CHROMATOGRAPHIC ANALYSIS OF THE ENVIRONMENT

CONTRIBUTORS

OSMAN M. ALY, Department of Environmental Engineering, Campbell Soup Company, Campbell Place, New Jersey

DANIEL F. BENDER, Environmental Protection Agency, Cincinnati, Ohio

ROBERT S. BRAMAN, Department of Chemistry, University of South Florida, Tampa, Florida

THOMAS G. BUNTING,* Chase Brass and Copper Company, Kennecott Copper Corporation, Cleveland, Ohio

GORDON CHESTERS, Water Resources Center, Department of Soil Science and Water Chemistry Program, University of Wisconsin-Madison, Madison, Wisconsin

RENATO C. DELL'ACQUA, Division of Laboratories and Research, New York State Health Department, Albany, New York

WALTER C. ELBERT, Water Science Branch, National Field Investigations Center — Cincinnati, Office of Enforcement and General Counsil, U.S. Environmental Protection Agency, Cincinnati, Ohio

SAMUEL D. FAUST, Department of Environmental Science, Rutgers — The State University, New Brunswick, New Jersey

D. A. GRAETZ,** Water Resources Center, Department of Soil Science and Water Chemistry Program, University of Wisconsin-Madison, Madison, Wisconsin

ROBERT L. GROB, Department of Chemistry, Villanova University, Villanova, Pennsylvania

CHARLES E. HAMILTON, Waste Control, The Dow Chemical Company, Midland, Michigan

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*Present Address: Ross Laboratories, Division of Abbott Laboratories, Columbus, Ohio

**Present Address: Soil Department, Institute of Food and Agricultural Sciences, University of Florida, Gainesville, Florida

JOSEPH V. HUNTER, Department of Environmental Science, Cook College, Rutgers University, New Brunswick, New Jersey

BARBARA S. JACOBSON, Ross Laboratories, Columbus, Ohio

KINGSLEY KAY, Department of Environmental Medicine, Mt. Sinai School of Medicine, New York, New York

EUGENE J. McGONIGLE, Merck Sharp and Dohme Research Laboratories, Pharmaceutical Research and Development, West Point, Pennsylvania

E. J. SOWINSKI, Western Electric Company, Inc., Allentown, Pennsylvania

IRWIN H. SUFFET, Department of Chemistry, Environmental Engineering and Science, Drexel University, Philadelphia, Pennsylvania

WAYNE THORNBURG, Del Monte Corporation Research Center, Walnut Creek, California

HAROLD F. WALTON, Department of Chemistry, University of Colorado, Boulder, Colorado

PREFACE

A monograph of this type, in order to cover the particular subject, must be complex. Environmental studies, by nature, are complex and a condensed survey-type book would serve little purpose to those engaged in the various environmental services. As a meaningful and working definition of environment I have chosen "the gross amount of surrounding entities and/or conditions that influence the well-being or preservation of mankind."

The need for a comprehensive series of methods for determining the various toxic substances in the atmosphere, water, waste effluents, and soil is generally recognized. This book has been written to provide a comprehensive work of chromatographic techniques that are of practical value to consultants, engineers, chemists, and students. It is hoped that it can end or lessen the need for tedious searches through the mass of scattered literature. Every effort has been made to present the material as simply and clearly as possible. Information contained herein may prove to be valuable in establishing the criteria for choosing one technique in lieu of another for a specific sample type and analysis. It certainly should be of value in teaching because it provides a primary framework for existing knowledge.

The ultimate goal in the scientific understanding of the environment as well as the development of scientific technology for its control is the benefit of mankind.

Some of our present-day drugs and pesticides are hazardous; their presence causes need for solicitude. Tobacco smoke, automobile exhaust fumes, drinking water, industrial effluents, and bad air may easily be included as of concern. Perhaps the two notorious examples of substances that hypothetically menace the health of mankind are pesticides and radioactive isotopes.

Chemists, because of their training and special skills, must play an important role in the understanding of the air, water, and land environment as well as in the prevention of their degradation. Due to the ecological interrelationships of the environment there needs to be more interdependence of research between chemists and other scientific disciplines concerned with man's environment. Our responsibility of monitoring and controlling toxic materials would be very simple if all such contaminants were radioactive—a radiation detector would suffice.

The term "environment" not only includes the vast out of doors (macroclimates) but the enclosed environment where man toils (localized or specific microclimates). Industry must have the capability of detecting and preventing atmospheric contaminants in these immediate surroundings. Toxic materials are a necessity for many industries; methods of detection and prevention means must be available so that concentrations are maintained at minimum levels. Thus, it is not amiss to emphasize that the most important single step toward prevention of environmental illness is the control of foreign bodies in our air, soil, and water supplies.

Frequently, speed, accuracy, and specificity of analyses have been greatly enhanced by the development and/or modification of procedures. Equally significant are the discoveries and utilization of powerful and improved methods of separation, indispensable in the investigation of complex systems where even the most refined of available methods are inadequate for distinguishing and measuring with sufficient precision.

In a field as extensive and as rapidly expanding as chromatography the practicing chemist is obliged to maintain close scrutiny over the current literature. He or she must be sufficiently grounded in the basic principles of chemistry to enable him or her to carry out tasks in the most intelligent, efficient, and scientific manner. It is hoped that the contributors to this monograph have aided in this understanding.

To have a self-contained reference source this volume commences with a plenary chapter on the theory and practice of chromatography. This enables minimization and repetition from chapter to chapter on such similar subjects as general theory, experimental techniques, and commonly used chromatographic systems. Thus, the book should be useful to the chemist (novice or expert in chromatography), practicing engineer, technician, or teacher.

In organizing the chapters of this monograph it has been decided to cover the main chromatographic techniques (gas, liquid, paper, thin-layer, and ion exchange) for each of the four environmental areas, i.e., air, water, soil, and waste. Only in the areas of air pollution and waste chemistry has it been decided not to cover all techniques. In these two areas, the extent to which ion exchange has been utilized does not warrant a chapter.

In preparing a work of this nature it is impossible to succeed without the support and cooperation of many people. I am grateful to many people, who in some way have made the monograph a reality. Special thanks would have to go to Dr. Calvin Calmon for aid in securing a contributor; to Dr. Harold F. Walton, Dr. Eugene J. McGonigle, and Mrs. Barbara S. Jacobson for their willingness to come to the aid of a fellow scientist; and to Dr. Thomas G. Bunting who read and commented on most of the manuscripts. Last, but by no means least, my thanks go to my family for their understanding during the long and quiet evenings.

Robert L. Grob

CONTENTS

PART I

PLENARY SECTION

Chapter 1

THEORY AND PRACTICE OF CHROMATOGRAPHY

Thomas G. Bunting*

Chase Brass and Copper Company
Kennecott Copper Corporation
Cleveland, Ohio

*Present Address: Ross Laboratories
Division of Abbott Laboratories
Columbus, Ohio

I. INTRODUCTION

A Russian botanist, Mikhail Tswett [1], used the word "chromatography" to describe his separation of plant pigments, which was effected by passing an extract of the pigments through a column packed with calcium carbonate. The result was a series of colored zones on the column and, thus, the name "chromatography" from the Greek chromatus and graphein, meaning "color" and "to write." Since Tswett, a wide variety of independent techniques that have little or nothing to do with color have come to be called chromatography. At least one, paper chromatography, was recognized centuries before Tswett, while most evolved from his work [2].

"Chromatography" now refers to any of a diverse group of techniques that effect a separation through a distribution of sample between two immiscible phases. Further qualification is necessary to distinguish chromatography from other separation techniques, such as extraction. The stipulation is thus added that one phase be stationary while the second phase be mobile and percolate through the first phase. Practically, the mobile phase is gas or liquid, while the stationary phase is a liquid or a solid. The separation of the components, or solutes, of a sample results from differences in their rates of adsorption, solution, or reaction with the mobile and stationary phases. The nature of the mobile and stationary phases, the type of interaction between the two phases and the solute, and the physical arrangement of the stationary phase must be considered in distinguishing the many types of chromatography. The physical states of the mobile and stationary phases give rise to four basic types of chromatography: gas-liquid chromatography, GLC; gas-solid chromatography, GSC; liquid-liquid chromatography, LLC; and liquid-solid chromatography, LSC.

Of the four basic types of chromatography, the two gas systems are independent and not subject to subdivisions. Thus, the terms GLC and GSC adequately identify the technique involved. The liquid systems are not so easily described and are not mutually exclusive, which can lead to considerable confusion. Liquid-solid chromatography may include column chromatography, thin-layer chromatography, and ion-exchange chromatography. "Liquid-liquid chromatography" generally is reserved for the liquid analog of gas-liquid chromatography, but other forms are possible. Finally, paper chromatography appears to be a combination of liquid-liquid and liquid-solid chromatography. Unfortunately, the profusion of nomenclature does not end here. Table 1, which omits some specialized systems, notably gel permeation and electrophoresis, describes 11 frequently encountered designations. The significance of Table 1 is that the common terms are insufficient to adequately describe a chromatographic system. Ideally, one should specify the physical states of the two phases, e.g., liquid-solid, the nature of the separation, e.g., adsorption, and the configuration of the system, e.g., columnar.

TABLE 1

Types of Chromatography

Adsorption	Any system where the solutes are resolved by selective adsorption on a solid stationary phase; generally refers to columnar liquid-solid chromatography but may be used for gas-solid, thin-layer, and paper
Column	Any technique in which the stationary phase is contained in a column: usually designates a liquid-solid adsorption system but may include ion exchange and, rarely, gas-liquid and gas-solid systems
Gas (GC)	Gas-liquid or gas-solid chromatography
Gas-liquid (GLC)	The system utilizing a gaseous mobile phase and a liquid stationary phase which is supported either by fine particles packed in a tube or by the walls of the tube itself
Gas-solid (GSC)	A gaseous mobile phase and a solid adsorbent stationary phase contained in a column
Ion exchange	Any system in which the stationary phase is an ion-exchange resin: configuration is usually columnar, but may be thin-layer or paper
Liquid (LC)	Technically refers to any system with a liquid mobile phase but is commonly used for columnar liquid-solid adsorption chromatography

TABLE 1 (Continued)

Liquid-liquid (LLC)	Mobile and stationary phases are liquid: generally refers to the analog of the gas-liquid system but may include ion-exchange and paper chromatography
Liquid-solid (LSC)	Liquid mobile phase; solid stationary phase: name used infrequently but technically includes columnar adsorption, ion-exchange, thin-layer, and paper chromatography
Paper	Paper strip or sheet is the stationary phase; cellulose or shredded paper in a column is generally treated as columnar liquid-solid adsorption chromatography
Thin-layer	Literally, any system in which the stationary phase is in the form of a thin layer: usually refers to liquid-solid adsorption but may be used for ion exchange in the form of a thin layer

TABLE 2

Chromatographic Systems

System	Mobile phase	Stationary phase	Configuration	Separation
Gas	Gas	Liquid	Column	Partition
	Gas	Solid	Column	Adsorption
Liquid	Liquid	Liquid	Column	Partition
	Liquid	Solid	Column	Adsorption
Paper	Liquid	Paper	Sheet or strip	Partition or adsorption
Thin-layer	Liquid	Solid	Thin film	Adsorption
Ion exchange	Liquid	Solid	Column	Ionic replacement reactions

For the purposes of environmental analysis, the classification of chromatographic systems according to Table 2 is expedient. The development of chromatographic theory and practice has been sufficiently nonstructured as to allow reclassification of the 11 systems of Table 1 into the five broad types in Table 2. This organization is convenient for a general consideration of chromatographic theory as well as for a specific treatment of chromatographic practice as applied to environmental analysis.

II. THEORY

A. General

1. Analysis Type

In a chromatographic system a solute is distributed between a stationary phase and a mobile phase that flows through the stationary phase. One may classify the analysis by the nature, not the physical state, of the mobile phase or eluent. If sample is used as the mobile phase, the technique is frontal analysis. Displacement analysis involves the use of an eluent that has a greater affinity for the stationary phase than does the solute. The use of a mobile phase that simply transports the solute through the system constitutes elution chromatography.

Frontal analysis, the simplest form of chromatography, requires the continuous addition of sample to the system. The results obtained from this system are depicted in Fig. 1. The chromatogram is interpreted in the following manner. If the components of the sample have different affinities for the stationary phase, a number of zones will be formed. The leading edge of a zone is called the "front"; thus the name, "frontal analysis." The first zone contains only the least retained solute A since it is moving fastest. The second zone will contain solutes A and B, the third zone, A and B and C, etc. The amount of A decreases as B appears and both A and B decrease as C appears because displacement analysis is involved in

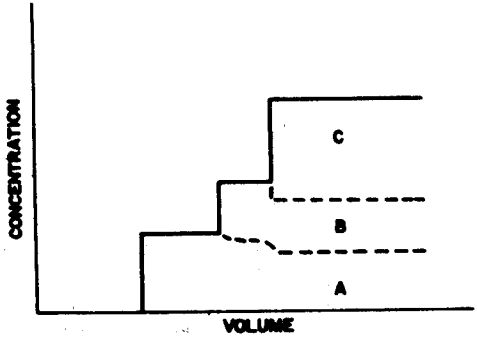

Figure 1. Frontal analysis.

all zones but A. Eventually, since sample is added continuously, the effluent from the system becomes identical in composition to the sample entering the system. In frontal analysis only one component, A, can be obtained in pure form, but the number of components in a sample can be determined since the steps in the chromatogram equal the number of components in the sample.

In displacement analysis, the mobile phase contains a substance that has a greater affinity for the stationary phase than does the solute. A single portion of sample is added and the components are moved through the system by virtue of their displacement in the stationary phase by the eluent. It should be noted that the displacer will replace the most strongly retained component C, which in turn will replace B, which will displace the least retained solute A. A chromatogram similar to Fig. 2 results. Each component can be recovered in pure form, but not quantitatively since the zones ideally have an interface and actually some overlap. One can, however, quantitatively measure each component with this technique. If equilibrium exists, a given amount of stationary phase can retain only a given amount of solute. As the solute concentration increases, then, the lengths, not the heights, of the zones must increase. Consequently, the volume of mobile phase required to elute a solute is proportional to the concentration of the solute.

Elution analysis involves the use of a mobile phase, which ideally serves only to transport the solutes through the system. Separation occurs because the various solutes have different affinities for the stationary phase and thus different speeds through the system. A typical elution chromatogram is presented in Fig. 3. Conceivably, elution analysis can completely resolve even the most complex mixtures into their individual components, which can then be analyzed by conventional techniques. The great separating

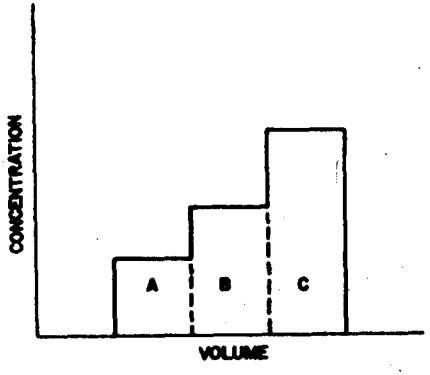

Figure 2. Displacement analysis.

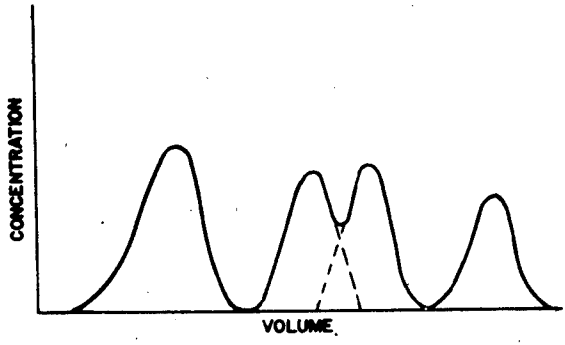

Figure 3. Elution analysis.

power of elution chromatography accounts for its being the most common form of chromatography, almost to the exclusion of the other forms. Consequently, unless otherwise noted, the remainder of this chapter applies specifically to elution chromatography.

2. The Chromatographic Process

A representation of the chromatographic process for the elution of a single solute is presented in Fig. 4. The sample is introduced to the system in what ideally would be an infinitely small volume and is immediately divided between the mobile and stationary phases through some physical or chemical process, e.g., adsorption, partition, or ion exchange. The unit volume Δx is described by:

$$\Delta x = \Delta V_m + \Delta V_s \tag{1}$$

where ΔV_m and ΔV_s are the unit volumes of the mobile and stationary phases, respectively. If C_m and C_s are the respective concentrations of solute in the mobile and stationary phases, then an equilibrium distribution coefficient K can be defined as the ratio of the concentration of the solute in the stationary phase to the concentration of solute in the mobile phase, i.e.,

$$K = C_s/C_m \tag{2}$$

This gives rise to the situation depicted in Fig. 4a. Now as the mobile phase progresses through the system, C_m is carried to the next unit volume and is redistributed between the two phases according to Eq. (2).

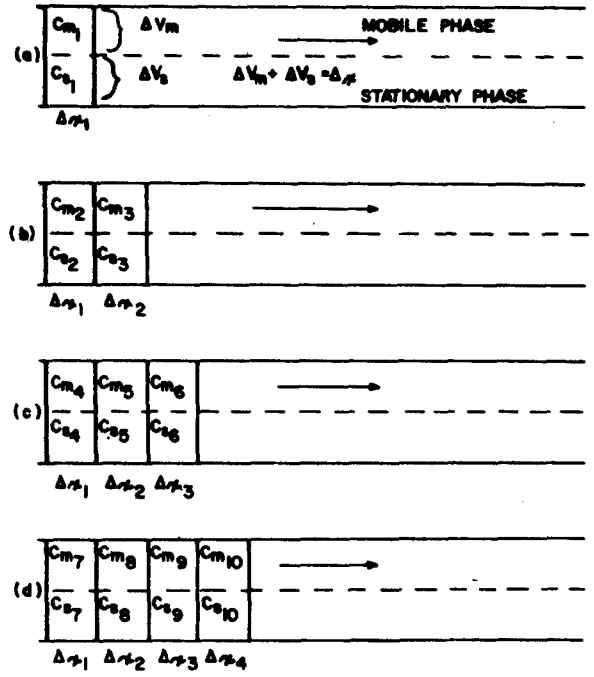

Figure 4. Schematic representation of solute distribution.

Simultaneously, C_s has remained at the first unit volume and has also redistributed according to Eq. (2). This leads to Fig. 4b, where:

$$K = C_{s_2}/C_{m_2} = C_{s_3}/C_{m_3} \tag{3}$$

The next step in the process leads to Fig. 4c, where C_{m_2} has moved to ΔV_2 and C_{m_3} has moved to ΔV_3. C_{m_2} plus C_{s_3} redistribute as does C_{s_2} and also C_{m_3}. This phenomenon of solute movement-solute distribution continues until the sample has moved through the system. It should be noted that the process, conveniently depicted here as discontinuous, is actually continuous.

Consideration of Eq. (2) and Fig. 4 leads to the observation that the relative rate of movement of a given solute is inversely proportional to the distribution coefficient K. For large values of K most of the solute is in the stationary phase and thus immobile. Conversely, if K is small, the solute moves rapidly through the system. Now, the various constituents of a multicomponent sample will behave as the single solute described in Fig. 4.