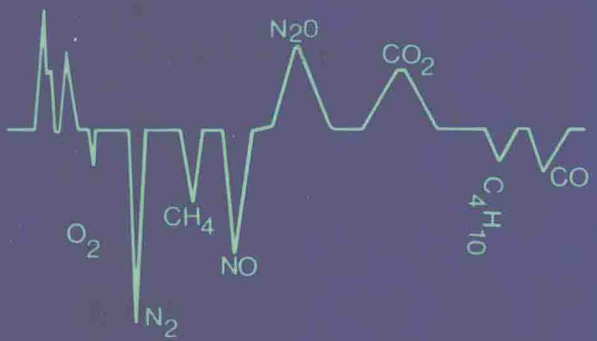

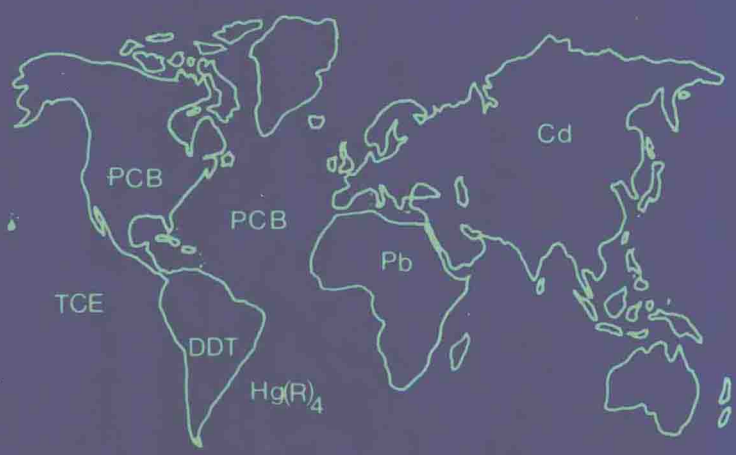

CHROMATOGRAPHIC ANALYSIS OF THE ENVIRONMENT

Second Edition, Revised and Expanded

edited by

ROBERT L. GROB

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CHROMATOGRAPHIC ANALYSIS OF THE ENVIRONMENT

TO MY WIFE AND CHILDREN

Preface

Since the publication of the first edition in 1975 many changes have occurred in the field of environmental analytical chemistry. These changes have produced numerous approaches to sampling the air we breathe, the water we drink, and the soil in which we grow our fruits and vegetables. More dramatically, these changes have brought to the forefront the manner in which we regard waste problems.

Our philosophy in this second edition has been very much like that of the first edition, with the additional highlighting of a couple of newer techniques that are being applied to environmental analyses, for example, ion chromatography. The topic of sampling has been given the position of a chapter of its own (Chap. 2). This was done with the hope of discussing the important aspect of environmental analyses in one place. Special modifications to sampling techniques are discussed in the various chapters. Some techniques (i.e., ion exchange techniques and paper chromatographic techniques) were originally meshed together to highlight their applications to the areas of environmental analysis. In this edition these two topics were wielded into separate chapters because of the limited application to some types of samples or areas of investigation.

Readers of the first edition will note changes in authorship of several chapters. These changes were effected because previous authors had either left the particular area of interest or the newer author(s) was becoming active in that specific area.

All readers are aware that the project of preparing a text of this type is not possible without the assistance, support, and cooperation of many people. This second edition is certainly no exception. The finalization of such an undertaking can be frustrating at the least. The most important persons are the editor's family, without whose understanding a task of this magnitude is not possible. I thank them very much. For many of the fine illustrations, I wish to thank my

daughter-in-law, Linda Grob. Special thanks must go to Dr. Harold F. Walton, who not only blended together the various applications of ion exchange chromatography (Chap. 15) but also wrote the chapter about liquid chromatographic applications in the area of water pollution (Chap. 7). Another thank you to Dr. Gerald R. Umbreit, who took time from his busy schedule operating a private consulting laboratory and gave us the knowledge and experience of his years of handling many types of environmental samples. Lastly, thanks also to several of my doctoral students (past and present) for their eagerness to participate in such an adventure: Eugene F. McGonigle, Matthew J. O'Brien, John F. Sullivan, Proespichaya Kanatharana, Mary Ellen P. McNally, and Susan Yates.

Robert L. Grob

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Part A
Chromatographic Theory and Environmental Sampling

Read no history: nothing but biography, for that is life without theory.

Contarini Fleming, pt. i, cha. 23
Benjamin Disraeli
1804-1881

It is a capital mistake to theorize before one has data.

The Adventures of Sherlock Holmes
"Scandal in Bohemia"
Sir Arthur Conan Doyle
1859-1930

Beauty is nature's brag, and must be shown
In courts, at feasts, and high solemnities,
Where most may wonder at the workmanship;
It is for homely features to keep home,
They had their name thence coarse complexions
And cheeks of sorry grain will serve to ply
The sampler, and to tease the huswife's wool.
What need a vermeil-tinchur'd lip for that,
Love-darting eyes, or tresses like the morn:

Comus, l. 745
John Milton
1608-1674

1
Theory and Practice of Chromatography

THOMAS G. BUNTING / The P. F. Laboratories, Inc., Totowa, New Jersey

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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—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]. Ettre [3] has reviewed the history of chromatography since Tswett's original paper.

"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 "gas-liquid chromatography" and "gas-solid chromatography" adequately identify the techniques involved. The liquid systems are not as 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.

For the purposes of environmental analysis, the classification of chromatographic systems according to Table 1 is expedient. The development of chromatographic theory and practice has been sufficiently

Table 1 Types of Chromatography

Type	Definition
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

Table 1 (Continued)

Type	Definition
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 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 absorbent 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
Liquid-liquid (LLC)	Mobile and stationary phases are liquid; generally refers to the analog of the gas-liquid system but many 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 or size exclusion
Liquid	Liquid	Liquid	Column	Partition
	Liquid	Solid	Column	Adsorption or size exclusion
Paper	Liquid	Paper	Sheet or strip	Partition or adsorption
Thin-layer	Liquid	Solid	Thin film	Adsorption
Ion-exchange	Liquid	Solid	Column	Ionic replacement or exclusion reactions