Physical Methods IN Chemical Analysis

EDITED BY WALTER G. BERL

VOLUME THREE

The contributions included in this volume continue the aims set forth in Volume I to describe those physical methods that have either proved of considerable value in analytical work or are destined to play an important role in the future. Electrical, magnetic, and miscellaneous techniques are discussed. In addition, a chapter on neutron spectroscopy and neutron interactions is included.

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PHYSICAL METHODS
IN
CHEMICAL ANALYSIS

Edited by

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VOLUME III

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PREFACE

Volume III of the "Physical Methods in Chemical Analysis" extends the ground covered in the previous volumes of this series. The adaptation and extension of newly discovered physical techniques to analytical ends continues at a rapid pace and thus strengthens the position and power of the analytical chemist. How rapid the advances are is shown by the fact that when the first two volumes were in preparation the principles of nuclear magnetic resonance had only just been disclosed to the scientific world. In less than ten years the method has become for the analyst a valuable new tool with unique and impressive capabilities. Gas chromatography and several other methods treated in this volume have had a similar history.

The scope of the analyst's functions is changing rapidly and fundamentally. Apart from identifications and quantitative estimations the problems of shape and structure on the molecular and on grosser levels have been added to his province. Much of this expansion is due to the wide adoption of physical methods of separation and measurement. Despite the frequent complexity of the techniques and the attendant expense in first cost and maintenance of the equipment they have become valuable and often indispensable companions to the well established classical methods. No analyst can practice his profession effectively without thorough acquaintance with this modern branch of analysis.

The editor has attempted to maintain the policy laid down previously which is to present a review of the status of physical measurements and their application as analytical tools. The discussion of principles is stressed. The reviews are intended to broaden the horizon of students and practicing chemists, acquainting them with the promising new research tools at their disposal and explaining the scientific basis upon which they are built. They also aim to indicate the areas of usefulness as well as the limitations to which they are subjected.

The chapters in Volume III range over many diverse fields of analytical interest. Gas chromatography represents an extraordinarily useful extension of chromatographic analysis and is rapidly gaining a firm foothold in the quantitative estimation of low-molecular-weight substances. Its capabilities are very wide and its use is so rapidly expanding that no review can hope to remain up to date for long. Electrochromatography is finding its main role in biochemical applications as a worthy companion to paper chromatography. The high precision and convenience of elec-

trical measurements is finding various outlets in electrochemical and polarographic micro-procedures and titrations. Although the range of applicability of the field ion microscope is limited it represents nevertheless one of the most sensitive devices for the detection of adsorbed films and for the study of individual crystal planes. It should find increased application in the analytical laboratory in the future.

No matter how elegant and precise the analytical techniques may be, faulty sampling of inhomogeneous mixtures may lead to incorrect conclusions. The chapter on sampling reviews the principles on which meaningful sampling procedures should be based. The spectroscopic armament of the analyst has received new additions through either the development of older principles or the introduction of quite new physical measurements. Flame photometry and fluorescent X-ray analysis belong to the former group where component developments have led to greatly improved practical utility. Microwave, nuclear resonance, and neutron spectroscopy, on the other hand, are based on quite new principles of physical measurements, now applied to analytical work. Finally, neutron activation opens up regions of versatility and sensitivity of detection unmatched by any other technique.

Without the unselfish cooperation of the authors of the individual chapters this book would be an empty shell. The publisher, as before, has assisted in every possible way.

WALTER G. BERL

August, 1956

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1. General Theory

1.1. Introduction

The term *gas chromatography* will be used to distinguish those chromatographic techniques in which the traditional moving liquid phase is replaced by a moving gas. The separations achieved in gas chromatography depend therefore upon repeated equilibrations between a moving gas and a fixed (or column) phase.

The most important advantage obtained by replacing the moving liquid by a gas is the greater rapidity with which equilibria involving gases are set up. This means that gas chromatographic columns work highly efficiently and can be run at greater speed than the corresponding liquid columns. The limits of the gas chromatographic techniques are not very severe. The substances to be chromatographed must be sufficiently volatile to be detectable in the gas phase at the temperature of operation, and the column materials must be sufficiently involatile to act as a separate phase. Small concentrations of vapor are easily measured in the moving gas by physical methods of general application, and the chromatographic separations can be followed and recorded automatically.

Despite the long history of chromatography and its wide practical applications, it is only relatively recently that the possibilities of gas chromatographic methods have been investigated in any detail. The development of gas chromatography can be traced largely to the fundamental contributions made by Claesson (4) in 1946 with displacement columns and by James and Martin (17) in 1952 with partition columns. In some ways it is curious that gas chromatography should have followed from conventional chromatography, for the behavior of gases is so much simpler and better understood than is the behavior of liquids.

1.2. Single Vapors

The word *vapor* will be used throughout to describe the substances which are being chromatographed, although in some cases these substances would be gases at the temperature of the column. The word *gas* will be reserved for the mobile phase.

We begin by considering the behavior of one vapor as it is carried through a long column by the gas until it finally emerges in the gas stream. The distribution of the vapor in this effluent stream is, ideally, directly related to the isotherm for the equilibrium distribution between the vapor and the fixed phase of the column. The distribution is recorded as a peak in the chromatogram. Three basic patterns can be distinguished for this peak (Fig. 1). Symmetrical (Gaussian) peaks result if the isotherm is linear, as is usually the case with partition isotherms (fixed liquid on the column) at low concentrations of vapor in the fixed phase. They are also found for adsorption at very low surface coverages. The detailed theory of these symmetrical peaks has been worked out by Martin and Synge (28) using the concept of the theoretical plate. This is defined as a layer at right angles to the column, the layer being of such thickness that the mean concentration of the substance in the fixed phase in this layer is in equilibrium with its vapor in the gas phase leaving the layer. The smaller the height of this theoretical plate, that is, the more rapidly equilibrium is

reached between the moving gas and the fixed phase, the more efficient is the column and the less the spread of the vapor peak. The column efficiency may be expressed in terms of the number of its theoretical plates r, which may be calculated from the peak shape. Two methods are given by

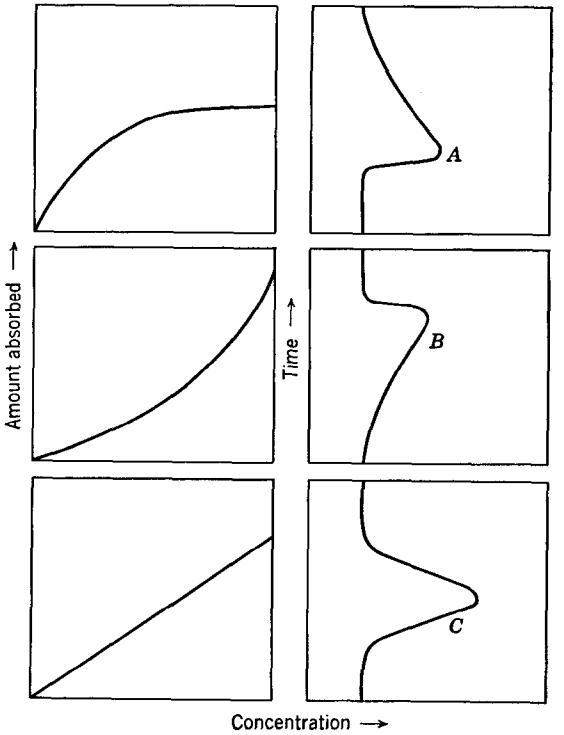

FIG. 1. Equilibrium isotherms and chromatogram peaks (22).

Martin and James (17). In the first the rate of removal of the vapor from the column is measured at the peak maximum, S. Then

$$r = 2\pi \left(\frac{St}{M}\right)^2$$

where M is the total quantity of substance put onto the column and t is the time taken before the peak maximum emerges from the column. In the second method the time (τ) taken for the center of the peak to leave the column (i.e., between ordinates one standard deviation on either side of the peak, or 68.3% of total quantity of material in the peak) is measured. Then

$$r = 4\left(\frac{t}{\tau}\right)^2$$

Some values taken from James and Martin (17) for a 4-ft.-long silicone/stearic acid column are given in Table I.

The peak maximum occurs when a certain volume of gas, the retention volume V_R, has emerged from the column. If the gas were an incompressible fluid, the retention volume V_R^0 would be given by the relation

$$V_R^0 = l(a + \alpha b)$$

where l is the length of the column, b is the cross-sectional area of the column occupied by the fixed (liquid) phase, a is the cross-sectional area

TABLE I

Determination of Column Efficiency
(r = number of theoretical peaks)

Flow rate of gas, ml./min.	r	
	Method I	Method II
35	550	400
18.2	718	600
10.3	765	730

of the column occupied by the moving gas, and α is the distribution (or partition) coefficient of the vapor between the fixed and the gas phase.

$$\alpha = \frac{\text{(weight of substance per unit volume of fixed phase at equilibrium)}}{\text{(weight of substance (vapor) per unit volume of gas at equilibrium)}}$$

In practice, as there is always a pressure drop across the column, the gas is compressed at the beginning and there is a gradient of gas velocity along the column. If p_1 is the pressure of gas at the column inlet and p_0 the pressure at the outlet, then (17)

$$V_R = \frac{2}{3} V_R^0 \frac{[(p_1/p_0)^3 - 1]}{[(p_1/p_0)^2 - 1]}$$

As α is a characteristic of the vapor (for a particular fixed phase and at a particular temperature), V_R^0 can be used to identify a substance being chromatographed. A typical relationship between V_R^0 and the number of carbon atoms in an homologous series is illustrated in Fig. 2.

Peaks with sharp fronts and diffuse tails result if the isotherm curves toward the vapor-pressure axis, as in Langmuir-type adsorption. In the case of such isotherms (2) high concentrations of vapor will move faster through the column than will low concentrations. The position of the

sharp front, unlike the position of the peak maximum for a linear isotherm, depends not only on the character of the vapor, but also on the amount. Peaks with diffuse fronts and sharp tails result if the isotherm curves away from the vapor-pressure axis, as is frequently the case for partition equilibria with high concentrations of vapor in the fixed liquid

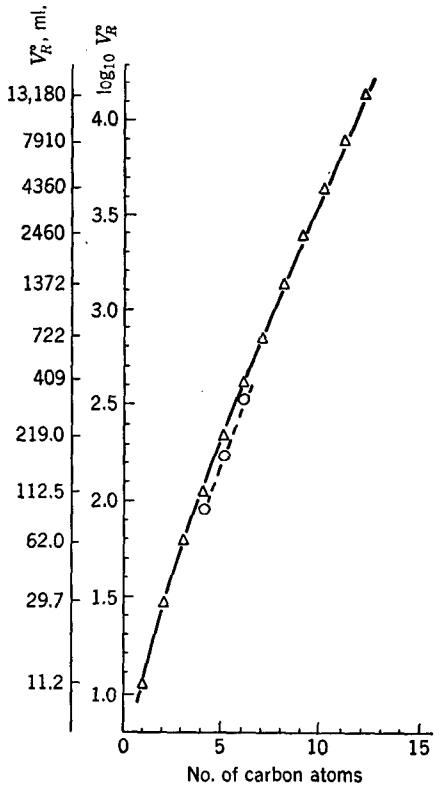

FIG. 2. Relationship between V_R^0 and the number of carbon atoms in the lower fatty acids.

Δ = *n*-acids o = *iso*-acids

Data for a 4-ft. silicone–stearic acid column at 137° C. (17).

phase. It is also observed with the adsorption of water vapor on charcoal at 20° C. (30).

1.3. Elution Analysis of Mixtures

If a small quantity of a mixture of volatile substances is brought to the beginning of the column, each substance will, to the first approximation,

behave independently of the others and produce its characteristic vapor peak in the effluent gas stream. The area (on the record) under each peak will measure the amount of the corresponding substance in the original mixture. In the case of linear isotherms (symmetrical peaks) each component of the mixture can be characterized by its retention volume, V_R^0.

With partition columns the components of the mixture, except insofar as they make slight modifications in the solvent properties of the fixed phase, interfere relatively little with one another. With adsorption columns, however, the various substances compete for lattice sites on the surface of the adsorbent. An important consequence of this [as has been shown most clearly by Hagdahl, Williams, and Tiselius for the case of Langmuir adsorption (11)] is that the more strongly adsorbed vapor will tend to push a more weakly adsorbed vapor ahead of it along the column. This means that the adsorption column has a "self-sharpening" property not possessed by partition columns. Substances not only separate by virtue of their differing individual rates of movement on an otherwise empty column, but in addition traces of a more weakly adsorbed component are rapidly accelerated out of a zone of a more strongly adsorbed component.

1.4. Displacement Analysis

This displacing action of one substance upon another during chromatography on an adsorbent column is the basis of the method of displacement analysis. In this method the mixture is first brought to the column

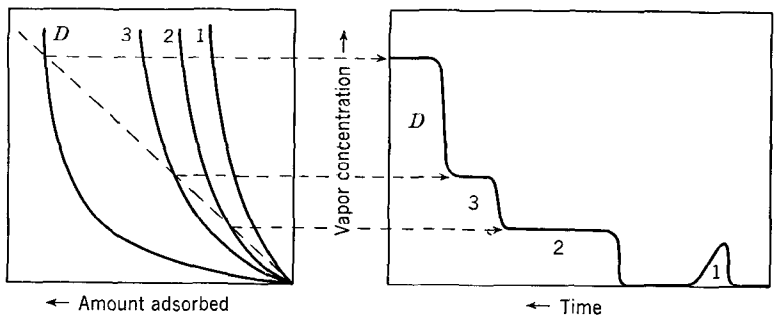

FIG. 3. Adsorption isotherms and displacement analysis.

as in elution analysis, but then a constant concentration of a substance (the displacer) more strongly adsorbed than any of the components of the mixture is fed into the moving gas stream at the beginning of the column. This displacer pushes the mixture ahead of it along the column, so that each component of the mixture acts as a displacer for the next most

strongly adsorbed component. The final chromatogram recorded from the effluent gas consists of a series of steps, each step corresponding to one component of the mixture leaving the column at a fixed concentration and finally to the displacer. Each concentration is a characteristic (for a fixed adsorbent, temperature, displacer, and displacer concentration) of the component, as is also its place in the displacement sequence. Qualitative analysis can thus be reduced to a measurement of step heights. The length of the step measures the quantity of the component present in the original mixture. The step heights may be deduced from the corresponding isotherms, as is shown in Fig. 3. In practice, these heights are obtained by calibration, and displacement analysis is used (22) to determine the isotherms rather than the reverse.

2. Apparatus

2.1. Introduction

There are thus three basic gas chromatographic methods: (*a*) gas-liquid partition chromatography (elution analysis only), (*b*) elution gas-adsorption chromatography, (*c*) displacement gas-adsorption chroma-

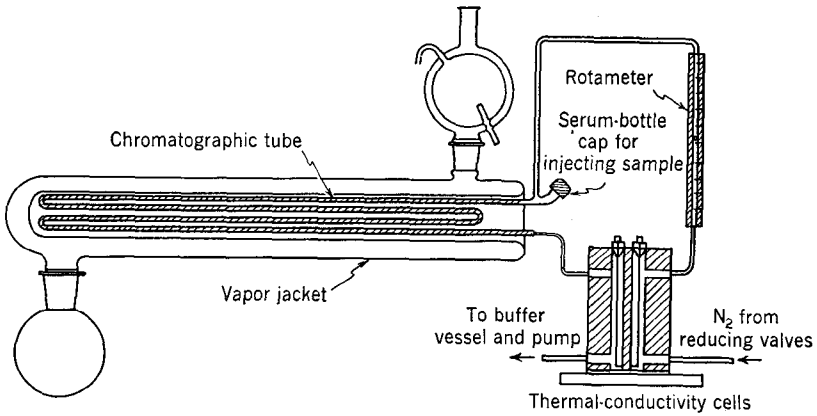

FIG. 4. A complete apparatus for elution (gas-liquid partition) analysis (32).

tography. Of these methods (*a*) is the simplest in principle and in general the most effective in practice. We shall therefore discuss the apparatus for gas-liquid partition chromatography in some detail and then only mention such modifications of this apparatus as are necessary for its application to the two gas-adsorption methods.

Figure 4 illustrates a typical partition apparatus, described by Ray (32). Nitrogen gas is taken from a cylinder via reducing valves and flows

through the column at a rate controlled by the pressure drop across the column and measured by means of the rotameter. The gas flows through the reference side of the thermal-conductivity vapor detector before passing onto the column and through the sensing side of the detector as soon as it leaves the column. The fixed liquid phase (dinonyl-phthalate) supported on an inert macroporous material (kieselguhr) is packed into a glass tube 6 ft. long and 4 mm. in internal diameter. The tube is formed into a *W* shape to restrict the length of the air jacket which maintains it at the temperature of operation. The air-jacket temperature is controlled by a surrounding vapor jacket. The sample is injected as a liquid into the gas stream through the serum-bottle cap by means of a hypodermic syringe. The component vapors are detected and their concentrations in nitrogen recorded by the sensing side of the detector.

2.2. Chromatographic Column

The following procedure has been found satisfactory for the packing of a partition column.

1. The inert solid support (e.g., Celite 545, Johns Manville Company, Ltd.) for the absorbing liquid is first graded by being suspended in water in a tall 3-liter beaker and allowed to settle for 3 min. The supernatant liquid is then decanted off.
2. The precipitate is washed with acid and distilled water and is dried at 100° C.
3. This material is treated with the appropriate amount of the immobile column liquid (e.g., 0.3 to 0.4 g. of liquid to 1 g. of Celite). The two are then thoroughly agitated together for 8 hr. in a cannister attached to a small electric motor. Alternatively the immobile liquid is dissolved in ether and the solution is added to the Celite to form a slurry, which is stirred continuously as the ether is evaporated off in a stream of air (26).
4. The column material is poured carefully into the column while the column is held against the rotating flattened spindle of an electric motor. The vibration of the motor causes the powder to pack in a uniform compact mass.

Very small particles are to be avoided as they cause excessive resistance in the column to passage of gas.

If the column liquid is, for all practical purposes, involatile at the temperature of operation of the column, then it is possible to use the same column repeatedly and reproducibly over long periods of time. However sharper resolution (larger number of theoretical plates) is frequently obtained with low-molecular-weight column fluids because of their greater solvent power and their lower viscosity. The following are examples of column liquids which have already found considerable application: liquid paraffin and silicone fluids (both nonpolar and especially suitable for the separation of saturated hydrocarbons), dinonyl-phthalate and tritolyl-phosphate (polar and therefore producing a selective retardation of polar molecules), benzyl-diphenyl (for selective retardation of aromatics)

polyethylene-oxide (Lubrol MO) (H bonding with "active" hydrogen, e.g., primary and secondary amines), glycerol (for selective retardation of alcohols and especially water vapor).

James and Martin (17) employed solutions of stearic acid or orthophosphoric acid (10% by weight) in silicone DC 550 fluid for the separation of fatty acids. The dissolved acid produces a marked increase in the linearity of the absorption isotherm.

2.3. Vapor Detectors

Vapor detectors for gas chromatography should be of high sensitivity to all vapors, should respond rapidly to changes in vapor concentration (hence be of small internal volume), and should not react with or adsorb any of the vapors. For quantitative work it is important that the detector signal should be directly proportional to vapor concentration and, if possible, independent of the nature of the vapor.

2.3.1. Thermal-Conductivity Cell. So far this has proved to be the most widely used detector in gas chromatography. It can be applied generally, is rapid in response and simple to construct, and with a little care can be made extremely sensitive. It gives a linear response to vapor concentration and, if helium (or hydrogen) be used as the carrier gas, a response which is very nearly proportional to molar concentration for a wide range of vapors of the same general type (13). A full account of the thermal-conductivity cell has been given by Weaver (35).

In the detector a heated wire (e.g., platinum) passes down the center of a tube, through which gas flows from the column. The wire loses heat via the gas to the walls of the tube, and the temperature and hence resistance of the wire are therefore dependent upon gas composition. The cell forms one arm of a Wheatstone bridge, the out of balance of which is fed to a recorder.

Metal tubes produce a slightly faster response than glass tubes do, because of their higher heat conductivity. Rapid temperature fluctuations of the tube walls give rise to unsteadiness in the base line, an effect which is overcome most simply by enclosing the tube in a metal block of high heat capacity. Slow temperature changes produce a drift of base line, which may be overcome by immersing the block in a very good thermostat or by using a second reference cell mounted with the sensing cell in the same block and placed in opposition in the bridge circuit. This latter method also provides a high measure of insensitivity to flow-rate variation and is adopted in most commercial instruments.

A considerable increase of sensitivity (and a reduction in detector volume) can be effected by use of thermistors in place of the heated wire.