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Plastics Analysis by Gas Chromatography

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INTRODUCTION

The main purpose of this chapter is to present the power of gas chromatography (GC) for the analysis of plastic materials—its simplicity, speed, and broad range of applicability. Generally speaking, plastic materials are mixtures of macromolecules (polymers) and smaller chemical entities (normally in minor concentrations), such as residual monomers, residual solvents, and additives. In the materials which we call plastics there is actually a wide variety of molecules, ranging from low-molecular-weight (relatively high-volatility) monomers and solvents to medium-molecular weight (medium-volatility) additives, to the very-high-molecular-weight (nonvolatile) polymers themselves. Each of these components plays a special role in the plastic material. Accurate information about the chemical composition plays a crucial role in predicting and controlling the physical as well as chemical properties of plastic materials. These properties in turn determine the processing behavior, mechanical properties, and end-use performance of the plastics materials.

Gas chromatography is a highly versatile analytical technique used widely in the plastics industry for the qualitative and quantitative determi-

nation of a broad variety of compounds ranging from small gaseous molecules to very-high-molecular-weight polymers. The many options available in gas chromatography offer great flexibility and capability in terms of the types of compounds that can be analyzed by this technique. GC offers a wide variety of options in terms of sample introduction, types of columns available, a great selection of detectors, and a host of other options to solve many types of plastics analysis requirements. The remainder of this chapter will present the different options available to the analyst to explain different ways to optimize analysis by this technique.

Numerous additives are used in plastic formulations to control end-use properties, processability, and stability. UV stabilizers for example, provide weatherability, antioxidants provide protection during processing, and other additives provide other desired end-use properties. Because knowledge of the concentrations and types of additives is essential to proper control of the compounding process, there is a need for reliable methods to analyze for these chemicals in resin formulations. Traditionally, gas chromatography has been the analytical technique of choice for the analysis of volatile and soluble additives. High-performance liquid chromatography (HPLC) has been used for a wider variety of additives but is less attractive than GC, mainly due to generation of large volumes of liquid waste, lower chromatographic resolution, and fewer available specific detectors for identification of different components.

Recent developments in gas chromatography have considerably enhanced the power and attractiveness of this technique to solve analytical problems. A special section at the end of this chapter highlights the nature of these developments and the advantages they bring to the analyst. New technical developments deserving special attention include: High-temperature gas chromatography, high-speed GC (fast GC), retention-time locking, and high-volume injectors.

This chapter is intended primarily to serve as a practical tool to the everyday user of gas chromatography. Specific applications, detailed explanations of theoretical principles, and mathematical equations can be found in the books and articles listed in the reference section.

THE GAS CHROMATOGRAPH

Since its introduction in the early 1950s, gas chromatography and later capillary gas chromatography has grown at a fast rate. Basically, any substance, organic or inorganic, which exhibits a vapor pressure low enough to elute from a GC column at the operating temperature can be analyzed by GC. The major limitation of GC is that sample mixtures, or their derivatives, must be volatile at the column operating temperature.

The GC instrument is a rather simple, yet very powerful. It is one of the most common analytical tools used in plastics analysis. When used properly, it can provide both qualitative (identification) and quantitative (amount) information about the individual components in sample mixtures. For a mixture to be suitable for gas chromatographic analysis it should be relatively volatile at temperatures below 350°C (450°C for high-temperature GC). In other words, the components of interest must become a gaseous form by rapid heating without any degradation or destruction of their chemical structure. This does not mean that other components are not amenable to GC analysis. In theory, most components can be analyzed by GC if a proper sample pretreatment or proper sample introduction technique is used (e.g., pyrolysis GC, sample derivatization) [1–5].

In general, the gas chromatographic system is comprised of six major components: gas supply and flow controllers, injector, detector, oven, column, and a recording device (Fig. 1). A high-purity gas flows into the injector, through the column, and through the detector. A liquid (or gas mixture) containing the dissolved sample components is introduced into the

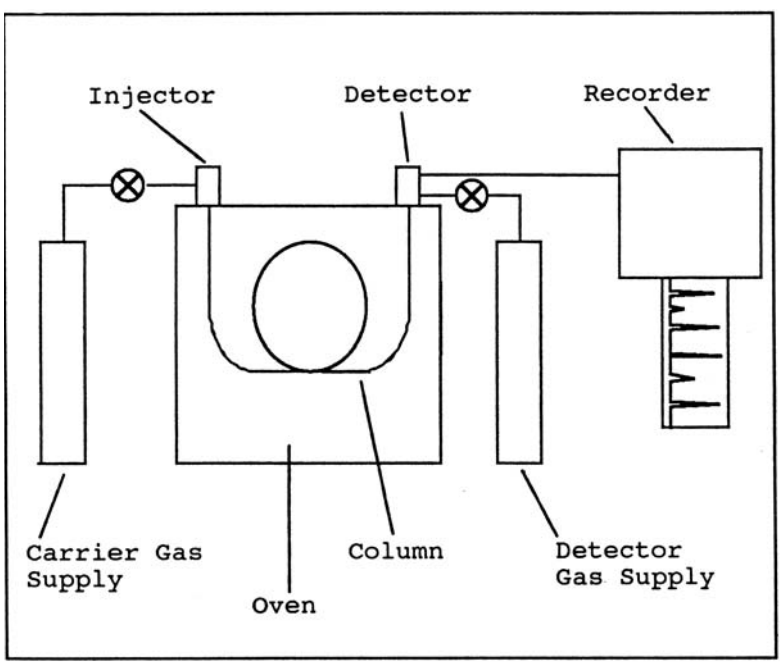

Figure 1 General diagram of a gas chromatograph.

heated injector, normally with a syringe. The sample components vaporize, and the gas flowing through the injector sweeps them into the column which is located inside the oven. The temperature of the oven is precisely and reproducibly controlled. Each compound in the sample interacts with the column to a different degree and so travels through the column at a different rate. The rate of travel through the column for each individual compound depends on the type of column, the gas flow rate, and the temperature of the oven. As each compound exits the column it is detected and an electrical signal is sent to a recording device (integrator or computer data system, etc.). The recorded signal will appear as a series of peak plotted versus time. This is called a *chromatogram*.

Normally, each peak represents an individual compound in the sample. In reality, however, it is not unusual for a peak to represent more than one compound when two peaks overlap. Using the proper column and operating conditions, this problem can be resolved or at least minimized. The time at which a compound exits from the column after introduction of the sample upon injection is called retention time. Most compounds have a unique *retention time* under particular conditions. This unique property is used for compound identification by GC.

The size of the peak provides quantitative information because the amount of the compound in the sample is proportional to the size of the corresponding peak in the chromatogram. By injecting a standard containing a known amount of the compound of interest, its retention time can be determined for the particular analysis conditions; the size of the peak (height or area) can then be compared to the corresponding peak of the known sample and a simple ratio used for quantitation. Like any other analytical technique, GC has some limitations and shortcomings, and even under various analysis conditions and columns some compounds will have identical retention times. This makes positive identification and quantitation of these compounds nearly impossible by gas chromatography. As the technique of gas chromatography expands and more technical innovations are introduced, however, the range of possible separations will definitely expand.

Numerous factors influence the successful identification and quantitation of compounds by GC. Understanding how all of these parameters can affect chromatographic analyses is critical if one is to obtain successful results.

One of the most important variables in GC is the GC column. The diameter, length, film thickness, and type of stationary phase depend on the column being used. With the exception of length, none of these factors can be changed without changing the column itself. On the other hand, oven temperature, carrier gas, and flow rate are factors which are readily con-

trolled by the GC operator. The proper setup and operation of the GC injector and detector is critical. It is important to remember that the quality of chromatographic separation is limited by the weakest component of the chromatographic system, whether it be the column, injector type, operational parameters, detector type, or the instrument itself.

Understanding the function of each component of the GC system is key to successful use of this technique in identification and quantitation of components in plastic and related materials. Furthermore, understanding the function of each component in the system will allow the analyst to optimize the system to best solve specific problems.

CAPILLARY COLUMNS: CHARACTERISTICS AND PROPER SELECTION

The GC column is considered the heart of the chromatographic system. Although there are many different types of GC columns (packed and capillary) available in the market today, the most widely used type in modern chromatography are the capillary columns. Highly efficient capillary columns do not tolerate the imprecision allowed with packed columns. For example, small deviations in gas flow from the optimal carrier gas flow rate in a packed column are acceptable, whereas small changes in flow rates for a capillary column will lead to potential errors in results. Capillary (open tubular or fused silica) columns are by definition very narrow in diameter. The diameter of the fused silica tubing used to make these columns is precisely controlled during the manufacturing process. Accurate control of the tubing's diameter is critical to the production of columns with consistent performance. Capillary columns can range in length from 5 to over 100 m. The most common lengths are from 10 to 60 m.

The outer surface of the finished column is coated with polyimide. This polymer coating serves a dual purpose. It fills flaws in the tubing which prevents breakage of the glass tubing, and it acts as a waterproof barrier to prevent corrosion coating. The polyimide coating has nearly indefinite stability at temperatures of 350°C or below. Fused silica tubing is very flexible, but it is inherently straight. This straightness and the protection provided by the polyimide coating allows the tubing to be wound on cages for easy handling and storage. A limitation of the polyimide coating is its upper temperature of about 360°C. Recently, aluminum-coated or -clad tubing has been used to manufacture capillary columns. This tubing has a much higher upper temperature limit. One drawback to aluminum-clad tubing, however, is its slight brittleness when exposed to continuous changes in temperature. It is satisfactory for isothermal temperature work since

the tubing becomes weak upon cycling of the oven temperature during temperature programming situations [1].

The Stationary Phase

The distinguishing feature of a column is its stationary phase. Capillary stationary phases are polymers that are deposited on the inner walls of the tubing in a thin, uniform film. The thickness and chemical nature of the stationary phase are critical to the overall performance of the column. High-efficiency capillary columns require relatively few types of stationary phase to achieve the separations necessary for complex samples. For this reason, only about three or four different stationary phases are actually necessary to accomplish most analyses of plastic materials. The first capillary columns had the stationary phase coated on the tubing walls, without any type of physical attachment. The stationary phase was easy to disrupt with solvents or contaminants. The advent of bonded and cross-linked phases substantially increased the stability and lifetime of capillary columns. The stationary phase is chemically bonded to fused silica capillary columns. Cross-linking is the joining of individual "strands" of polymer so that a larger and more stable stationary phase is formed. Practically every nonbonded liquid stationary phase has a bonded counterpart. There is virtually no difference in separation behavior between bonded and nonbonded equivalent phases. It is recommended, however, to use bonded and cross-linked phases if they are available. These stationary phases include polysiloxanes, polyethylene glycols, and solid adsorbents.

Polysiloxanes

The most common stationary phases are the polysiloxanes. These phases are considered to be the most resistant to abuse and have superior lifetimes. The type and amount of substitution groups on the polysiloxane backbone distinguishes each stationary phase and its properties. The most widely used phase is dimethyl polysiloxane. The interactions between solutes and this phase are limited to dispersive forces, thus solute elution occurs in the order of increasing solute boiling points. Compounds that cannot be differentiated on the basis of their boiling points (i.e., they have very similar or equal boiling points) require a different stationary phase for separation. Different stationary phases are made by changing the functionalities on the polysiloxane backbone. To obtain the differentiation of solutes by forces other than dispersion, a more selective stationary phase is required. Stationary-phase selectivity is controlled by the substitution of phenyl, cyanopropyl, and/or trifluoropropyl groups in place of some of the methyl groups on the polysiloxane backbone. This substitution enables the solutes

to use dipole, acidic, and/or basic interactions in addition to dispersive interactions. The relative magnitude of each of the four interactions determines the selectivity of a stationary phase. Injecting the same sample into two columns with different selectivities will result in two chromatograms with the corresponding peaks differing in retention times and often in elution order as well. The degree of substitution of the siloxane polymer affects the selectivity of the stationary phase as well as the thermal stability and "bleed level" of the column. In general, as the amount of polar substitutions on the polysiloxane backbone increases, there is a corresponding decrease in the upper temperature the stationary phase will tolerate. Less substituted stationary phases (i.e., more methyl substitution) usually offer longer lifetimes and lower bleed levels. Columns coated with bonded and cross-linked stationary phases will usually exhibit longer lifetimes, especially for splitless and on-column injection applications.

Polyethylene Glycols

Polyethylene glycol is the second most common stationary phase after polysiloxane. Carbowax 20M is the most widely used for gas chromatography. The major disadvantage of the Carbowax phase is its extreme sensitivity toward oxygen, especially at high temperatures. Phase solubility in water and low-molecular-weight alcohols and a lower temperature limit are other drawbacks to columns coated with Carbowax 20M. Upon analysis of acidic or alkaline compounds, the column mimics their behavior. For example, if a large number of amine samples are injected into the column, it will become slightly alkaline. Subsequent injections of an acidic compound will give a poor peak or no peak at all. This behavior is reversible by solvent-rinsing the column with water, acetone, and hexane. Bonded and cross-linked Carbowax phases eliminate the phase and water/alcohol solubility problems, but the high sensitivity to damage by oxygen is still a problem. Nevertheless, the superior selectivity for certain solutes renders the Carbowax 20M stationary phases very useful in some applications such as hindered amines and phenolic additives.

Porous-Layer Phase

Several gas–solid adsorption capillary columns are available. They are commonly called porous-layer open tubular or PLOT columns. These columns contain a layer of adsorbent particles coated on the inner wall of the fused silica tubing. Phases of aluminum oxide (alumina), molecular sieves, and porous polymers (Poraplot-like) are commercially available. Gas–solid adsorption rather than a gas–liquid partition is the separation mechanism involved. PLOT columns are well suited for the analysis of light hydrocarbons, sulfur gases, permanent gases, or other very volatile solutes at or

above ambient temperature conditions. Some of the disadvantages of PLOT columns are lower efficiencies, some loss of inertness, and problems with stability and reproducibility over time.

General Guidelines for Column Selection

The following guidelines are helpful for the selection of the appropriate stationary phase, depending on the type of analytes present in the mixture of interest.

1. For general purposes (screening purposes) use a nonpolar phase.
2. Use a stationary phase with polarity closely matching that of the solutes (i.e., nonpolar phase for nonpolar mixtures).
3. Use the least polar phase that will provide satisfactory separation; nonpolar phases have higher lifetimes than polar phases.
4. For solutes with dipoles or hydrogen bonding capabilities (i.e., amines and hydroxy-type additives), use a cyanopropyl or Carbowax stationary phase. Always consider polarity and temperature performance.
5. For light hydrocarbons or inert gases, use packed columns or PLOT columns (alumina, or molecular sieve).
6. Whenever possible, avoid using phases containing the specific element which interferes with specific detectors [e.g., do not use cyanopropyl phases with a nitrogen-phosphorous detector (NPDs) or trifluoropropyl phases with an electron-capture detector (ECD)].
7. In general, the widest range of compounds can be analyzed by using any of three or four columns: nonpolar, medium polarity, and polar (wax) columns. More than 99% of all analyses can be adequately performed with these three columns.

Column Diameter Considerations

The most popular column diameters available for fused silica capillaries are 0.18, 0.25 narrow bore), 0.32 and 0.52 mm (magabore or wide bore). Other diameters are also available from various manufacturers. The following guidelines apply to selection of a column diameter.

1. Use a 0.25-mm-I.D. column for split and splitless injections when sample overloading is not a problem. High column efficiencies (higher resolution) are achieved with small-diameter columns.

2. Use 0.32-mm-I.D. columns for splitless and on-column injections, especially when injecting large amounts of sample.
3. Use 0.53-mm-I.D. (megabore) columns as replacements for packed columns or for high sample loading applications. Use of these columns also permits lower split ratios, resulting in carrier gas savings.
4. A 0.18-mm-I.D. column can be very useful for GC/MS systems with low pumping capacities or when very high resolution is needed.

Film Thickness Selection

Column capacity is highly affected by the film thickness and column diameter. The capacity of a column is defined as the maximum amount of sample that can be injected into a column before significant peak distortion occurs. Capacity is related to film thickness, column diameter, and the solubility or polarity match between the solute and the stationary phase. Capacity increases as the column's film thickness or diameter is increased. The more soluble a salute is in the stationary phase, the greater is the column capacity for the solute. For example, a polar solute (e.g., an alcohol) will have greater solubility in a polar stationary phase (e.g., Carbowax) than in a nonpolar phase (e.g., dimethylsilicone). Exceeding column capacity or *overloading* is indicated by peak broadening or asymmetry.

Fused silica columns are available in different film thicknesses. Depending on the column diameter, film thicknesses are available from 0.10 to 5.0 μm. In most cases, a "standard" film thickness column is satisfactory. These columns have phase ratios of between 100 and 400. The phase ratio is defined as the column radious divided by 2 times the film thickness. In general, a standard film column is 0.25 μm for 0.25-mm- and 0.32-mm-I.D. columns, and 1.0–1.5 μm for 0.53 mm diameter columns.

The following guidelines can be used to select the optimal film thickness:

1. Use of a standard film thickness column is desirable for most applications.
2. Thin film columns are useful for high-boiling compounds, trace analysis, and for instances when column bleeding must be minimized at high temperatures.
3. Thick film columns should be used when higher capacity and longer column lifetime is desirable. Normally, thick films are used with wide-bore columns.

Column Length Selection

Column length has a direct effect on retention times when using isothermal analysis conditions. A nearly linear increase in retention time with increase in column length is seen. However, only about 40% increase in resolution is achieved. For temperature program analysis conditions, the increases in retention and resolution with column length are much less than those for isothermal conditions. Only a small increase in resolution is realized with longer columns. This is especially true for volatile compounds. Using thick-film columns is the best method to obtain better separation of volatile or early-eluting compounds. In general, the following guidelines can be used to select an optimum column length.

1. A 30-m column is suitable for most applications.
2. Fifteen-meter columns have been used conventionally for simple mixtures (less than 10 components) or for sample screening purposes. However, the advent of "fast chromatography" technology is opening new possibilities for the use of short columns for more complex mixtures. This issue is discussed in more detail later in this chapter.
3. Use of a column 60 m or longer is recommended for very complex samples or for situations requiring the highest possible number of theoretical plates. The use of long columns could provide resolution of components not possible with shorter columns. This normally results in the cost of a much longer run time.

Overall Considerations for Column Selection

If all other chromatographic conditions remain the same, it is the structure of the stationary phase that determines the relative retention time and elution order of compounds. The stationary phase determines the relative amount of time required for two compounds to travel through the column. It retains the compounds as they move through the column. If any two compounds take the same amount of time to migrate through the column, these two compounds are not separated; they co-elute. If two compounds take different times, the two compounds will be separated. The stationary phase is often selected on the basis of its polarity. Polarity of the stationary phase is determined by the chemical structure of the resin (polymer). Polarity affects several column characteristics. Some of the most important are column lifetime, temperature limits, bleed level, and sample capacity.

The selectivity of the stationary phase directly influences column separation properties. Stationary phase selectivity is not well understood, but

selectivity can be thought of as the ability of the stationary phase to differentiate between two compounds by a difference of their chemical and/or physical properties. If there is a difference in the properties of two compounds, the amount of interaction between the compounds and the phase will be different. If there is a significant difference in the interactions, one compound will be retained more than the other and separation occurs. If there are no differences, co-elution occurs. The compounds may have different structures or properties, but if a particular stationary phase cannot distinguish between the compound differences, co-elution takes place. Most analyte properties, such as hydrogen-bonding dipole strength, are not easily determined. The column stationary phase increases resolution by increasing the relative time the compound spends in the stationary phase. *Resolution*, the degree of separation of two adjacent peaks, is defined as the distance between the peaks centers divided by the average bandwidth. Strictly speaking, this is valid only when both peaks have the same height.

SELECTING THE PROPER INJECTOR

There are two main purposes when introducing the sample into the GC instrument. One purpose is to introduce the sample into the column in a short band. The smaller the sample band at injection, the sharper and more narrow the peaks will be on the chromatogram. The end result is more sensitivity and better resolution. The second goal is to have the composition of the sample introduced into the column be as representative as possible of the sample injected. There should be no sample degradation or adsorptive losses occurring during injection. With the exception of on-column injection, all injectors utilize vaporization to introduce the sample into the capillary column. The injected sample is rapidly vaporized in the heated injector, and the carrier gas flowing through the injector carries the sample into the column. A significant problem with vaporization injection techniques is backflash. Upon sample vaporization, the gaseous sample expands to fill the injector liner volume. Backflash occurs when the vaporized sample expands beyond the capacity of the liner volume and into the injector body. Since the sample now occupies a larger volume, it takes longer for the sample to be carried into the column. A large (and tailing) solvent peak is obtained. If the vaporized sample comes in contact with cold spots such as the septum and gas inlets of the injector, small amounts of the sample may condense. This condensation may result in carryover problems on subsequent injections. Backflash problems can be minimized by:

1. Using a septum purge with split/splitless injectors
2. Using small injection volumes
3. Using large-volume injector liners
4. Using the optimal injector temperature

The following discussion should serve as a general guide to the selection of injector configuration, proper injector setup and proper injection technique.

Injector Temperatures

The injector temperature should be just hot enough to ensure quick vaporization of the entire sample without thermally degrading the sample components. If the injector temperature is too low, carryover problems, incomplete sample vaporization, or broad peaks (especially the solvent front) will result. If the injector temperature is too high, excessive backflash or sample thermal degradation may occur. Using an injector temperature above the upper temperature limit of the column does not damage the column. For most samples, 200–250°C is a good injector temperature. Some screening may be needed to obtain the smallest amount of backflash and the maximum amount of sample throughput.

Inlet Discrimination

Upon injection, the less volatile sample components will not vaporize as rapidly as the more volatile sample components. Immediately following injection, the vaporized sample has a greater proportion of the more volatile compounds than the less volatile compounds. Therefore, more of the volatile compounds are introduced into the column. This effect is called inlet discrimination. The peaks for the less volatile compounds will be smaller than the more volatile compounds. The longer the sample spends in the heated injector, the less severe this type of discrimination is experienced by the sample. If inlet discrimination needs to be eliminated, an on-column injector should be used.

Septum Purge

Most split/splitless capillary injectors have a septum purge function. The septum purge minimizes the amount of septum bleed materials that may contaminate the GC system. The septum purge gas sweeps the bottom face of the septum and carries the contaminants out through the septum purge vent. The septum purge flow is usually between 0.5 and 5 ml/min. Higher than optimum septum purge flows may result in the loss of some of the more volatile sample components. The septum purge function is not essential in order to obtain good chromatographic results; however, any septum bleed and inlet contamination problems will be minimized.

INJECTION TECHNIQUES

There are four major capillary injection techniques: split, splitless, on-column, and megabore or direct injection. Nearly every standard capillary injector is capable of split and splitless injections. On-column injections require a dedicated capillary on-column, injector and is a required injector for high-temperature gas chromatography and to minimize inlet discrimination [1,2].

Split Injection

Split injection is very simple and the most common of the capillary injection techniques. The highest resolution and system efficiencies are obtained with split injections (Fig. 2). Split injections are used for highly concentrated samples with typical per-component concentrations of 0.1–10 μg/μl. Injection volumes of 0.5–2 μl are normally used, but volumes up to 5 μl can be used without significant problems. Split injection is a vaporization

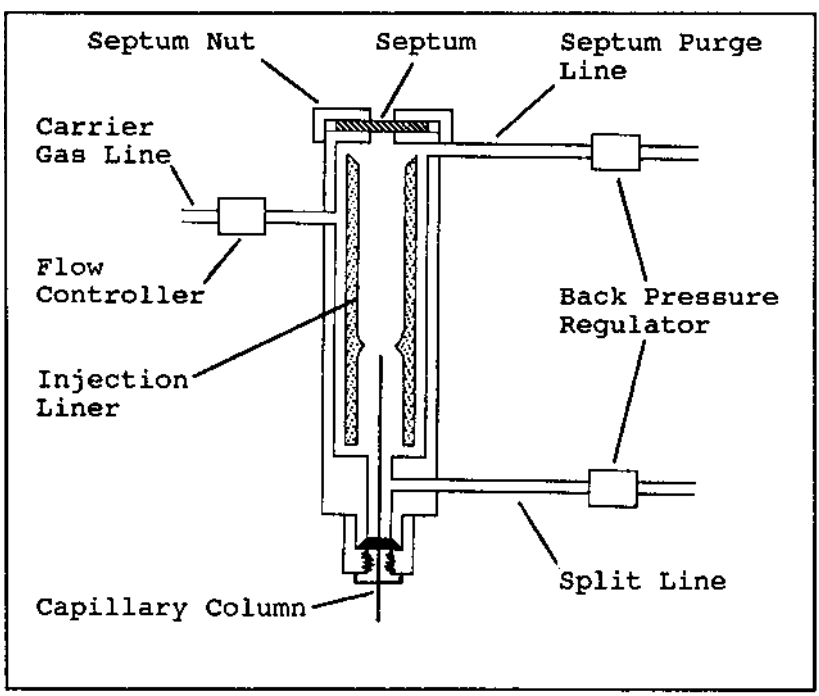

Figure 2 Split injector.

technique (Fig. 2). The sample is vaporized upon injection and rapidly mixed with carrier gas. A small amount of the carrier gas enters the column, and a much larger amount leaves the injector through the split vent. Since the vaporized sample is mixed with the carrier gas, only a small amount of the injected sample actually enters the column. The total gas flow through the injector at the moment of injection is quite high (the sum of the column and split vent flows). The sample is rapidly swept into the column, which accounts for the high efficiency of split injections. This also accounts for the severe discrimination obtained with split injections. The less volatile compounds do not have sufficient time to vaporize fully before they are discarded via the split vent.

Split Ratio

The amount of sample entering the column depends on the carrier gas flows into the column and out of the split vent. By measuring the column flow and the split vent flow, the amount of sample going into the column relative to the amount of sample being split can be calculated. This value is called the *split ratio*. The split ratio is normally reported with the column flow rate normalized to 1. A split ratio of 1:50 indicates that one part of the sample enters into the column and 50 parts are discarded out of the split vent. Therefore, 1/51 of the total sample theoretically makes it into the column. Typical split ratios range from 1:10 to 1:100, depending on the column diameter being used and the column loading desired for the analysis. Applications involving highly concentrated samples or very-small-diameter columns may require the use of higher split ratios. Split ratio is measured using a flow meter. The split ratio is equal to vent flow/column flow. For example: Column flow = 5 ml/min split vent flow = 100 ml/min split ratio = 100/5 = 20. Therefore, the split ratio is 1:20.

Splitless Injection

Splitless injections are used for trace analyses or when the component concentration in the mixture of interest is about 200 ng (Fig. 3). The injected sample is vaporized and carried into the column by the carrier gas. At the moment of injection, the flow through the injector is the same (1–2 ml/min) as the column flow. About 15–60 s after injection, additional carrier gas flow is introduced into the injector. This extra gas purges the injector of any remaining sample that has not entered the column. The time at which the extra gas flow is introduced is called the *purge activation time* (or *purge on*).

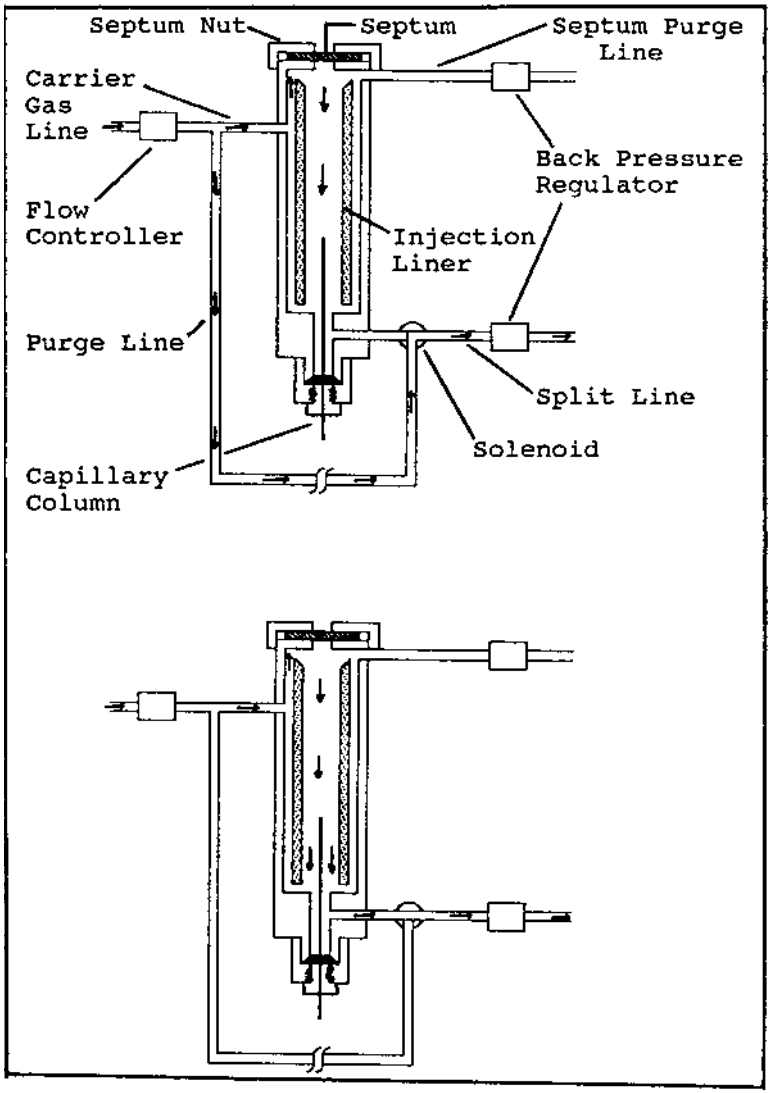

Figure 3 Splitless injector.

Solvent Effect and Cold Trapping

With splitless injections, the sample is introduced into the column at a much slower rate than for split injections. To prevent peak broadening, the sample needs to be refocused before starting the chromatographic process. One requirement of most splitless injections is that the initial temperature of the column oven be at least 10°C below the boiling point of the sample solvent. When the vaporized solvent leaves the injector and enters the cooler column, the solvent rapidly condenses at the front of the column and will trap and refocus the sample. This is called the *solvent effect*. Starting at too high a column temperature can result in broad peaks. If refocusing does not take place, the earlier-eluting peaks will suffer greater peak shape degradation than the later-eluting peaks. If this occurs, either a lower initial column temperature or a higher-boiling solvent should be used. If the sample components boil at 150°C or above the initial column temperature, the solvent effect does not have to occur for good peak shapes. The high-boiling compounds cold-trap in the column and refocus into a short band without help from the solvent effect. Injection sizes are usually limited to 2 µl or less for splitless injectors. Large injection volumes will normally result in broader peaks. Another limitation of splitless injections is that peaks that elute before the solvent front do not show good peak shapes. Changing to a lower-boiling solvent may help this situation.

On-Column Injection

On-column injection offers great advantages. This technique provides the optimum in capillary column performance by eliminating discrimination and degradation effects that can result from using a vaporization technique and is highly recommended for high-temperature GC applications (Fig. 4). With this technique, the sample is deposited directly into the column with a syringe. On-column injections are particularly useful for high-boiling compounds such as high-molecular-weight additives (e.g., waxy mold release agents) and thermally labile compounds. On-column injection requires the solvent effect or cold trapping to obtain acceptable peak shapes. Some on-column injectors use a secondary cooling function to eliminate the need to cool the entire column down to the appropriate temperature for the solvent effect. Only a small portion of the front of the column is cooled at the moment of injection. Megabore columns can tolerate large injection volumes (1–2 µl) and high sample concentrations (1–10 µg). Megabore columns are used for converted packed column instruments or for situations where large sample capacities are needed. Megabore injections are well suited for trace-level analyses. Highly concentrated samples may have to be diluted to avoid overloading the column. Small-diameter capillary

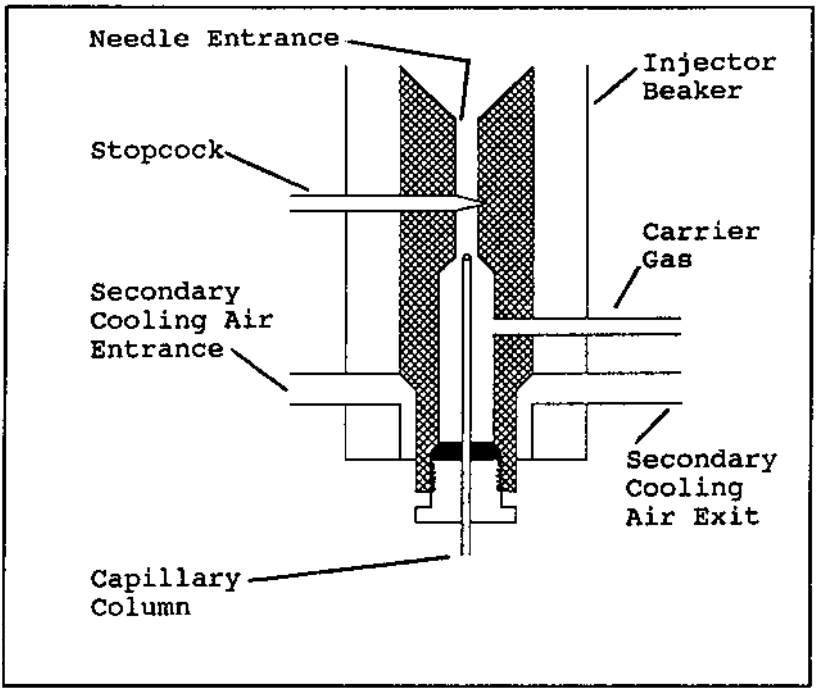

Figure 4 On-column injector.

columns (0.32 mm I.D. or less) are not compatible with megabore injectors. Some on-column injectors are temperature-programmable, permitting vaporization of solvent while the analytes still remain focused in a narrow band at the head of the column.

Direct Injection

Direct injection relies on vaporization processes to introduce sample into the column. However, it lacks a purge activation function, a septum purge flow, or secondary cooling (Fig. 5). The direct injection mode is used with packed columns or wide-bore (0.53-mm-I.D.) capillary columns. Wide-bore columns are used as higher-efficiency replacements for packed columns without the need to extensively modify the packed-column injector.

The process to convert a packed-column injector for use with wide-bore columns is relatively simple. The packed column is removed from the GC along with any injector (or detector) fittings attached to the base injector (or detector) body. A glass, direct-injection liner is placed into the packed

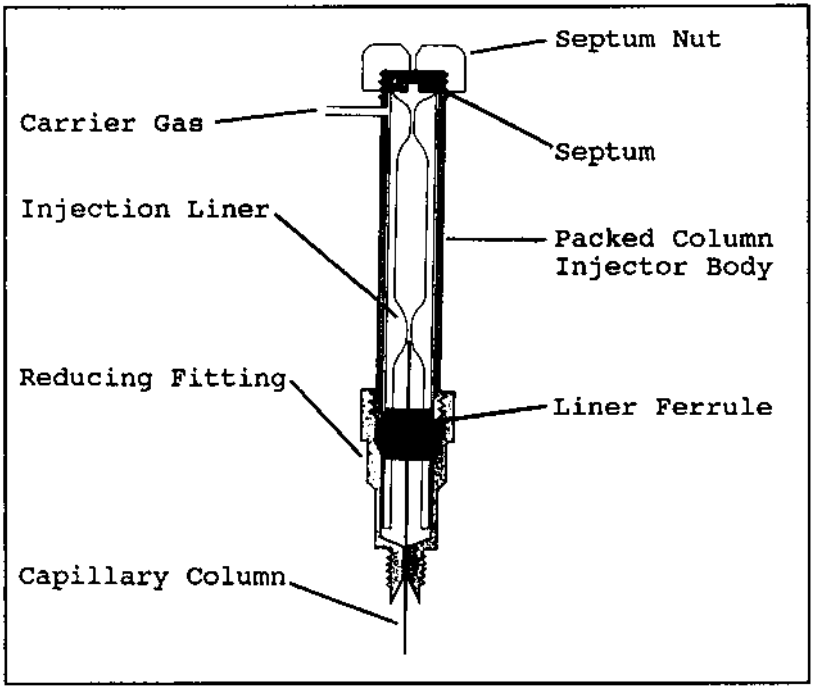

Figure 5 Direct injector.

injector. This liner serves two purposes. First, it decreases the volume of the injector so that excessive dead volumes and the resulting peak broadening effects are significantly reduced. Second, it serves as the vaporization site and means to transfer the vaporized sample directly into the wide-bore column. A ferrule and metal fitting is used to seal the liner and hold it in place. The metal fitting reduces the larger packed injector fitting down to the size normally used for capillary columns. Another fitting is used to reduce the packed detector fitting and to add makeup gas, if desired. A variety of different and specially designed conversion kits can be purchased for nearly every packed column

Injector Port Liners

Injector liners provide an inert environment in which the sample can vaporize and be properly introduced into the column. The liner design will vary depending on the type of injection technique being used. Liners that are

dirty, poorly installed, or incorrectly selected will contribute to poor chromatographic results.

Split Injector Liners

The split injector liner must have a large enough volume to accommodate the expansion of the vaporized sample. However, the volume must be small enough for the gas flow to quickly sweep the vaporized sample into the column. Liners with too small a volume will be subject to severe backflash problems. Larger liner volumes become less important at high split ratios, since the high carrier gas flows rapidly sweep the injector. Flow disruption within the liner ensures thorough mixing of the sample, thus minimizing discrimination problems. Various types of flow disruption liners are available. The greatest discrimination is obtained with straight-bore liners, while the inverted-cup liners discriminate the least. Hourglass-shaped liners provide good sample mixing, and they are easier to clean than inverted-cup liners. Packing a split injection liner with silanized glass wool is another way to ensure flow disruption. The packed liner has a higher thermal mass, which aids in the rapid volatilization and mixing of the less volatile components. Additionally, the glass wool acts as a filter to help trap some of the nonvolatile materials in the injected sample. The glass wool should be lightly packed so that unnecessary peak broadening will not occur.

Splitless Injector Liners

Splitless injector liners are normally straight tubes without any flow-disruption devices. Any flow disruption in the injector usually causes peak broadening. Therefore, it is not recommended to pack a splitless liner with glass wool. Sometimes there is a restriction at the bottom of the liner. This is to keep the column centered in the liner and away from the liner walls. Use of small-volume liners will result in greater inlet efficiency, since the sample will be transferred into the column over a shorter period of time. However, smaller-volume liners are more subject to backflash problems. For small injection volumes (< 0.5 μl), the 2-mm-I.D. splitless liner is recommended; for larger injection volumes, the 4-mm liner is recommended to minimize backflash problems.

Megabore Injector Liners

The type of direct injection liners used greatly affects the quality of megabore chromatography. There are three general types of direct injection liners: the straight tube, the direct flash vaporization liner, and the hot on-column.

Straight-Tube Liners

Using a straight-tube type of megabore liner is not recommended. It typically gives a very broad and tailing solvent front, which may interfere with some of the early-eluting peaks of interest. Due to the lack of any type of restrictions, the vaporized sample can readily backflash out of the liner. The severity of solvent front tailing will be more pronounced for large injection volumes, volatile sample solvents and solutes, low carrier gas flows, and excessively hot injectors.

Direct Flash Vaporization Liners

The direct flash vaporization liner has a restriction at the top of the liner and another restriction several centimeters below the upper restriction. The sample is injected into the chamber formed by the two restrictions. When the syringe needle is inserted into the liner for injection, the needle blocks most of the upper restriction. This prevents the vaporized sample from escaping from the top of the liner. The lower restriction is tapered so that the megabore column becomes lightly wedged in the taper. Carrier gas (or sample) will not escape around the column. Backflash is greatly reduced, so the solvent front is narrow and without significant tailing. Direct flash vaporization liners can be packed with silylated glass wool, provided there is no top restriction. The glass wool should be lightly packed so that unnecessary peak broadening will not occur. The column end should be cleanly cut and checked with a magnifying lens. The column is inserted into the liner until it fits snugly in the restriction. Too much force will crush the column end, and too little force will not seal the column in the restriction. If the column is not sealed properly, the solvent peak will show tailing. Also, any debris in the injection liner taper will prevent a proper seal.

Hot On-Column Liners

The hot on-column injection-port liner has a single tapered restriction at the top of the liner. The megabore column seals in this region in the same manner as for the direct flash vaporization liner. The needle of a standard GC syringe can be inserted directly into the megabore column. The syringe needle should be straight, and the end should not have burrs or hooks. Injection volumes are limited to 0.5 μl or less. Hot on-column megabore injections are suitable for high-boiling samples that are difficult to vaporize by standard vaporization techniques. Since the injector temperatures are lower than those used for vaporization techniques, thermally labile samples can also be chromatographed with the on-column megabore liner. A direct flash vaporization liner system is more suitable and better in greater than

95% of all megabore applications. Hot on-column megabore liners should be used only when direct flash vaporization liners are not suitable.

THE CARRIER GAS

Selecting/Setting the Carrier Gas

The carrier gas is chosen for its inertness. Its only purpose is to transport the analyte vapors through the chromatographic system without interaction with the sample components. The gas is obtained from a high-pressure gas cylinder and should be free from oxygen and moisture. High-purity grades of carrier gas are usually less expensive in the long run. Helium is the most popular GC carrier gas in the United States.

The effects of the type of carrier gas and its flow rate upon a capillary column performance can be significant. The flow rate has to be accurately set, measured, and reproduced to fully experience the high efficiencies available with capillary columns. Unlike packed columns, small variations in the carrier gas flow rate can have significant effects on the separations obtained with capillary columns. Even the type of carrier gas can affect separation quality [2].

Instead of volumetric flow rate, a better way of assessing carrier flows is the average linear velocity. It can be thought of as the rate of travel for a nonretained compound through the column. It is the speed of the carrier gas through the column. The average linear velocity is a measure of carrier gas flow that is independent of the diameter of the column. Linear velocities are ideal for comparing carrier gas flows when the columns differ in diameter. There are small differences between the optimal linear velocities for columns of different diameters, film thickness, and length. In the laboratory environment, usually only one linear velocity per carrier gas type must be known, regardless of the column dimensions. van Deemter curves are usually given in terms of the linear velocity; in many cases, therefore, linear velocities are of the greatest practical use to the analyst (Fig. 6).

The volumetric flow rate of the carrier gas is still important for a number of applications and GC configurations. Typically a flow rate that is greater than the value corresponding to the minimum of the van Deemter curve is recommended. This is especially important for analyses using a temperature program, because at a constant inlet pressure, as the temperature of the oven increases, the viscosity of the carrier gas increases with a subsequent decrease in the carrier gas flow rate. This means that the carrier gas velocity and flow rate do not remain constant throughout the course of a temperature-programmed run. If the flow is set at the exact minimum in the van Deemter curve, a decrease in efficiency will result as the carrier gas flow decreases with the increasing oven temperature. If the flow rate is set slightly

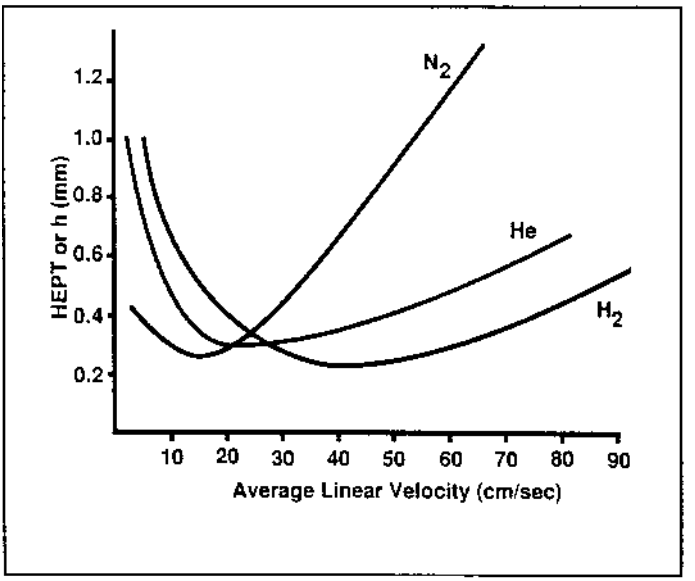

Figure 6 van Deemter curves for three main carrier gases: N_2, He, and H2.

above the minimum, an increase in separation efficiency with increasing temperature will result, since a shift toward the minimum in the van Deemter curve occurs. For helium and hydrogen as carrier gases, the minimum in the efficiency curves occurs over a much broader range and at higher linear velocities than for nitrogen. Using nitrogen provides the greatest column efficiency, but the minimum efficiency value occurs over a very narrow range at low linear velocities. Efficiency drops sharply with increasing linear velocities. Substantial analysis speed must be sacrificed for optimal resolution. For helium and especially hydrogen, high flow rates can be used for fast analysis times without sacrificing a large amount of separation efficiency. Large changes in oven temperatures will not grossly affect the column's efficiency due to flow-rate changes with temperature. In general, helium and hydrogen will provide nearly equivalent separations to nitrogen, but within a much shorter period of time. Also, helium and hydrogen provide the best separations when the analytes of interest elute over a wide temperature range. Although nitrogen is not normally recommended as a carrier gas for capillary columns, it can perform as well as helium, depending on the conditions chosen to run the analysis. There may be reluctance to use hydrogen as a carrier due to perceived explosion hazard. However, the ratio of air to hydrogen must be within a very narrow range (4–10%) before

the possibility of an explosion exists. Hydrogen is very diffusive in air, so it is very unlikely that such a buildup of hydrogen might occur.

Before analysis and after proper conditioning of the column, the carrier gas flow rate has to be accurately set. The carrier gas flow rate depends on the column temperature. It is important, therefore, to set the carrier gas at the same column temperature for a given analysis. Significant changes in the resolution can occur with small changes in the carrier gas flow rate. The carrier gas is normally set at the initial temperature of the temperature program. For capillary columns, carrier gas flow is normally expressed as an average linear velocity (cm/s) instead of a volumetric flow rate (ml/min), as discussed previously. The average linear velocity can be thought of as the average rate at which a nonretained compound travels through the column, or the "speed" of the carrier gas. The linear velocity is determined by injecting a highly volatile compound that is not retained by the column. From the retention time of the nonretained peak, the average linear velocity can be calculated. The following compounds are recommended for the determination of average linear velocity for various detectors.

For FID and TCD, methane or butane
For ECD, methylene chloride or other halogenated methanes
For PID, ethylene or acetylene
For NPD, acetonitrile
For MS, butane, air, or halogenated methanes

It is not recommended to inject the neat liquid sample directly into the column for estimation of carrier gas velocity, as overloading may take place. Instead, make a headspace injection by placing a small volume of the appropriate compound in a septum-capped vial. Shake the vial, then insert the syringe needle into the headspace above the liquid. Pull up about 1 μl of the headspace vapors and inject. The nonretained peak should be very sharp and symmetrical. Leaks in the injector, a poorly installed column, or a lack of sufficient makeup gas flow will cause tailing or broadening of nonretained peaks. The effect of the carrier gas linear velocity on column efficiency is described using the van Deemter curves (Fig. 6). The curves show that there is an optimal linear velocity that provides the highest efficiency. This point is where the curve reaching the smallest value is used (the point of greatest column efficiency). The best resolution is obtained when a linear velocity that generates the highest efficiency for a column is used. Figure 6 also shows that using a linear velocity that is too low or too high will result in a rapid loss of column efficiency. Usually a linear velocity that is greater than the value corresponding to the minimum in the van Deemter curve is used. Setting the linear velocity at a higher value also compensates for the decrease in linear velocity with increasing column temperature, as encoun-

tered when using a temperature program. With helium and hydrogen as carrier gases, the minimum in the van Deemter curves occurs over a much broader range and at higher linear velocities than with nitrogen. Using nitrogen provides the greatest column efficiency, but the minimum in the van Deemter curves occurs over a very narrow range and at a low linear velocity. Substantial analysis speed may be sacrificed for optimal resolution when using nitrogen. For helium and hydrogen, high linear velocities can be used to reduce analysis times without sacrificing a lot of efficiency. The faster flow rates also sweep the injector faster, which improves the sample introduction process. Helium, and especially hydrogen, provide the best resolution when the analytes elute over a wide temperature range. Use of the highest-purity carrier gas will maximize column life. The use of impurity traps (water and oxygen) on the gas lines is highly recommended to extend column lifetime and to improve detector sensitivities.

Gas Purity and Gas Purification

Gas traps are strongly recommended, even if high-purity carrier gases are used. Trace amounts of contaminants can cause baseline problems, detector noise, and possible column damage. Contaminated detector gases can lead to artificially high baseline readings and poor performance. Individual traps are designed to remove moisture, oxygen, hydrocarbons, and other contaminants from the gas supply. The trap system recommended is a moisture trap, a high-capacity oxygen trap, and an indicating oxygen trap. The moisture trap should be first in line, because moisture will quickly deactivate the oxygen traps. The high-capacity oxygen trap should be installed second, followed by an indicating oxygen trap. An expired trap should be replaced immediately.

Moisture Traps

A moisture trap should be installed in the carrier and detector gas line(s). It will remove trace levels of water, some nonpermanent gases, and light hydrocarbons.

Oxygen Traps

Trace levels of oxygen in the carrier gas can dramatically shorten the life of a gas chromatographic column. Generally, the polyethylene glycol-based stationary phases (i.e., Carbowax) are readily oxidized, especially at elevated temperatures. Polysiloxane phases can also be irreversibly damaged by oxidation at high temperatures, but much more slowly than polyethylene glycol-based phases. Oxidized phases exhibit poor chromatographic performance and higher than normal bleed. Oxygen has a negative effect on many

GC detectors: it degrades the performance of electrolytic conductivity detectors (ELCDs), reduces filament lifetime in thermal conductivity detectors (TCDs), and reduces the linearity and sensitivity of electron capture detectors (ECDs). Both the column and detector benefit when oxygen is removed from the carrier gas supply. Oxygen contamination can usually be attributed to small leaks in the gas lines, septum leaks, or low-purity carrier gas. The most efficient oxygen traps are 99% efficient at reducing oxygen in carrier gases such as helium, nitrogen, hydrogen, argon, argon–methane, or CO_2 at 99.999% purity. A 20- to 40-fold reduction in oxygen in the gas is often obtained. These traps will effectively remove oxygen from argon–methane mixtures (used with ECDs) without disturbing the ratios of these gases. Metal-bodied traps avoid the signal noise associated with any plastic-bodied trap. The use of an indicating oxygen trap is recommended to determine when the high-capacity oxygen trap needs replacing. A glass indicating oxygen trap should be placed downstream of the high-capacity oxygen trap as a means of indicating when to replace the high-capacity nonindicating trap. This will prevent premature disposal of the high-capacity oxygen trap. The indicating material undergoes color change as it is depleted. The high-capacity oxygen trap must be replaced immediately upon the first indication of color change in the indicating trap. Fully expired oxygen traps will contaminate the gas with previously trapped materials.

Use of Gas Generators

Traditionally, compressed-gas tanks have been used as the source of laboratory gases. However, laboratory-size generators capable of producing ultrapure and ultradry (99.999%) hydrogen gas, nitrogen gas, and high-purity air are now available and are highly convenient and much less expensive in the long run compared to the traditional gas tanks. Hydrogen is conveniently produced by the electrolysis of deionized or distilled water. Separation of hydrogen from other electrolysis products is done by permeation through a palladium membrane. Nitrogen and high-purity air are produced from an air source. Because of the high-purity gas obtained from gas generators, further purification for use in gas chromatography is not normally required.

SELECTING THE RIGHT DETECTOR

In addition to high resolution and speed, gas chromatography offers the great advantage of interfacing with a large variety of detection methods. The detector is the critical link between the separation of the sample components by the column and the generation of a chromatogram. The signal generated by the detector is relayed to a recording device, such as an integrator or a computer which produces a corresponding chromatogram.

Capillary columns are compatible with most of the commonly available detectors used in gas chromatographic systems. However, each type of detector has a different set of requirements for optimal performance. In theory, the ideal situation is where the compounds are detected as they exit the column, thus preserving the separation achieved by the column.

Makeup Gas

Most detectors require a high volume of gas flow for optimal sensitivity and peak shape. For capillary columns, these gas volumes are much greater than those delivered by carrier gas alone. Even megabore (0.53-mm-I.D.) columns used at their highest recommended flow rates (10–20 mi/min) do not deliver the necessary flows (30–40 ml/min) required by most detectors for optimal performance. The difference in gas flows is even much greater for smaller-diameter columns. For optimum detector performance this difference is made up by the addition of makeup gas. The makeup gas is added at the detector side independently of the carrier gas. The carrier gas flow is not affected by the flow rate or type of makeup gas. In many cases the best makeup gas may be different than the carrier gas.

Detector Sensitivity, Selectivity, and Linear Range

Sensitivity

The detector response should is proportional to the mass of solute passing through the detector per unit time. In theory, these detectors are not affected by changes in the carrier gas flow rate. However, in practice, large changes in carrier-gas flows have a significant effect on detector behavior. For mass flow-rate detectors, sensitivity is defined as the peak area divided by the sample weight. The peak area can be obtained directly from the integrator. Concentration-dependent detectors are affected by the amount of gas flowing through the detector. The greater the amount of carrier and makeup gas is mixed with the sample, the less is the response from the detector. A concentration-dependent detector responds to changes in the concentration of the solute in the gas within the detector rather than to the presence of the substance itself; no response is obtained unless the composition of the flowing gas mixture changes. Sensitivity is defined as the product of the peak area and flow rate divided by the sample weight.

Selectivity

Some detectors respond to almost every compound in the column effluent. These detectors are called general or universal detectors. Flame ionization detectors (FIDs) and thermal conductivity detectors (TCDs) are examples of

these types of nonspecific detectors. Other detectors respond to the presence of organic compounds containing certain functional groups or chemical structure. These detectors are called specific or selective detectors and are able to discriminate between compounds containing and not containing the particular functionality. Some specific detectors may respond to high concentrations of compounds that lack the particular functionality. Examples of specific detectors include the electron capture detectors (ECDs), nitrogen–phosphorus detectors (NPDs) and flame photometric detectors (FPDs).

Linear Range

Any change in the analyte concentration in a sample should result a corresponding change in the compound's peak size. If the amount of compound introduced into the detector is doubled, the size of the resulting peak should double. This normally occurs only over a certain range of compound concentrations—this is called the *linear range* of the detector. If the concentration of compound is outside this range, the response of the detector does not reflect the amount of analyte passing through the detector. To find the linear range of a detector, a simple test is performed. Increasing concentrations of the compounds of interest are injected and the response plotted versus the compound concentration. The linear range is the region where a straight line can be drawn through the resulting points.

Ideally, a GC detector should have the following attributes:

1. High sensitivity
2. Low noise level (background level)
3. Linear response over a wide dynamic range
4. Good response to all components being analyzed
5. Insensitivity to flow variations and temperature changes
6. Stability and ruggedness
7. Simplicity of operation
8. Positive compound identification

The Thermal Conductivity Detector

The thermal conductivity detector (TCD) is the most common universal detector used in GC. It is rugged, versatile, and relatively linear over a wide range and is highly useful in the analysis of components which do not give a signal by FID (water, CO_2, etc.). In operation it measures the difference in the thermal conductivity between the pure carrier gas and the carrier gas plus components in the gas stream from the separation column. The detector uses a heated filament (often rhenium–tungsten) placed in the emerging gas stream. The amount of heat lost from the filament by conduc-

tion to the detector walls depends on the thermal conductivity of the gas. When substances are mixed with the carrier gas, its thermal conductivity goes down (except for hydrogen in helium); thus, the filament retains more heat, its temperature rises, and its electrical resistance goes up. Monitoring the resistance of the filament provides a means of detecting the presence of the sample components. Of all the detectors, only the thermal conductivity detector responds to anything mixed with the carrier gas. Since it is nondestructive, the eluent may be passed through a thermal conductivity detector and then into a second detector or a fraction collector (i.e., preparative GC). The linearity of the detector is good at the lower concentration range but not in the high-percent range. In the high-percent range, a multipoint calibration is a way to ensure accurate measurements. Even gold- and nickel-coated tungsten–rhenium hot wires are susceptible to oxidation, which may unbalance the detector to the point where it cannot be zeroed properly. Oxide formation on the hot-wire surface will minimize the detector's ability to sense changes in thermal conductivity and thus decrease its sensitivity. Thus, it especially important to remove oxygen from the carrier gas when using a TCD.

The Flame Ionization Detector

The flame ionization detector (FID) is the most popular detector because of its high sensitivity and wide linear dynamic range [1]. The FID is an ionization detector that exhibits a nearly universal response to all organic compounds. The sensitivity, stability, excellent linear range, ease of operation and maintenance, along with wide applicability and low cost has made this detector the most popular gas chromatographic detector in use today [2].

A voltage is applied to the flame jet and the collector. Carrier gas exiting from the column is mixed with hydrogen and burned at the tip of the jet. Excess oxygen, usually as an air mixture, is supplied to the combustion chamber to ensure efficient ionization of the column effluent. Movement of the generated ions from the flame to the positively charged collector produces a small current. A background or baseline signal is always present and is a result of trace levels of gas impurities, system contamination, and normal column bleed. The introduction of an organic compound into the flame results in the compound's ionization and an increase in the detector current above the background level.

Most commercially available FIDs require 30–40 ml/min of total gas flow for optimal performance. Carrier gas flows for capillary columns are usually 0.5–10 mi/min; therefore, makeup gas must be added to supplement the column carrier flow. Nitrogen is a better makeup gas than helium.

Detector sensitivity will be increased by about 20% using nitrogen rather than helium as the makeup gas.

Sensitivity also depends on the flow of makeup gas. The sum of carrier and makeup gas flows should be 30–40 ml/min. The flows of the hydrogen and air combustion gases are critical for optimal sensitivity. Usually the air flow is about 10 times the flow of hydrogen (30–40 ml/min hydrogen and 300–400 ml/min for air).

The Nitrogen–Phosphorus Detector

A very widely used selective detector for the analysis of compounds containing nitrogen or phosphorus is the nitrogen–phosphorus detector (NPD). This detector is used in a number of novel applications including trace analysis of nitrogen-containing or phosphorous-containing additives, monomers, or residual solvents. Special applications requiring specificity for components present in complex mixtures take advantage of this detector, since it responds only to compounds that contain nitrogen or phosphorus. Its fabrication is similar to that of a flame ionization detector and, consequently, NPD equipment is usually designed to mount on an existing FID-type detector base. The thermionic source has the shape of a bead or cylinder centered above the flame tip. This bead is composed of an alkali metal compound impregnated in a glass or ceramic matrix. The body of the source is molded over an electrical heating wire. A typical operating temperature is between 600 and 800°C. A fuel-poor hydrogen flame is used to suppress the normal flame ionization response of compounds that do not contain nitrogen or phosphorus. With a very small hydrogen flow, the detector responds to both nitrogen and phosphorus compounds. Enlarging the flame size and changing the polarity between the jet and collector limits the response to phosphorus compounds only. Located in proximity to the ionization source is an ion collector. The thermionic source is also polarized at a voltage that causes ions formed at the source to move toward the ion collector. Compared with the flame ionization detector, the thermionic emission detector is about 50 times more sensitive for nitrogen and about 500 times more sensitive for phosphorus.

The Electron-Capture Detector

The electron-capture detector (ECD) is highly sensitive and selective for halogenated and other electronegative compounds, and as such remains one of the most widely used GC detectors. Applications in the plastics industry are relatively wide, especially in trace analysis or analyses of residual halogenated solvents or monomers and halogenated additives such as

flame retardants. As with the NPD detector, one of the main advantages of the ECD in the analysis of complex mixtures is its specificity. The ECD responds only to electrophilic species such as oxygenated and halogenated compounds. The ECD is a selective electrode that is capable of providing extremely sensitive responses to specific substances that might be present in a sample containing a large excess of little or not responsive substances. It consists of two electrodes. On the surface of one electrode is a radioisotope (usually nickel-63 or tritium) that emits high-energy electrons as it decays. Argon mixed with 5–10 % methane is added to the column effluent. The high-energy electrons bombard the carrier gas (which must be nitrogen when this detector is used) to produce a plasma of positive ions, radicals, and thermo electrons. A potential difference applied between the two electrodes allows the collection of the thermo electrons. The resulting current when only carrier gas is flowing through the detector is the baseline signal. When an electron-absorbing compound is swept through the detector, there will be a decrease in the detector current, a negative excursion of the current relative to the baseline as the effluent peak is traced. The potential is applied as a sequence of narrow pulses with a duration and amplitude sufficient to collect the very mobile electrons but not the heavier, slower negative ions. The ^{63}Ni sources can be safely heated up to 400°C with no loss of activity. The carrier gas and makeup gases must be free from residual oxygen and water [6–8].

After the TCD and FID, the ECD has the highest usefulness in the GC field. Unlike the FID, the ECD has neither ease of operation nor dynamic range. What it does have is detectability on the order of picograms and good specificity. Additives containing amines or acid functionalities can be converted to perfluoro derivatives, which give a signal with this detector.

The Flame Photometric Detector

The flame photometric detector (FPD) is a highly useful detector in the analysis of components containing sulfur and phosphorous functionalities. In this detector, the column effluent passes into a hydrogen-enriched, low-temperature flame contained within a shield. Air and hydrogen are supplied as makeup gases to the carrier gas. Two flames are used to separate the region of sample decomposition from the region of emission. Flame blowout is no problem because the lower flame quickly reignites the upper flame. Phosphorus compounds emit green band emissions at 510 and 526 nm that are due to HPO species. Sulfur compounds emit a series of bands from excited diatomic sulfur; the most intense is centered around 394 nm. Phosphorus and sulfur can be detected simultaneously by attaching a photomultiplier tube and an interference filter for sulfur on one side of the flame, and a photo-

multiplier tube with an interference filter for phosphorus on the opposite side of the flame. The detector response to phosphorus is linear, and the response to sulfur depends on the square of its concentration. Carbon dioxide and organic impurities in the makeup and carrier gases must be limited to below 10 ppm. The quenching effect of carbon dioxide is very significant.

The Photoionization Detector

The photoionization detector (PID) is a highly selective and sensitive detector for chemical compounds containing aromatic components. The PID is a concentration-sensitive detector with a response that varies inversely with the flow rate of the carrier gas. A typical PID has two functional parts: an excitation source and an ionization chamber. The excitation source may be a discharge lamp excited by direct current, radio frequency, microwave, or a laser. The discharge lamp passes ultraviolet radiation through the column effluent from one of several lamps with energies ranging from 8.3 to 11.7 eV. Photons in this energy range ionize most organic species, but not the permanent gases. A potential of 100–200 V is applied to the accelerating electrode to push the ions formed by UV ionization to the collection electrode at which the current is measured. The most popular PID lamp is the 10.2-eV, which has the highest photon flux and therefore the greatest sensitivity. There are certain applications in which the 9.5-eV lamp is preferable to the 10.2-eV lamp; these include aromatics in an aliphatic matrix, mercaptans in the presence of H_2S, and amines in the presence of ammonia.

The discharge ionization detector (DID) uses far-ultraviolet photons to ionize and detect sample components. Helium gas is passed through a chamber in which high-voltage electrodes generate a glow discharge and cause it to emit a high-energy emission line at 58.84 nm This energy passes through an aperture to a second chamber in which it ionizes all gas or vapor species present in the sample stream that have an ionization potential less than 21.2 eV (which embraces practically all compounds including hydrogen, argon. oxygen, nitrogen, methane, carbon monoxide, nitrous oxide, ammonia, water, and carbon dioxide). A polarizing electrode directs the resulting electrons to a collector in which they are quantitated with a standard electrometer.

The Tandem PID/FID Combination Detector

The tandem PID/FID combination detector system is available commercially and incorporates the photoionization and flame ionization detectors. With both detectors in tandem, dual detector traces for benzene, toluene, ethyl benzene, and xylenes are possible, eliminating the need for two sepa-

rate analyses. Both detectors can be used separately if so desired, and excellent results can be obtained with either packed or capillary columns. The first commercially available tandem PID/FID detector with no transfer lines eliminates the transfer line and improves peak shape and performance and enables the analyst to obtain screening and confirmatory information on sample in only one injection. The sample stream elutes from the column through the detector's reaction chamber, where it is continuously irradiated with high-energy ultraviolet light. When compounds that have a lower ionization potential than that of the irradiation energy (10.2 eV with a standard lamp) are present, they are ionized. The ions formed are collected in an electric field, producing an ion current that is amplified and output by the gas chromatograph's electrometer. The sample stream flows from the PID into the FID, which uses a flame produced by the combustion of hydrogen and air. As the analytes pass through this flame, they are ionized and attracted to the collector electrode due to an applied electric field in the ionization chamber. The collected ions produce a current proportional to the amount of sample in the flame. The PID shows the aromatic compounds, while the FID will detect all organic compounds present in the sample.

The Electrolytic Conductivity Detector

Because of its high versatility, the electrolytic conductivity detector (EICD) detector is used in analysis of plastic additives and solvents requiring high sensitivity and selectivity. When compared to other selective detectors, such as the nitrogen–phosphorus detector or the electron-capture detector, electrolytic conductivity detector chromatograms typically are much cleaner. In the electrolytic conductivity detector, also called the Hall detector, organic compounds in the effluent are first converted to carbon dioxide by passing the column eluent through a high-temperature reactor in which the hetero atoms of interest (halogen-, sulfur- and nitrogen-containing compounds) are converted to small inorganic molecules. The reaction-product stream is then directed into a flow-through electrolytic conductivity cell. Changes in electrolytic conductivity are measured. Ionic material is removed from the system by water that is continuously circulated through an ion-exchange column. The combustion products may be mixed with hydrogen gas and hydrogenated over a nickel catalyst in a quartz-tube furnace. Ammonia is formed from organic nitrogen, HCl from organic chlorides, and H_2S from sulfur compounds. If one wants to detect halogen compounds, a nickel reaction tube, hydrogen reaction gas, a reactor temperature of 850–1000°C, and 1-propanol are used. Under these conditions, compounds containing chlorine will be converted to HCl, methane, and water. The HCl will

dissolve in 1-propanol and change its electrolytic conductivity, whereas the nonhalogen products and will not dissolve in the alcohol and not change its conductivity to any significant degree. In the detection of sulfur compounds, the compound must be converted to SO. Collection of SO in methanol containing a small amount of water converts the SO into ionic species. Although water is a satisfactory solvent for the sulfur or halogen modes, water containing an organic solvent is preferred for the nitrogen mode [9].

Mass Spectrometer and Fourier Transform Infrared Detectors

The mass spectrometer is a very widely used detector in gas chromatography. More detailed information about the use and capabilities of the mass spectrometer are presented in the chapter on mass spectrometry. The Fourier transform infrared (FT-IR) detector is also used in GC to provide structural information about components eluting from the GC column. The FT-IR detector is nondestructive and is often used in line with the mass spectrometer. This combination of detectors provide two very powerful complementary pieces of information for structural elucidation of analytes being eluted from the GC column. The FT-IR can also be used as a single detector and in many instances is also used off-line to identify components eluting from the GC column. In this instance, the components are trapped in a cool medium to prevent thermal losses and then analyzed off-line by FT-IR [10–13].

Other Gas Chromatographic Detectors

The Chemiluminescence-Redox Detector

The chemiluminescence-redox detector (CRD) is based on specific redox reactions coupled with chemiluminescence measurement. An attractive feature of this detector is that it responds to compounds such as ammonia, hydrogen sulfide, carbon disulfide, and sulfur dioxide. Hydrogen peroxide, hydrogen, carbon monoxide, sulfides, and thiols that are not sensitively detected by flame ionization detection can be detected with the CRD detector. Compounds that typically constitute a large portion of the matrix of many industrial samples are not detected, thus simplifying matrix effects and sample cleanup procedures for some applications.

The Helium Ionization Detector

The helium ionization detector (HID) is often used for the detection of inert gases.

The Surface Ionization Detector

Over the past few years, surface ionization detectors (SIDs) have been given considerable attention for the determination of organic compounds with low ionization potentials. Recently, however, a novel design based on hyperthermal positive surface ionization has been available. The primary requirement for the operation of this detector is the use of a supersonic free jet nozzle to introduce the sample to a high-work-function surface of rhenium oxide. The primary advantage of this new SID is that it produces a higher sensitivity for all organic compounds, providing a universal GC response.

The Ion Mobility Detector

The number of applications of ion mobility spectrometry (IMS) as a detector for gas chromatography continues to grow. In recent years, much of the emphasis on ion mobility detection after gas chromatography has been in the area of portable analytical instruments. IMS has been used as a detection method for pyrolysis GC.

Isotope Ratio Mass Spectrometry

Isotope ratio mass spectrometry (IR-MS) is used with GC for the high-precision measurement of isotopic ratios of D/H, $^{13}C/^{12}C$, and $^{15}N/^{14}N$ from organic mixtures. In general, gas chromatography is coupled to isotope ratio mass spectrometry via a combustion furnace [9].

Inductively Coupled Plasma Ionization

A powerful technique for the separation and speciation of volatile organometalic compounds is capillary gas chromatography coupled to inductively coupled plasma mass spectrometry (ICPMS) The main advantage of GC-ICPMS is that the total analyte is transferred into the ICPMS without loss due to nebulization. In some instances the interface does not require any changes in the ICP and can be completed in a relatively short time. Applications of GC/ICPMS include analysis of organometallic components.

Combination Detectors

The ability to combine GC detectors in a single analysis is a powerful approach for the investigation of complex mixtures and the identification of unknown compounds. Combinations of various detectors have also been used in novel ways to solve analytical problems during the past few years.

THE GC OVEN: TEMPERATURE CONTROL

The purpose of the oven is to ensure that the column is either kept at a constant temperature (isothermal GC) or programmed during the run. The temperature should be monitored, adjusted, and regulated at the injection port, in the oven surrounding the column, and at the detector. The temperature of the injection port must be sufficiently high to vaporize instantly the sample, yet not so high that thermal decomposition or molecular rearrangement can occur. The column temperature need not exceed the boiling point of the sample in order to keep the analytes in their vapor phases. Actually, the column will produce better separations if the temperature is below the sample's boiling point (above its condensation point), in order to increase the interaction with the stationary phase. The smaller the amount of the stationary phase, the lower is the temperature at which the column can operate: open tubular columns are usually required to run at lower temperatures than packed columns. The temperature of the detector housing should be sufficiently high so that no condensation of the effluent occurs, yet not so high that the detector malfunctions. In general, the detector must be kept at a higher temperature than the injector and higher or equal to the highest temperature of the CG column temperature program.

Isothermal Operation

Selecting the column temperature for isothermal operation is a complex problem. Although most often temperature-programmed analysis is preferred, in some instances isothermal analysis is convenient (i.e., when uniform flow rate due to detector response is required). A sample whose components have a wide range of boiling points cannot be satisfactorily chromatographed in a single isothermal run. A scouting run at a moderate column temperature may provide good resolution of the lower-boiling compounds but requires a lengthy period for the elution of high-boiling materials. One solution is to raise the column temperature to a higher value at some point during the chromatogram so that the higher-boiling components will be eluted more rapidly and with narrower peaks. A better solution to this problem is to change the band migration rates during the course of separation by using temperature programming.

Temperature Programming

In temperature programming, the sample is injected into the chromatographic system when the column temperature is below the lowest-boiling-point component of the sample, preferably 90°C or below. Then the column temperature is raised at some preselected heating rate. As a general rule, the

retention time is halved for a 20–300°C increase in temperature. The final column temperature should be near the boiling point of the final solute but should not exceed the upper temperature limit of the stationary phase. Heating rates of 3–50°C/minute should be tried initially and then fine-tuned to achieve optimum separation.

DATA RECORDING AND PROCESSING

Chromatography data acquisition, processing, and archiving can be performed with the aid of a simple integrator or strip-chart recorder, with a highly sophisticated computer data system, or with any system in between. There are a great many choices for the analyst today. Depending on the type of analysis, the requirements may vary. For example, for high-speed GC, fast data acquisition systems are a prerequisite.

For complex operations with numerous instruments, a chromatographic network data system with the power needed to organize, store, and retrieve chromatography data quickly and easily is highly recommenced. Most commercially available systems offer the flexibility of working with a single system and then going to multiple instruments while still conserving the simplicity of the client personal computer. One of the most important and unique design capabilities of these systems is the fact that a single workstation will have exactly the same look and feel as very large client/server systems. Users have the ability to grow from a small single user systems to large client/server systems without the need to learn a new system protocol each time they expand.

The specific capabilities of simple or complex data acquisition and processing devices can vary significantly from source to source and is beyond the scope of this chapter.

SAMPLE PREPARATION

A key to successful chromatographic analysis lies in proper sample preparation. Ideally, it is preferred to dissolve the sample in a suitable solvent and analyze that solution directly, provided the presence of dissolved polymer does not complicate the chromatographic analysis. These cases are indeed rare. Normally, filtration or precipitation followed by final filtration is desirable to remove interferences in sample components (polymers) and higher-molecular-weight components. This approach works well when the polymers are, first, soluble, and second, can be precipitated with an antisolvent. Less soluble polymers, such as highly crystalline resins, require extraction to remove the components of interest from the resin matrix. Numerous extraction techniques (supercritical fluid extraction, solvent extraction, resin dissolution followed by antisolvent precipitation, etc.) are also available [14].

In many instances the dissolved polymer matrix (along with the components of interest in the solution) can be injected in the GC instrument directly (Fig. 7). This requires that the polymer be retained in the injector liner and that it is thermally stable at the injector temperatures of the analysis to minimize undesirable matrix interference. In reality this approach can work relatively well for some polymer systems if the injector liner is replaced or cleaned on a routine basis to prevent or minimize column contamination or degradation. A relatively new device which permits injection of polymer solutions for trace analysis of residual solvents or additives is the high-volume injector. This is further described at end of this chapter. In theory, any type of sample can be introduced into a GC for analysis. All that is required is the right accessory to provide the right conditions for sample introduction to make the sample amenable to gas chromatographic analysis. This includes GC-pyrolysis (for polymers and high-molecular-weight additives), headspace (to separate volatile components from nonvolatile matrix), purge-and-trap, thermal desorption devices (to extract volatile components from polymer matrix), etc. These techniques are presented in more detail later in the chapter.

A good approach for sample cleanup for GC analysis is solid-phase extraction (SPE). SPE is used primarily to clean up samples for analysis

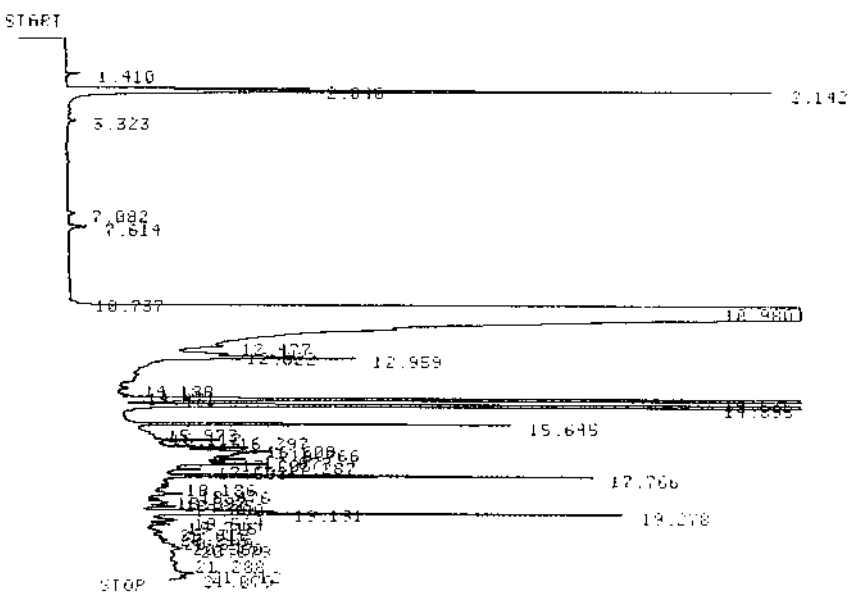

Figure 7 Analysis of trace monomers by GC by injection of whole polymer solution. Frequent change of the injector liner is required for this technique.

and/or concentrate samples to improve detection limits. SPE techniques usually provide better sample cleanup and recovery than liquid–liquid extraction techniques. SPE uses small volumes of common solvents, does not require the use of highly specialized laboratory equipment, and allows rapid sample preparation. A liquid or solid sample is dissolved in a proper solvent and poured into the conditioned SPE cartridge. Vacuum or pressure is used to force the sample through the sorbent in the cartridge. An SPE vacuum manifold can be used to process multiple cartridges simultaneously. Usually, SPE methods are designed to retain the analytes of interest; other sample components similar to the analytes may also be retained. A properly designed SPE method will minimize the amount of unwanted sample components retained by the sorbent. Weakly retained sample components are rinsed from the sorbent using a solvent. The analytes of interest are then eluted from the sorbent using a second solvent. This solvent is collected for analysis. In some cases, the analytes of interest are allowed to pass through the sorbent without being retained and are collected as they exit the sorbent. Most of the sample interferences are retained by the sorbent and thus are isolated from the analytes of interest. In most cases, retaining the analytes of interest followed by elution results in better sample cleanup [15].

SPE cartridges are commercially available from several manufacturers or can be packed by the analyst using commercially available resins to solve individual problems.

The cartridge body usually is a syringe-like barrel made of serological-grade polypropylene. Some manufacturers may also offer glass barrels. The barrel normally terminates in a male luer tip for ease of use. Different sizes of barrels are available to accommodate the various amounts of stationary phase used in SPE cartridges.

The stationary phase (sorbent) is the most important part of an SPE cartridge. The most common SPE phases are bonded silica-based materials. Various silanes are used to attach functional groups to the accessible areas of the silica particle. The functional group determines the identity and chromatographic characteristics of the phase. In addition, several non-silica-based phases are also available. Samples that are dirty, complex, or highly concentrated will require larger amounts of phase for sufficient sample cleanup.

GC ANALYSIS

Quantitative Analysis

Most chromatographic detectors respond to the concentration of the solute and yield a signal that is proportional to the solute concentration that passes through the detector. For these detectors the peak area is proportional to

the mass of the component. This is true if the analyte concentration is located in the detector's working range. Peak quantitation is nornmally based on peak height or peak area.

Modern integrators or computers equipped with signal processing software make peak integration and quantitation a relatively easy task. These devices also provide the flexibility required to process complex chromatograms automatically or manually under different sets of conditions. In the case of overlapping peaks and complex chromatography, special algorithms allot areas to each component. During isothermal runs the software can automatically alter the slope sensitivity with time. This allows both sharp, narrow peaks and low, broad peaks to be measured with equal precision. If the peak height or peak areas are measured, there are four main methods that can be used to translate these numbers to the amounts of solute.

Area Normalization

For application of the area normalization method, the entire sample must elute from the column and all components must be separated. This is not a requirement if the composition of components not eluting from the GC is known or can be calculated by a different technique. The area under each peak is measured and corrected (if necessary) by a response factor. All the peak areas are added together. The percentage of individual components is obtained by multiplying each individual calculated area by 100 and then dividing by the total calculated area. Results are not correct if a sample component does not elute from the column or does not give a signal with the detector used. This type of report can be automatically obtained from a GC integrator or a computer acquisition system.

Internal Standard

A known quantity of an internal standard can be injected along with known amounts of the compound of interest. The area versus concentration is calculated to crate a calibration curve. Then an appropriate quantity of the internal standard is added to the raw sample prior to any sample analysis. The peak area of the standard in the sample run is compared with the peak area when the standard is run separately. This ratio serves as a correction factor for variation in sample size, losses during sample preparation, or incomplete elution of the sample. The internal standard must be completely resolved from adjacent sample components, should not interfere with the sample components, and should never be present in material to be analyzed.

External Standard

Calibration curves for each component can also be prepared from pure standards using identical injection volumes and operating conditions for standards and samples. The concentration of solute is read from its calibration curve. In this approach, only the areas of the peaks of interest need to be measured. This method is highly operator-dependent and requires good laboratory technique. The sample amount (volume) to be injected for this approach is critical. The variation in injection volume will compromise results, so it is recommended to use an auto-injector whenever possible for this technique.

Standard Addition

The standard addition approach is useful when only a few samples are to be analyzed. The chromatogram of the unknown is recorded. Then a known amount of the analyte(s) is added, and the sample is reanalyzed using the same reagents, instrument parameters, and procedures. From the increase in the peak area (or peak height), the original concentration can be computed by interpolation. The detector response should be linear for the analyte. Sufficient time should be allowed between addition of the standard and the analysis to allow equilibrium of the added standard with any matrix interferant.

The following equation can be used to calculate analyte concentration:

$$X = \frac{(A_1)(a)}{(A_2 - A_1)}$$

where A_1 = area count of analyte in original chromatogram
A_2 = area count of analyte in chromatogram of spiked sample
X = original concentration
a = known (added concentration)

The amount to spike should be around the expected concentration of the analyte in the original sample. Example: If expected concentration is 1%, spike sample to a known concentration (a) of 1% in sample.

A correction for dilution must be made if the amount of standard added changes the total sample volume significantly. Additions of analyte ranging from twice to one-half the amount of analyte present in the original sample are optimum conditions.

Qualitive Analysis (Identification of Unknowns)

Retention Time

Retention time is widely used in GC analysis as a way to identify components of mixtures. This is due mainly to the fact that retention time under

fixed operating conditions is constant for a particular component. This is readily accomplished by comparing the retention times of the sample components with the retention times of pure standards. Additionally, retention index can be calculated for different analytes. This can be done by using isothermal (GC) elution times. Retention times usually vary in a regular and predictable fashion with repeated substitution groups (homologous series). One must be cautious, however, in interpretation of results because of the possibility of co-elution of an unknown with the standard.

Identification by Ancillary Techniques

Under normal circumstances, retention time is a good tool to identify components by GC. Often, however, retention time alone is not definitive because many compounds have similar retention times. Structural information can be obtained independently from several spectroscopic techniques. This has led to hyphenated techniques, such as gas chromatography-mass spectroscopy, gas chromatography-infrared spectroscopy and others. If spectroscopic, reference spectra are available, confirmation of analyte identity is very likely.

Enhancing GC Analysis

Derivatization Reactions

The majority of analytical derivatization reactions used for chromatography fall into three general reaction types: silation, alklylation, and acylation. These reactions are used to:

- Improve the thermal stability of compounds, particularly compounds that contain certain polar functional groups
- Enhance the volatility of (nonvolatile or polar) compounds
- Improve sensitivity by tagging a molecule that gives higher response with certain detectors

For analysis by gas chromatography, additives containing functional groups such as $-COOH$, $-OH$, $-NH$, and $-SH$ are of primary concern because of their tendency to hydrogen-bond. This affects the inherent volatility and thermal stability. Many derivatization methods are also intended to enhance detectabiliry by special detectors such as NPDs or ECDs.

Silylation

Silyl derivatives, which are widely used for gas chromatographic applications, are formed by the replacement of active hydrogens atoms from acids, alcohols, thiols, amines, amides, enolizable ketones, and aldehydes with trimethylsilyl groups. A wide variety of reagents are available. These

reagents differ in their reactivity, selectivity, side reactions, and the character of the reaction by-products from the silylation reagent. The trifluoro group is commonly used for sensitizing substances to detection by electron capture. This derivatization method makes feasible the quantitative and qualitative analysis of amino acids.

Alkylation

Alkylation is used in the derivatization of additives and analytes containing active hydrogen atoms, aliphatic or aliphatic-aromatic substituents. This method is also used to modify compounds containing acidic hydrogen, such as carboxylic acids and phenols, which are converted into esters. Alkylation reactions can also be used to prepare ethers, thioethers and thioesters, N-alkylamines, amides, and sulfonamides. Although silyl derivatives of carboxylic acids are easily formed, these compounds suffer from low stability.

Acylation

Acylation is used to convert compounds containing active hydrogens into esters, thioesters, and amides through the action of carboxylic acid or a carboxylic acid derivative. The use of deuterated derivatives provides critical information for interpreting the mass spectra of silylated compounds.

Reagents to Enhance Detectability

When the detection sensitivity of certain analytes is low, the detection can be improved by adding (tagging) a component to which a specific detector is highly sensitive. Addition of halogen-containing tags enhances detectability and specificity for analysis by ECD. Addition of nitrogen-containing tags enhances detectability and specificity for analysis by NPD.

SAMPLE INTRODUCTION/SAMPLE CONCENTRATION

Pyrolysis Gas Chromatography

Pyrolysis gas chromatography has been used extensively to determine compositional analysis of polymeric materials. It is a technique that has long been used in a variety of investigative fields because it produces volatile compounds from macromolecules that are neither volatile nor soluble. Examples are polymers, rubbers, paint films, and resins. Volatile fragments are formed and introduced into the chromatographic column for analysis. A polymer can be used as an example to illustrate the use of this technique, which consists of two steps. The injection port is heated to about 250C;

when the sample is injected, the volatile ingredients that are driven off provide a fingerprint of the polymer formulation. Then the pyrolysis step develops the fingerprint of the nonvolatile components. Known monomers of suspected polymers can be injected with a microsyringe for identification of the peaks of an unknown pyrogram [15–18]. Specific identification of the peaks appearing in pyrograms is most effectively carried out by directly coupling gas chromatography-mass spectrometry together with the retention data of the reference samples. Gas chromatography-Fourier transform infrared spectrometry also can provide effective and provides complementary information.

Pyrolyzers can be classified into three groups:

1. Resistively heated electrical filament
2. High-frequency induction (Curie point)
3. Furnace types

The resistively heated pyrolyzer uses either a metal foil or a coil as the sample holder. The heat energy is supplied to the sample holder in pulses by an electric current. This permits stepwise pyrolysis at fixed or increasing pyrolysis temperatures. This feature makes it possible to perform discriminative analysis of volatile formulations and high polymers in a given compound without any preliminary sample treatment.

The Curie-point pyrolyzer uses the Curie points of ferromagnetic sample holders to achieve precisely controlled temperatures when the holder containing the sample is subjected to high-frequency induction heating. Foils of various ferromagnetic materials enable the analyst to select pyrolysis temperatures from 150 to 1000°C.

In the furnace pyrolyzer type, the sample is introduced into the center of a tubular furnace held at a fixed temperature. Temperature is controlled by a proportioning controller that utilizes a thermocouple feedback loop.

Pyrolysis GC has been used in the determination of compositional analysis and microstructure of chlorinated polyethylene (CPE). This method utilized specific aromatic compounds which were formed through dehydrochlorination of trimers after pyrolysis of CPE polymers at elevated temperatures. The composition and microstructure calculation was based on the difference between the levels of ethylene and vinyl chloride trimers formed [19–22].

A pyrolysis gas chromatography has also been used to study the composition and microstructure of styrene/methyl methacrylate (STY/MMA) copolymers. The composition was quantified by pyrolysis-GC using monomer peak intensity. Because of the poor stability of methyl methacrylate oligomers, neither MMA dimer nor MMA trimers were detected under normal pyrolysis conditions. The number-average sequence length for STY

was determined by pure and hybrid trimer peak intensities. The number-average sequence length for MMA was determined by using formulas that incorporate composition and the number-average sequence length of STY [23].

Thermal degradation mechanisms under pyrolysis conditions have also been studied using a variation of this technique. It has been shown that the enhanced monomer production of poly(alkylvinylcarboxylate) during pyrolysis makes possible qualitative analysis of poly(vinylcarboxylic acid) through its derivatized alkyl ester. In this study, copolymers containing poly (methacrylic acid) and methacrylic acid were used to demonstrate the pyrolysis gas chromatography qualitative analysis of derivatized polymer [18].

Purge-and-Trap

The analysis of low levels of volatile organic compounds in samples is commonly performed using the technique of purge-and-trap gas chromatography. Using this technique it is possible to detect and identify various flavors, fragrances, off odors, and manufacturing by-products in a wide diversity of products and chemical formulations, colloidal suspensions, and liquid pastes, including perfumes, food products, blood, and latex paint. In the purge-and-trap method, samples are contained in a gas-tight glass vessel. With a sparging needle dipping nearly to the bottom of the sample vessel, the sample is purged by bubbling high-purity helium or nitrogen through the sample. If desired, the sample can be heated for the removal of higher boilers, but the temperature should be kept well below the boiling point of the sample. Volatile compounds are swept out of the sample and carried into and trapped in an adsorbent tube packed with Tenax or other adsorbent material such as activated carbon. Tenax has a low affinity for water. Also, a dry-gas purge is added just before the adsorption tube. Volatile organic materials can be efficiently collected from a relatively large sample, producing a concentration factor that is typically 500- to 1000-fold greater than the original and resulting in detection limits of parts per billion or parts per trillion (Fig. 8). The trapped material on the adsorbent is heated to release the sample and then backflushed using the GC carrier gas. This sweeps the sample directly onto the GC column for separation and detection by normal GC procedures. Trapped samples can easily be stored or shipped to another site for analysis.

Headspace Sampling

Headspace sampling is another technique that is widely used in the plastics industry for the analysis of volatile components in plastic resins. A major advantage of headspace GC is the relative cleanliness of the sample entering

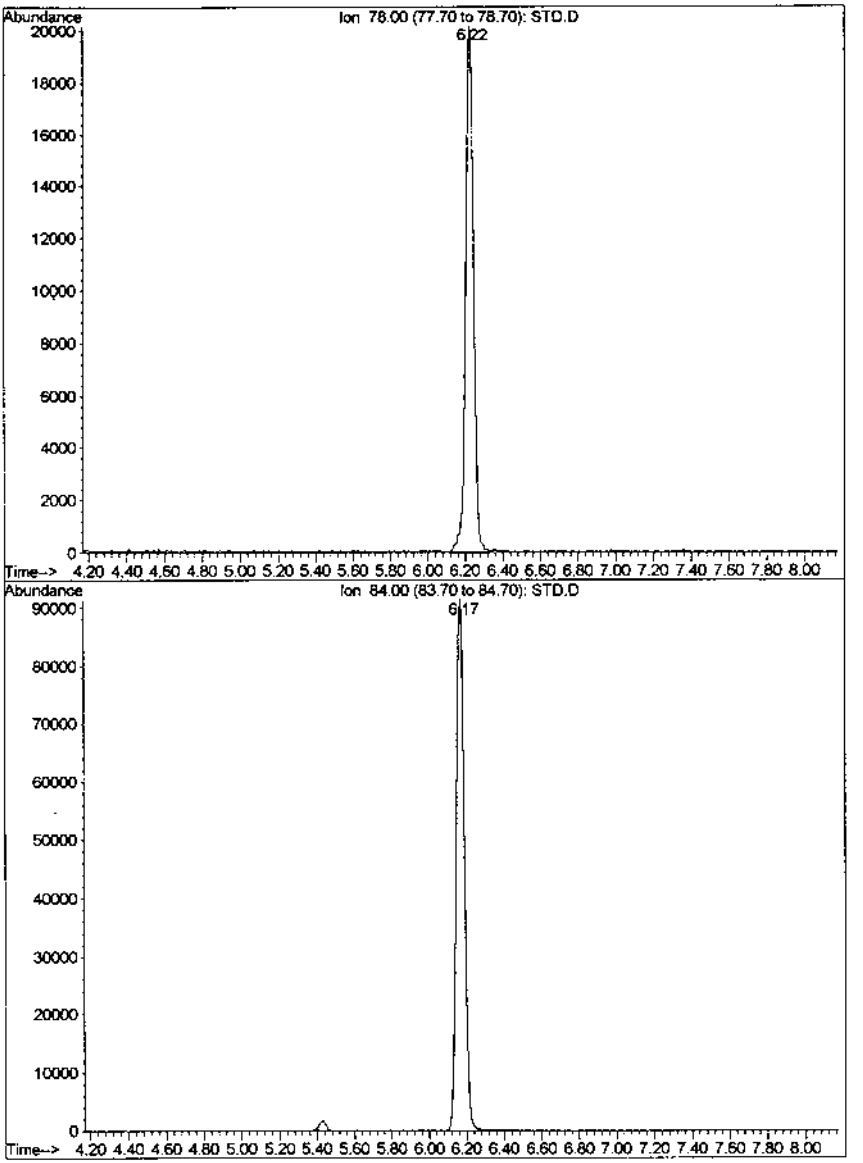

Figure 8 GC chromatogram: trace analysis of benzene in polymer by purge-and-trap GC-MS. The single-ion signal for benzene (m/z, 78) is displayed on top, while the single-ion signal for deuterated benzene (m/z, 84) is displayed below.

the GC (gas phase), free from nonvolatile, matrix interferences. This in turn results in chromatography of excellent signal-to-noise ratio. Headspace sampling can be done when only the vapor above the sample is of interest and the partition coefficient allows a sufficient amount of analyte into the gaseous phase. This is normally not a severe limitation, since temperature or matrix manipulation can be used to drive the compounds of interest into the vapor phase. Samples may be solid or liquid.

In a typical analysis a measured amount of sample, and often an internal standard, are placed in a vial, and then the septum and cap are crimped in place. The vials, contained in a carousel, are immersed in a heated oven or silicone oil bath operating from ambient temperature to up to 300C. A heated flexible tube that terminates in a needle samples each vial in turn. A gas-sampling valve provides a fixed volume of vapor sample to transfer into the GC injection port [19].

Headspace sampling is an excellent technique for the analysis of compounds that produce, odors in many commercial products, such as plastics, rubbers, paints, resins, etc. Interfacing of a headspace GC with a mass spectrometer provides valuable information for the identification of such components. Figure 9 shows the output from head space-GC analysis of residual benzene and toluene in polymeric material.

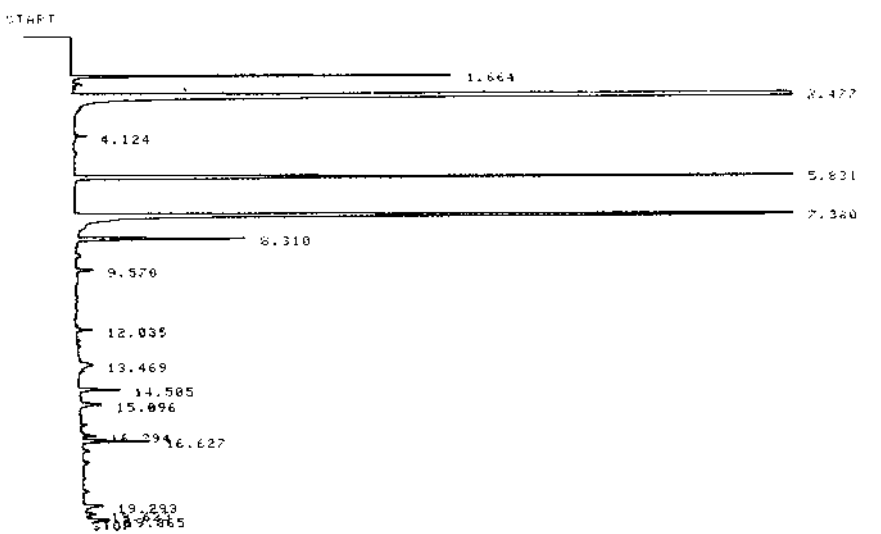

Figure 9 GC chromatogram: trace analysis of benzene and toluene in polymer by headspace GC-FID.

Thermal Desorption

Thermal desorption permits the analysis of plastic resins and other solid material samples without any prior solvent extraction or other sample preparation. Solid samples between 1 and 500 mg are placed inside a glass-lined, stainless steel desorption tube between two glass-wool plugs. After attaching a syringe needle to the tube and then placing the tube in the thermal desorption system, the desorption tube is purged with carrier gas to remove all traces of air or oxygen. The preheated heater blocks are closed around the adsorption tube to desorb samples at temperatures from 20 to 350°C and for program desorption times from 1 s up to 5 min or more. The procedure permits the thermal extraction of volatiles and semivolatiles from the sample directly into the GC injection port. The GC column is maintained at subambient temperatures or at a low enough temperature to retain any samples at the front of the GC column during the desorption step. This enables the desired components to be collected in a narrow band on the front of the GC column [20]. As an alternative to cryofocusing, a thick-film capillary column or a packed column with a high loading capacity may be used. After desorption is complete, the needle is removed and the GC gas turned on. The components trapped on the front of the GC column are separated and eluted via a temperature program in the GC oven. By selection of the desorption temperature, the number and molecular-weight distributions of components in the samples can be selected. Adsorbent tubes with samples collected during either dynamic headspace purging or purge-and-trap of liquids can also be analyzed with a thermal desorption unit [20,21].

Solid-Phase Microextraction

Solid-phase microextraction (SPME) is a straitforward sample extraction process. As pointed out above, the extraction of organic compounds from a sample matrix usually consists of purge-and-trap, thermal desorption, or headspace methods for concentrating volatiles; and liquid–liquid extraction, solid-phase extraction, or supercritical fluid extraction for semivolatiles and nonvolatiles. These methods have various drawbacks, including high cost and long sample preparation times. This relatively new sample preparation technique eliminates this to extract organic compounds from various matrices. SPME requires no solvents or complicated apparatus. It can concentrate volatile and nonvolatile compounds, in both liquid and gaseous samples, for analysis by GC or GC-MS. An SPME unit consists of a length of fused silica fiber coated with a phase material. The phase can be mixed with solid adsorbents, e.g., divinylbenzene polymers, templated resins, or porous carbons. The fiber is attached to a stainless steel plunger in a

protective holder. In a relatively short step (a few minutes), the organic compounds of interest are concentrated by direct exposure to the fiber and subsequently injected directly into the instrument for characterization.

SPME has been applied to the analysis of various volatile components in plastic resins with gas chromatography with great success. Recently, it has also been demonstrated that SPME can be conveniently used with high-speed GC for quick sample analysis. While SPME offers a rapid sampling procedure for volatile analytes, the gas chromatographic analysis becomes the limiting factor in the speed of analysis. High-speed GC has been used to allow for the analysis of volatile components a factor of 10 times more rapidly than conventional GC. SPME allows the selectivity necessary to make these determinations, while rapid gas chromatography provides great speed of analysis, making this combination an excellent candidate for analysis of various products in the laboratory.

MULTIDIMENSIONAL GAS CHROMATOGRAPHY

Multidimensional gas chromatography has enjoyed a dramatic increase in usage recently to solve problems of materials characterization. Much activity has taken place in the coupling of liquid chromatography (LC) with GC, despite a first impression of apparent incompatibility of LC and GC for the analysis of large nonvolatile molecules. This field has further benefitted by new developments in high-volume injectors and sophisticated switching devices. However, in LC-GC, the liquid chromatograph has been used principally for prefractionation of complex mixtures to isolate a targeted GC-compatible substance. The availability of high-temperature GC should provide a brighter future to this approach.

In multidimensional gas chromatography, the components of a sample are separated by using series-connected columns of different capacities or selectivities. Two common multicolumn configurations are the packed-column and capillary-column combination and two capillary columns in series [21,22,24]. Two independently controlled ovens may be needed, and such a configuration is available commercially. In addition to decreased analysis time, this arrangement provides an effective way of handling samples containing components that vary widely in concentration, volatility, and/or polarity. Used in conjunction with techniques such as heart-cutting, backflushing, and peak switching, useful chromatographic data have been obtained for a variety of complex mixtures.

NEW TECHNOLOGIES IN GAS CHROMATOGRAPHY

Recent developments in gas chromatography have given this technique an additional boost in terms of power and attractiveness to solve analytical

problems. New technical developments deserving special attention are high-temperature gas chromatography, high-speed GC (fast GC), retention-time locking, and high-volume injectors.

High-Temperature Gas Chromatography

High-temperature gas chromatography has extended the capability of GC analyses to analyses of samples previously not possible by this technique. Oven temperatures up to 450°C can be reached with this new equipment. A cool on-column injector, temperature programmable, is normally required for these applications, as well as high-temperature, aluminum-clad capillary columns that can take these temperatures without column bleeding. Most conventional GC detectors are available for this applications. While analytes of molecular weight of about 800 amu represent the upper limit for conventional CG, the upper limit for high-temperature GC is about 1200–1400 amu, depending on the nature of the analytes of interest. This means that many of chemical compounds previously analyzed by liquid chromatography can now be easily analyzed by high-temperature GC. Figure 10 illustrates the chromatographic and temperature capabilities of high-temperature GC.

Aluminum-Clad Columns

High-temperature capillary columns which are capable of operating at temperatures up to 420°C are coated with a thin (approximately 20 μm) uniform layer of aluminum replacing the conventional polyimide outer coating (typical maximum temperature of 370°C). Aluminum-clad columns offer excellent heat transfer and the same flexibility and inert fused silica surface as the polyimide coated columns. These columns are ideal for the analysis of a wide variety of high-molecular-weight compounds such as crude oils, waxes, polymers, etc. In order to obtain the best results with any of these high-boiling compounds, the injection technique is very important. Either cold on-column, movable needle, or programmable temperature injectors must be utilized to prevent component discrimination.

Stainless Steel Columns

The inertness of stainless steel columns matches that of fused silica and is derived from a multistep process which utilizes a multilayer pretreatment of the inner surface of the stainless steel. Each layer is chemically stable at elevated temperatures and has the same or higher mechanical properties as the steel tubing. The layers are chemically bonded together. Stationary phases are easily bonded to this stable inert surface, resulting in high-performance columns.

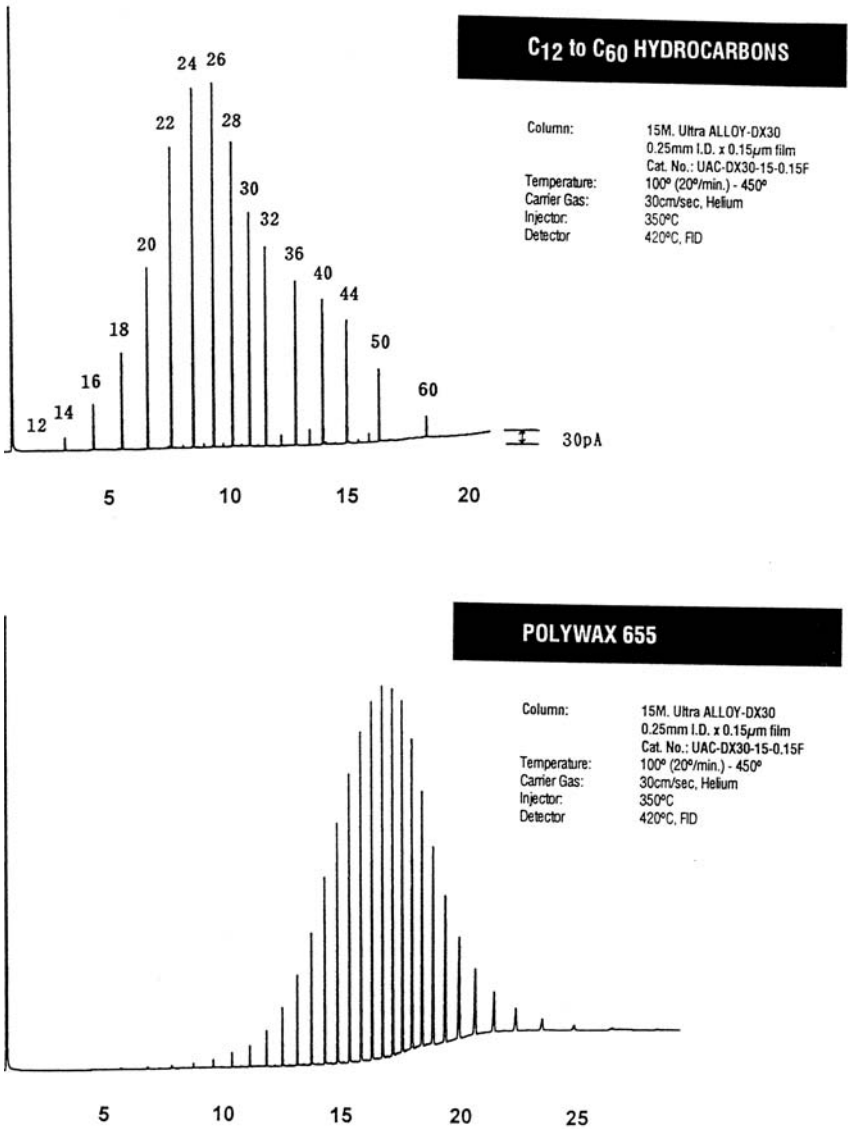

Figure 10 Analysis of high-molecular-weight waxes, illustrating the power of high-temperature GC columns. Note the high temperature limit for the column and the relatively short retention time. (Courtesy of Quadrex Corporation.)

Stainless steel columns are not lined with fused silica, which can crack or flake off when flexed or bent, thus exposing active sites. As a result, these columns can be tightly coiled to fit small GC ovens. Stainless steel capillary columns are available in three internal diameters, the standard 0.25-mm, 0.50-mm, and 0.80-mm I.D., and in lengths up to 60 m.

High-Speed Gas Chromatography

In recent years, the need for rapid GC analysis has led to the development of gas chromatographs with fast separation times. Several recent technologies have been developed to decrease analysis times in GC, such as using short narrow-bore columns and optimizing the flow rates, temperature rates, and sample focusing parameters. Two major requirements for successful fast GC are fast data acquisition rates and fast detector response.

High-speed GC offers several benefits:

Quicker results for timely decisions about sample or product fate
Faster sample turnaround times
Lower operating costs per sample analysis
Ability to handle more samples with fewer pieces of equipment

There are three major commercially available systems providing high-speed GC. They use different approaches to accomplish high speed of analysis. Their principles and capabilities are briefly described below.

High-Speed GC Using a Standard Instrument

High-speed GC analysis is now possible with the recent development of GC equipment that allows rapid heating of the CG oven as well as precise control of the carrier-gas pressure. Although this is not yet a widely used approach in chromatography, it has already been demonstrated that this new technique can reduce the analyses time by a factor of 5 or better, compared with conventional GC analyses. The advent of high-frequency sampling devices has been crucial in the development of this new technology.

One of the many remarkable features of modern GC instruments is their ability to perform fast GC without special modifications or expensive accessories. High-speed GC can be achieved using short, narrow-bore columns, resulting in analyses that are 5 times faster than with traditional methods run on conventional laboratory GCs. These GCs offer the capability to carry out fast GC without the need for cryofocusing or thermal desorption devices which may limit the flexibility or performance of the instrument. Properly configured for fast GC, the system can perform all types of analyses using existing detectors, injectors, and flow controllers.

Minimal system requirements are a GC equipped with electronic pneumatic control (EPC), off-the-shelf capillary columns, split/splitless or on-column inlets, standard detectors optimized for capillary columns, and a fast acquisition data system. At any time, users can switch from fast GC back to the original method without major difficulties, or optimize new methods to meet new analytical demands.

Flash GC

Flash temperature programming is a new technique for rapidly heating capillary GC columns. The technique utilizes resistive heating of a small-bore metal sheath that contains the GC column. This technology is based on the flash GC system, an innovative chromatographic system that accomplishes in 1–2 min what takes a conventional GC from 30 min to a 1 h or more. The flash GC can be over 20 times faster than conventional GC (Fig. 11) and is also more sensitive and far more versatile. Additionally, the flash GC can be used to concentrate samples as part of its purge-and-trap capabilities. On-column cryotrapping procedures can be accomplished within the system and incorporated as part of the very fast analysis procedure.

Development of the flash GC began in the 1980s. The first application was for the detection of explosives. The basic concepts, the proof of principle, and the initial designs were initially classified by the U.S. government. The patents were declassified in the early 1990s. and are now been issued to produce this equipment for public use.

Flash GC systems feature the following.

1. Reduction of total system cycle time exceeds other forms of temperature programmed "high-speed gas chromatography." This is possible thanks to rapid cool-down capabilities.
2. Increased sensitivity over conventional GC. The chromatographic peaks produced by the flash GC are typically only a fraction of a second wide. With mass-sensitive detectors, such as the FID, narrowing the peak widths of the same sample will give the user an additional signal-to-noise advantage.
3. Conventional GC columns 6 m or 12 m long are used in the flash column assemblies; (standard fused silica columns with typical column diameters and coatings are compatible with the flash GC). The flash column consists of a standard column inserted into a metal sheath designed for both rapid heating and cooling.
4. Sample introduction can be by direct on-column injection or isolated from the flash columns using "cold spots." Either method can be optimized for maximum performance.

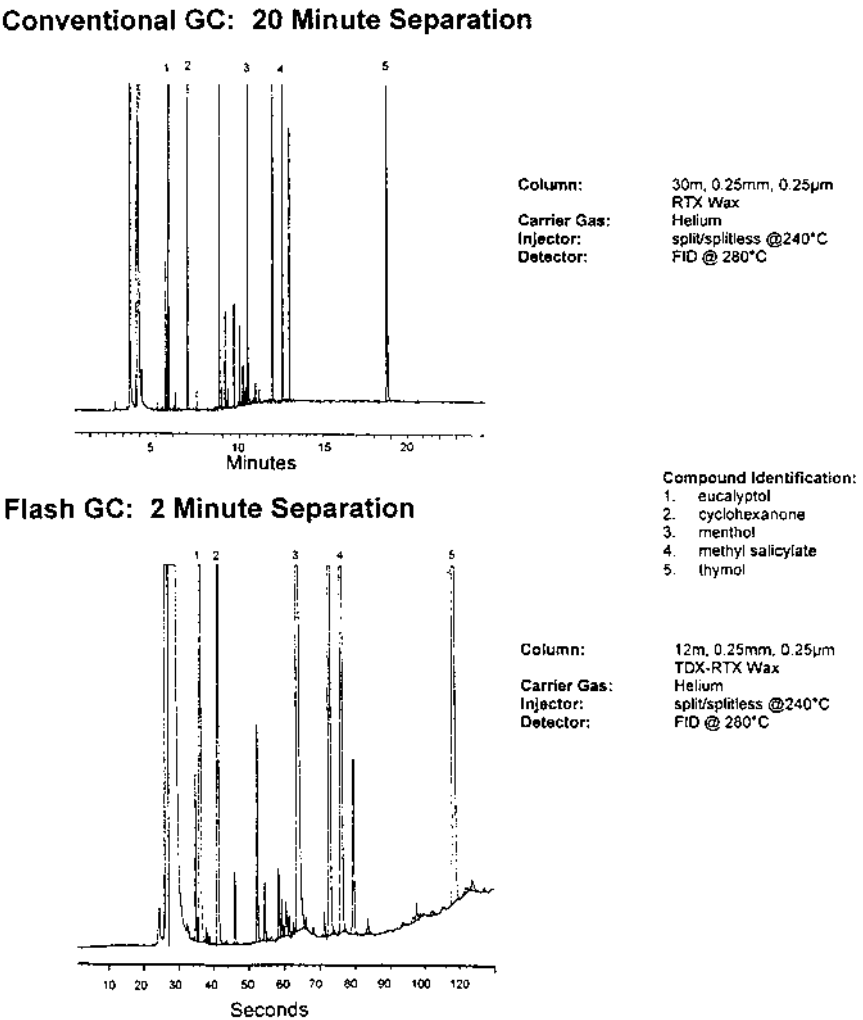

Figure 11 GC chromatograms comparing conventional GC versus high speed flash GC. Notice the reduction in run time by 10-fold by the use of the flash GC versus conventional GC. (Courtesy of Thermedics Detection.)

Samples can be introduced onto the cold spots, which serve to concentrate and focus the sample prior to introduction onto the flash columns. Samples can also be directly injected on to cooled flash columns.

5. The flash-GC comes equipped with up to four cold spots. The cold spots are computer-controlled independently of each other. These cold spots can be heated at rates from 4°C/s to 3000°C per second. Since standard column materials are used in the cold spots, their maximum upper temperatures are limited by the temperature rating of the column selected.
6. Because the sample compounds are typically in the hot zone of the flash columns for only a few seconds, thermally labile compounds, those compounds which are not normally amenable to GC, can often be analyzed.
7. The flash GC comes equipped with exceptionally fast electronics and software designed to handle the high-speed chromatographic data. The on-board A/D can operate at up to 200 Hz, providing 5-ms chromatographic resolution.

In summary, the flash GC provides great speed and flexibility to the analyst for the charaterization of a great variety of chemical compounds. This technology has been proven to work in conjunction with mass spectrometry.

There is also an upgrade kit available to easily convert a conventional GC into a flash GC. It is called the EZ Flash. This kit converts a conventional GC to a flash GC, providing the benefits from the speed and accuracy of flash GC technology with minimal investment. EZ Flash columns mount inside the oven of a conventional GC, replacing the existing column. The system offers column heating rates up to 20°C/s and a temperature control range of ambient to 400°C.

Cryofocusing Technology

Cryofocusing technology permits high-speed GC on already-existing GC equipment. ChromatoFast's proprietary Fast-GC technology enhances conventional capillary gas chromatographs with a novel sample inlet system to allow very rapid separations to take place (Fig. 12). It is ideal for use in a wide range of applications including plastic materials, industrial chemicals, and environmental applications. Using a unique cryofocusing inlet system, samples can be preconcentrated and are subsequently desorbed onto the analytical column in a very narrow band, thus eliminating the band broadening that occurs with conventional inlet systems. It can also be interfaced to other automated sample introduction devices such as autosamplers,

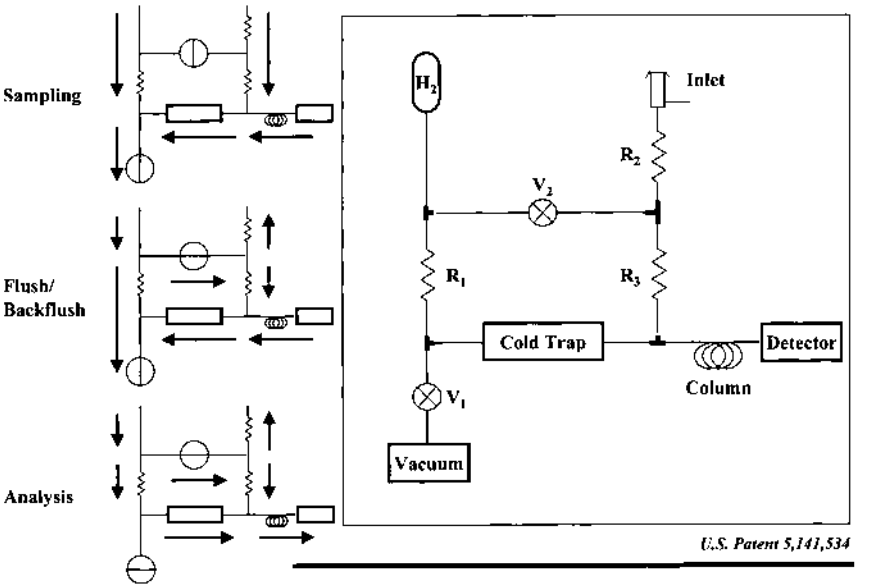

Figure 12 General diagram of a ChromatoFast GC. (Courtesy of ChromatoFast.)

purge-and-trap, headspace, and SPME. The Fast-GC is extremely sensitive, capable of subparts-per-billion detection This approach allows high-speed separations to take place using short lengths of conventional 0.25-mm columns, which provide increased sample handling capacity over microbore columns. Figure 13 shows a typical chromatogram using this technique.

The main advantages and applications of cryofocusing are

Affordable, can be installed on existing GC equipment
At least 10 times faster than conventional GC
Liquid and air analysis capabilities
Compatible with automated sample preparation/introduction devices
Enhanced sensitivity: sub-ppb limit of detection for air analysis
Utilizes conventional 0.25-mm columns and a wide range of stationary phases
Multiple detector options

Figure 12 is a diagram of a ChromatoFast system. This high-speed inlet system can deliver injection bandwidths of 5 ms. The main components

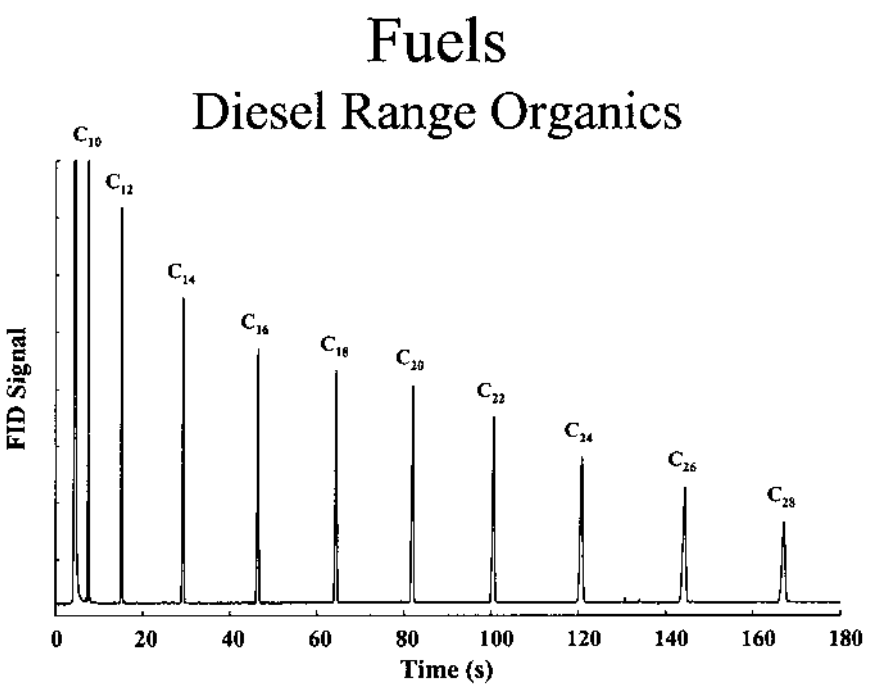

Figure 13 GC chromatogram illustrating the high speed of analysis using ChromatoFast technology. (Courtesy of ChromatoFast.)

include restrictor columns, solenoid valves, source of hydrogen or helium carrier (CG), vacuum pump, detector, and split injector for sample introduction. Short lengths of 0.25-mm capillary columns are typically used at high linear velocities. This provides the maximum rate of plate production as opposed to number of plates. The cold trap consists of a metal tube with inert coating that is cooled using liquid nitrogen and rapidly heated using a capacitive discharge power supply. This technology contains a high level of sophistication with several advantages. Three sequential stages of operation are dictated by the states of valves V1 and V2. All stages are controlled through an automated process for ease of use. Here are summarized the three main stages of operation.

1. *Sampling*. Sample is pulled through R2 and R3 and cryofocused at the right side of the trap. The solenoid valves used in the system are not in the sample flow path. This eliminates problems of sample carryover or decomposition from sample contact with valve surfaces. Since the sample is being pulled onto the trap by the vacuum pump, this system is available as

a separate model designed to sample directly from air or other sample containers. Large amounts of preconcentration can be obtained by varying the duration of the sampling stage.

2. *Flush*. A clean purge flow of carrier gas travels through V2 and splits between R2 and R3. Residual sample in R3 is swept onto the trap and purge flow through R2 eliminates any memory effect or sample carry-over from the split inlet.

3. *Analysis*. The flow reverses in the cold trap and the trap tube is rapidly heated at a rate of up to 100,000°C/s. Because the sample is trapped and injected from the same end of the trap, it is in the heated metal trap tube for a minimal period of time. This reduces the possibility of decomposition of thermally labile samples. Broadening from the dead volume of the tube itself is also reduced.

High-Volume Injection

The use of high-volume injectors is a specialized option in gas chromatography which provides additional power to standard sample introduction techniques. This technique permits introduction of injection volumes of up to 1000 μl (versus 1–5 μl in conventional injectors). The major advantage provided by this technique is increased sensitivity, i.e., lower detection limits. Although there are various suppliers of high-volume injectors, essentially the technology is based on a sophisticated combination of cryogenic or chemical sample concentration and automatic valving [23,25].

A large-volume injector permits a speed-programmed injection of sample volumes of 5 μl to up to 1000 μl, with simultaneous venting of the solvent. These devices function as a cryotrap, focusing and concentrating the components to be determined, and then transferring them to the capillary column. Large-volume injectors are available as a single-shot system and as a fully automatic systems for processing up to 100 samples by using an autosampler tray. Specialized software packages are also commercially available to optimize the injection parameters. Critical parameters such as the sample injection speed as a function of initial injection temperature, and solvent split and split flow, can be easily determined. The programmed values can be transferred to a method and from instrument to instrument with a few keystrokes [26,27].

The major advantages provided by this technique are

Lower detection limits by injecting sample volumes of 5 μl to 1000 l
Reduced sample preparation time by eliminating solvent evaporation or preconcentration step
Solvent evaporation step is performed at optimal injection speed

Adjustable sampling height allows for automated injection of solvent layer for ''in vial'' liquid/liquid extraction
Protection of the capillary column and the detector through solvent venting

Some attractive applications for the analyst are

Lowering of detection limits for almost any analysis
Detection of impurities in ultrapure solvents
Elimination of solvent evaporation step when combined with solid-phase extraction and liquid–liquid extraction techniques

Retention-Time Locking

Retention-time locking (RTL) is a unique feature available in some GC equipment which has revolutionized gas chromatography by reproducing retention times within hundredths of a minute from one instrument to another. This capability is possible thanks to highly reliable electronic pneumatic control (EPC), (pressure and flow control), good temperature control; and high reproducibility of capillary columns. The result is ultimately retention time stability between any GC systems with EPC.

Once a method is developed, a compound is selected, which becomes the locking compound in the usual standard to establish the pressure-versus-retention time relationship using the RTL software. Once developed, this information can be used to lock the method on another GC system with EPC.

To lock a method on another GC system, you only have to make a single run and enter the retention time of the locking compound into the software. The software then calculates the new inlet pressure to match chromatograms exactly. Furthermore, the software automatically updates the method with the new pressure and records the change in the instrument log file that is saved with the method.

Retention-time locking provides the immediate benefits of increased sample throughput, greater confidence in results, easier analysis for compliance, and lower costs of sample analysis. All you need is a GC equipped with the RTL software, EPC, and a GC ChemStation. With RTL, all peaks match and elution order is constant. Retention-time locking eliminates the need to update calibration tables, timed events tables, and integration events tables when a method is transferred, a new column is installed, or routine maintenance is performed.

Pattern Recognition and Artificial Intelligence

In recent years, multivariate data analysis has been used powerfully in the analysis of complex mixtures. This is an excellent tool for coping with the

large information density presented by high-resolution chromatography. Data processing has thus become an element of foundational significance in handling chromatographic data, extending and expanding the meaning of chromatographic resolution. Although the best examples come from complex petroleum or environmental samples, this tool can be valuable in the analysis of plastic materials, particularly for the analysis of trends in product quality when many samples must be compared to assess process improvement or product variability. Complex processes can be successfully modeled by the use of advanced artificial intelligence methods and chromatography data.

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