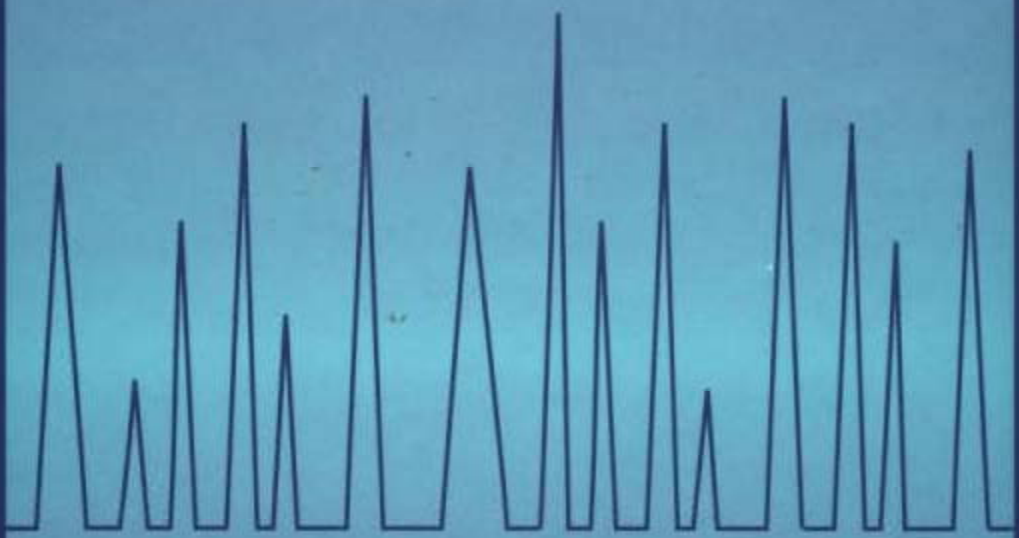
Analytical Gas Chromatography

SECOND EDITION



WALTER JENNINGS
ERIC MITTLEFEHLDT PHILIP STREMPLE

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CONTENTS

CHAPTER 3
Sample Injection

CHAPTER 4
The Stationary Phase

CHAPTER 5
Variables in the Gas Chromatographic Process

CHAPTER 6
Column Selection, Installation, and Use

CHAPTER 7
Instrument Conversion and Adaptation

CHAPTER 8
Special Analytical Techniques

PREFACE

Some forty years after the process was first conceived, gas chromatography remains the world's most widely used analytical technique. However, the real expertise of a large proportion of today's chromatographers lies in other fields. Lacking opportunity or time to develop a better understanding of the chromatographic principles that underlie their analyses, they use chromatography merely as a means to an end. Because the technique is so powerful, they are still able, however, to generate useful data. Some are under pressure to produce results using equipment that was purchased specifically to generate those results. Others, including a number of GC/MS analysts in environmental laboratories, often perform their analyses using procedures established by regulatory agencies that often discourage deviations from these methods that would otherwise permit improvements in analytical procedure. The net result—which is certainly understandable—is that a large proportion of users have little real knowledge of the actual variables in the chromatographic process, the interaction between those variables, how they are best controlled, how the quality of analytical results could be improved, and how analysis times can be shortened to facilitate the generation of a greater number of more reliable results on the same equipment.

An analyst with a more comprehensive understanding of chromatographic principles, however, can often improve the quality of the data generated and reduce the analytical time. As the laboratory workload increases, shorter analysis times help accommodate increased demands on the available equipment. In turn, this forestalls the need to purchase an additional chromatograph or another mass spectrometer. Knowledgeable users can also extend the usable lifetime of the

equipment. Equally important is the sense of personal satisfaction that comes when a "black-box" approach changes to a real understanding of the process. One of W.J.'s most rewarding experiences occurred when a senior professor in Germany who had been publishing chromatographic papers for some twenty years thanked the instructor at the end of a course and remarked, "I never realized how little chromatography I actually knew."

We have taken pains to prepare this second edition in a form that will permit its use as an instructional college-level text, as a "brush-up" manual that the practitioner can read straight through, and as a reference source for the user who merely wishes to review one subject or area. To fulfill these multiple goals properly, some degree of redundancy has been necessary. The user wishing to quickly review the options for increasing retention factors will be reminded of the roles played by K_c, temperature, and β, with a brief mention of their interrelationships. He or she will then be referred to other sections where each of these topics is discussed in greater detail.

Many of our colleagues have generously contributed suggestions and ideas. We are particularly indebted to Roger Schirmer for assistance in the areas of the physical and chemical nature of glass and fused silica, to Shawn Reese and Roy Lautamo for their contributions in the areas of stationary phases, surface treatments, and deactivations, and to Allen Vickers, Mitch Hastings, and others for invaluable help in applications and other areas.

September, 1996

Walter Jennings
Eric Mittlefehldt
Philip Stremple

ABOUT THE AUTHORS

Complementing a research career that began in 1952, Professor Walter Jennings has taught gas chromatography for over 40 years. His teaching has included graduate instruction and regularly scheduled courses at the University of California, Davis. Beginning about 1970, these instructional activities were supplemented by a series of extra-curricular one- to three-day courses, some of which were open enrollment, while others were restricted, in-house courses specially tailored for a variety of industrial concerns. Eventually these evolved into a comprehensive, fast-paced, continuously updated one-day course that is still presented 30 to 40 times each year at points all over the world. To date, it has been estimated that well over 30,000 chromatographers have attended these courses.

Dr. Eric Mittlefehldt is a Senior Research Scientist and Manager of J&W's Custom Column Shoppe. Eric is an accomplished physical–analytical chemist whose experience extends well beyond the practical aspects of capillary column gas chromatography. Originally trained as a surface scientist, Eric has made significant contributions to the characterization of multicomponent polymeric materials routinely used as stationary phases in gas chromatography. His unusual background brings to this edition a solid foundation in chromatographic theory as well as considerable practical experience with regard to the design and implementation of new stationary phases and column technology.

Dr. Philip Stremple received his Ph.D. at the University of Iowa in 1983 and was a postdoctoral fellow at MIT until 1985. He then spent nine years as a practicing analytical chemist exclusively in the area of gas chromatography for the Clorox Company. His areas of expertise then included the GC analysis of industrial

raw materials, fragrance and flavors, finished products, and competitive product analysis. For the past two and a half years Phil has been the manager of applied science at J&W Scientific specializing in applications, technical support, and training.

CHAPTER 1

INTRODUCTION

1.1 General Considerations

In the late 1800s, Mikhail Tswett separated natural pigments into colored zones by percolating plant extracts through adsorbent-packed columns. He later used the word "chromatography" to describe this process [1, 2]. Our use of the word has broadened, and "chromatography" is now used for a number of processes in which the substances to be separated are subjected to equilibrium partitioning between two phases. In most cases, one of those phases is stationary and the other is mobile. The principles of liquid–liquid chromatography (LLC) are employed by the separatory funnel at one end of the spectrum, and by the Craig countercurrent distribution apparatus at the other extreme. Applications of liquid–solid chromatography range from paper—through column—to some forms of thin-layer chromatography.

Their work on liquid–solid chromatography (LSC) earned Nobel Prizes for A. J. P. Martin and R. L. M. Synge. It was in his award address that Martin suggested a gas might be used as the mobile phase in chromatographic processes. Some years later, James and Martin [3] subjected to the passage of ethyl acetate vapor a mixture of fatty acids that had been affixed to an adsorbent. In doing so, they demonstrated the sequential elution of the fatty acids. Coupled with an automated titration system, this generated a graph composed of a series of "steps" depicting the sequential additions of base as each successively eluted acid was neutralized by automated titration.

In 1954, Ray [4] inserted the sensing filament of a thermal conductivity cell, constituting one leg of a Wheatstone bridge, into the outlet of a gas chromatographic column. He generated the first modern-day "chromatogram" where each eluting

substance generated a Gaussian-type peak. The schematics and chromatograms that Ray published stimulated a number of workers to enter what promised to become a new and exciting field. Within a decade, some hundreds of individual scientists were engaged in both basic and applied research in gas chromatography. Many of these contributions have been detailed elsewhere (e.g., [5, 6]), but several fundamental steps in the development of modern analytical gas chromatography deserve special mention. These include Golay's invention of the open tubular column [7], Desty's elegantly simple design for a glass-capillary-drawing machine [8], and the concept of a thin-walled fused silica column [9].

When a gas is employed as the mobile phase, either a liquid or a solid can be utilized as the stationary phase. These processes are "gas–liquid chromatography" (GLC) and "gas–solid chromatography" (GSC), respectively. The former has greater general utility and is more widely used, while the latter is especially useful for the separation of highly volatile compounds, including fixed gases (see later chapters). In popular usage, the term "gas chromatography" and the abbreviation "GC" are often applied to both processes.

1.2 A Simplistic Approach

In the process of gas chromatography, a thin film of the stationary phase is confined to the column, and continuously swept by a stream of mobile phase (i.e., carrier gas). The two extremes in column types are packed columns and open tubular columns.

Packed columns are typically 2–5 m long, 1–5 mm in internal diameter (ID) (d_c), and are filled with an "inert" granular support, each particle of which is coated with the stationary phase. As implied by the name, micropacked columns are a smaller version of the packed column, usually having IDs of less than 1 mm, and smaller packing granules. The length of a packed column is practically limited by the pressure drop generated by the resistance it offers to gas flow.

There are three general types of open tubular columns. The most widely used is the wall-coated open tubular (WCOT) column, in which the stationary phase exists in the form of a uniform thin film affixed to the inner periphery of an open tube, the column. In porous layer open tubular (PLOT) columns, a porous layer exists on the inner wall of the column, while the central portion is open. Porosity of that layer is sometimes achieved by chemical means such as etching of the wall per se, and in other cases by deposition of the porous particles from a suspension. The porous layer may serve as a support for a stationary phase, or as the "stationary phase" per se. SCOT (support coated open tubular) columns are a form of PLOT column. Commonly used sorbents include porous polymers, aluminum oxide, and selected zeolites. In some open tubular columns, the d_c may be as large as 0.5–0.75 mm. While these are open tubular columns, they should not be regarded as true "capillaries." We will consider all of the above columns in this book, but

the use of the word "capillary" will be restricted to columns whose inner diameters do not exceed 0.35 mm.

Whether it is packed or open tubular, the column, which in the normal GC system is connected to the inlet of the gas chromatograph at one end and to the detector at the other, is adjusted to some suitable temperature and continuously swept with the mobile phase (carrier gas). When a mixture of volatile components is introduced to the inlet end of the column, each solute in that sample engages in a highly dynamic equilibrated partitioning between the stationary phase and the mobile phase in accordance with its distribution constant ($K_c = c_S/c_M$). Let us consider a single band of solute at some one point in time: as the solute molecules in the gas phase are swept forward by the carrier gas, those in the stationary phase are carried downcolumn a finite distance. At that instant, the equilibrium distribution K_c is violated at the rear of the band (where c_S is finite and c_M is zero) and at the front of the band (where c_S is zero and c_M is finite). To reestablish the distribution constant throughout the band, the dominant partitioning is from stationary phase to mobile phase at the rear of the band, and from mobile phase to stationary phase at the front of the band. In other words, the flow of carrier gas disrupts the equilibrium distribution at the front and rear of each chromatographing solute band, causing continuous evaporation at the rear and reestablishment at the front of each solute band as it chromatographs through the column (Fig. 1.1). Because all solutes are injected simultaneously, separation is obviously contingent on differences between the K_c values of the individual solutes. The proportion of a solute that is in the mobile phase at any given time is a function of the "net" vapor pressure of that solute; molecules of those components exhibiting higher vapor pressures partition more toward the mobile phase. They are swept toward the detector more rapidly and are the first solutes eluted from the column. Other solutes exhibit lower vapor pressures, either because they are higher-boiling or because they engage in interactions with the stationary phase that effectively reduce their vapor pressures under the chromatographic conditions employed. Individual molecules of these solutes venture into the mobile phase (carrier gas) less frequently, their concentrations in the mobile phase are lower, and they require longer periods of time to reach the detector; hence separation is achieved.

These superficial considerations lead to two credulous generalities. First, gas chromatography is a volatility phenomenon that is applicable only to materials that can be vaporized; it is not useful in the analysis of proteins or metals per se, although we will, in later chapters, discuss methods of converting some nonvolatile substances to volatile derivatives. Second, because separation depends on partitioning between the two phases, the temperature of the column is critical to the analysis. If the column temperature is too low, the solutes remain largely (or wholly) in the stationary phase, and rarely (or never) enter the mobile phase. They neither separate from each other nor (in the extreme case) elute from the column. If the column temperature is too high, the solutes spend most (or all) of their time

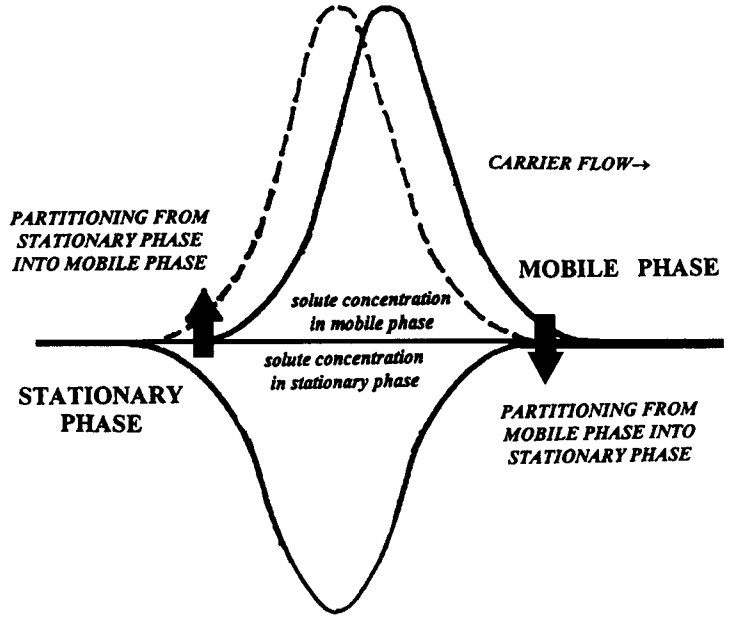

Fig. 1.1. In gas chromatography, each chromatographing solute partitions between the mobile phase (*above the horizontal line*) and the stationary phase (*below the horizontal line*) in accordance with its K_c ($K_c = c_S/c_M$). At time "T," c_S is represented by the curve below, and c_M by the dotted curve above, the horizontal line. Those solute molecules in the mobile phase are continuously swept down stream, and an instant later, at time "$T + t$," c_M is represented by the solid curve above the horizontal line. The K_c has now been violated in the regions marked by the dark arrows. At the left, solutes in stationary phase must migrate to mobile phase to re-establish the K_c; at the right, solutes in mobile phase must partition toward the stationary phase to re-establish the K_c. In traversing the column, each solute band continuously evaporates at the rear and is re-established at the front.

in the mobile phase, rarely (or never) enter the stationary phase, and elute from the column as an unseparated mixture.

It can be useful to (incorrectly) visualize gas chromatography as a stepwise process and to begin by considering the separation of a simple two-component mixture containing (e.g., acetone [boiling point (bp) 57°C]) and ether bp 37°C). If a small amount of that mixture is introduced into a chromatographic column which is continuously swept with carrier gas and held at a temperature where each solute exhibits a suitable vapor pressure, both solutes will immediately partition between the moving gas phase and the immobile stationary phase. All other things being equal, the molecules of the lower-boiling ether that are dissolved in the stationary phase will vaporize before (or more frequently than) the molecules of the higher-boiling acetone [10]. As they enter the mobile gas phase they progress through the column and pass over the virgin stationary phase, where they redissolve. A fraction

of a second before the acetone molecules revaporize to be carried downstream again by the carrier gas, the ether molecules move again. Hence the more volatile ether molecules continuously increase their lead over the less volatile acetone molecules, and separation is achieved.

Although this concept may prove helpful in visualizing that a multiplicity of vaporizations and resolutions on the part of the individual solute molecules is one major factor influencing the degree of separation efficiency, it must be stressed that this oversimplification results in an inaccurate picture. For one thing, the chromatographic process is continuous and highly dynamic rather than being a series of discrete steps. At any point in time, some of the molecules of each solute are in the stationary phase and others are in the mobile phase. As the mobile phase moves over virgin stationary phase, some of the mobile-phase-entrained solute molecules dissolve in the stationary phase, while immediately behind the moving front, an equivalent number of dissolved solute molecules vaporize into the mobile phase. Because ether and acetone exhibit different vapor pressures, the ratio

Molecules in stationary phase/molecules in mobile phase

will be larger for the less volatile acetone than for the more volatile ether. Hence, ether is less retained and spends a greater percentage of its transit time in the mobile phase. Hence it will move through the column more rapidly, and at the conclusion of the process a "plug" of ether molecules dispersed in the mobile phase (carrier gas) will emerge to the detector, followed by a second mobile phase "plug" carrying acetone molecules. Under constant chromatographic conditions, the degree of separation (i.e., the distance between the two eluting plugs) will be a function of the solute retention factors and the concentrations (or "sharpness" of the solute plugs).

These concepts are also helpful in emphasizing that the vapor pressure of the solute strongly influences its chromatographic behavior. Solutes undergo no separation in the mobile phase, nor do they undergo separation in the stationary phase. Solute separation is dependent on the differences in solute volatility, which influence the rates (or frequencies) of solute vaporizations and resolutions. This differentiates solute concentrations in the stationary and mobile phases. Hence it is desirable to subject solutes to as many "vaporization steps" as possible (without having other adverse effects; *vide infra*), and this will require that they undergo an equal number of "resolution steps." If the vapor pressures of the solutes are too high, they spend most (or all) of their transit time in the mobile phase and little (or no) separation is achieved. If the vapor pressures are too low, the solutes spend too long in the stationary phase, analysis times become disproportionately long, and sensitivity is also adversely affected (*vide infra*). Column temperature is an obvious method of influencing solute vapor pressures. Another method is through the choice of stationary phase. A "polar" stationary phase reduces the vapor pressures of polar solutes by means of additional solute-stationary phase interactions

that may include hydrogen bonding and/or dipole–dipole interactions. These interrelationships are discussed in greater detail in later chapters.

1.3 Simplistic Comparisons of Packed and Open Tubular Columns

Most chromatographers recognize that the open tubular (or "capillary") column is capable of separations that are vastly superior to those obtained on packed columns [11]. Figure 1.2 illustrates separations of an essential oil on a packed column and on two types of open tubular column [12]. One of us (WJ) once experienced instructional difficulties with workers in a developing country who preferred the packed column "because it generated fewer peaks." They viewed with dismay the greater challenge imposed by the large number of peaks generated during the separation of their sample on a more efficient capillary column. The folly of that

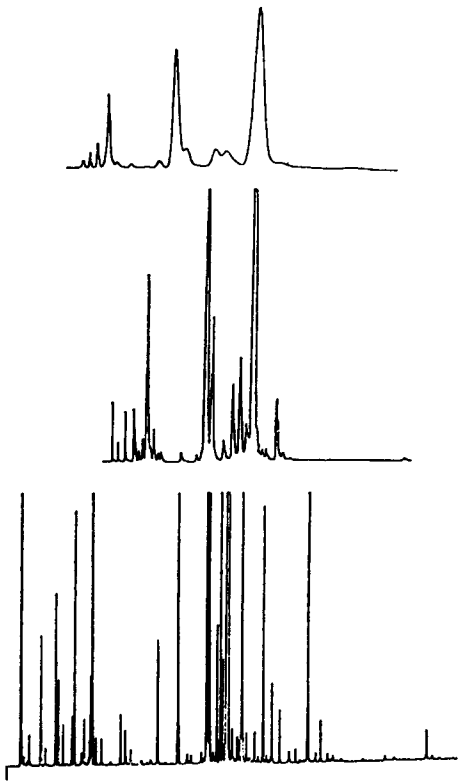

Fig. 1.2. Chromatograms of a peppermint oil on (top) a 6 ft × 1/4 in packed column, (center) a 500 ft × 0.03 in stainless steel open tubular column, and (bottom) a 30 m × 0.25 mm fused silica open tubular (capillary) column. *Adapted from [12], p. 445, and reprinted with permission.*

prejudice is easily emphasized by pointing out that the chromatogram can be made even simpler by omitting the stationary phase. The chromatogram will then consist of a single peak that includes all components.

On the other hand, there are occasions where the required degree of separation can be obtained on a packed column and separation on an optimized open tubular column results in more resolution than is required ("overkill") at the expense of longer analysis times. In situations of this type, some of the superior resolving power of the open tubular column can be traded off to yield equivalent (or improved) separation in a fraction of the analysis time required by the packed column, while generating higher sensitivities in a much more inert system (quantitative reliability is improved). As compared to packed columns and packed column analyses, the open tubular column can also confer distinct cost advantages [13].

These points are illustrated in Fig. 1.3 [14], where the short capillary column delivers separation "equivalent" to that obtained in the much longer packed column analysis. Actually, the capillary resolution is superior. Integrated peak areas from the packed column analysis will include appreciable solvent contributions. The solute peaks are well removed from the solvent in the capillary analysis, and quantitation will be enhanced.

Returning to Fig. 1.2, the striking difference between the two sets of chromatographic results illustrated is best attributed to inequalities in the degree of

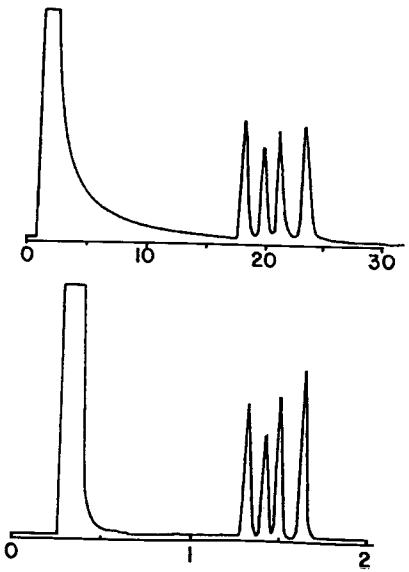

Fig. 1.3. Off-line monitoring of a mixture of methyl benzoates. Top, packed column analysis (25 min), and bottom, 1.7 m × 0.25 mm glass capillary analysis (1.7 min).

randomness exhibited by identical molecules of each individual solute. All identical molecules of each solute exhibit a narrow range of retention times in the bottom chromatogram, but as the ranges of retention times become greater, neighboring peaks exhibit overlap and resolution suffers. These behavioral differences between identical molecules can be attributed to three factors [10]:

1. The packed column offers solute molecules a multiplicity of flow paths: some short, the majority of average length, and some long. Hence identical molecules of each given solute would be expected to spend disparate times in the mobile phase. The open tubular column, on the other hand, has a single flow path, and molecules would be expected to exhibit mobile phase residence times that were much more nearly identical.
2. A similar rationale can be drawn for the randomness of stationary phase residence times. There is much more stationary phase in the packed column, and the film thickness is nonuniform. Thicker regions of stationary phase would be expected to occur in particle crevices and where two or more coated particles come into contact. A solute molecule dissolving in a thinner region of stationary phase would become dispersed and then reemerge to the moving gas phase in a relatively short period. An identical molecule, dissolving in a thicker patch of stationary phase, would take a longer time to reemerge. The times that identical molecules of a given solute spent in the stationary phase would be quite diverse. In the open tubular column, the stationary phase is in a thinner and much more uniform film. Hence, the range of times that identical molecules spent in the stationary phase would be expected to be much narrower.
3. It was previously mentioned that solute volatility (i.e., solute vapor pressures) constitutes an important variable in gas chromatography. The vapor pressure of a solute is an exponential function of the absolute temperature, ergo a minor shift in temperature can have a major effect on vapor pressure. At our present state of instrumental development, solute temperatures are controlled by the temperature of the air in the column oven—the oven air conveys heat to the column wall, the column wall conducts heat to the particles of solid support in contact with the wall, these conduct heat to the stationary phase with which it is coated and to the next particle of solid support, and so on. Packed column support materials, however, are notoriously poor heat conductors. *A temperature range must exist across any transverse section of the packed column.* The range of temperature will be greater for larger-diameter columns and for faster program rates, but even in an isothermal mode, there must be a temperature difference between that packing in contact with the column wall and that packing at the central axis of the column. In an isothermal mode, solute molecules whose flow path is down the center of the packed column will be at a lower temperature, exhibit lower vapor pressures, and spend more of their time in the stationary phase than will identical molecules whose flow paths are closer to the column wall. The problem is exacerbated by

larger diameter-columns and fast heating rates. The fact that these individual flow paths through the column undoubtedly switch back and forth from the central area of the packing to peripheral areas bounded by the column wall does not compensate for this variation. This is one more factor causing identical molecules to exhibit a broadened range of retention times. In the fused silica column, the stationary phase exists as a thin film deposited directly on the inner wall of a tube of very low thermal mass. There should be no temperature variation across any transverse section of the column, provided that the column is not exposed to radiant heat but is heated only by convection. The latter point is an important distinction between the oven requirements for packed and capillary columns and is considered again in a later chapter.

Our goal in chromatography can now be better defined. Gas chromatography should be performed under conditions where (1) solute molecules undergo many interphase transitions (vaporizations and resolutions), (2) identical molecules of each solute exhibit the narrowest possible range of retention times (i.e., the chromatographing band formed by each molecular species is short, hence the standard deviation of the resultant peak is small), and (3) negative contributions (e.g., remixing caused by longitudinal diffusion) must not be permitted to cause excessive degradation of the separation achieved by the processes described above.

1.4 A Simplified Theory of the Chromatographic Process

The primary objective of this book is to hone the practical skills of those using gas chromatography. Practical skills include judicious selection, proper installation, evaluation, and optimized use of state-of-the-art open tubular columns. While a basic comprehension of elementary gas chromatographic theory is essential to attaining these goals, this section is intended as neither a comprehensive nor a rigorous treatment of chromatographic theory. Theoretical considerations have been well covered elsewhere (e.g., [5, 15, 19]). In an attempt to avoid contributing further to the confusion caused by a variety of nonuniform "systems" of nomenclature, the symbols and nomenclature used throughout this discussion are based largely on those suggested by the International Union of Pure and Applied Chemistry (IUPAC) [20] and the American Society for Testing and Materials (ASTM) [21] and are detailed in the Appendix.

A compound subjected to the gas chromatographic process (a "solute") is, on injection into the column, immediately partitioned between the mobile phase and the stationary phase. Its apportionment between the two phases is reflected by the distribution constant K_c, defined as the ratio of the weights of solute per unit volumes of the stationary and mobile phases:

$$K_c = \frac{\text{mass of solute per unit volume stationary phase}}{\text{mass of solute per unit volume mobile phase}} = \frac{W_{i(S)}/V_S}{W_{i(M)}/V_M} \qquad (1.1)$$

K_c is a true equilibrium constant, and its magnitude is governed only by the compound, by the stationary phase, and by the temperature. Polar solutes would be expected to dissolve in, disperse through, and engage in intermolecular attractions with polar stationary phases to a much greater degree than would hydrocarbon solutes exposed to the same stationary phase. Logically, the K_c of a polar solute in a polar stationary phase is higher than the K_c of the analogous aliphatic hydrocarbon in the same polar stationary phase. As the temperature of the column is increased, both types of solute exhibit higher vapor pressures and their K_c values (c_S/c_M ratios) decrease, although (in this polar stationary phase) those of the polar solute remain larger than those of the hydrocarbon. Among the members of a homologous series, of course, higher-molecular-weight homologues have lower vapor pressures and higher K_c values.

During its passage through the column, a chromatographing solute spends a fractional part of its total transit time in the stationary liquid phase and the remainder in the mobile gas phase. The mobile phase residence time can be determined by direct measurement. Whenever a solute emerges to the mobile phase, it is transported toward the detector at the same rate as in the mobile phase. Hence, under a given set of conditions, every solute in a given chromatogram *must spend the same length of time in the mobile phase*. This mobile phase residence time can therefore be determined by timing the elution of a substance that never enters the stationary phase, but spends all its time in the mobile phase. Ideally, this could be determined by timing the transit period of an injection of mobile phase (carrier gas), but detection of carrier gas in carrier gas would be impractical. Methane is normally used for this purpose, and although it is recognized that methane does have a discrete stationary phase residence time (particularly in some PLOT columns), it is assumed that this is minuscule and can be ignored in columns of "standard" stationary phase film thickness at reasonable column temperatures.

The column residence time for methane is assigned the symbol t_M, and, as discussed earlier, a solute in the mobile phase is transported toward the detector at the same velocity as the mobile phase. Hence *everything spends t_M time in the mobile phase*. This is the "gas holdup time" (or "gas holdup volume") of the system. The total retention time is equal to the mobile phase residence time t_M, plus the stationary phase residence time. It therefore follows that the stationary phase residence time or the "adjusted retention time" t'_R is

$$t'_R = t_R - t_M \tag{1.2}$$

Ideally, solute bands will be introduced into the column in such a way that they occupy a very short length of the column (see injection mechanisms in Chapter 3). It is highly desirable that the length of each band increase by a minimum amount as the solute bands traverse the column. Toward this goal, it is desirable that the ranges of retention times exhibited by identical molecules be extremely narrow, i.e.,

that the standard deviation exhibited by each molecular species is small. As these tight, concentrated bands leave the column, they can be delivered to the detector as narrow, sharp peaks. In actuality, even if the times that identical molecules spend in mobile phase and in stationary phase are precisely the same, other factors such as longitudinal diffusion (occurring primarily in the mobile (gas) phase and to a negligible degree in the stationary phase) cause lengthening of the solute bands during the chromatographic process. The centers of the bands of solutes that have different K_c values will become increasingly separated as they progress through the column, but if the range of retention times exhibited by identical molecules is large or if longitudinal diffusion is excessive, band lengthening may cause the trailing edge of the faster component to interdiffuse with the leading edge of the slower component, resulting in incomplete separation and overlapping peaks. Hence the efficiency with which two components can be resolved is governed not only by their separation factors (see below) but also by the degree of band lengthening that occurs. Insofar as the column is concerned, the separation efficiency is inversely related to the degree of band lengthening. All other things being equal, a minimum degree of band lengthening occurs per unit of column length in a column of high efficiency, and a higher degree of band lengthening occurs per unit of column length in a less efficient column. There also exist extracolumn contributions to band lengthening. These also detract from the separation process and will be considered in later chapters. The term "band broadening" is usually used to describe these phenomena, but as discussed in later chapters, bandwidths are constant and limited by the column diameter. It is really the lengths of those bands that are of concern, because long bands lead to broad peaks.

Inasmuch as both are methods for separating mixtures of volatile compounds, it is not surprising that gas chromatography was promptly compared with the process of fractional distillation, and distillation terminology (i.e., "theoretical plates") was employed (albeit imperfectly; see below) to describe gas chromatographic separation efficiencies.

As detailed above, the separation efficiency of a gas chromatographic column is related to the degree to which a solute band lengthens (which correlates with peak width and affects the standard deviation of the peak, σ) relative to the time the band requires to traverse the column (i.e., its retention time, t_R). The "number of theoretical plates" N is defined as

$$N = (t_R/\sigma)^2 \tag{1.3}$$

where t_R is the time (or distance) from the point of injection to the peak maximum, and σ is the standard deviation of the peak. To avoid the necessity of determining σ, the peak is assumed to be Gaussian (which is usually doubtful; see below), and the problem is simplified. For a Gaussian peak, peak width at base (w_b) is equal to 4.0σ, and peak width at half height (w_h) is equal to 2.354σ (Fig. 1.4). Substitution