Modern Practice of Gas Chromatography

SECOND EDITION

Edited by

ROBERT L. GROB

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PREFACE

Since the appearance of the first edition of *Modern Practice of Gas Chromatography* in 1977, the technique of gas chromatography (GC) has continued to expand. During this time interval (1977–1985) we have seen many advances in the related area of high-performance liquid chromatography (HPLC). These are two complementary techniques in the ever important field of analytical chemistry.

The technique of GC has been widely accepted and proved successful by many investigators. The analytical chemists have utilized its simplicity, short analysis time, high sensitivity of selective detectors, efficiency of separation, and varied applications very well. The measurement of parts per million (ppm) and parts per billion (ppb) has become routine. Combining the technique of concentrating analyte amount (adsorption columns and dynamic and static headspace techniques) and GC, the analytical chemist is lowering the analyte concentration detectable limits.

The first edition was a result of an annual short course in GC sponsored by the Chromatography Forum of the Delaware Valley. This course not only continues to be given, but its enrollment continues to be filled. Because of the continued success of the short course and the book (eight printings), it was decided to bring forth a second edition.

We have followed the same nomenclature guidelines as in the previous edition. The order of the chapters is what we consider a logical sequence for the student of chromatography as well as the scientists who use the technique on a daily basis. The discussion on columns has been expanded to three chapters: the packed column, capillary column technology, and optimization of separations in GC. These latter two topics have become very important since the publication of the first edition. The application chapters have been modified, and several new chapters have been added—for ex-

ample, petroleum and petrochemicals, polymers, and environmental applications.

No book will please everyone. Each person has certain ideas concerning what should be covered and how much detail should be given to each topic. The coverage of the theory and basics of GC are what we consider necessary to the beginner for this technique, and the instrumentation section is greatly detailed. The application chapters cover topics that would be of interest to most people.

The editor wishes to thank the contributing authors for their cooperation and professional attitudes. I wish to thank the Chromatography Forum of the Delaware Valley and hope that it continues to serve its function as an educational group as well as a scientific society for the dissemination of chromatographic information. Thanks also are extended to the Chemistry Department Staff of the University of Hawaii at Manoa for the friendly and professional atmosphere during my leave in which the final stages of this book were completed. I would like to thank Villanova University for providing the encouragement and understanding for such a rewarding project. Finally, I wish to thank my wife for her encouragement during this project.

ROBERT L. GROB

Villanova, Pennsylvania
March 1985

FOREWORD TO THE FIRST EDITION

It is appropriate that a book on modern gas chromatography (GC) be written by member-experts from the Chromatography Forum of the Delaware Valley. This active scientific body, which lists as a chapter member the well-known GC pioneer, the late Stephen Dal Nogare, has long been active in the development and dissemination of chromatographic technology. The Chromatography Forum has held meetings, organized symposia, sponsored books on liquid and thin-layer chromatography, and presented awards in chromatography. For several years the Forum has presented a practical course in GC that inevitably has been oversubscribed because of its popularity. This textbook is an outgrowth of this highly successful course.

The chapters in this book have been prepared by those personally skilled in the various areas they have developed. Professor Grob has welded these chapters together into a cohesive treatment, but the individuality of each expert remains so that the reader is able to sample the unique experiences and insights of the writer. It is fortunate that the many contributors to an edited book live and work in the same area and are members of the same organization. Thus, the ability to easily communicate and exchange ideas, develop formats, and closely interact has resulted in an edited book with unusual coverage and readability.

This is a practical book that can be used by workers with a variety of scientific backgrounds. It contains topics and experiences that have not been developed in other books. Current information, references, and data all are combined to produce an up-to-date treatment.

For several personal reasons I am very gratified that this new book on

PREFACE TO THE FIRST EDITION

Gas chromatography (GC) is one of the most widely employed analytical techniques today. It is used in the academic and research laboratories as well as in industry. GC, in the form of gas–liquid chromatography, had its beginning at the end of 1952 in the accounts of James and Martin [*Biochem. J.*, **50**, 679 (1952) and *Analyst*, **77**, 915 (1952)].

The wide acceptance and success of this technique have been due to such features as simplicity, rapidity of analysis, high sensitivity of detector systems, efficiency of separations, varied applications, and the use of very small samples (microgram or smaller). Presently GC is finding use in the concentration of impurities in the parts per million (ppm) and parts per billion (ppb) range and in addition to the actual measurement of impurities at these levels. Without the use of GC many analytical problems could not be solved or would involve more intricate and time-consuming techniques.

This text represents a blending of the basic theories of chromatography with the experiences of each author. It is the product of a Gas Chromatography Short Course which has been presented annually in Philadelphia by the Chromatography Forum of Delaware Valley. The course has been offered each year with the highest level of participation. It has been structured for not only beginners, but for existing workers in the field and specialists of other fields who wish and need to know more about this powerful technique.

The authors feel that there is a current need for a textbook about gas chromatography. Existing books on the topic are either out of date or do not place the proper emphasis on the technique's modern practices. This

situation became painfully apparent when deciding on a text for the short course that subsequently gave birth to this book.

The nomenclature recommended by the IUPAC Committee of Chromatography (1972) and the now fashionable SI units have been utilized as much as possible.

The gas chromatographic technique is explained on the basis of a physical process with correlations to distillation, liquid–liquid extraction, countercurrent distribution, and other separation techniques to give the reader a better appreciation of the basic process of chromatography. Explanation of fundamentals is followed by chapters on columns and column selection, theory and use of detectors, instrumentation necessary for a gas chromatographic system, techniques used for qualitative and quantitative analyses, and data reduction and readout. Subsequent chapters cover specialized areas in which gas chromatographic literature is more scattered and data collection and evaluation are more important.

The format of the book represents what the various authors, collectively and individually, consider to be essential to the student of chromatography. We have tried to be consistent in nomenclature and have furnished representative and comprehensive bibliographies to allow the reader to explore further and in more depth the topics presented. The book is presented in a chapter order that we feel flows smoothly for the explanation of the gas chromatographic process.

Any book, whether a textbook or reference work, cannot be produced without the help and cooperation of many people. I wish to acknowledge the members of the Chromatography Forum of the Delaware Valley, the contributing authors for their cooperation, professional attitude, and unselfish availability of their time, my son Duane for the drawings in several of the chapters and the creation of the cover drawing, Dr. Gerald R. Umbreit for assistance and cooperation beyond those of a contributor, and Drs. Mary A. Kaiser, Matthew J. O'Brien, and John F. Wojcik for helping with the reading of the chapters. A special acknowledgment is extended to Dr. J. J. Kirkland, who reviewed and offered much assistance with the manuscript. I also thank him for writing the foreword. Last, but by no means least, I gratefully acknowledge my wife Marjorie for her typing and encouragement throughout this project.

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Villanova, Pennsylvania
February 1, 1977

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APPENDICES

CHAPTER ONE

Introduction

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1.1 HISTORY AND DEVELOPMENT OF CHROMATOGRAPHY

Many publications have discussed or detailed the history and development of chromatography (1–3). Rather than duplicate these writings, we present

TABLE 1.1 Development of the Field of Chromatography

Year (Reference)	Scientist(s)	Comments
1834 (4) 1834 (5)	Runge, F. F.	Used unglazed paper and/or pieces of cloth for spot testing dye mixtures and plant extracts
1850 (6)	Runge, F. F.	Separated salt solutions on paper
1868 (7)	Goppelsroeder, F.	Introduced paper strip (capillary analysis) analysis of dyes, hydrocarbons, milk, beer, colloid drinking and mineral waters, plant and animal pigments
1878 (8)	Schonbein, C.	Developed paper strip analysis of liquid solutions
1897–1903 (9–11)	Day, D. T.	Developed ascending flow of crude petroleum samples through column packed with finely pulverized fuller's earth
1906–1907 (12–14)	Tswett, M.	Separated chloroplast pigment on $CaCO_3$ solid phase and petroleum ether liquid phase
1931 (15)	Kuhn, R., et al.	Introduced liquid–solid chromatography for separating egg yolk xanthophylls
1940 (16)	Tiselius, A.	Earned Nobel Prize in 1948; developed adsorption analyses and electrophoresis
1940 (17)	Wilson, J. N.	Wrote first theoretical paper on chromatography; assumed complete equilibration and linear sorption isotherms; qualitatively defined diffusion, rate of adsorption, and isotherm nonlinearity
1941 (18)	Tiselius, A.	Developed liquid chromatography and pointed out frontal analysis, elution analysis, and displacement development
1941 (19)	Martin, A. J. P. and Synge, R. L. M.	Presented first model that could describe column efficiency; developed liquid–liquid chromatography; received Nobel Prize in 1952
1944 (20)	Consden, R., Godon, A. H., and Martin, A. J. P.	Developed paper chromatography

TABLE 1.1 (*continued*)

Year (Reference)	Scientist(s)	Comments
1946 (21)	Claesson, S.	Developed liquid–solid chromatography with frontal and displacement development analysis; co-worker A. Tiselius
1949 (22)	Martin, A. J. P.	Contributed to relationship between retention and thermodynamic equilibrium constant
1951 (23)	Cremer, E.	Introduced gas–solid chromatography
1952 (24)	Phillips, C. S. G.	Developed liquid–liquid chromatography by frontal technique
1952 (25)	James, A. T. and Martin, A. J. P.	Introduced gas–liquid chromatography
1955 (26)	Glueckauf, E.	Derived first comprehensive equation for the relationship between HEPT and particle size, particle diffusion, and film diffusion ion exchange
1956 (27)	van Deemter, J. J., et al.	Developed rate theory by simplifying work of Lapidus and Ammundson to Gaussian distribution function
1957 (28)	Golay, M.	Reported the development of open tubular columns
1965 (29)	Giddings, J. C.	Reviewed and extended early theories of chromatography

in Table 1.1 a chronological listing of events that we feel are the most relevant in the development of the present state of the field. Since the various types of chromatography (liquid, gas, paper, thin-layer, ion exchange) have many features in common, they must all be considered in the development of the field. Although the topic of this text, gas chromatography (GC), probably has been the most investigated during the past 30 years, results of these studies have had a great impact on the other types of chromatography, especially modern (high-performance) liquid chromatography (HPLC).

There will, of course, be those who believe that the list of names and events presented in Table 1.1 is incomplete. We simply wish to show a development of an ever-expanding field and to point out some of the important events that were responsible for the expansion. To attempt an account of contemporary leaders of the field could only result in disagreement with some workers, astonishment by others, and a very long listing that would be very cumbersome to correlate.

1.2 SEPARATION TECHNIQUES

1.2.1 Various Techniques Used for Separations

Most separation techniques involve the formation of at least two phases, in which the object is to separate and measure the various constituents. There are various ways of describing a phase, that is, gas, liquid, and solid. By proper choice of conditions (temperature and pressure), one is able to convert a solid to a liquid (melting) or a gas (sublimation), a liquid to a solid (freezing) or a gas (distillation) and a gas to a liquid (condensation) or a solid (condensation). When the phase transition(s) are completed, one phase should contain the material of interest and the other(s), materials not of interest. The phases can then be mechanically or physically separated, and the phase containing the component of interest is retained.

Since the component(s) of interest can be in one of three states of matter and these, in turn, can be converted into one of three phase types, many types of separation can be used. The major classifications are shown in Table 1.2. Chromatography is used in four of the nine major types shown.

In our discussion of separations we include not only homogeneous equilibria, but also heterogeneous equilibria and the rates at which these equilibria are obtained. If the equilibrium point and the rate of attainment of said equilibrium are both favorable, the separation can usually be attained in one step. Less favorable systems utilize multistage operations. Multistage separations are both feasible and attractive.

The separations are classified according to mechanical, physical, or chemical processes, as shown in Table 1.2. This is illustrated in Table 1.3. The measurements of the separated components can be made by physical, chemical, or biological means. Several techniques are used within each of these three types of analysis. In the majority of analysis studies most of the discussion relates to an examination of the theoretical background, the experimental limitations, and the applications of the various techniques for making useful measurements. Methods of analysis are usually defined in terms of the final measurement made and thus many give the impression that this stage constitutes the entire subject of analytical chemistry. A more realistic view of analytical chemistry involves decisions regarding what information is needed from a system, how to obtain that information, utilization of one or more separations and measurements, collection and evaluation of the experimental data, and finally drawing some conclusions from the data.

In analysis of materials, any one of the above categories (sample, separation, measurement) may assume more importance than another. It may be more difficult to obtain a representative sample than the separation, or measurement or the separation may be more difficult than the sampling and measurement. Two objectives should be paramount for any analysis: the data must have the *required accuracy and precision* and be produced in the *minimum time*.