

# CRC Handbook of Chromatography

Carbohydrates

Volume I

Editor

Shirley C. Churms, Ph.D.

# **CRC Handbook of Chromatography**

## **Carbohydrates**

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# CRC HANDBOOK OF CHROMATOGRAPHY

## SERIES PREFACE

This *Handbook of Chromatography, Carbohydrates* by Shirley C. Churms, is one in a series of separate volumes devoted to a single class of chemical compounds or to compounds with a similar use pattern, like the prospective volumes on pesticides and drugs. When Volumes I and II of the *Handbook of Chromatography* were first published in 1972, the editors made an attempt to select the data that would cover most organic and inorganic compounds in a volume of about one thousand pages. However, during the ensuing 10 years, the literature of chromatography, especially high-performance liquid chromatography (HPLC), has grown to such an extent that, after an initial intent to update Volumes I and II, it was decided to publish separate volumes devoted to specific subjects. The present volume on the chromatography of carbohydrates is an example of the expanded handbook series. In selecting Volume Editors, the Editors-in-Chief endeavored to select scientists with extensive knowledge and expertise in the chromatography of specific compounds. The Editor of this volume, Dr. Shirley C. Churms, is renowned in the field of chromatography of carbohydrates, which is evident from the comprehensive and authoritative treatment of the subject found in this volume. We have given each Volume Editor wide latitude in designing a format that would be most useful to the reader and do justice to the particular subject being covered. Subsequent volumes of this series will include the chromatography of drugs, steroids, lipids and fatty acids, terpenoids, plant pigments, hydrocarbons, amino acids, inorganic compounds, polymers, and nucleic acids and associated compounds.

We invite readers to communicate with the Volume Editor for comments and corrections and to the Editors-in-Chief for suggestions for future volumes. The Editors-in-Chief want to thank Dr. Shirley C. Churms for her outstanding effort and the cooperation of her associates.

Gunter Zweig, Ph.D.  
Joseph Sherma, Ph.D.  
Spring 1981

## PREFACE

This handbook is intended to serve as a working manual and reference book for carbohydrate chemists and biochemists using the chromatographic methods that are indispensable in this field. Emphasis is on newer methods, such as high-performance liquid chromatography (HPLC) and other automated liquid chromatography systems; and the material included was compiled mainly from literature published during the years 1970 to 1978. Data appearing in Volumes I and II of the *Handbook of Chromatography* are not repeated here, but references to relevant tables in Volumes I and II are given at the start of corresponding sections of this handbook. In some cases material published before 1970 that was omitted from Volumes I and II of the series is included here; this applies particularly to the sections dealing with paper chromatography and electrophoresis.

## THE EDITORS-IN-CHIEF

**Gunter Zweig, Ph.D.**, received his undergraduate and graduate training at the University of Maryland, College Park, where he was awarded the Ph.D. in biochemistry in 1952. Two years following his graduation, Dr. Zweig was affiliated with the late R. J. Block, pioneer in paper chromatography of amino acids. Zweig, Block, and Le Strange wrote one of the first books on paper chromatography which was published in 1952 by Academic Press and went into three editions, the last one authored by Gunter Zweig and Dr. Joe Sherma, the co-Editor-in-Chief of this series. *Paper Chromatography* (1952) was also translated into Russian.

From 1953 till 1957, Dr. Zweig was research biochemist at the C. F. Kettering Foundation, Antioch College, Yellow Springs, Ohio, where he pursued research on the path of carbon and sulfur in plants, using the then newly developed techniques of autoradiography and paper chromatography. From 1957 till 1965, Dr. Zweig served as lecturer and chemist, University of California, Davis and worked on analytical methods for pesticide residues, mainly by chromatographic techniques. In 1965, Dr. Zweig became Director of Life Sciences, Syracuse University Research Corporation, New York (research on environmental pollution), and in 1973 he became Chief, Environmental Fate Branch, Environmental Protection Agency (EPA) in Washington, D.C.

During his government career, Dr. Zweig continued his scientific writing and editing. Among his works are (many in collaboration with Dr. Sherma) the now 11-volume series on *Analytical Methods for Pesticides and Plant Growth Regulators* (published by Academic Press); the pesticide book series for CRC Press; co-editor of *Journal of Toxicology and Environmental Health*; co-author of basic review on paper and thin-layer chromatography for *Analytical Chemistry* from 1968 to 1980; co-author of applied chromatography review on pesticide analysis for *Analytical Chemistry*, beginning in 1981.

Among the scientific honors awarded to Dr. Zweig during his distinguished career are the Wiley Award in 1977, Rothschild Fellowship to the Weizmann Institute in 1963/64; the Bronze Medal by the EPA in 1980.

Dr. Zweig has authored or co-authored over 75 scientific papers on diverse subjects in chromatography and biochemistry, besides being the holder of three U.S. patents.

At the present time (1980/81), Dr. Zweig is Visiting Scholar in the School of Public Health, University of California, Berkeley, where he is doing research on farmworker safety as related to pesticide exposure.

**Joseph Sherma, Ph.D.**, received a B.S. in chemistry from Upsala College, East Orange, N.J. in 1955 and a Ph.D. in analytical chemistry from Rutgers University in 1958. His thesis research in ion exchange chromatography was under the direction of the late William Rieman III. Dr. Sherma joined the faculty of Lafayette College in September 1958, and is presently full professor there in charge of two courses in analytical chemistry. At Lafayette he has continued research in chromatography and has additionally worked a total of 12 summers in the field with Harold Strain at the Argonne National Laboratory, Illinois, James Fritz at Iowa State University, Ames, Gunter Zweig at Syracuse University Research Corporation, New York, Joseph Touchstone at the Hospital of the University of Pennsylvania, Philadelphia, Brian Bidlingmeyer at Waters Associates, Framingham, Mass., and Thomas Beesley at Whatman Inc., Clifton, N.J.

Dr. Sherma and Dr. Zweig [who is now with U.S. Environmental Protection Agency (EPA)] co-authored Volumes I and II of the *CRC Handbook of Chromatography*, a book on paper chromatography, and 6 volumes of the series *Analytical Methods for Pesticides and Plant Growth Regulators*. Other books in the pesticide series and further

volumes of the *CRC Handbook of Chromatography* are being edited with Dr. Zweig, and Dr. Sherma will co-author the handbook on pesticide chromatography. A book on quantitative TLC (published by Wiley-Interscience, New York) was edited jointly with Dr. Touchstone. Dr. Sherma has been co-author of 7 biennial reviews of liquid chromatography (1968 to 1980) and the 1981 review of pesticide analysis for the journal *Analytical Chemistry*. Dr. Sherma has authored major invited chapters and review papers on chromatography and pesticides in *Chromatographic Reviews* (analysis of fungicides), *Advances in Chromatography* (analysis of fungicides), *Advances in Chromatography* (analysis of nonpesticide pollutants), Heftmann's *Chromatography* (chromatography of pesticides), Race's *Laboratory Medicine* (chromatography in clinical analysis), *Food Analysis: Principles and Techniques* (TLC for food analysis), *Treatise on Analytical Chemistry* (paper and thin layer chromatography), and *CRC Critical Reviews in Analytical Chemistry* (pesticide residue analysis). A general book on thin layer chromatography co-authored by Dr. Sherma is now in press at Marcel Dekker.

Dr. Sherma spent 6 months in 1972 on sabbatical leave at the EPA Perrine Primate Laboratory, Perrine, Fla., with Dr. T. M. Shafik, and two additional summers (1975, 1976) at the U.S. Department of Agriculture (USDA) in Beltsville, Md., with Melvin Getz doing research on pesticide residue analysis methods development. He spent 3 months in 1979 on sabbatical leave with Dr. Touchstone developing clinical analytical methods. A total of more than 200 papers, books, book chapters, and oral presentations concerned with column, paper, and thin layer chromatography of metal ions, plant pigments, and other organic and biological compounds; the chromatographic analysis of pesticides; and the history of chromatography have been authored by Dr. Sherma, many in collaboration with various co-workers and students. His major research area at Lafayette is currently quantitative TLC (densitometry), applied mainly to clinical analysis and pesticide residue determinations.

Dr. Sherma has written an analytical quality control manual for pesticide analysis under contract with the U.S. EPA and has revised this and the EPA Pesticide Analytical Methods Manual under a 4-year contract (EPA) jointly with Dr. M. Beroza of the Association of Official Analytical Chemists (AOAC). Dr. Sherma has also written an instrumental analysis quality assurance manual and other analytical reports for the U.S. Consumer Product Safety Commission, and is currently preparing a manual on the analysis of food additives for the U.S. Food and Drug Administration, both of these projects also in collaboration with Dr. Beroza of the AOAC.

Dr. Sherma taught the first prototype short course on pesticide analysis with Henry Enos of the EPA for the Center for Professional Advancement. He is editor of the Kontes TLC quarterly newsletter and also teaches short courses on TLC for Kontes and the Center for Professional Advancement. He is a consultant for several industrial companies and federal agencies on chemical analysis and chromatography and regularly referees papers for analytical journals and research proposals for government agencies.

Dr. Sherma has received two awards for superior teaching at Lafayette College and the 1979 Distinguished Alumnus Award from Upsala College for outstanding achievements as an educator, researcher, author, and editor. He is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, Society for Applied Spectroscopy, and the American Institute of Chemists.



## THE EDITOR

**Shirley C. Churms, Ph.D.**, is Research Associate in the Carbohydrate Chemistry Research Unit (sponsored by the South African Council for Scientific and Industrial Research) of the Department of Organic Chemistry at the University of Cape Town, Republic of South Africa.

Dr. Churms (born Macintosh) was educated at Rustenburg School, Rondebosch, Cape Town and the University of Cape Town, where she obtained the degrees of B.Sc. (with distinction in chemistry) in 1957 and B.Sc. (Hons) in 1958. She then undertook research, at the same University, on cation-exchange processes in aqueous monoethanolamine, for which the degree of Ph.D. was awarded in 1962. During this period she served as a Junior Lecturer, and in 1961 as Lecturer in a temporary capacity, in the Department of Chemistry. In 1962 she was awarded the Ohio State Fellowship by the International Federation of University Women, which enabled her to spend her post-doctoral year at the Imperial College of Science and Technology in London, England. While there she carried out an extensive survey of the properties of inorganic ion-exchangers in general and commenced an investigation of the ion-exchange properties of hydrated alumina in particular. This work was continued after her return to the University of Cape Town in 1964, and during the period 1964 to 1968 Dr. Churms was also involved in the supervision of research students who were extending her own earlier work on ion-exchange in nonaqueous solvents. Another research project, concerned with fundamental aspects of cation exchange on the high-capacity carboxylic acid resins, to which she made a major contribution resulted in the publication, in 1967, of a paper for which she was awarded, with two co-authors, the African Explosives and Chemical Industry medal conferred annually by the South African Chemical Institute.

In 1965 and 1967 Dr. Churms held temporary lecturing posts in the Department of Chemistry at the University of Cape Town, while in 1964 and 1966 her work was supported by grants administered by the South African Council for Scientific and Industrial Research. In 1968, shortly after the latter body had commenced support of a Carbohydrate Chemistry Research Unit, under the direction of Professor Alistair M. Stephen, at the University of Cape Town, she assumed her present position in this Unit.

Her involvement in carbohydrate studies resulted in a change of research interest from ion exchange *per se* to the application of chromatographic methods, and in particular gel-permeation chromatography, to the examination of polysaccharides and of the complex mixtures of products obtained in the degradation processes used for investigation of the molecular structures of polysaccharides. Dr. Churms has contributed chapters on this topic to two books already published, and a further two at present in the course of publication. She was also the author of a series of five review articles on inorganic ion-exchangers, published in 1965, and the research papers of which she has been author or co-author number approximately 40.

Dr. Churms is a Member of the Royal Society of Chemistry (London) and is thus a Chartered Chemist. She is also a member of the South African Chemical Institute and of the interdisciplinary Experimental Biology Group of the Cape, and has served as Secretary of the latter association.



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Special thanks are due to Miss Margaret Dreyer for her sterling efforts in typing most of the manuscript of this handbook. The assistance of Ms. Eleanor Stenton and Mrs. Jean Goode in the typing is also gratefully acknowledged, as is the cooperation of the editorial staff of CRC Press.

## DEDICATION

My interest in carbohydrate chemistry in general, and in carbohydrate chromatography in particular, has developed under the inspiring guidance of Professor Alistair M. Stephen, to whom this volume is dedicated.

Shirley C. Churms  
April 1979

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# Section I

## *Chromatographic Data*





## Section I.I

## GAS CHROMATOGRAPHY TABLES

These tables are grouped according to the type of volatile derivative prepared for GC of the carbohydrates, with the derivatives arranged in alphabetical order. Some earlier GC data for alditol acetates, isopropylidene acetals, trifluoroacetates, and trimethylsilyl ethers of carbohydrates will be found in Section A, Volume I, Section II.I, Tables GC 13-15, 76, and 124.

The co-operation of Dr. E. H. Merrifield (University of Cape Town) in the compilation of Tables GC1, GC2, and GC22 is gratefully acknowledged.

**Table GC 1**  
**PERACETYLATED ALDITOLS, AMINODEOXYALDITOLS, AND**  
**REDUCED OLIGOSACCHARIDES**

Packing	P1	P2	P3	P4	P5
Temperature (°C)	220	T1	190	240	260
Gas; flow rate (ml/min)	N <sub>2</sub> , 40	N <sub>2</sub> , 34	N <sub>2</sub> , 40	He, 100	N <sub>2</sub> , 20
Column					
Length, cm	152	150	170	152	183
Diameter (I.D.), cm	0.6	0.3	0.6 (O.D.)	0.6	0.3
Form	na	na	coiled	U-tube	na
Material	glass	glass	glass	glass	glass
Detector	FI	FI	FI	FI	FI
Reference	1	2	3	4	5
Parent sugar	r <sup>a</sup>	r <sup>a</sup>	r <sup>a</sup>	r <sup>b</sup>	r <sup>c</sup>
Rhamnose	—	—	0.72	—	—
Fucose	—	0.76	0.80	—	—
Ribose	0.88	—	—	—	—
Arabinose	1.00	1.00	1.00	—	—
Xylose	1.23	1.24	1.32	—	—
Mannose	2.32	2.11	2.76	—	—
Galactose	2.75	2.27	3.04	—	—
Glucose	2.68	2.43	3.24	1.00	—
2-Amino-2-deoxy-D-glucose	—	4.7	—	2.87	—
2-Amino-2-deoxy-D-galactose	—	5.1	—	3.32	—
2-Amino-2-deoxy-D-mannose	—	—	—	3.54	—
2-Amino-2-deoxy-D-gulose	—	—	—	3.59	—
2-Amino-2-deoxy-D-talose	—	—	—	2.69	—
Sucrose <sup>d</sup>	—	—	—	—	0.83
Trehalose <sup>d</sup>	—	—	—	—	1.00
Maltose	—	—	—	—	1.34
Lactose	—	—	—	—	1.65

Note: This table supplements Table GC 14 in Section A, Volume 1, Section II.1.

<sup>a</sup> *t*, relative to arabinitol pentaacetate (absolute retention 6.4 min for Reference 1, 9.1 min for 2, 5 min for 3).

<sup>b</sup> *t*, relative to glucitol hexaacetate (8 min).

<sup>c</sup> *t*, relative to trehalose derivative (79 min).

<sup>d</sup> Peracetylated derivatives of sugars.

Packing	P1 = 5% poly(ethylene glycol adipate) on acid-washed Diatomite C (85 to 100 mesh BSS).
	P2 = 1% OV-225 on Chromosorb G-HP (80 to 100 mesh).
	P3 = 3% OV-225 on Chromosorb W, acid-washed, DMCS (80 to 100 mesh).
	P4 = 10% neopentyl glycol sebacate polyester on acid-washed Chromosorb W (80 to 100 mesh).
	P5 = 3% OV-225 on Gas-Chrom Q (100 to 120 mesh).
Temperature	T1 = temperature programmed, 170 → 230°C, 1°/min to end temperature, 15 min isothermal.

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