CONTENTS

VI. HYDRIDES

VII. ORGANOMETALLIC COMPOUNDS

VIII. METAL CHELATES

IX. ISOTOPES

X. SOME EXAMPLES OF ANALYTICAL APPLICATIONS

XI. NONANALYTICAL APPLICATIONS

INTRODUCTION

In 1952, A. T. James and A. J. P. Martin [1] expanded the "chromatographic method" of M. Tswett [2], described in 1906 for the separation of colored pigments, to the analysis of volatile compounds with the use of a gas as the mobile phase and a liquid as the stationary phase, and gas chromatography was born. Since then, this technique has grown remarkably. The number of publications devoted to it increases yearly, and today few research or industrial control laboratories are without at least one gas chromatograph.

The success of the method is due to its exceptional performance. Qualitative and quantitative analyses of the most complex mixtures can be obtained with a better resolution and in a shorter time than with the majority of other analytical methods in current use. However, an important factor in the increasing popularity of gas chromatography is that the equipment developed for current needs is simple, rugged, economical, and easy to handle.

Technological progress has made it possible to improve the column efficiency, to increase the sensitivity and precision of quantitative analyses, and to realize separations on a preparative scale. At the same time, theoretical knowledge has grown, and gas chromatography has become a method of choice for physicochemical determinations and the thermodynamic study of gas-liquid or gas-solid interactions required for the development of the theories of solutions and of adsorption.

The extremely rapid progress of gas chromatography has occurred primarily in connection with organic chemistry, and its applications to the separation of inorganic compounds came later. Very few inorganic separations, with the exception of some so-called permanent gases, were studied in the first ten years of gas chromatographic history, *i.e.*, up until about 1962.

The explanation for this phenomenon may be sought first of all in the nature of inorganic materials which, in contrast to organic compounds, generally have low volatility and great chemical reactivity. Furthermore, organic chemistry had an urgent need for a simple, rapid, and sensitive method permitting the analysis of highly complex mixtures, *e.g.*, mixtures originating directly from synthesis, crude oil fractions, volatile oils, pyrolysis products of plastic materials, etc. Finally, the development of gas chromatographic theories was undoubtedly facilitated by the existence of series of organic compounds permitting systematic studies.

Inorganic compounds are often liquids or solids with high boiling or sublimation points. Their study by gas chromatography is possible only at a

temperature at which their vapor pressure is sufficient, *i.e.*, generally above 200°C and sometimes much higher. Moreover, numerous inorganic compounds have high chemical reactivity. Many are highly sensitive to hydrolysis by traces of water vapor or by hydroxyl radicals resulting in irreversible decomposition reactions. In this situation it is necessary to take special care during manipulation and injection of samples. All of this results in a complication of the equipment and in difficulties in the choice of construction materials for the chromatograph components in contact with the compounds analyzed (injector, column, detector). The search for suitable stationary phases often presents problems which still remain difficult to solve.

Generally, solid adsorbents have good thermal stability, but it is sometimes difficult to eliminate the active groups (especially hydroxyl groups) on their surface. Furthermore, the adsorption isotherms are linear only at very low partial pressures. Specific adsorption often interferes, and the polar compounds are eluted with strongly tailing peaks. Consequently, gas-solid chromatography is still frequently limited to the analysis of gases.

Numerous liquid phases employed for the chromatography of organic compounds are often not suitable for the analysis of certain inorganic compounds. These liquid phases must satisfy numerous requirements: they should not be volatile at the temperature of the analysis, be thermally stable at this temperature, and be good solvents for the compounds analyzed, but not undergo chemical decomposition or irreversible association reactions with them.

Several types of inorganic compounds have a volatility making them suitable for gas chromatographic analysis:

Compounds which are gaseous at temperatures near room temperature:

so-called permanent gases (hydrogen and the constituents of air);

nonmetallic oxides (carbon, nitrogen, sulfur);

halogens;

nonmetallic halides (hydrogen halides, interhalogen compounds, and the halides of boron, oxygen, nitrogen, phosphorus, and carbon); and

hydrides of electronegative elements, such as O, S, N, P, Si, Ge, B.

Metal halides:

certain transition metal chlorides or fluorides.

Organometallic compounds:

alkyl or aryl derivatives of elements such as boron, antimony, silicon, germanium, tin;

chelates such as the β-diketones formed between metals and organic molecules; and

metallocenes, metal carbonyls and their derivatives.

The metals are volatile only at very high temperatures, but some investigators are presently developing a technology for their gas chromatography at 1000°C or more. Under this condition, some results are obtained, *e.g.*, the cadmium enrichment of a zinc–cadmium alloy (boiling points of the two elements, 907 and 765°C respectively).

Several reviews have been published on the analysis of inorganic compounds by gas chromatography: J. Tadmor in 1963 [3], V. I. Anvaer and B. P. Okhotnikov in 1964 [4], R. S. Juvet and F. M. Zado in 1965 [5], and C. Pommier in 1966 [6].

After an intentionally brief review of the theoretical principles and the experimental technique of gas chromatography, this book will examine the solutions offered in the analysis of different types of inorganic compounds. We have made efforts to emphasize the difficulties encountered as much as the results obtained and attempt to draw attention to fields in which the applications of this technique seem to be promising. Finally, the non-analytical possibilities of gas chromatography, though still not widely used in inorganic chemistry, are mentioned.

We are particularly indebted to Professor A. Chrétien, who directed the first scientific research of one of us (C.P.), for suggesting this book, and for writing the preface.

REFERENCES

1. A. T. James and A. J. P. Martin. *Biochem. J.*, 50, 1952, p. 679.
2. M. Tswett. *Ber, Deutsch. Botan. Ges.*, 24, 1906, p. 384.
3. J. Tadmor. *Chromatographic Reviews*, 5, M. Lederer (Ed.), Elsevier, New York, 1963, pp. 223–235.
4. V. I. Anvaer and B. P. Okhotnikov. *J. Anal. Chem, U.S.S.R.*, 19, 1964, pp. 444–459.
5. R. S. Juvet and F. M. Zado. *Advances in Chromatography*, 1, J. C. Giddings and R. A. Keller, (Eds.), Marcel Dekker, New York, 1965, pp. 249–307.
6. C. Pommier. *Revue de Chimie minérale*, 3, 1966, 401–437.

NOMENCLATURE OF PRINCIPAL SYMBOLS

d_g	Mean film thickness of the liquid phase
d_p	Diameter of the packing particles
D_g	Diffusion coefficient of the solute in the gas phase
D_L	Diffusion coefficient of the solute in the liquid phase
f	Relative peak width
F	Separation factor
F_o	Volume flow rate of the carrier gas at the outlet pressure of the column
h	Peak height
H	Height equivalent to a theoretical plate
I	Retention index
j	James and Martin factor (column pressure gradient correction factor)
k	Column permeability
k'	Capacity factor: $(1-R)/R$
K	Partition coefficient
K_e	Equilibrium constant
L	Column length
M	Molecular weight of the liquid phase
n	Number of theoretical plates
N_i	Mole fraction of compound i
p^o	Saturated vapor pressure of the pure compound investigated at the column temperature
$P=\frac{p_i}{p_o}$	Ratio of the column inlet and outlet pressures
R	Retention ratio: t_M/t_R
$R_{1,2}$	Resolution of compounds 1 and 2
t_M	Retention time of "air" (gas hold-up time)
t_R	Retention time

T_c	Absolute column temperature
u	Mean linear carrier gas velocity
u_0	Linear carrier gas velocity at the column outlet
V_g	Specific retention volumn
V_L	Volume of liquid phase in the column
V_M	Retention volume of "air" (gas hold-up volume)
V_N	Net retention volume: jV'_R
V_R	Retention volume
V'_R	Adjusted retention volume: $V_R - V_M$
V^o_R	Corrected retention volume: jV_R
α	Relative retention
γ	Activity coefficient at infinite dilution defined by Raoult's law
η	Carrier gas viscosity
ρ or ρ_L	Molecular weight of the liquid phase
σ	Standard deviation of the peak
ω	Baseline peak width
ΔH_E	Excess (or mixing) enthalpy of one mole of solute at infinite dilution in the liquid phase
ΔH_v	Vaporization enthalpy of the pure solute
ΔH_s	Vaporization enthalpy of the solute from the infinitely dilute solution

EDITOR'S NOTE: Nomenclature and symbols have been edited or altered to conform with "Recommended Practice for Gas Chromatography Terms and Relationships," *ATSM*, E355-68.

I. THEORETICAL CONCEPTS

For the convenience of the reader who is not familiar with gas chromatography, a few theoretical concepts which are necessary for an understanding of the following chapters are summarized here. A more complete development of the theory of this method can be found in general books [1, 2, 38].

1. Definition of Chromatography; Principles

Chromatography is a separation method in which the constituents of the mixture to be analyzed are distributed between two phases in a sequence of dynamic solution or adsorption equilibria. One of the two phases is stationary and has a very large specific surface; the other is mobile and percolates through the stationary phase [1].

The mobile phase can be either a gas or a liquid. The stationary phase can be either a solid adsorbent or a liquid. In the later case, the liquid phase is coated on a support of sufficiently large area, the specific surface of which is as inert as possible in order to avoid the disastrous effects of solid surface adsorption; this guarantees optimum contact with the mobile phase. In this way, four types of chromatography are available. Here we will study only gas-liquid and gas-solid chromatography.

The characteristics of gas chromatography result from the use of a carrier gas as the mobile phase, a low-viscosity compressible fluid in which the diffusion coefficients are high and the interaction between molecules, if any, is very low. Except in rare applications (see Chapter XI, §1), it can be assumed that an ideal gas is involved. The constituents to be analyzed must be soluble in the mobile phase, sufficiently volatile at the column temperature to be transported by the carrier gas.

In addition to the different types of chromatography enumerated above, several operating techniques exist: elution chromatography, frontal analysis, and displacement chromatography [1].

The most common of these is the elution method, in which a plug of the mixture to be studied is injected into the mobile-phase stream just upstream of the column. When the analysis is suitable, each component is eluted separately from the others but mixed with the carrier gas in the form of a more or less broadened band. The concentration of each component in the carrier gas is lower than its concentration in the analyzed mixture, in accordance with the second principle of thermodynamics as it applies to gas

chromatography: *chromatographic separation is accompanied by more or less extensive dilution in the carrier gas.*

In frontal analysis, the vapor of the mixture is introduced continuously into the carrier gas stream. Only the constituent with the least retention is eluted from the column in pure form; the other components of the mixture are then obtained, each containing more or less large quantities of the components not retained as strongly as the one with the least retention.

In displacement chromatography, a small quantity of sample is introduced at the head of the column and is swept by a carrier gas containing a constant concentration of a compound more strongly retained than each of the constituents of the mixture; the latter are then eluted in successive zones as in frontal analysis.

Preparative chromatography (see Chapter XI, §3) uses a method intermediate between elution and frontal analysis: a large sample of the vapor of the mixture to be separated is injected during a rather long time, and, after elution of the last band, this operation is repeated as many times as necessary [42].

In this chapter, we will study only the problems involved in the elution analysis of small samples of a mixture; therefore, we can consider the concentrations as negligible and the gas phase as ideal. The deviations from ideal behavior (*i.e.*, the case of large samples) are considered in Chapter XI.

The object of the theory of chromatography is to predict the elution time for each compound, the corresponding relative band width as a function of the column characteristics and operating parameters, and the degree of resolution between two adjacent bands.

2. Parameters Measured by Chromatography

At this point, it is of interest to compile the definitions of the principal chromatographic parameters. However, this section may appear superfluous to the reader. It is recommended that he scan it rapidly and refer to it whenever he later encounters an unfamiliar term.

We shall distinguish between the raw experimental data resulting directly from the chromatogram and those which are derived directly or are important to a theoretical interpretation. These parameters are generally defined for chromatograms obtained with pure products or binary mixtures, but it is evident that they can be generalized to any kind of mixture.

2.1 Raw Data Generated by the Chromatogram

Five parameters can be defined from the chromatogram obtained for a pure compound, and all other parameters necessary for interpretation of the

experiment should be calculated from them. In the case of a mixture, these same parameters can be defined for each of the components; however, their precise measurement is not always possible.

Figure 1 is a schematic chromatogram which indicates these parameters.

The retention time of the compound, t_R. This is the period of time which elapses between the time of injection and the time when the detector indicates the maximum concentration of the compound in the carrier gas leaving the column (OB in Figure 1).

Retention time of "air", t_M (OA in Figure 1). This time is important because it involves the transit time of an unretained compound (air in gas-liquid chromatography) through the column and the equipment. The residence time of a retained compound in the stationary phase therefore is $t_R - t_M$.

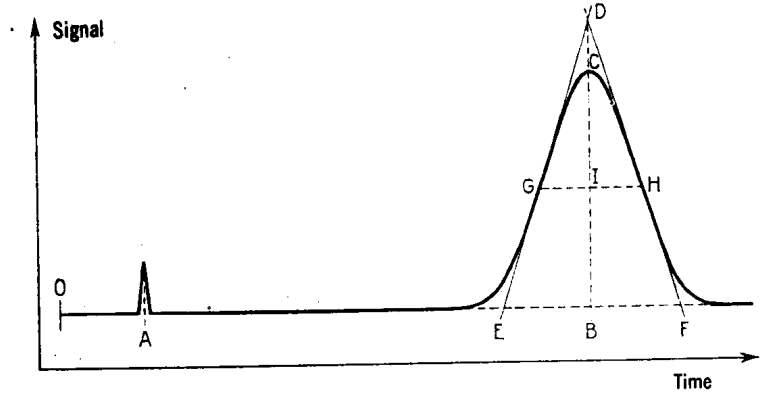

Figure 1. Schematic chromatogram showing the raw chromatographic data.

Peak width of the compound. Generally, use is made of the baseline width or the length of the segment intercepted on the baseline by tangents to the curve through the inflection points (EF in Figure 1).

Since the peak generally has the shape of a Gaussian curve, the half-width or any other equivalent definition can be used just as well.

Peak height (BC in Figure 1). The latter parameter is, in principle, proportional to the quantity of injected solute. It can be used in quantitative analysis, but the fluctuations of various factors (flow rate, temperature, injection time) lead to significant peak height variations, and the area is, therefore, often preferred. If the curve remains Gaussian, the area is proportional to the product of the height and the baseline width. However, frequently it will be preferable to determine the peak area directly by graphic integration or, better yet, by electronic integration of the signal obtained (*cf.* §7).

In general, these parameters can be expressed either in units of length as they are measured on the chromatogram or in physical units corresponding to the variables which are really measured (time, detector signal). Table I lists the names and symbols generally used as well as the designations employed in Figure 1.

Table I
Names and Symbols

Figure 1	*Symbol*	*Description*
O	—	Zero time, injection time, origin.
OA	t_M or d_M	Retention time (t_M) of a component not retained in the column or the corresponding retention distance (d_M) measured on the recording.
OB	t_R or d_R	Measured retention time or distance of solute B.
AB	$t_R - t_M = t'_R$	Retention time corrected for the air retention time or adjusted retention time.
—	d'_R	Adjusted retention distance.
EF	w	Baseline peak width, length of the segment intercepted by the tangents to the inflection points H and G
GI	σ	Standard deviation. When the peak is a Gaussian curve, the standard deviation is one-half of the distance GI between the inflection points and one-fourth of the baseline width EF; I is located at such a height that BI = 0.609 BC.
BC	h	Peak height

From these five raw data, a certain number of parameters can be derived characterizing the gas flow, the retention of a compound, the column efficiency, and the resolution of two components.

2.2 Derived Parameters Characterizing Flow

Flow in a column of length L is characterized by the average carrier gas velocity: $u = L/t_M$.

Later on, it will be apparent that it is possible to calculate all other

characteristic parameters for flow from it and from the inlet and outlet pressures (§3.7).

2.3 Derived Parameters Characterizing the Retention of a Compound

From the retention values obtained above, the following values are derived:

Measured retention volume, V_R. This is the volume of carrier gas flowing through the column during the retention time:

$$V_R = t_R F_o \tag{1}$$

where F_o is the volumetric flow rate measured at the outlet pressure and column temperature. If F_o is not constant, V_R is defined by an integral.

The gas hold-up volume, V_M, is the uncorrected retention volume of a gas not retained in the column (air in gas-liquid chromatography):

$$V_M = t_M F_o \tag{2}$$

Adjusted retention volume, V'_R. This is the volume of carrier gas flowing through the column during the residence time of the compound investigated in the stationary phase:

$$V'_R = V_R - V_M = (t_R - t_M) F_o = t'_R F_o \tag{3}$$

Corrected retention volume, V_R^o. When the flow rate F_o increases, the retention time t_R decreases; but V_R increases rather than remaining constant. In fact, to increase the flow rate, it is necessary to raise the pressure at the column inlet. Since the carrier gas is compressible, it expands as it progresses through the packing. Consequently, a larger volume of gas is necessary to elute a component when the column inlet pressure is higher. Therefore, $V_R = t_R F_o$ increases with F_o. The retention volume which would be obtained for zero flow rate, at which there is no pressure gradient, is called the limit or corrected retention volume. The ratio

$$j = \frac{V_R^o}{V_R} \tag{4}$$

is smaller than unity and decreases with increasing pressure. If the carrier gas can be considered ideal, it can be demonstrated (see §3) that this correction factor, called the James and Martin factor [4], is given by

$$j=\frac{3}{2}\frac{\left(\frac{P_i}{P_o}\right)^2-1}{\left(\frac{P_i}{P_o}\right)^3-1}=\frac{3}{2}\frac{P^2-1}{P^3-1}, \qquad (5)$$

where p_i is the inlet pressure and p_o the outlet pressure of the carrier gas.

Generally, p_o is atmospheric pressure and the ratio p_i/p_o then is equal to the absolute inlet pressure expressed in atm. Generally it has the notation P.

The net retention volume, V_N, or the completely corrected retention volume, results from the uncorrected retention volume to which the two corrections of gas hold-up and carrier gas compressibility have been applied:

$$V_N=jV'_R=j(t_R-t_M)F_o. \qquad (6)$$

By convention, V_R, V'_R, V^0_R, and V_N are measured at the column temperature and at the carrier gas outlet pressure, consequently requiring a correction of the experimental value of F_o, usually measured downstream from the detector at ambient temperature.

Specific retention volume, V_g. This is the net retention volume reduced to normal temperature and pressure conditions (0°C, 76 cm Hg) and referred to the unit mass of stationary phase:

$$V_g=\frac{V_N}{m_f}\frac{273}{T_c}\frac{p_o}{p_n}, \qquad (7)$$

where T_c is the absolute column temperature (°K), m_f is the weight of stationary phase in the column, p^o the outlet pressure and p_n is the normal pressure.* The specific retention volume is a physical constant depending only on the solute-solvent combination and temperature (see §5).

Retention volumes are absolute parameters which depend on frequently imprecise flow rate measurement. Relative parameters are often used as an alternative.

Frontal ratio, R. This is the ratio of the uncorrected retention times of air and of the compound investigated:

$$R=\frac{t_M}{t_R} \qquad (R<1). \qquad (8)$$

It will be demonstrated (see §4) that R is equal to the fraction of solute

*EDITOR'S NOTE: V_g defined by ASTM does not include correction to $p_n=1$ atm, it being assumed that $p_o \backsim 1$ atm.

molecules present in the gas phase at a given time, and this gives this parameter its theoretical interest. The fraction $1 - R$ is dissolved in the stationary phase. (In paper chromatography, a similar parameter, R_f, is used.)

Capacity or partition ratio, k'. It is defined by the following relation:

$$k' = \frac{t_R - t_M}{t_M} = \frac{d'_R}{d_R - d'_R} = \frac{1-R}{R} \tag{9a}$$

and therefore we have

$$R = \frac{1}{1+k'} \tag{9b}$$

In equation 9a, $1 - R$ represents the average number of molecules present in the stationary phase at a given time and having zero velocity; R represents the number of molecules in the mobile phase at the same time having velocity u; k' is the ratio of these two values. Thus, it is the partition coefficient of the solute between the gas phase and the stationary phase present in the column. Factors k' and R are two different expressions characterizing the same phenomenon: retention. They are directly dependent on the partition coefficient K of the solute.

Partition coefficient, K. This coefficient is defined by the following ratio at equilibrium:

$$K = \frac{\text{solute concentration per unit of volume of stationary phase}}{\text{solute concentration per unit of volume of mobile phase}} \tag{10}$$

K is a thermodynamic parameter depending only on the solute–solvent system and on temperature. Therefore, K is directly related to V_g. In fact, it will be demonstrated (see §5) that

$$V_g = \frac{K}{\rho_L}, \tag{10a}$$

where ρ_L is the density of the liquid phase. Furthermore, by definition of K and k', we have

$$k' = K\frac{V_L}{V_G}, \tag{10b}$$

where V_G and V_L are the gas and liquid volumes present in the column.

2.4 Derived Parameters Characterizing the Efficiency

The baseline peak width characterizes the ability of the column to produce narrow peaks and thus to separate complex mixtures. Several other absolute or relative parameters permit expression of this ability.

Standard deviation σ. The classical parameter, σ, permits a description of a Gaussian curve. Since the peaks generally have profiles differing somewhat from a Gaussian curve, this parameter is often taken as equal to one-fourth of the baseline width. It may also be considered as experimental data. The entire statistical theory of peak broadening is based on a calculation of the standard deviations produced by the different phenomena playing a role in peak broadening. For this reason, we will review a few properties of standard deviations.

Properties of the standard deviation, σ. We assume that a large number of molecules is forced to move randomly by jumps of path lengths l in one dimension of space in either direction but not in the other two dimensions. When each molecule has made n jumps, n being very large, the center of mass of the population will have remained immobile, but the distribution of molecules will be a Gaussian curve with the standard deviation given by

$$\sigma = l\sqrt{n}. \tag{11}$$

This is the equation for unidirectional random walk which we will use in the following.

In general, several processes of different origin contribute to the random motion. The overall result can be determined with the following rules.

1. When several interrelated random processes are simultaneously active, the total standard deviation is given by

$$\sigma = \sum \sigma_i. \tag{12}$$

2. When several independent random processes are active simultaneously, the total standard deviation is given by

$$\sigma^2 = \sum \sigma^2_i, \tag{13}$$

σ^2 is called the *variance*.

3. In the case of two partially dependent phenomena between which there is no strict relation but only a statistical correlation, the total variance is given by

$$\sigma^2 = \sigma_1^2 + \sigma_2^2 + 2\rho\sigma_1\sigma_2, \tag{14}$$

where ρ is a coupling coefficient between 0 (complete independence) and 1 (strict dependence).

Generally ρ is difficult to estimate.

Different standard deviations. For each peak, we distinguish the standard deviations expressed in unit of length (σ) and unit of time (τ). Since the solute band moves at velocity Ru as we will see (see §§3, 4, and 5), the following relation exists between these two standard deviations:

$$\sigma = Ru\tau.$$

Relative peak sharpness, f. This is the parameter.

$$f = \frac{d_R}{\omega} = \frac{t_R}{4\tau} = \frac{d_R}{4\sigma} \tag{15}$$

Resolution value, W:

$$W = 2\frac{d_R - d_m}{\omega} = \frac{t'_R}{2\tau} \tag{16}$$

Number of theoretical plates of the column, n. This parameter was introduced by a purely phenomenological theory of little interest because it offers no concrete prediction:

$$n = 16\left(\frac{d_R}{\omega}\right)^2 = \left(\frac{d_R}{\sigma}\right)^2 = \left(\frac{t_R}{\tau}\right)^2 = 16f^2. \tag{17a}$$

This parameter nevertheless remains useful because it permits a simple classification and comparison of columns. If columns are prepared under the same conditions with the same packing, n is proportional to their length. Unfortunately, since n increases with the square of the relative peak sharpness, it is subject to a certain inflation. The value n is particularly useful because it permits us to calculate another parameter, the plate height.

Effective number of theoretical plates, N. This parameter is similar to n but is defined on the basis of the adjusted retention time t'_R:

$$N = 16\left(\frac{d'_R}{\omega}\right)^2 = \left(\frac{t'_R}{\tau}\right)^2 = 4W^2. \tag{17b}$$

Height equivalent to a theoretical plate, $\bar{H}$. If the column length is L, the height of each theoretical plate will be

$$\bar{H} = \frac{L}{n}. \tag{18a}$$