Organic Functional Group Analysis by Gas Chromatography

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PREFACE

The past two decades have seen tremendous developments in gas chromatography and the appearance of many publications on this subject. Since the gas chromatographic apparatus was originally designed for the sole purpose of separating vapors, it is understandable that most investigators have devoted their efforts to improve the instrument or to study the optimal conditions for the separation of specific gaseous mixtures. In the present monograph I wish to discuss a different aspect of gas chromatography, being concerned with the application of existing instruments and known separation techniques to the quantitative analysis of organic compounds through the formation of suitable derivatives.

This book is an offshoot of my comprehensive project on micromethods of organic functional group analysis which was undertaken during the 1950s. When the said project was near completion, the gas chromatograph became an accepted analytical tool. Realizing the potential of this instrument, I assigned several students to work out experimental procedures to convert certain functions into simple gaseous products and measure the latter by means of gas chromatography. I also encouraged practicing analysts to adopt this approach in devising new methods of analysis—I called attention to its two distinct advantages, namely (a) gas chromatography provides a simple way to isolate the measurable product and (b) the high sensitivity of the instrument can be utilized to extend the lower limit of microdetermination of organic functional groups beyond the 0·1 millimole level.

With the assistance of my former student A. S. Ladas, I have compiled this volume to cover the literature up to 1975. Inspection of the table of contents will reveal that the various functional groups are treated systematically according to my scheme of classification. A number of experiments are described in detail so that the reader can use this book as a laboratory manual. In the case of some functional groups that may be determined by means of gas chromatography but for which published procedures are not available, I have attempted to make suggestions on how to carry out the analysis.

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New York, N.Y. *T. S. Ma*
May 1975

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1. INTRODUCTION

1. OBJECTIVE AND SCOPE OF THIS MONOGRAPH

The present monograph is concerned with the utilization of gas chromatography for the determination of organic compounds based on the chemical reactions of their functional groups. Thus, this book differs from other volumes on gas chromatography in several respects: (a) It discusses analytical methods in which the gas chromatograph serves primarily as an instrument for measurement instead of for separation. (b) When separation is involved in the determination, the specific component can be easily isolated from the matrix. (c) The original organic material submitted for analysis undergoes chemical transformation in such manner that an identifiable product is obtained from the analyzed compound. Understandably, the product must be a gas or can be vaporized at the temperature of the chromatographic column.

There are certain advantages in using gas chromatography for the analysis of organic substances through the functional group reactions. First, since gas chromatography is discriminative, the gaseous product to be measured is easily distinguishable from the extraneous gases. For instance, in the determination of primary amino groups by nitrosation (see Chapter 4, Section III.B), the nitrogen formed is mixed with the oxides of nitrogen, but it is not necessary to remove the latter by means of scrubbers. Secondly, extremely sensitive detectors are available for gas chromatographic measurements. Whereas precise determination at the nmol (10^{-9} mol) level can be carried out in the gas chromatograph, great difficulty is encountered when μmol amounts of gas are collected in a gasometer for measurement. In the analysis of carbamates (Ladas and Ma, 1973), gas chromatography makes it possible to determine the alcohols produced by hydrolysis at the μmol level, while titrimetric determination of alcohols is not recommended below the 0·1 mmol region (Cheronis and Ma, 1964).

When the gas chromatograph was first introduced in the analytical laboratory, it was used exclusively for the separation of gaseous mixtures. No attempts were made to modify the compounds in the sample to be

analyzed. Hence gas chromatography was restricted to the analysis of volatile materials and dependent on the availability of authentic compounds for comparison of retention times. In connection with the investigation of organic functional group analysis, one of the writers (Ma, 1965) called attention to the applicability of gas chromatography in this area. It may be mentioned that, even for an organic compound which can be analyzed conveniently by direct gas chromatography, determination of a suitable product formed from its functional group serves as a complementary method to check the reliability of the analytical results.

In this monograph, the literature published during the past two decades has been surveyed. A number of representative experimental procedures are described in detail so that the reader may use this book as a laboratory manual. At the same time, many conventional gasometric methods which can be adapted to gas chromatography are suggested, in order to stimulate further development of this area of organic analysis.

II. GENERAL ASPECTS OF GAS CHROMATOGRAPHY

A. Historical

Chromatography is a process in which chemical species are distributed between a stationary phase and a mobile phase, and migrate in the direction of flow with a certain characteristic velocity (see Ma and Horak, 1975). The stationary phase may be solid or liquid. If it is the latter, the liquid is fixed on the surface of an inert adsorbent. In the case of gas chromatography, the mobile phase is in the gaseous state. Hence, for organic functional group analysis *via* gas chromatography, the species determined can either be vaporized below 200° without decomposition, or are permanent gases.

The term chromatography was coined by the botanist Tswett (1906) because he was concerned with colored materials. Later, in the 1930s, Kuhn *et al.* (1931) revived Tswett's technique and they also worked on colored compounds. It should be recognized, however, that color plays no role in gas chromatography.

Martin and Synge (1941) developed liquid–liquid partition chromatography in which they used silica gel to hold one liquid immobile while passing another liquid (the mobile phase) over it; subsequently they replaced silica gel with cellulose fiber (paper) and their work was rewarded with the Nobel Prize in 1952. Although Martin and Synge suggested in their first paper that the mobile phase could be a gas rather than a liquid, the concept of gas–liquid partition chromatography remained dormant for about ten years until James and Martin (1952) employed this technique to separate volatile fatty acids. It should be mentioned that, previously, a number of workers

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had described analytical techniques to separate gas mixtures by passing the sample through a column of solid material (Schuften, 1931; Eucken and Knick, 1936; Damköhler and Thiele, 1943; Turner, 1943).

B. Gas–solid chromatography and gas–liquid chromatography

As mentioned above, the stationary phase in gas chromatography is either a solid or a fixed liquid packed into a column, and the mobile phase is an inert gas. The gaseous or vaporized material to be separated is distributed between these two phases. The specific term gas–solid chromatography (GSC) is applied to the method when the stationary phase is a solid adsorbent. The most commonly used solid adsorbents are alumina, silica gel, charcoal, and molecular sieves. Selective sorption on these solids allows the separation of certain permanent gases and low molecular weight hydrocarbons. On the other hand, when the stationary phase is a liquid distributed on an inert support, the method is known as gas–liquid chromatography (GLC). Undoubtedly, gas–liquid chromatography is much more commonly used in the analytical laboratory. In the succeeding chapters of this monograph, the general term gas chromatography (GC) is employed, since it is clear from the description of the column packing in a particular operation whether the method involves gas–solid or gas–liquid chromatography.

C. Techniques

Frontal, displacement, and elution analyses are the three techniques by which gas–solid chromatographic (GSC) separations are performed. Although, theoretically, all three of these techniques can be used in gas–liquid chromatography (GLC), in practice, the elution analysis technique is the most versatile and most easily accomplished. The gas chromatographic methods described in this monograph utilize the elution technique nearly exclusively.

1. *Frontal Analysis*

In the frontal analysis technique, the entire multicomponent sample is introduced continuously into the column. The least adsorbed component passes through the adsorbent column first and leaves the column in its pure state until the next less adsorbed component emerges together with the first component. Each successive component leaving the column contains small amounts of all of the preceding components. The last component emerges in a mixture corresponding to the original sample composition. As an analytical tool, therefore, the frontal analysis technique is of very little

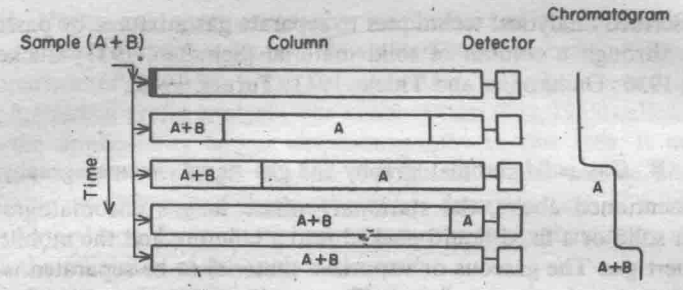

FIG. 1.1. Schematic diagram for frontal analysis, after Dal Nogare and Juvet (1962). (Courtesy of J. Wiley and Sons.)

value. A schematic diagram for the frontal analysis technique is given in Fig. 1.1.

2. *Displacement Analysis*

In the displacement analysis technique (Claesson, 1946), a small amount of the sample is introduced into the inlet of the adsorbent column. A strongly adsorbed vapour, called the displacer, is then used to displace the components of the sample from the column. As the displacer saturates the column behind the sample, the components of the sample are desorbed and pushed toward the outlet of the column. The least adsorbed component emerges first, followed by the next least strongly adsorbed component. Each component of the sample is displaced by the next most strongly adsorbed component. This process continues until the displacer itself emerges from the column. Obviously, in this type of analysis, mixing of adjacent components is inevitable. Despite this, displacement analysis is superior to frontal

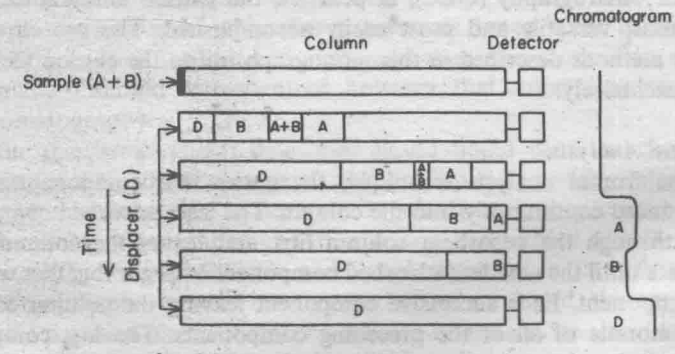

FIG. 1.2. Schematic diagram for displacement analysis, after Dal Nogare and Juvet (1962). (Courtesy of J. Wiley and Sons.)

analysis, since good purity portions of the individual components can be obtained. The technique, however, is rarely used, since much better separations can be obtained by elution analysis. Displacement analysis is illustrated schematically in Fig. 1.2.

3. *Elution Analysis*

In the elution analysis technique (Fig. 1.3), a sample is introduced into

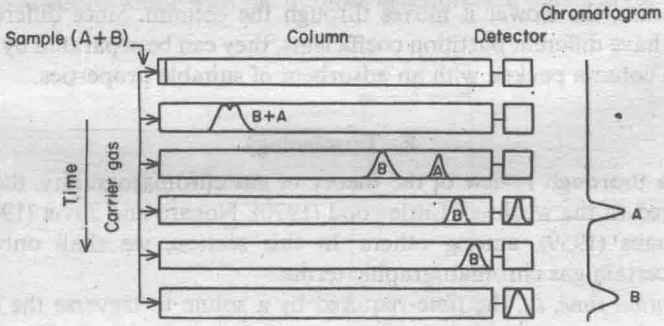

FIG. 1.3. Schematic diagram for elution analysis. (Acknowledgment as in Figs. 1.1 and 1.2.)

the column and its individual components are swept through the column by a stream of inert gas. Each individual component is eluted from the column as a distinct peak in contrast to both frontal and displacement analyses, where the emerging components are partially mixed. This differential migration is a result of the selective retardation of the individual components by the solid adsorbent (GSC) or the liquid (GLC) of the stationary phase. Under specified conditions, the time required for a component to emerge from the column is characteristic for this particular component, and the area of the resulting peak is proportional to the amount present. The self-purging of the column after each analysis is a distinct advantage of the elution technique over both frontal and displacement analyses.

D. Operation

The essential part of the apparatus for gas chromatography is the chromatographic column, which is a long tube packed with either a solid adsorbent (GSC) or with an inert support coated with a non-volatile liquid phase (GLC). A stream of an inert gas passes continuously through the column. The sample containing a mixture of components to be separated is introduced into the gas stream where it is first evaporated to form a vapor and then swept by

the carrier gas on to the column. After a series of equilibria between the adsorbent of the column and the carrier gas, the vapor is finally carried through the column by the carrier gas. The speed at which the different components move through the column is mainly a function of two variables: (a) their respective vapor pressures and interactions with the non-volatile liquid phase, and (b) the flow rate of the carrier gas. The higher the flow rate of the carrier gas, the faster the vapor moves through the column. On the other hand, the more strongly the vapor is adsorbed by the adsorbent of the column, the slower it moves through the column. Since different substances have different partition coefficients, they can be separated by making use of a column packed with an adsorbent of suitable properties.

E. Terminology

For a thorough review of the theory of gas chromatography, the reader is referred to the works of Littlewood (1970), Nogare and Juvet (1962), and Keulemans (1959), among others. In this section, we shall only define briefly certain gas chromatographic terms.

Retention time, t_R, the time required by a solute to traverse the column, is inversely proportional to the flow rate of the carrier gas. In Fig. 1.4, t_M is

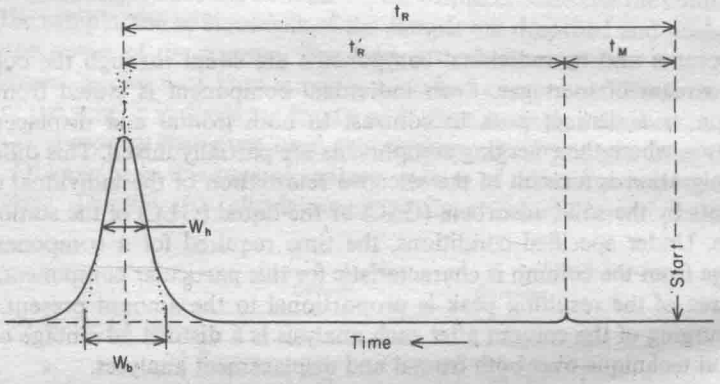

FIG. 1.4. Simplified chromatogram. (Courtesy of Perkin–Elmer Corp.)

the retention time for an unretained solute, such as air, and t'_R is the adjusted retention time for the solute being analyzed.

Retention volume, V_R, is the volume of gas required to sweep the solute from one end of the column to the other end, and is independent of the flow rate of the carrier gas. V'_R is called the *corrected retention volume* and is the retention volume corrected for the compressibility of the gas.

Relative retention is the ratio of the retention volume of two components and is an indication of the separation of these two components.

The separation of two adjacent peaks as a whole is measured by the *peak resolution*, R (see Fig. 1.5).

$$R = \frac{2d}{W_1 + W_2} \tag{1.1}$$

Peak resolution along with the number of theoretical plates in the column

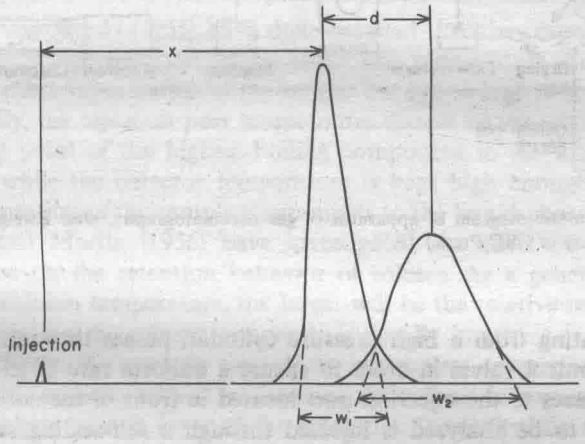

FIG. 1.5. Calculation of N and R from a chromatogram. (Courtesy of CRC Press.)

determines the efficiency of the column. The *number of theoretical plates*, N, can be measured from the chromatogram, by making use of the equation:

$$N = 16\left(\frac{X}{W_1}\right)^2 \tag{1.2}$$

where X is the distance from the point of injection to the peak maximum, and W_1 is the width of the peak along the baseline.

Height equivalent to the theoretical plate, HETP, is the column length divided by the number of theoretical plates (N). In a given experiment, the retention time is proportional to the retention volume, and the retention volume is proportional to the number of theoretical plates or the length of the column.

Both the relative retention and the number of theoretical plates are very important considerations for the description of the column performance.

III. INTEGRAL PARTS OF THE GAS CHROMATOGRAPH

The schematic diagram of instrumentation involved in a typical gas chromatograph is shown in Fig. 1.6 (Zweig and Sherma, 1972). The carrier

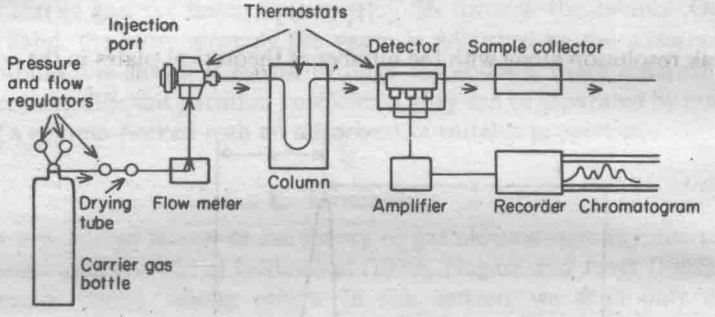

FIG. 1.6. Schematic diagram of apparatus of gas chromatography, after Zweig and Sherma (1972). (Courtesy of CRC Press.)

gas, originating from a high pressure cylinder, passes through regulators and flow-control valves in order to ensure a uniform rate of gas flow. The gas then passes to the injection port located in front of the column, where the sample to be analyzed is injected through a self-sealing septum. The carrier gas elutes the components of the mixture through a coiled, bent, or straight column made from copper, stainless-steel, or glass tubing. The separated components of the original material are then detected as they emerge from the column one by one. The amplifier amplifies the signal from the detector and feeds it to the recorder where the chromatogram is recorded on a chart. If desired, individual components can be collected from the column effluent into sample collectors. During all this process, the temperature is controlled accurately in three parts of the gas chromatograph. The injection port is kept hot enough to vaporize the sample. The temperature of the column is kept as low as possible, but high enough to obtain fast separations. Finally, the detector is kept hot enough to resist condensation of the sample components or any other products formed. Descriptions of the most important parts of the gas chromatograph are given below.

A. Carrier gas

One important factor to be considered in the selection of the carrier gas for gas–solid chromatography is the adsorptivity of the gas on the adsor-

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