CRC

ANALYSIS of PESTICIDES in WATER

Volume II

Alfred S. Y. Chau
B. K. Afghan

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Analysis of Pesticides in Water

Volume II
Chlorine- and Phosphorus-Containing Pesticides

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ANALYSIS OF PESTICIDES IN WATER

Volume I: Significance, Principles, Techniques, and Chemistry of Pesticides
Volume II: Chlorine- and Phosphorus-Containing Pesticides
Volume III: Nitrogen-Containing Pesticides

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CHEMICAL ANALYSIS OF INORGANIC CONSTITUENTS OF WATER

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ORGANIC ANALYSIS OF WATER POLLUTION: CHEMICAL ANALYSIS

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FOREWORD

The assessment of the environmental impact of man's endeavors must be made as rapidly and painlessly as possible. It is not only aesthetically rewarding to retrieve clean lakes, rivers, air, and countrysides; it is possibly vital to man's continued existence. Emotional reaction serves no useful long-range purpose, but in fact eventually boomerangs and disenchants the public. Nevertheless, it is incumbent upon man to safeguard his environment. Clearly, the forces involved are quite beyond our comprehension at this time. When we are operating from a position of ignorance as we are today, it is most important to be sure that the risks we take are minimal, although in many cases a 'fail safe' posture has been adopted which can be extremely expensive. Discussion on the possible short-term and long-term impacts of various pollutants is valuable but probably endless. The truth ultimately emerges from reliable data interpreted with wisdom and understanding. Analytical chemistry provides the invaluable bridge between speculation and firm data. We can generate firm data only with reliable analytical techniques, skilled scientists, and clear minds.

In an effort to provide means of collecting and dispersing this information to all interested parties, we have invited a number of scientists of stature to produce monographs in their field of expertise. The objective of these monographs is to document analytical procedures and techniques that are useful to the environmentalists.

In general, three groups of people will be interested in these monographs: industrial engineers and scientists who are monitoring both liquid and gaseous effluents from industrial effluents; and environmentalists who are trying to assess pollution levels and amass data on long-term health effects and other effects of pollution.

This book, collected by Mr. Chau and Dr. Afghan, is devoted to the broad and important topic of Pesticides. It examines important facets such as the Significance of the Problem, the Chemistry of Pesticides, and Principles and Techniques. It will provide excellent reference material for producers, users, and testing agencies.

J. W. Robinson
Editor-in-Chief
June 1977

EDITOR-IN-CHIEF

J. W. Robinson is Professor of Chemistry and Chairman of the Analytical Division at Louisiana State University, Baton Rouge, Louisiana. He earned his degrees at The University of Birmingham, England (B.Sc., 1949; Ph.D., 1952; D.Sc., 1977) and obtained American citizenship in 1965.

He worked at both Exxon Research Company and Ethyl Research Corporation for a number of years before returning to Louisiana State University to join its Chemistry Faculty.

Dr. Robinson has written more than 130 publications, as well as two texts: *Undergraduate Instrumental Analysis,* the 3rd edition of which is currently in press, and *Atomic Absorption Spectroscopy,* the 2nd edition of which was published in 1975. He is Editor of two international journals, *Spectroscopy Letters* and *Environmental Science and Engineering.* He is also assistant editor of *Applied Spectroscopy Reviews.* He is a former chairman of the Gordon Research Conference on Analytical Chemistry and of the L.S.U. International Symposium on Analytical Chemistry. He is also director of the Saul Gordon Workshop on Atomic Absorption Spectroscopy.

Dr. Robinson is a Guggenheim Fellow and an Awardee of the Honor Scroll of the American Institute of Chemists.

PREFACE

Recently, there have been an increasing number of xenobiotic materials entering into our environment. Many of them are hazardous to human health and to the ecosystem. Indeed, the problem of environmental protection and pollution control has become one of modern man's preoccupations.

One prerequisite for decision making in environmental protection and pollution control is the ability to identify and measure these xenobiotic materials in our ecosystem. In fact, nearly every phase of environmental protection and pollution control depends upon analytical data. However, it is not sufficient merely to generate data. These data must be reliable and truly represent the situation.

Since the analytical data are used for various stages in the activities of international and national environmental protection and pollution control, the analytical data thus have far-reaching political, scientific, and financial implications and impact. When there is no information on the quality of data, the decisions based on them, at best, are questionable. At worst, if the data are poor, irrational decisions will result. Therefore, an effective quality assurance program is needed to ensure the reliability of data. Suitable analytical methodology is the first consideration in an effective quality assurance program for the generation of reliable data.

Unlike the situation for inorganic pollutants, the nature of organic pollutants is extremely complex and diversified. The number and types of organic pollutants including pesticides are also constantly increasing and changing. Due to the numerous variables (sample matrix, and concentration and types of pollutants), analysis and method development for these materials is a challenge even to the experienced chemist. In fact, for the analysis of many organic pollutants in several environmental substrates, suitable methodology is still lacking.

In these three volumes on pesticides, we have tried to present a detailed survey of the analytical methodology and the essential background information emphasizing the practical aspects derived from evaluation of literature data and the authors' own experience. The pros and cons of the different methods, viewpoints, and approaches are also discussed. Equal amounts of data and discussion from both sides are presented so that there is sufficient information for readers to derive their own conclusions, even though they may not agree with us.

The first volume of this series provides background information on pesticides, while the subsequent two volumes detail analytical methodology on the different classes of pesticides. These volumes were written for the analyst as well as for university students, scientists, and researchers for other disciplines. For the latter groups, an attempt was made, whenever possible, to explain terminology, basic principles, and theories that might be unfamiliar to them.

We wish to acknowledge the pleasant and fruitful relationships with all the contributors. The patience, assistance, and understanding of the publisher are greatly appreciated. I wish to thank my wife Linda for typing and retyping the various versions of my early manuscripts and also for her understanding during the two and one-half years I spent working on these volumes. A special acknowledgment of gratitude is extended to M. Chiba, W. Sans, B. Ripley, M. Forbes, and D. McGregor for their valuable suggestions and critical review of the chapter on the chemical derivatization-gas chromatographic techniques.

A. S. Y. Chau, 1981

THE SENIOR EDITOR

Alfred S. Y. Chau is Head, Quality Assurance Methods Section of the Analytical Methods Division, National Water Research Institute, Canada Centre for Inland Waters.

He obtained his B.Sc. degree from the University of British Columbia in 1961 and the M.Sc. degree from Carleton University in 1966.

From 1965 to 1970, Alfred Chau held the position of pesticide analyst in the Department of Agriculture and later joined the Department of the Environment, first as Head of Organic Laboratories and then as Head, Special Services Section. He has held his current position since 1980.

Alfred Chau is the General Referee and member of the Association of Official Analytical Chemists, a member of the Chemical Institute of Canada, and a task group chairman of the American Society for Testing and Materials. He is included in American Men and Women of Science and Who's Who in Finance and Industry and is the recent recipient of the annual Caledon Award for his contribution to analytical chemistry.

Alfred Chau has engaged in research in a number of areas. In addition to a manual of analysis of pesticides in water, and serving as an associate editor for a book on the analysis of chlorinated hydrocarbons and hydrocarbon, he has published some 90 papers on the analysis of pesticides and other contaminants in water and in sediment. Recently, he has been involved in the development of the first Environmental Standard Reference Materials for organic contaminants such as PCBs in lake sediment.

Furthur, Alfred S. Y. Chau is well known as an accomplished nature artist, being represented in commercial galleries across Canada. His works are in many private and permanent collections including the Dofasco Canadian Art Collection and the Beckett Collection.

THE CO-EDITOR

B. K. Afghan is research scientist in environmental analytical chemistry in the Analytical Chemistry Research Section, Canada Centre for Inland Waters, Burlington, Ontario.

Dr. Afghan received the B.Sc. degree from Sind University, Pakistan, in 1962, and the D.I.C. and Ph.D. degrees in analytical chemistry from the University of London in 1964 and 1969, respectively.

Following positions in research at Dalhousie University (1966 to 1968) and the University of Montreal (1968 to 1969), Dr. Afghan served as a research scientist in analytical methods development in the Department of Energy, Mines, and Resources in Ottawa and has been with the Canadian Centre for Inland Waters since 1972.

Dr. Afghan is a fellow in the Chemical Institute of Canada, member of the editorial board of the *Canadian Journal of Spectroscopy,* and chairman of the task group of the American Society of Testing and Materials. His research has been concerned with modern polarographic and electroanalytical techniques, high speed liquid chromatography, atomic and molecular absorption and fluorescence spectroscopy, trace analysis, and environmental analytical chemistry.

Dr. Afghan has published more than 50 research papers over his research career in the areas of automation, atomic/molecular spectroscopy, luminescence, nutrients, heavy metals, trace organics, and pesticide residues.

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ANALYSIS OF PESTICIDES IN WATER

Volume I
SIGNIFICANCE, PRINCIPLES, TECHNIQUES, AND CHEMISTRY OF PESTICIDES

Environmental Impact and Significance of Pesticides
Basic Principles and Practices in the Analysis of Pesticides
Positive Identification of Pesticide Residues by Chemical Derivatization-Gas Chromatographic Technique
The Chemistry of Cyclodiene Insecticides

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CHLORINE- AND PHOSPHORUS-CONTAINING PESTICIDES

Organochlorine Pesticides
Organophosphorus Pesticides
Phenoxyalkyl Acid Herbicides (CPHs)

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Chapter 1

ORGANOCHLORINE PESTICIDES

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I. CHEMICAL AND PHYSICAL PROPERTIES OF ORGANOCHLORINES

A. Introduction

In the broad field of water management, surveillance of various bodies of water is one of several important activities which provide information on present pollutant levels and their future trends in waters. This activity also identifies "hot" spots where concentrations of particular pollutants are unacceptably high. This information alerts pollution control authorities to assess the degree of hazard and to take appropriate action. The success of any surveillance and monitoring program depends largely on the availability of good analytical data. Suitable analytical methodologies including sample handling and collection are needed to generate reliable data and quality control and assurance programs are required to maintain the data quality.

One of the important parameters in surveillance activity and environmental impact study is pesticide residues. A pesticide is generally considered to be a chemical or chemical formulation used to kill plants, insects, or animals injurious to man or unwanted by man. In a broader sense, pesticide is defined under the Ontario Pesticides Act and Regulation as "any organism, substance or thing that is manufactured, represented, sold or used as a means of directly or indirectly controlling, preventing, destroying, mitigating, attracting or repelling any pest or of altering the growth, development or characteristics of any plant life that is not a pest." These are the residues remaining after pesticides are applied to a system. Such residues can be the unchanged parent compounds, their degradation products, metabolites, or any combination.

At present, most pesticides are synthetic chemicals, and could be classified by chemical type. However, pesticides can be more usefully classified by considering their intended targets, as stated in Volume I, Chapter 2. Here, we are concerned with organochlorinated pesticides, also known as organochlorines, organochlorine pesticides, organochlorinated hydrocarbon pesticides or simply o.c.s. These compounds are insecticides in target, i.e., they kill or control insects. Organochlorines consist of two different major groups based on their molecular structures, namely, the cyclodiene or diene group and the DDT group.

Cyclodiene insecticides are cyclic compounds possessing the characteristic "endomethylene bridged" structure. With one exception, all the cyclodiene insecticides are the Diels-Alder reaction products of hexachlorocyclopentadiene and a suitable unsaturated compound. Chlordane, heptachlor, isodrin, and aldrin are products of Diels-Alder reactions; dieldrin, heptachlor epoxide, and endrin are prepared by the epoxidation of aldrin, heptachlor, and isodrin, respectively. Toxaphene, the exception, is produced by the chlorination of camphor. All these compounds contain six or more chlorine atoms in the molecule.

DDT and its analogs that contain two aromatic rings represent the other major group in o.c. pesticides. Methoxychlor, DDD, perthane, and kelthane are some examples of this group.

There are a few other o.c. pesticides which do not belong to either of these two groups. BHC (benzene hexachloride) isomers, and hexachlorobenzene (HCB) are important examples. It may be pointed out that BHC is a misnomer. BHCs are, in fact, hexachlorocyclohexane isomers prepared from chlorination of benzene and are saturated cyclic hydrocarbons.

In pesticide residue analysis for environmental studies, cyclodiene and DDT-type insecticides together with lindane (γ-BHC) are often encountered. This is due partly to their widespread application and toxicity and partly to their persistence in the environment. Although many o.c.s are now curtailed or drastically limited in their use, they are still found because of their resistance to chemical and biological degradation.

Before discussing the analysis of o.c.s, we shall first briefly describe their structures, synthesis, and physical and chemical properties.

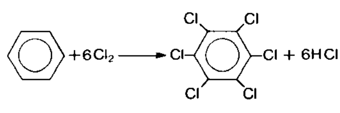
B. Structures

The chemical structures, common names, formulae, molecular weights, and nomenclatures of the common o.c. insecticides are listed in Table 1.[1,2]

C. Synthesis[1,2]

Only the outlines of synthetic routes are given here. The interested reader is referred to the original reference for more experimental details.

1. HCB — Chlorination of benzene in the presence of catalyst.



2. BHCs — Chlorination of benzene in the presence of UV light gives a mixture of α, β, γ, δ, and ε-BHC isomers. Pure (99%) isomers can be obtained by selective recrystallization from crude BHC (see, e.g., U.S. Patent 2,502,258).

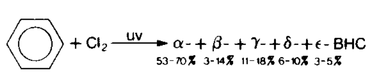


Table 1
NOMENCLATURE, STRUCTURES, FORMULA, AND MOLECULAR WEIGHTS OF SOME COMMON O.C. PESTICIDES

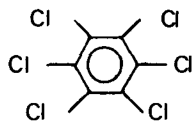
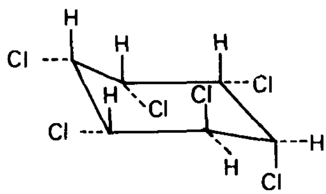
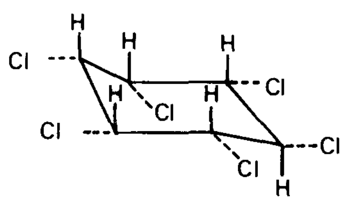
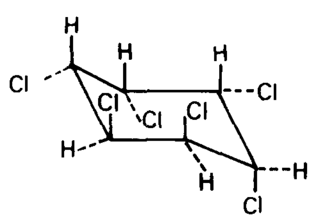
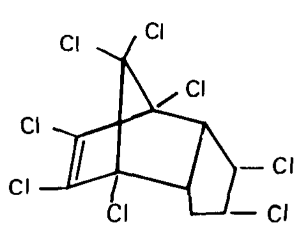
Common name	Structure	Formula and mol wt	Nomenclature
HCB		C_6Cl_6 (284.8)	Hexachlorobenzene
α-BHC		$C_6H_6Cl_6$ (290.8)	α-1,2,3,4,5,6-Hexachlorocyclohexane
β-BHC		$C_6H_6Cl_6$ (290.8)	β-1,2,3,4,5,6-Hexachlorocyclohexane
γ-BHC (lindane) (active form)		$C_6H_6Cl_6$ (290.8)	γ-1,2,3,4,5,6-Hexachlorocyclohexane
α-Chlordane (*cis*-Chlordane)		$C_{10}H_6Cl_8$ (409.8)	1-exo, 2-exo, 4,5,6,7,8,8-Octachloro 2,3,3a,4,7,7a-hexahydro- 4,7-methanoindene

Table 1 (continued)
NOMENCLATURE, STRUCTURES, FORMULA, AND MOLECULAR WEIGHTS OF SOME COMMON O.C. PESTICIDES

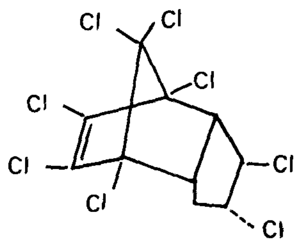
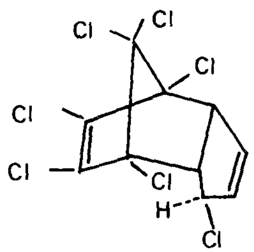
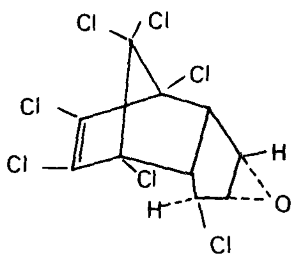
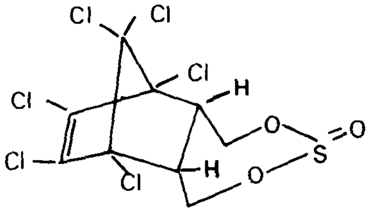
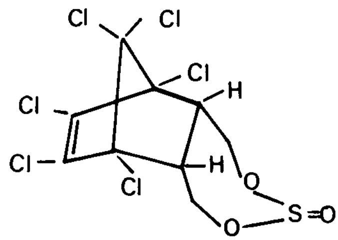
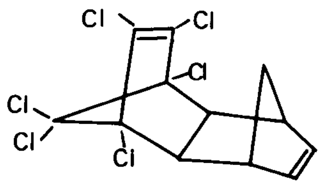
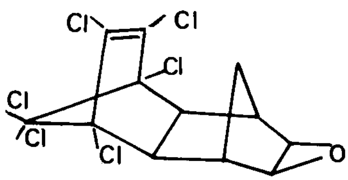
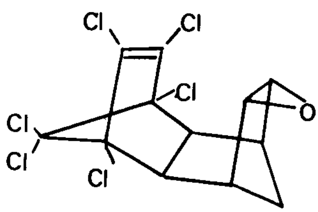
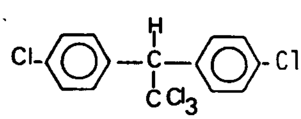
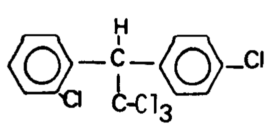
Common name	Structure	Formula and mol wt	Nomenclature
γ-Chlordane (*trans*-Chlordane)		$C_{10}H_6Cl_8$ (409.8)	1-exo, 2-endo, 4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
Heptachlor		$C_{10}H_5Cl_7$ (373.3)	1,4,5,6,7,8,8-Heptachlor-3a,4,7,7a-tetrahydro-4,7-methanoindene or 1,4,5,6,7,8,8-heptachloro-4,7-endomethylene-3a,4,7,7a-tetrahydroindene
Heptachlor epoxide		$C_{10}H_5Cl_7O$ (389.3)	2,3-epoxy-1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
α-Endosulfan (Thiodan - I)		$C_9H_6Cl_6O_3S$ (406.9)	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide (α-isomer)

Table 1 (continued)
NOMENCLATURE, STRUCTURES, FORMULA, AND MOLECULAR WEIGHTS OF SOME COMMON O.C. PESTICIDES

Common name	Structure	Formula and mol wt	Nomenclature
β-Endosulfan (Thiodan - II)		$C_9H_6Cl_6O_3S$ (406.9)	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide, (β-isomer)
Aldrin		$C_{12}H_8Cl_6$ (364.9)	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-endo-1,4-exo-5,8-dimethanonaphthalene
Dieldrin (HEOD)		$C_{12}H_8Cl_6O$ (380.9)	1,2,3,4,10,10-Hexachloro-exo-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, exo-5,8-dimethanonaphthalene
Endrin		$C_{12}H_8Cl_6O$ (380.9)	1,2,3,4,10,10-Hexachloro-exo-6,7-epoxy-1,4,4a,5,-6,7,8,8a-octahydro-1,4-endo, endo-5,8-dimethanonaphthalene
p,p'-DDT		$C_{14}H_9Cl_5$ (354.5)	1,1,1-Trichloro-2,2-*bis* (*p*-chlorophenyl)-ethane
o,p'-DDT		$C_{14}H_9Cl_5$ (354.5)	1,1,1-Trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenyl-ethane