CHEMICAL SEPARATIONS AND MEASUREMENTS

Theory and Practice of Analytical Chemistry

Dennis G. Peters, John M. Hayes, and Gary M. Hieftje

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About the Cover:

The superimposed images of a high-resolution gas chromatogram and the glass capillary column tubing essential in its production. The chromatogram happens to be that of marijuana smoke. The full recording, not shown here, reveals well over 200 components. Only 2.5 ml of unenriched smoke was taken as the sample. The column temperature was programmed from −70° to +130° C. The average width at half height of the peaks is 9 seconds. In the chromatogram as shown, time is increasing linearly from right to left, with retention times varying from about 20 to 60 min. Chromatogram and column provided by M. V. Novotny and M. L. Lee, Indiana University. (See M. V. Novotny and M. L. Lee: Detection of Marijuana Smoke in the Atmosphere of a Room. Experientia *29*:1038, 1973.)

Chemical Separations and Measurements:
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PREFACE

Virtually all of "modern chemistry" has been developed through the application of new analytical technology. Taken together, these analytical techniques form a fascinating subject for study and investigation. There is a very strong synergism in the unified study of analytical chemistry—it is immensely more fruitful to focus on the objective of accurate chemical measurement than to attempt to separate techniques according to their present applications. It is, for example, well known that the methods useful to organic chemists today might be taken up by inorganic chemists next year (or *vice versa*). In addition, workers in related fields such as biology, geology, and engineering often have use for analytical chemical techniques. Workers in these "client" disciplines have frequently made important contributions to the science of chemical analysis, and the subject has become an important and stimulating interface between a wide variety of research fields. Our goal has been to capture this diversified vitality in a way which will stimulate students.

It would be nice, we think, to have a textbook that introduced students to genuine modern practice without first leading them through too much history. The composition of such a textbook is made very difficult by the breadth of topics to be considered, and the task is compounded by our philosophy that any topic chosen for discussion must be treated in enough depth to make it truly understandable. Our solution has been to edit very carefully the content of a normal analytical chemistry text and to supplement it with material generally new to the first analytical chemistry course. The latter material has been chosen with care, and we have made every effort to avoid merely listing techniques. In the areas of chemical separations and spectrochemistry, for example, we have provided highly generalized introductions and then have moved quickly to the detailed consideration of a few examples. In all cases, we have tried to avoid a preoccupation with metal ions in aqueous solutions and to introduce more organic, biochemical, solid-state, and gas-phase technology.

In its organization, the present text falls naturally into five units:

I. Introduction and statistics
II. Chemical equilibria and their analytical applications
    A. General aspects
    B. Acids and bases
    C. Complexes
    D. Precipitates
III. Redox equilibria, techniques, and electrochemistry
IV. Separations, particularly chromatography
V. Spectrochemical analyses

These units are not strongly interdependent, and instructors should find it easy to adapt the text to their individual needs. Section I might become the introduc-

tory unit of the laboratory course or be covered in lectures. The chapter on statistics is designed to introduce the student to principles, not formulas. The generally available tables of the normal distribution and of the statistic t are used rather than any special tables available only in this text. Sections II and III have been completely rewritten from the earlier text (Fischer and Peters, *Quantitative Chemical Analysis*, third edition), with, for example, the Brønsted-Lowry definitions of acids and bases being used throughout. An extensive treatment of potentiometric measurements with ion-selective electrodes is provided. The four new chapters on separation techniques emphasize chromatography, certainly one of the most widely applied modern analytical tools. In order to allow treatment in some depth, only three examples are discussed, but these represent a partition technique, an adsorption technique, chromatography with a liquid mobile phase and with a gaseous mobile phase. Like the section on separations, the new material on spectrochemical analysis begins with a broadly general introductory chapter. A generalized spectrochemical instrument based on transducer definitions is described, and various techniques are classified according to whether they involve absorption, luminescence, or emission, and whether the species involved are atomic or molecular. The remaining chapters deal with specific examples within this unified context.

Each chapter is abundantly provided with illustrative problems, a number of which are quite challenging. Answers are compiled in an appendix. A program of experiments appropriate to an analytical chemistry laboratory can be obtained from the companion text, *Chemical Separations and Measurements: Background and Procedures for Modern Analysis*, by W. E. Harris and B. Kratochvil (W. B. Saunders Co., 1974).

We would like to acknowledge the assistance and invaluable cooperation of a number of our friends, colleagues, and students. First of all, this book would probably not even exist were it not for the preceding texts principally authored by Dr. Robert B. Fischer, now at California State College, Dominguez Hills. His cooperation in the creation of this new text is greatly appreciated. *Quantitative Chemical Analysis*, third edition, by Fischer and Peters, was very carefully reviewed by Professors Byron Kratochvil, University of Alberta; Richard Ramette, Carleton College; and George Wilson, University of Arizona. Their extensive comments were very helpful in the preparation of the present text, which was in turn reviewed by Professors Stanley Crouch, Michigan State University; A. James Diefenderfer, Lehigh University; Dennis Evans, University of Wisconsin; W. E. Harris and Byron Kratochvil, University of Alberta; Milos Novotny, Indiana University; and Harry Pardue, Purdue University. Kaye Fichman and Robert Yount, two excellent students who were subjected to manuscript versions of text, provided enormously helpful reviews. The tasks of production were eased by the assistance of Norman Clampitt, Larry Games, Janice Hayes, Terry Hunter, Gary McNamee, and Robert Sydor, all of whom helped in the preparation of figures and tables; and by the cooperation of Pam Hieftje, who figured out how to keep the third author at the table. At W. B. Saunders, John Vondeling moved things along with the finesse of a Roman galleymaster and the tactics of Niccolo Machiavelli (he succeeded, however), and Joan Garbutt mediated with cheerful patience, for which we are most grateful.

The entire manuscript was typed twice by Shirley Williams and Sue Hughes and relentlessly reproduced by Dan Logan. Ann Forsee prepared the index. Their extraordinary speed, skills, and cooperation are very sincerely appreciated. Draft versions of the text have been used for two years at Indiana Univer-

sity, and we sincerely appreciate the tolerance and very helpful cooperation of our students.

We hope the text will be worthy of revision, and that the present version is lively enough to stimulate some comments. We invite letters of comment and correction from all readers, especially students.

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