually from a melt or an appropriate solvent), and the wire is retracted into the syringe needle. When the syringe is inserted into a heated injector, the wire is pushed through the needle, until the sample is in the carrier stream.

The transfer of a gaseous sample to the chromatographic injector must involve the consideration of temperature and pressure since these variables have a profound effect on the density (and therefore the number of moles) of a gas. The simplest and least expensive method to transfer a gas to the injector is the use of a gas-tight syringe having a volume between 0.001 and 50 mL. If the ambient room temperature is constant to within ± 3 C, a reproducibility of between 2 and 5 percent is possible.

Gas Sampling Valves

A better method of gas sampling involves the use of a thermostatted sampling valve with a fixed volume sample loop as the injector. The valve consists of a stainless-steel body which accommodates the necessary transfer lines, a loop of tubing to contain the sample, and a channeled rotor (usually made from graphite-filled polyimide) which changes the flow path. In the fill position, the gas to be analyzed is allowed to flow into the sample loop. Enough sample gas should be allowed to flow through the valve to ensure that any residual carrier gas is swept from the loop and rotor. While residual carrier gas will not show up on the chromatogram, its presence will impair quantitative performance since carrier molecules will displace molecules of sample. This will cause problems in achieving good reproducibility among a set of replicate analyses. To assist in carrier removal, some operators plumb a vacuum line into the vent manifold.

In the injecting position, the sample gas is swept into the column by the carrier gas. The valve is usually maintained at an elevated temperature in a separate oven. Temperatures of 150 to 250°C are normally employed to prevent the adsorption of sample gas on the surface of the loop or rotor. The rotors are usually made from a thermally stable polyimide material which retains mechanical integrity over many cycles, and which in fact provides a better seal at higher tem-

peratures. The use of a sampling valve is the most accurate way to introduce gaseous or very volatile samples into the chromatograph. The total volume of sample injected is very reproducible since the volume of the loop and rotor do not change from run to run. The injection process is very reproducible since the valves are usually actuated using an electronically controlled solenoid or a pneumatic cylinder. This provides for very rapid injection, which minimizes the pressure pulse caused by the momentary disruption of the carrier gas flow. The use of helium as the pneumatic actuation gas usually provides the fastest switching, especially if the pneumatic actuator is equipped with high-flow pilot valves.

Flash Vaporizer Injectors

The most common type of chromatographic injector used with all types of packed columns is the flash vaporization injector, shown schematically in Figure 3a. The injector consists of a heated cylinder containing a concentrically positioned liner, usually made of deactivated (silanized) glass or quartz. The internal volume of the liner must be at least as large as that of the vaporized sample to prevent sample flashback into carrier gas transfer lines. At the top of the inlet is a self-sealing elastomer septum, through which the syringe needle penetrates to introduce the sample.

Some comments on septa are in order, since they are required for most of the injection ports that are used in gas chromatography. Septa are available in a variety of sizes, and are usually selected on the basis of thermal stability and inertness toward samples. The septa used for lower temperature applications are soft silicone rubbers, and reseal very well after being punctured by a syringe needle. The septa used for higher temperature applications are harder, and cannot be used for as many injections as the softer septa. High temperature silicones and layered septa allow for operation at temperatures up to 350°C. Septa are available in prepunctured varieties, which provide better resealing and a longer useful life (approximately 200–300 injections).

The carrier gas inlet is usually at the base of the injector, and the gas is warmed as it travels to the top, thus providing a preheated flow stream. Flash vaporizers are relatively high volume devices, sometimes having internal volumes as high as several milliliters. They are usually maintained at a high temperature (upwards of 200°C) to ensure complete vaporization of the sample. This can be a disadvantage for a number of reasons. Septum bleed, responsible for unassignable "ghost" peaks, is always more severe at higher temperatures. This is aggravated by the large volume of the injector, much of which may be poorly swept by the carrier gas. In addition, flash vaporizers cannot be used with heat sensitive samples. They all suffer from a problem called "sample discrimination," which is especially pronounced when the sample consists of a complex mixture of compo-

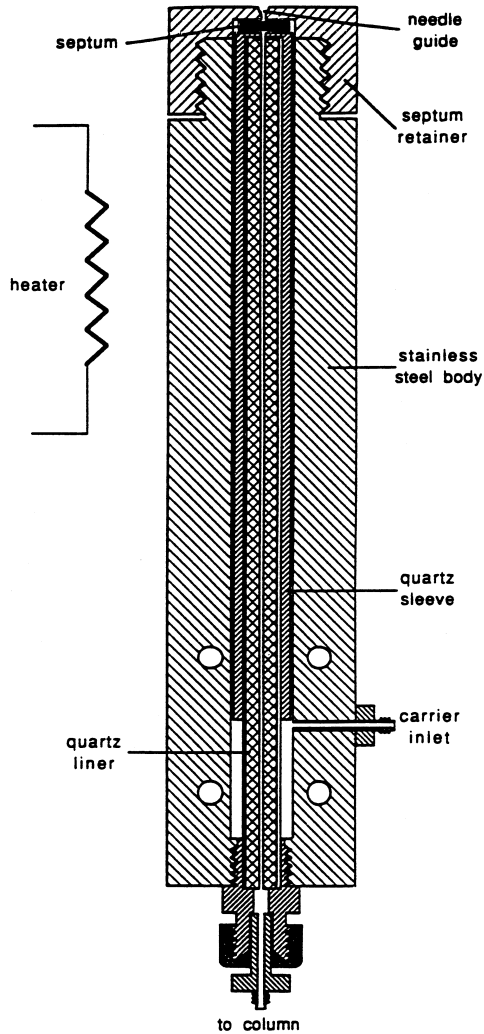

Figure 3a. A typical flash vaporization injector for packed and large bore open tubular columns.

nents with widely varying boiling points. The more volatile components of the sample will be more easily vaporized; therefore the sample delivered to the column may be of different composition than the one applied by the syringe. This makes the flash vaporizer a marginal choice for the quantitative analysis of complex mixtures. On the positive side, flash vaporizers are low-cost devices and are easy to maintain. Periodic cleaning of the inlet liner with solvent in an ultrasonic

cleaner will minimize contamination problems. A single unit can be used with packed columns made of different materials and of different diameters.

Splitter Injector

Injection of samples into open tubular columns is a somewhat more demanding process than injection onto packed columns. As we discussed in the previous section, the sample capacity of open tubular columns is much lower than that of packed columns. This requires much smaller injector volume, since sample volumes will rarely be larger than 2 μL, and usually closer to 0.5 μL. In general, the more efficient the column being used, the smaller must be the internal volume of the injector.

While flash vaporizers have been used for injection into open tubular columns, such devices are relatively rare. To handle the low sample capacity, the splitter injector (shown schematically in Figure 3b) was developed. This injector consists of a heated liner (like the flash vaporizer, usually made from deactivated or silanized quartz) where the sample is introduced by syringe and vaporized. A small plug of silanized glass wool, silanized glass beads or chromatographic support is sometimes located downstream from this area in the split liner, to facilitate mixing of the vaporized sample with the carrier, and to trap any particulates that may be inadvertently injected with the sample. Alternatively, baffles or inverted cups are sometimes used. The flow of the mixture is then split into two streams,

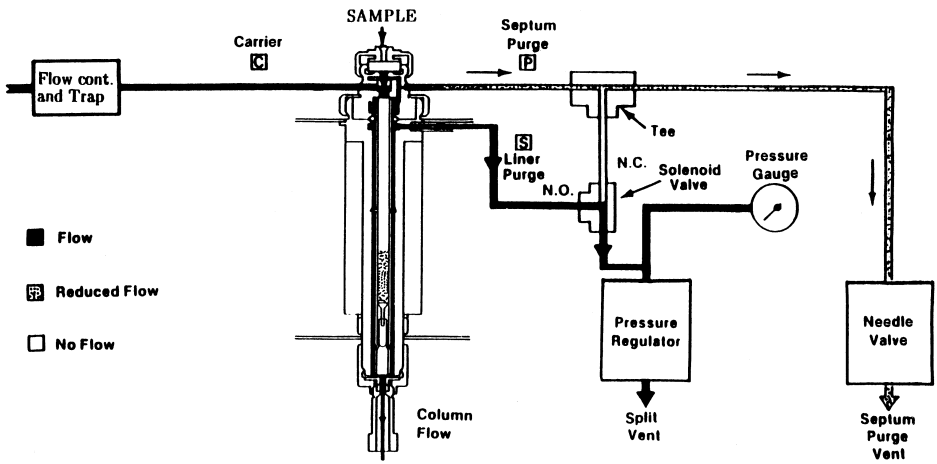

Figure 3b. A typical split injector for open tubular columns. (courtesy of Hewlett-Packard Corp*).

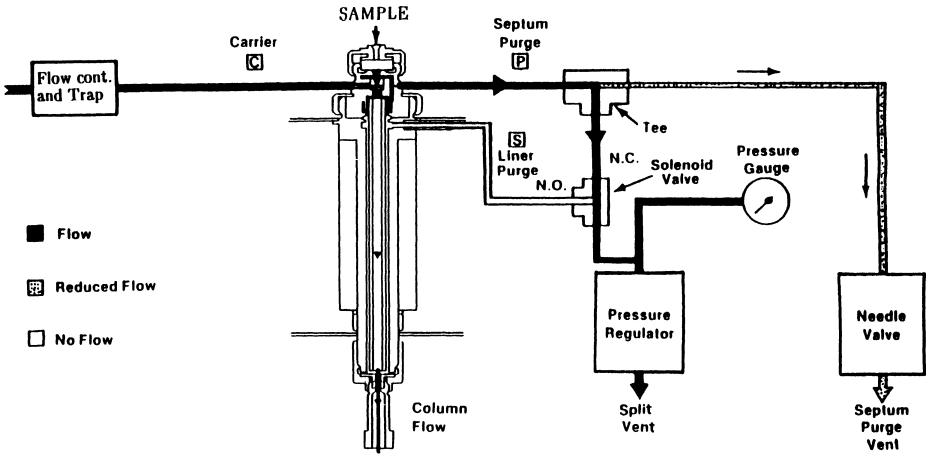

Figure 3c. A split/splitless injector for open tubular columns. (courtesy of Hewlett-Packard Corp*).

one entering the capillary column and the other vented through a back pressure regulator. Typical split ratios (ratio of vented flow/column flow) are between 10:1 and 1000:1, controllable by the back pressure regulator. This method of decreasing the column flow is done without affecting the column pressure, and ensures that column overload does not occur. Sample transfer to the column is fast, resulting in little band broadening due to the injector volume. To minimize the potential for ghost peak formation caused by the septum, most splitter injectors are equipped with a septum purge line (operated at approximately 3 mL/min) which carries off the slipstream from the underside of the septum.

Splitter injectors are more complex and costly than the flash vaporizers used for packed columns. All splitters will cause sample discrimination to some extent, although the problem can be minimized more easily than with the flash vaporizer. Inlet discrimination is more pronounced at higher split ratios. The elevated temperatures make the device unsuitable for use with thermally labile samples, although decomposition for these compounds is lower at higher split ratios. Obtaining reproducible data with a splitter can be problematical, since the split ratio which is set by the operator before a run is not the ratio which is obtained when sample appears at the splitter. The actual split ratio which results is a complex function of sample volume and boiling point range, solvent characteristics, injector temperature, syringe technique, and the magnitude of the pressure pulse produced upon vaporization. Many of these variables are hardly reproducible or predictable. For the best results, one must reproduce the injection process precisely from run to run, especially in terms of liquid volume injected and the time taken

for injection. It is also advisable, where possible, to use internal standardization as the calibration method.

Splitless Injector

An alternative injector for open tubular columns is the splitless injector (Figure 3c), which is similar enough in external construction to the splitter that a single injection port can be modified to provide both split and splitless modes. As with the splitter, small (0.5 to 1.0 μL) volumes of liquid are injected, making it attractive for trace analysis. This injector uses a deactivated straight glass or quartz liner in place of the split liner, and a solenoid valve diverts the purge flow during injection so all carrier and sample present in the liner is deposited into the column. The injection process is therefore much slower (the rapid vaporization step required for the other injectors is not needed) than that used in split mode, and is usually done at lower temperatures. This makes the splitless injector attractive for the injection of thermally labile samples, those samples with components which elute near the tail of the solvent front, and samples that are very dilute. The lower temperature is used to refocus the sample volume, which is then deposited as a whole into the column. An alternative to this thermal refocusing is to make use of the so-called "solvent effect" in which the solvent plug is used as a secondary stationary phase to retard and reform the solute components at the head of the column.

The splitless injector, while relatively simple in construction and easy to maintain, can be difficult to operate and optimize. The use of cool refocusing or the solvent effect usually requires careful adjustment of the chromatographic pneumatics, a trial-and-error process which can take longer than the analysis itself. The sample size must be reproducible within experimental error for the most precise quantitative work. Septum bleed can be a serious problem even with lower operating temperatures, since any septum impurities present in the liner during the splitless phase of the injection will be deposited on the column. When the injector is operated in split mode, the septum purge line will minimize the column uptake of septum generated impurities, as is the case with the splitter injector. In general, higher column flow rates are used with splitless injection than are used with split injection, to minimize the residence time of the sample in the injector.

Cool On-Column Injector

An injector which can be adapted for both packed columns and larger diameter open tubular columns is the cool on-column injector. With this device, the sample is syringe-deposited directly into the packing or inside the capillary column. An on-column injector is inherently simple, and is often found as a home-

made device modified from a flash vaporizer. Injection is done quickly with the temperature maintained at or below the boiling point of the solvent. Sample volumes are usually 2 μL or less. This method of injection is well suited to trace analysis, or work involving dilute solutions, since all of the sample is deposited on the column. The effects of catalytic or thermal degradation of the sample are minimal, as is sample discrimination. It is generally the most precise injection method, and is relatively easy to implement and optimize, especially with packed columns.

The application of on-column injection to the smaller diameter capillary columns (and capillary columns with large phase ratios) can be impossible, however. Another disadvantage is that involatile material can be deposited at the head of the column, accumulating over time. This is sometimes remedied by installing a guard column, usually consisting of a 1 m long section of uncoated fused silica tubing placed before the analytical column. Also, this injector does not lend itself well to automation. The sample volume that can be applied with this injector is smaller than with other injectors. Sample peaks that elute immediately before the solvent peak cannot be focused and are thus difficult to analyze using this injection method.

An accessory that is sometimes used with cool on-column injectors is a secondary cooling compartment immediately following the injector. This compartment uses a gas purge line to cool the first 30 to 100 cm of an open tubular column. After injection, the cooling gas is turned off, and the column heats to the initial temperature of the oven. This accessory allows the use of higher than normal starting temperatures in the column oven.

Programmed Temperature Vaporizer Inlets

The programmed temperature vaporizer inlet is an attempt to combine the useful features of the split, splitless and cool on- column inlets. The sample is injected into a cool inlet liner that is made of quartz, and is usually packed with silanized glass wool. If the sample is labile and might be decomposed by the glass wool, a fluted or baffled liner is used. The temperature is then programmed to a value that vaporizes the sample, with optional concurrent split venting at a user-selected time. This injector eliminates syringe discrimination and minimizes inlet discrimination. Relatively large injection volumes may be applied, and solvent removal can be accomplished by the splitter.

Automatic Samplers

A very useful accessory that can be applied to almost any injector is the automatic sampler. This device contains a tray capable of holding approximately

100 samples in small, special crimp or screw cap vials that are equipped with septum closures. A small robot arm selects a vial from the tray following a programmed set of instructions, and places it in a smaller sampling tray or turret. Here, a chromatographic syringe mounted on a carriage samples the contents of the vial and injects it into the injector. The carriage assembly is purged or ventilated to remove any fugitive vapors that might escape from the vials. After injection, the syringe is rinsed a specified number of times with one or more solvents. Injection by automatic sampler has many advantages over manual injection, beyond the obvious savings in operator time. Injections can be performed much more reproducibly with an automatic sampler than by injecting manually. The syringe needle is held precisely, and pierces the septum in the same location for each injection. This increases septum life by up to 50 percent. It is possible to equip the automatic sampler with a bar code reader that will automatically identify and log each sample vial.

Electronic Pressure Control and Pressure Programming

As a final note to the treatment of injection devices, a brief discussion on the topic of electronic pressure control and programming is in order. The concept of temperature programming of the chromatographic column is, of course, central to the application of gas chromatography. On the other hand, column head pressure programming, introduced in the early 1960's, was abandoned as being too complex for too little benefit. The development of electronic pressure control using a microprocessor or computer caused pressure programming to be reintroduced in the 1990's.

There are several reasons that one might want to change the column head pressure during a chromatographic analysis. Temperature programming from relatively low to relatively high column temperatures will cause a corresponding increase in the carrier gas viscosity, and thus a decrease in the flow rate. It is possible to make a column operate in an essentially constant flow mode by programming the column head pressure to compensate (or at least partially offset) this decrease in flow rate. Another application of pressure programming is the enhanced elution of very high boiling compounds at the end of an analysis. In these situations, the column temperature may approach the thermal limit of the stationary phase before all of the heavy materials are out of the column. The only alternatives are to wait an excessively long time, or to increase the column temperature beyond its design limit. If the pressure is instead increased, it is often possible to elute the heavy components without the application of excessively high column temperatures. The pressure program only applies the higher pressure after all of the earlier peaks have eluted, thus avoiding the degradation of the chromatographic separation of early eluting compounds. Another technique is the applica-

tion of higher pressure upon injection (early in the run) to quickly elute a solvent front, followed by a decrease to the optimal column head pressure for the remainder of the analysis.

Automatic Headspace Analyzers

Another accessory that is used with chromatographic injectors are automatic headspace analyzers. These are devices that sample the vapor space that is above a liquid or solid sample, usually contained in an automatic sampler vial. This method has important applications in environmental analyses. Headspace analysis is also very useful if the sample matrix will potentially interfere with the analysis, because the technique is very effective at matrix minimization.

It is important to understand that when the vapor of a sample is analyzed, the sample taken is representative of the vapor composition but not necessarily of the condensed phase composition. In fact, these compositions may be very different. It is possible to approximately relate the concentrations of species in the vapor phase to those in the liquid phase by applying some fundamental principles of solution thermodynamics to the chromatographic results.

For our purposes, the chromatographic detector signal output can be related to the partial pressure of a component:

$$\mathbf{ACi} = \mathbf{ciP_i'}, \tag{6}$$

where **AC** is the total area count of the peak of species **i** integrated from the detector, $\mathbf{P_i'}$ is the partial pressure of **i**, and $\mathbf{c_i}$ is a material dependent proportionality constant. We now apply Henry's law, which relates the partial pressure of an analyte above a solution to its liquid mole fraction $\mathbf{x_i}$, its saturated vapor pressure, $\mathbf{P_i^o}$, and its activity coefficient, γ_i:

$$\mathbf{P_i'} = \mathbf{x_i}\gamma_i\mathbf{P_i^o}. \tag{7}$$

We can combine these two equations to obtain an expression for the mole fraction $\mathbf{x_i}$ in the liquid:

$$\mathbf{x_i} = \mathbf{AC}/(\mathbf{c_i}\gamma_i\mathbf{P_i^o}). \tag{8}$$

The material dependent term $\mathbf{c_i}$ can be determined for a solute **i** by independently measuring the mole fraction $\mathbf{x_i}$ by sampling the liquid. Once $\mathbf{c_i}$ is determined, it is possible to use equation (8) to approximate $\mathbf{x_i}$ in the liquid phase by vapor measurements alone.

The experimental arrangement required for automated headspace analysis is usually very simple, consisting of little more than a thermostatted vessel (capable of withstanding moderate pressures) to accommodate the two-phase sample, and a provision to withdraw an aliquot of vapor. The sensitivity can often be controlled

by careful adjustment of the temperature of the sample container. Sometimes the sensitivity can be improved by "salting out", performed by the addition of a non-electrolyte such as water to the sample. The principal disadvantage of headspace analysis is that careful and extensive calibration is usually required. In addition, one must be careful to avoid adsorption of the vapor sample in the vessel or on vessel closures, and one must ensure that the two phase system has achieved equilibrium before withdrawing a sample.

Detectors for Chromatography

The function of the chromatographic detector is to provide a recordable, reproducible, quantitative response to the presence of separated components as they emerge from the column exit. We would like the response of the detector to produce a signal that is proportional to the quantity of each component, and be linear over the concentration range of interest. The nature of the sample, the required level of sensitivity and the mode of chromatography we wish to employ will play major roles in our choice of detector.

Thermal Conductivity Detector

The first detection device we will consider is the thermal conductivity detector (TCD). This detector measures the change in a bulk transport property of the gas stream, and is therefore universal in response. This bulk transport property is actually a heat transfer coefficient that is a composite of thermal conductivity and heat capacity of the gas passing through the detector. There are two basic TCD varieties available, hot wire based detector and thermistor based detectors.

The most commonly used TCD is the hot wire version or katharometer, is shown schematically in Figure 4, along with the relevant Wheatstone bridge circuit. The carrier gas is passed over short sections of coiled wire made from gold- or rubidium-sheathed tungsten. Two cell compartments contain wires bathed by the sample stream, while two additional compartments accept the flow from a reference column. The wires in these four compartments form the legs of the Wheatstone bridge circuit, with the chromatographic integrator or recorder in place of the electrometer. The wires are electronically heated to between 300 and 450°C, but the continuous stream of carrier serves to remove much of the heat from the cell. High thermal conductivity gases such as hydrogen and helium are especially efficient heat removers. When sample elutes from the column and enters the sample part of the detector cell, there will be a differential change in the rate at which heat is removed from the two sets of hot wires. This is due to the different (usually lower) heat transfer coefficient of the sample rel-

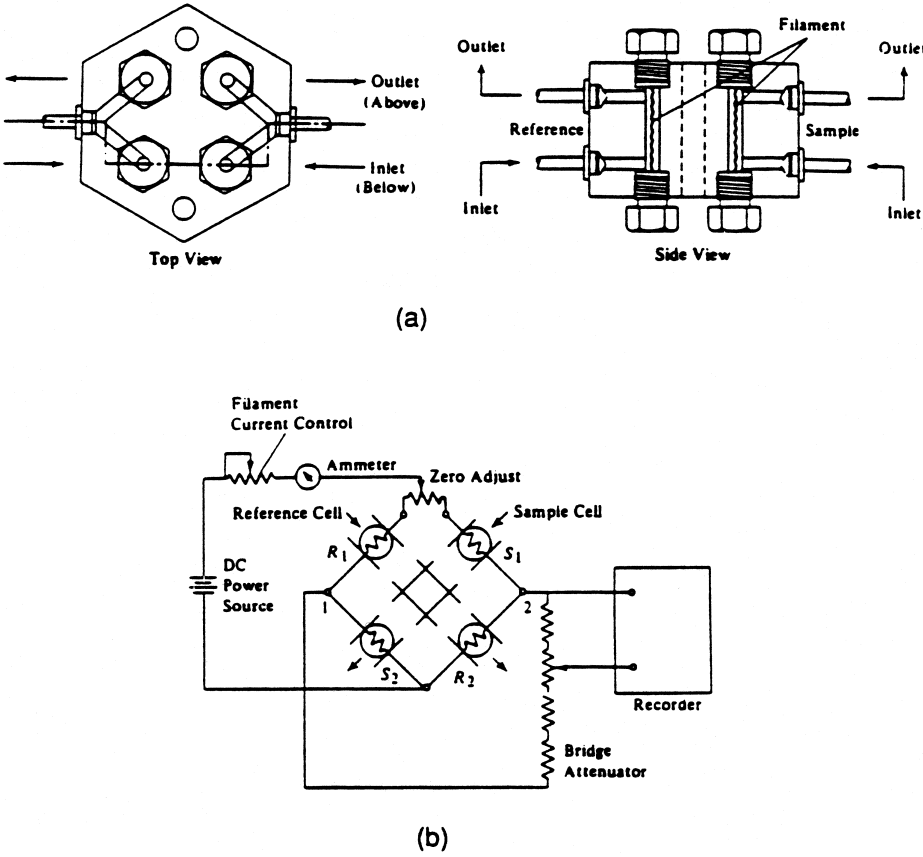

Figure 4. A hot wire thermal conductivity cell (a) and a typical Wheatstone bridge circuit (b) (courtesy of the Gow Mac Instrument Company*).

ative to that of the carrier. This leads to an increase in temperature of the wires in the sample stream, and consequently an increase in their electrical resistance. It is this electronic measurement of resistance which provides the output. Alternatively, the wires can be maintained at a constant temperature (regardless of the presence or absence of sample) using a feedback circuit. The response signal is then derived from the measurement of the marginal change in current applied to the wires that is needed to maintain the isothermal condition of the wires. This eliminates the temperature gradient at the wire support headers that occurs when the wire temperature is allowed to change, thus decreasing the time constant of the detector.

The best response from the hot wire cell is obtained when the temperature difference between the wires and the gas stream is maximized. For this reason, it is best to maintain the detector block at a temperature just hot enough to prevent sample condensation, since higher temperatures will result in a decrease in sensitivity.

A hot wire TCD is prone to oxidation damage, and therefore must not be operated without the constant flow of carrier gas. The sheathed tungsten wires are susceptible to attack by sulfur-containing compounds, and extensive use with halogenated compounds will require special nickel alloy wires. In addition, the volume of gas required for the TCD is relatively high, even for the newer microscale cells. This usually limits the usefulness of the hot wire TCD for applications with packed columns only, where flow rates on the order of 20 to 40 mL/min are possible. Large bore open tubular columns can be used with the TCD if appropriate make up gas is provided.

The other type of TCD is one based on thermistor elements instead of hot wires. The thermistors are semiconductors in which the resistance decreases sharply with increasing temperature. This type of TCD has a somewhat higher sensitivity, but at a cost of a decreased operating temperature range. The thermistors will fail at temperatures much above 150°C; thus the detector cannot be used with high boiling point solutes. The thermistor TCD is, however, very useful for work on gaseous samples. The thermistor elements are much less prone to oxidative damage than the hot wires, but they tend to be sensitive to reducing agents. This usually precludes the use of hydrogen as the carrier gas, or the analysis of samples that contain large concentrations of hydrogen. Since the thermistors are small, it is often possible to build detectors of much lower internal volume than the hot wire based cells. This allows the use of thermistor detectors with larger bore capillary columns.

When carrier gases other than hydrogen or helium are used with a TCD, there is the possibility of obtaining negative peaks on the chromatogram. This is because many materials have higher thermal conductivities than the other common carrier gases such as nitrogen and argon. This is a problem since integrators and chromatographic computer software usually cannot process negative peaks. The TCD is a flow sensitive detector which cannot be used easily for analyses that require the column temperature to be programmed. The temperature-dependent viscosity of the carrier gas will change the flow rate to the detector and thereby cause severe baseline drift, even if mass flow controllers are used on the carrier pneumatics. Electronic pressure programming can be used to minimize this problem, however.

While the sensitivity of the thermal conductivity detector is somewhat low as compared to other detectors, it does offer some unique advantages which make it very popular. Since the detector is universal, the TCD will respond to water, carbon dioxide, carbon monoxide, and permanent gases. It is low in cost, easy to operate, and requires very little maintenance to provide good performance.

Flame Ionization Detector

The flame ionization detector (FID) is as popular for routine analysis as the TCD. In fact, it is rare to find a gas chromatograph which is not equipped with both of these detectors. It is relatively simple in construction, and is easy to operate and maintain. The FID may be considered universal in response for organic compounds. A typical flame ionization detector is shown schematically in Figure 5. A hydrogen-air flame is maintained above the tube which delivers carrier and sample from the column. The flame itself, in the absence of an organic sample species, contains few ions and has a high electrical resistance. When a sample containing carbon-hydrogen bonds leaves the column and enters the flame it is burned, and a cascade of ions is produced. This increases the electrical conductivity of the flame by many orders of magnitude. A collector electrode above the flame is maintained at a potential of 180 to 300 V above that of the sample delivery tube. This system of electrodes, in combination with a sensitive electrometer, measures the flame conductivity and produces the response signal.

The FID is one of the most sensitive and fast responding detectors available. It can easily sense the presence of 10^{-11} g of hydrocarbon, and the response will

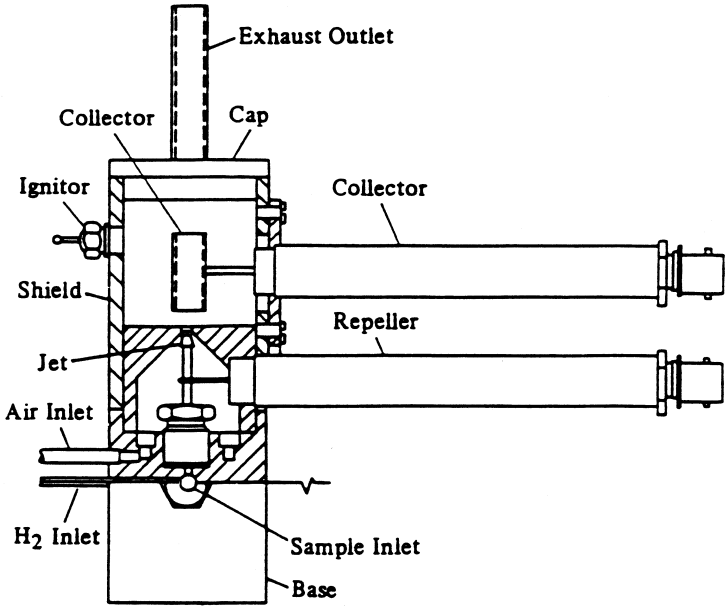

Figure 5. A schematic diagram of a flame ionization detector (courtesy of the Gow Mac Instrument Co. *).

be linear over a wide concentration range. The high sensitivity makes the FID very suitable for use with capillary columns, where very small amounts of material are analyzed. The device has high baseline stability and shows little or no sensitivity to changes in the carrier gas flow rate. It can therefore be used in temperature programmed applications without the viscosity-induced disruptions which plague the TCD. The dead volume of the detector is very small, since the sample is released directly into the flame.

Since any heated metal object will be a source of thermal electrons, the FID performance is optimized at lower detector temperatures. The body of the detector is usually heated just enough to prevent sample or water condensation. Water is a product of combustion of the hydrogen-air flame, and must not be allowed to drip back into the base of the detector, since it will cause temperature fluctuations and may even extinguish the flame.

The FID will not show a response to water, carbon dioxide, permanent gases and most inorganic species. This is a drawback, although very often the chromatogram is "cleaner" due to the absence of these peaks. When the FID is used with samples dissolved in chlorinated solvents, soot formation in the flame can be a problem. Soot can also form from a low level bleed of silicone liquid phases, resulting in an insulating deposit of silica in the detector. The response of the FID to species containing heteroatoms (organic nitrogen and phosphorus compounds, for example) can be unpredictable. It is sometimes difficult to keep the flame lit when eluting these materials. For this reason, most detectors can be operated with the igniter energized and continuously glowing. The potential of thermal electron interference makes this a last resort, however.

Several important operational disadvantages of the FID must be considered. Since a hydrogen flame is used in the detector, there is a slight but finite explosion hazard. An FID would not generally be usable in an explosion-proof laboratory (as defined in Class A, Group b of the National Electrical Code in the United States). The detector is destructive to the sample and cannot usually be followed downstream by another detector. The major exception to this is the sulfur chemiluminescence detector, which analyzes the FID flue gas stream for sulfur species. It is not usually easy to determine the carrier gas flow rate at the exit of an FID; one is often forced to disconnect the column exit for this measurement.

Thermionic Detector

A modification of the FID is the thermionic detector, a device which is specific for nitrogen or phosphorus compounds. For this reason, it is also called the nitrogen-phosphorus detector (NPD). It is similar in construction to the FID, except that a small pellet of alkali metal salt is held in the vicinity of the flame. The bead is sometimes electrically heated (under separate control from the detector

block) to provide flexibility in analyzing very dilute solutions. The salts of potassium, rubidium, cesium and sodium have been used as the bead material. The detector is very sensitive for certain compounds, approaching the level of the electron capture detector (see the following section). The use of this detector is confined mainly to the analysis of pesticides. Not all nitrogen or phosphorous compounds give good detector responses. It appears that carbon-nitrogen or carbon-phosphorous bonds are needed for good signal to noise ratios.

This detector is very sensitive to changes in gas flow rates, and it is also very sensitive to sources of contamination such as sampling glassware that has been cleaned with phosphates. Related to this, phosphate-based leak detector solutions, glass wool and columns that have been washed in phosphoric acid, polyimide-coated open tubular columns, or cyano-modified stationary phases should be avoided when using this detector. The passage of a large solvent front through this detector can cause quenching (the bead cools to a temperature at which ion production is too low). This can be remedied by an increase in the power applied to the bead heater, or by increasing the air flow rate.

Electron Capture Detector

A simplified schematic diagram of an electron capture detector is shown in Figure 6. There has been surprisingly little change in the design of these devices ever since the first viable unit was made in 1958. Naturally, significant advances have been made in the sensing and control electronics since that time, however. A radioactive source ionizes the carrier gas as it leaves the column. The carrier used must be either pure nitrogen or argon that contains between 5 and 10 percent methane, since these gases are the most easily ionized. The carrier gas must be ultra-pure, because any contaminants will interfere with optimum operation. The radioactive source used most often today is a ^{63}Ni foil, although some older models use adsorbed tritium, ^{3}H. The ionization of the carrier gas caused by the β-radiation produces a high background level of current measured across the anode and cathode. A sample eluting from the column enters this region, and will participate in ionization processes. If the sample contains atoms that will absorb electrons (such as halogens, nitrogen or organometallic moieties), the background ion current will drop sharply. It is this dramatic decrease in the current which provides the high level of response from the ECD.

The response sensitivity of the ECD is strongly dependent on the sample itself, and increases with the electronegativity of the functional groups. Some "ideal" cases (for example, the analysis of sulfur hexafluoride) have been reported in which an ECD provided a response to 10^{-14} g/s of sample. The response to an aliphatic hydrocarbon will be very slight, however. The response will also be related to the operating temperature, which is usually maintained at a level just high

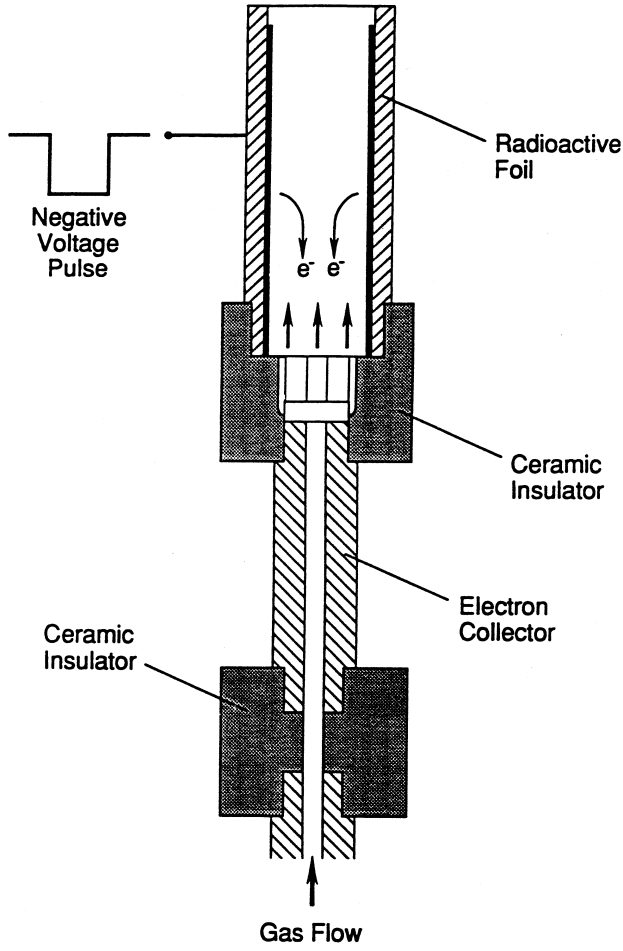

Figure 6. A schematic diagram of an electron capture detector (courtesy of The Varian Corp. *).

enough to prevent sample condensation. The presence of trace quantities of interfering species (such as oxygen, which is an electron absorber) will also affect sensitivity. Even the careful control of these factors does not guarantee reproducible results between separate ECD's, however. It is very important to use non-bleeding stationary phases, such as the cross-linked methyl silicones. Septa used in the injectors should be heat-conditioned to minimize bleed, and the pneumatic lines should be baked out to drive off adsorbed impurities.

It can be difficult and time consuming to optimize the performance of the electron capture detector. Even in the ideal situation, disadvantages persist. The

linearity of the detector over sample concentration ranges is comparatively low, being two to four orders of magnitude. One can compare this with the eight-decade linearity of the flame ionization detector. This is not a fatal flaw, however; the main consequence of the short linear range is the need for a more careful and extensive calibration.

Mass Selective Detector

The routine use of a mass spectrometer as a detector for gas chromatography began the trend toward what have come to be called hyphenated techniques (GC-MS). This combination of two major instrumental analysis methods provides one of the most powerful analytical techniques available. This is because mass spectrometry is the single most useful tool for organic structure elucidation and compound identification.

It is difficult to consider the mass spectrometer (or mass selective detector, MSD, a term that will often be used interchangeably) in the same vein as the TCD or FID. The cost and complexity of the combination requires the consideration of the GC-MS instrument as a system unto itself. A schematic diagram of such a system is provided in Figure 7. Only a brief outline of the mass spectrometer will be given here, since this topic is covered elsewhere in this issue. The mass spectrometer consists of a vacuum chamber pumped to a level of 1.3×10^{-3} to 1.3×10^{-4} Pa (10^{-5} to 10^{-6} torr). This can be accomplished using a turbomolecular pump or a diffusion pump, both of which must be backed by a mechanical rough pump which produces a vacuum of at least 0.13 Pa (10^{-3} Torr).

Inside the vacuum chamber are the ion source, the mass filter and the electron multiplier detector. The ion source usually consists of an "electron gun" filament which ionizes the sample eluting from the chromatograph. Actually, only a small fraction of the sample is ionized. Most of the sample leaving the column will be pumped away without ever encountering an electron from the source. Some instruments allow the use of chemical ionization reagent gases as an alternative to electron impact ionization. The ion source also contains a series of electronic lenses which accelerate and focus the positive ions which are formed by the electrodes. The beam of ions is passed to the mass filter, which is most often of the quadrupolar type. The electron multiplier amplifies the electron current signal, and a computer system is required to process this signal into the familiar mass histogram format. Usually, the output consists of a total ion chromatogram, which is displayed as peaks as a function of time, just as the output from any GC detector.

The advantage of the GC-MS system is that one can choose any peak on the chromatogram, and at the punch of a button, have a mass spectrum of that peak. The computer allows manipulation of spectra, such as the addition, subtraction, and averaging of spectra, and the searching of measured spectra against libraries.

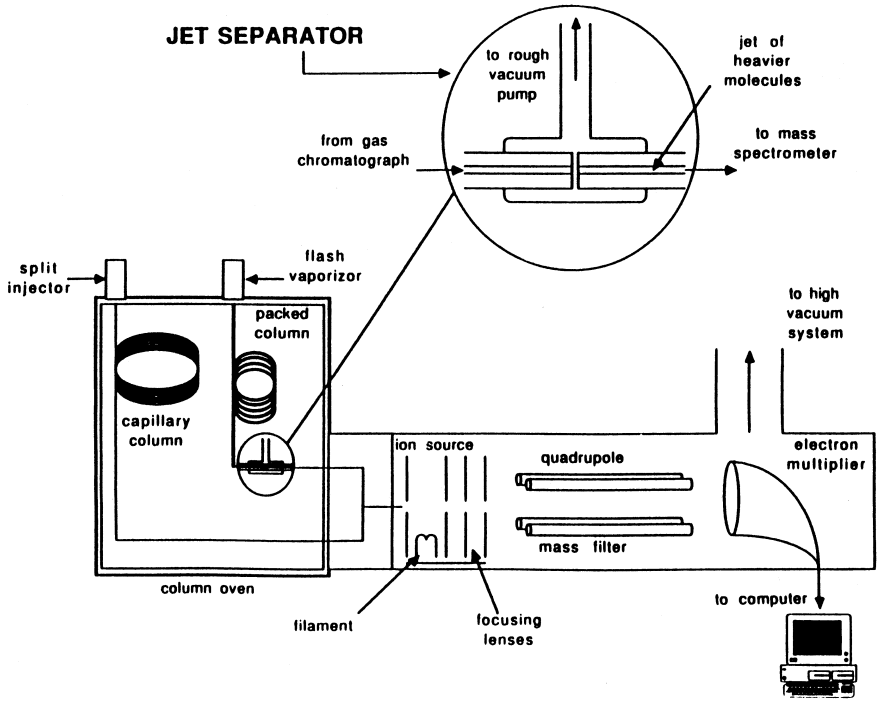

Figure 7. A schematic diagram of a gas chromatograph interfaced with a mass spectrometer.

This is of great value in the qualitative identification of eluted samples. These libraries can be built up by the user or purchased from the manufacturer and other sources. The commercial libraries are usually based on the 110,000 compound library (containing more than 130,000 spectra) developed jointly by the U.S. National Institute of Standards and Technology, the U.S. Environmental Protection Agency (EPA), and the Mass Spectrometry Data Center of the Royal Society of Chemistry (England).

The mass selective detector can be used in one of two modes: mass scanning mode or single ion monitoring mode. When operating in scan mode, the MSD will record complete mass spectra over the molecular mass range selected by the operator. It is usual to keep the molecular mass range which is scanned as small as possible without sacrificing needed information, since a finite time is require to sweep the spectrum. This means that if a large relative molecular mass range is scanned, there will be relatively fewer spectra obtained per second than if a smaller range is scanned. Single ion monitoring is used primarily for high sensitivity quantitative analysis. Instead of scanning over hundreds of molecular mass

units, one (or several) individual molecular mass values are selected for continuous intensity measurement. When the MSD is used in this fashion, the sensitivity approaches that of the electron capture detector.

The MSD is one of the most expensive detectors available for the gas chromatograph. It can easily cost three or four times more than the chromatograph itself. It is relatively complex and requires some degree of training in order to be used effectively. The interface between the chromatograph and the high vacuum of the MSD requires some discussion as well. The low mass flow rate of a capillary column can be accommodated directly by most MSD pumping systems, but packed columns usually require the use of a molecular jet separator or some other device to divert and vent the bulk of the carrier flow. A jet separator, shown on the inset of Figure 7 draws off most of the column flow in low vacuum. The solute molecules, which are usually much heavier than the carrier, remain roughly focused at the center of the jet and are drawn into the ion source of the MSD by the high vacuum. The use of a jet separator results in some degradation of performance of the overall GC-MSD system. The major manifestations of this are lower sensitivity and resolution. The only other option for the use of packed columns is to equip the MSD with a much larger capacity vacuum system.

Another consideration in the operation of a MSD is maintenance, which, relative to other GC detectors, is hardly routine. Pumping system service, source cleaning, filament replacement, and electron multiplier replacement must be done periodically. This is usually requires extreme care, ultra clean conditions, and a very steady hand.

Data Collection

As shown in Figure 2, the output from whatever detector is chosen is fed into a data collection system that can consist of a strip chart recorder, a digital electronic integrator, or a computer driven with special peak-processing software. A strip chart recorder is not usually used in analytical applications of GC, but is still quite useful in physicochemical work in which the main experimental parameter is the retention time or retention volume. For analytical work, the use of a dedicated electronic integrator is now standard. The purpose of the integrator is to measure the area under each chromatographic peak, since this quantity is most easily related to the quantity of sample. The relationship between the peak area and sample quantity or concentration is obtained by the calibration method. The analog output of the detector is converted to a digital signal by the integrator, and is internally manipulated as area slices in units of voltage. Most of the modern integrators allow calculation of concentration directly after the appropriate calibration method is chosen and the standard values are stored in the internal memory. Calculation of peak height and peak widths is also standard, thus making theoret-

ical plate height calculations a simple matter. Many integrators can provide macro programming, disk storage and various data display and presentation formats of chromatographic data as options.

Using appropriate software, a personal computer or work station may be used to process chromatographic data. The programs are quite sophisticated, and allow deconvolution and manipulation of very complex chromatograms. Data from different detectors can be processed and displayed in real time in separate windows on the computer screen. As was mentioned earlier, the use of a computer with a dedicated software system is necessary when using the mass selective detector. It is also possible to achieve a high degree of connectivity between chromatographic instrumentation using laboratory information management systems (LIMS).

SUGGESTED READING

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