CHEMICAL SEPARATIONS

VOLUME I. PRINCIPLES

C. JUDSON KING
AND
JAMES D. NAVRATIL

LITARVAN LITERATURE

CHEMICAL SEPARATIONS

VOLUME I. PRINCIPLES

Developed from selected papers presented at the First International Conference on Separations Science and Technology, New York, NY, U.S.A., April 15-17, 1986.

Edited by

C. JUDSON KING
University of California
Berkeley, California, U.S.A.

and

JAMES D. NAVRATIL
Colorado School of Mines
Golden, Colorado, U.S.A.

LITARVAN LITERATURE

DENVER VIENNA

For cataloging in publication data use main entry under title: Chemical Separations.
Volume I. Principles.

"Developed from selected papers presented at the First International Conference on Separations Science and Technology, New York, NY, April 15-17, 1986."
Bibliography:p.
Includes index.
1. Separation (Technology) I. King, C. Judson
II. Navratil, James D., 1941-

LC 86-81868
ISBN 0-937557-02-1 (V. I)
ISBN 0-937557-03-X (V. II)
ISBN 0-937557-04-8 (Set)

This book represents either original work or information obtained from highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. Although the data and information are regarded as reliable, the editors and publisher cannot assume responsibility for the validity of the information or its use. Furthermore, the papers contained herein were refeered by at least one competent expert in the field. To expedite publication, the authors' revised typescripts were, for the most part, directly reproduced; we hope this will not inconvenience the reader.

International Standard Book Number 0-937557-02-1 (Volume I)
Library of Congress Card Number 86-81868
Printed in the United States of America

CHEMICAL SEPARATIONS

VOLUME I. PRINCIPLES

PREFACE

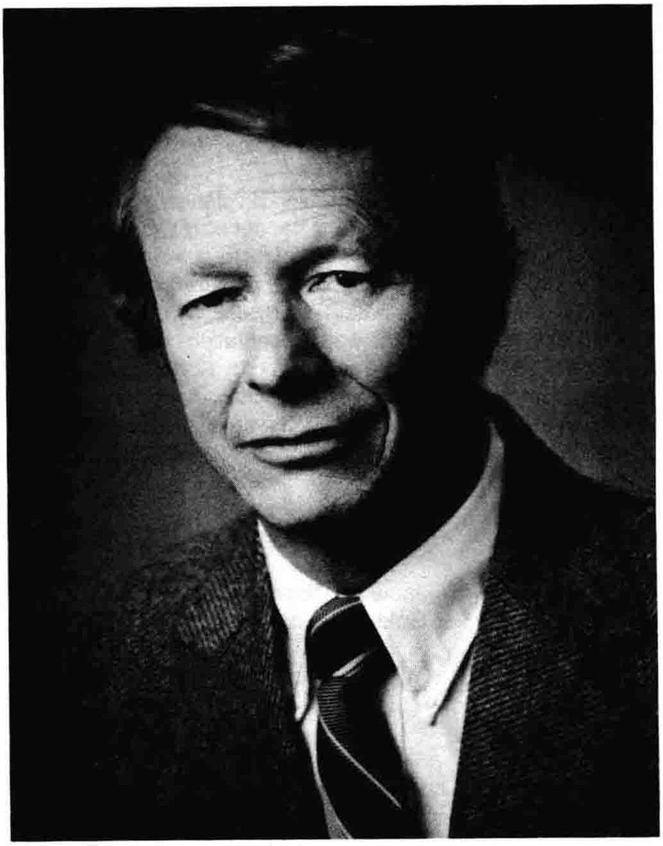
The First International Conference on Separations Science and Technology was held April 15-17, 1986, in New York, in conjunction with the 191st National Meeting of the American Chemical Society. The Conference was sponsored by the Subdivision of Separations Science and Technology, Industrial and Engineering Chemistry Division, American Chemical Society with financial support from the U.S. National Science Foundation and the Donors of The Petroleum Research Fund (administered by ACS).

This volume contains selected papers based on plenary and poster presentations made at the Conference. The papers cover some of the principal techniques used in separations, namely, field-flow fractionation, chromatography, electrophoresis, ion exchange, adsorption, solvent extraction, inclusion phenomena, membranes, and information retrieval.

A special feature of the Conference was presentation of the Third ACS Award in Separations Science and Technology, sponsored by Rohm and Haas Company, to Professor J. Calvin Giddings of the University of Utah. Associated with the Conference was an award symposium, including several papers relating to field-flow fractionation and other areas of separation of interest to Professor Giddings.

C. Judson King
Berkeley, California

James D. Navratil
Golden, Colorado



J. Calvin Giddings

ACS AWARD IN SEPARATIONS SCIENCE AND TECHNOLOGY*

Professor J. Calvin Giddings is recipient of the Separations Science and Technology Award for 1986. Dr. Giddings is honored for his outstanding and unique contributions to separations science and especially to the field of analytical chemistry.

It is fitting that Cal Giddings receive this award, as many of us would not be doing research in liquid chromatography if it were not for his brilliant insight into – and development of – the theory of chromatography.

Dr. Giddings was not always an analytical chemist. However, one day his advisor, Professor Henry Eyring, burst through the door – and posed a fateful question: "Would you like to know all about chromatography?" Since a graduate student did not readily say "No" to Dr. Eyring, Cal indeed learned everything he could about chromatography; thus, a most distinguished career in separations science was born. I have no doubt whatever direction he had taken in his research, Cal Giddings would have risen to the top and been on the cutting edge of that area of chemistry. But I personally am glad that he applied his genius to the field of separations.

Professor Giddings is a native son of Utah, and obtained both his graduate and undergraduate degrees in Utah; his B.S. at Brigham Young University and his Ph.D. at the University of Utah. However, he wandered afar and did postdoctoral work at the University of Wisconsin under Joseph Hirshfelder. Early in his career he developed models to explain chromatographic behavior. In 1958 he developed the random walk theory of chromatography; and in 1959 his generalized non-equilibrium theory of chromatography was published.

In 1963 he said that for the analogy between gas chromatography and liquid chromatography to be complete, a comparison of column efficiencies was important. He predicted that column parameters would be found that would make liquid chromatography as powerful as gas chromatography. He also predicted that particle size for liquid chromatography would be smaller than in gas chromatography, that large pressure drops would be required, and that liquid chromatography would be better than gas chromatography for very difficult and complex separations. In 1965, Dr. Giddings compared the theoretical limit of the

*The Separations Science and Technology Award, sponsored by Rohm and Haas Company and administered by the American Chemical Society, was established in 1982 to recognize outstanding accomplishments in fundamental or applied research directed to separations science and technology. Previous awardees are D. B. Broughton and A. S. Michaels.

speed of separation of gas chromatography with that of liquid chromatography and proposed that the comparative speed of separation depends on the relative viscosity and diffusivity of gases and liquids.

Dr. Giddings' work was not just in the theoretical realm. His theoretical work was done in conjunction with sound experimental investigations, and in 1964 he did a classical study concerned with the theoretical limit of separability. In addition, his famous book, *The Dynamics of Chromatography,* Volume I, published by Marcel Dekker, Inc. in 1965, is a classic in the field.

Besides chromatography, he has worked on chemical kinetics, as well as snow and avalanche physics.

Dr. Giddings has continued to be interested in separations and in the last decade has turned his attention to field-flow fractionation. He is a tireless innovator, and his contributions to the development and understanding of this technique are unique and monumental. Developments in this area are presented in this book.

Dr. Giddings has received worldwide recognition for his pioneering work in analytical chemistry and chromatography. Among the many awards he has received are the ACS Award in Chromatography, the Stephen Dal Nogare Award in Chromatography, the T. S. Tswett Chromatography Medal, the ACS Award in Analytical Chemistry, a Fulbright Fellowship for work in Peru, and the Romcoe Award for Outstanding Environmental Achievement in Education.

In addition to being an outstanding scientist and superb (but demanding) teacher, Professor Giddings is a renaissance man who has many interests. He is a person with great intellectual curiosity, and his curiosity extends way beyond the confines of chemistry. He is interested in other cultures and has traveled and lectured extensively. He recently returned from a trip to South America; in November of 1985 he was an invited speaker in Russia.

Cal loves nature and the out-of-doors. He is an avid white river kayaker, a skier and mountain climber. His knowledge of the environment is extensive, and his broad approach to science resulted in a textbook for non-science majors entitled, *Chemistry, Man and Environmental Change.* This beautifully written book, which integrates his concern for the environment with his vast knowledge of chemistry, demonstrates his extraordinary writing ability. Published in 1973, its contents are still as relevant today as are Dr. Giddings' basic theories of chromatography. I quote from the book's preface:

> "The main characters in the drama of man's changing environment are chemicals. The roles are acted out by H_2O, O_2, DDT, CO, SO_2, etc. – as fine a

cast of heroes and villains as one is likely to find anywhere. But this drama is deadly serious. With man's fate hinging on the outcome. The rules of the play are the rules of chemistry. In this book I have attempted to present these rules simply and clearly. I have used the rules to follow the ebb and flow of the cast across the landscape of earth; to chart their repercussions for man; and to predict the direction of future entanglements between the chemical actors and human society."

Phyllis R. Brown
Kingston, Rhode Island

CONTENTS

FIELD-FLOW FRACTIONATION

CHROMATOGRAPHY

ELECTROPHORESIS

ION EXCHANGE AND ADSORPTION

SOLVENT EXTRACTION

INCLUSION

MEMBRANE PROCESSES

INFORMATION RETRIEVAL

APPENDIX

INDEX

FIELD-FLOW FRACTIONATION

SEPARATION IN THIN CHANNELS: FIELD-FLOW FRACTIONATION AND BEYOND

J. Calvin Giddings
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

The capabilities and limitations of field-flow fractionation (FFF) in the broad scheme of separation technology are noted. Despite the great power and versatility of present-day FFF methods in the analytical scale separation of macromolecular and particulate materials, it appears that the frontiers of FFF (more generally of thin channel systems) could be pushed back significantly by invoking other approaches and modes of operation. Accordingly, both existing and potential variants of FFF are described and their promise evaluated. Among one-dimensional FFF systems, in addition to "normal" FFF using a variety of fields, such operating modes as represented by steric FFF, hyperlayer FFF, and cyclical-field FFF are described. The potential of two-dimensional FFF for both analytical and small-scale preparative separations is then discussed. The advantages of using split-flow channels in FFF are also noted. Finally, continuous separation in split-flow thin (SPLITT) cells, in which separation takes place over the thin (generally sub-millimeter) dimension of the channel, is shown to have several important advantages for small-scale preparative work.

INTRODUCTION

The extensive development in recent years of the field-flow fractionation (FFF) family of techniques has illustrated the versatility and power of separation systems based on thin channels subject to an externally imposed driving force (1-9). FFF, operated with a variety of driving forces adjusted to different appropriate strengths, has been shown to be widely applicable to complex macromolecular and particulate material over a 10^{15}-fold mass range, spanning from 10^3 molecular weight up to 100 μm particle diameter (5). The species in this range can generally be separated at high resolving power according to increments in different properties, the specific property depending upon the nature of the driving force employed. They can be separated while dissolved or suspended in virtually any organic or aqueous fluid, thus assuring applicability to biological macromolecules and particles, synthetic polymers, industrial latices and other colloids, and a broad spectrum of environmental contaminants. There appears to be no major limitation, either theoretical or practical, to applicability across the entire spectrum of the macromolecular/particulate domain.

Yet, from a broader point of view, the demands of our technological society for separations are so pervasive that no single method or approach appears capable of excelling in more than a small fraction of needed applications. We must call on an extensive arsenal of techniques--chromatography, membrane methods, extraction, adsorption, distillation, electrophoresis, and many more--to seriously approach the combined needs of preparative and analytical-scale separations. Even then, many separation problems are poorly addressed.

Normal FFF, like every other separation method or family of methods, has serious limitations when measured against the totality of separation needs. First, FFF is by its nature an analytical technique, suffering a degradation in resolution when samples significantly exceed 1 mg in size. Second, the method is not competitive in dealing with small molecules, an area where chromatography excels. Third, FFF, as normally applied, separates species according to only a single property (mass, density, thermal diffusion factor, diffusion coefficient, electrical charge, etc.) or a fixed combination of properties. That is to say, FFF is normally applied as a one-dimensional technique.

The latter limitation appears of little consequence when it is realized that such high-resolution techniques as chromatography and electrophoresis, in normal operation, are also one-dimensional, with separation based on a spectrum of distribution coefficients (chromatography) or electrical mobilities (electrophoresis). Nonetheless, the enormous separation power recently demonstrated by two-dimensional electrophoresis (10-13) and coupled column (sometimes called multidimensional) chromatography (14-17) demonstrates that separation according to a single property is not adequate for the analytical-scale separation of many enormously complicated materials of interest.

While it is almost certain that the above limitations will never be so completely removed that FFF and allied techniques will apply to every separation problem, we have developed some strategies to begin to bypass some of these limitations and thus to achieve applicability across an even broader spectrum of separation needs than now possible. Because some of these extensions go beyond FFF methodology, we do not refer to them collectively as FFF. Rather, what these approaches have in common is the achievement of separation within a thin channel whose contents are subject to flow displacement and to a transverse driving force. These characteristics are illustrated in figure 1. In this paper we will discuss the numerous approaches for harnessing this simple channel system both for analytical and preparative ends. We will also outline our progress in implementing the various approaches described.