

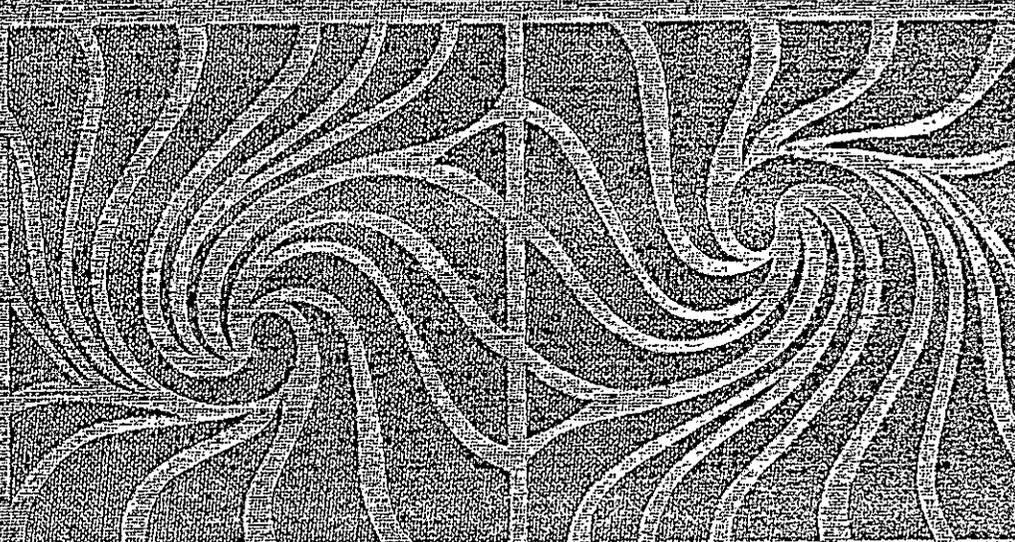
G. TECHNICAL COMPLIANCE GUIDELINES

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4

STANDARD METHODS

For the Examination of
Water and Wastewater



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STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER

101 APPLICATIONS

The procedures described in these standards are intended for the examination of waters of a wide range of quality, including water suitable for domestic or industrial supplies, surface water, groundwater, cooling or circulating water, boiler water, boiler feed water, and treated and untreated municipal or industrial wastewater. The unity of the fields of water supply, receiving water quality, and wastewater treatment and disposal is recognized by presenting methods of analysis for each constituent in a single section for all types of waters.

An effort has been made to present methods that apply as generally as possible; and where alternative methods are necessary for samples of different composition, to present as clearly as possible the basis for selecting the most appropriate method. However, samples with extreme concentrations or otherwise unusual com-

positions may present difficulties that preclude the direct use of these methods. Hence, some modification of a procedure may be necessary in specific instances. Whenever a procedure is modified, state plainly the nature of modification in the report of results.

Certain procedures are intended for use with sludges and sediments. Here again, the effort has been to present methods of the widest possible application, but when chemical sludges or slurries or other samples of highly unusual composition are encountered, the methods of this manual may require modification or may be inappropriate.

The analysis of bulk chemicals received for water treatment is not included herein. A committee of the American Water Works Association prepares and issues standards for water treatment chemicals.

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102 LABORATORY APPARATUS, REAGENTS, AND TECHNICS

1. Containers

For general laboratory use, the most suitable material for containers is resistant borosilicate glass.* Special glassware is available with characteristics such as high resistance to alkali attack, low boron content, or exclusion of light. Choose stop-

pers, caps, and plugs to resist the attack of material contained in the vessel. Cork stoppers wrapped with a relatively inert metal foil are suitable for many samples. Metal screw caps are a poor choice for samples that will cause them to corrode readily. Glass stoppers are unsatisfactory for strongly alkaline liquids because of their tendency to stick fast. Rubber stoppers are excellent for alkaline liquids but unacceptable for organic solvents, in which they swell or disintegrate. Use

*Pyrex, manufactured by Corning Glass Works; Kimax, Kimble Glass Co., Division of Owens-Illinois; or equivalent.

2. American Public Health Assoc., American Water Works Assoc., Water Pollution Control Federation. Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater: Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency. 15th Edition, 1981

2

Supplement to the Fifteenth Edition of
*Standard Methods for the Examination of
Water and Wastewater.*

SELECTED ANALYTICAL
METHODS APPROVED AND
CITED BY THE UNITED
STATES ENVIRONMENTAL
PROTECTION AGENCY

Prepared and Published by:

American Public Health Association
American Water Works Association
Water Pollution Control Federation

INTRODUCTION

This "Supplement to the Fifteenth Edition of *Standard Methods for the Examination of Water and Wastewater*" (Supplement) presents selected analytical methods for which no equivalent methods are found in the Fifteenth Edition of *Standard Methods for the Examination of Water and Wastewater* (*Standard Methods*), and which may be of use in complying with certain requirements of the National Pollution Discharge Elimination System (NPDES) regulations and the National Interim Primary Drinking Water Regulations promulgated by the U.S. Environmental Protection Agency (EPA).

EPA's regulations which approve and cite analytical water methods were promulgated prior to the publication of the Fifteenth Edition of *Standard Methods*, and therefore cite methods in the Fourteenth Edition. Many methods of analysis not included in the Fourteenth Edition, but required by EPA's regulations, have now been included in the Fifteenth Edition of *Standard Methods*, and it is expected that these methods will be approved and cited by EPA in the next revision of these regulations.

This Supplement provides information on analytical methods cited in regulations contained in Title 40 of the Code of Federal Regulations (C.F.R., July 1, 1980 ed.), primarily Part 136 (the NPDES regulations approving water

methods) and Part 141 (the safe drinking water regulations). One of the several tables prepared by the Editors of the Supplement presents a listing of all the Federal regulations of EPA and other Federal agencies as of December 31, 1980 which refer to water methods.

Many of these regulations cite EPA's Table I.--List of Approved Test Procedures, set forth at 40 C.F.R. §136.3, which cites approved water methods for over 115 parameters, pollutants, and characteristics. The entire text of this basic regulation is presented in the Supplement.

The Government methods published by EPA which are included in the Supplement have not been subjected to the rigorous consensus approval procedures used to develop the standards methods contained in the Fifteenth Edition of *Standard Methods*. These Government methods are being presented without endorsement or sanction by the sponsors of *Standard Methods* as a service to the analyst. In addition, the publication of these supplemental methods should not be construed as approval of trade names cited by EPA or implied disapproval of comparable unlisted products. The mention of trade names or commercial products in the Supplement or the original EPA publications is for illustration purposes and does not constitute endorsement or recommendation for use by EPA or other agencies of the U.S. Government or by *Standard Methods*.

The methods presented in the Supplement include metals, inorganic non-metals, organic compounds, and radioactive metals. Table I is the primary reference source for methods to be used in the analysis for pollutants. The term "pollutants" is also used to define the naturally occurring constituents of drinking water. Table I as presented in the Supplement does not include any of the changes in a proposed rule issued by EPA in the Federal Register on December 3, 1979 (44 Fed. Reg. 69464-575, as corrected by 44 Fed. Reg. 75029-52 (Dec. 18, 1979)), because those regulations have not yet been promulgated as a final rule. When EPA promulgates a revised version of Table I in Part 136, it will approve and cite methods in the Fifteenth Edition.

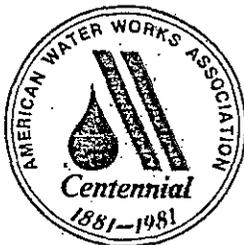
The Editors of the Supplement have prepared five tables, Tables A-E, to assist analysts in understanding EPA's TABLE I, the Federal regulations of all agencies, and the correlation between the Fourteenth and Fifteenth Editions.

It should be noted that there are several stages of method "approval". The official source of approved methods is the C.F.R., but there are appreciable delays in incorporating changes into the C.F.R. Moreover, once the final revised regulations are published in the Federal Register, it takes some time before the changes are incorporated in the C.F.R. Consequently, to meet new analytical demands, methods may be temporarily acceptable as recommended, proposed, interim, or as part of a proposed rule not yet incorporated into the current issue of the C.F.R. The status of a new method for reporting purposes is best determined by consultation with the agency in your State exercising primacy in the enforcement of State or Federal regulations.

The sponsors of *Standard Methods* wish to acknowledge the efforts of the Consulting Editor of the Supplement, Robert E. Mittendorff, Esq., for his thorough research of Federal regulations and Government water methods, and preparation of the various tables. Mr. Mittendorff is an attorney in Washington, D.C. who previously served in the Office of General Counsel of EPA. The sponsors also wish to recognize the diligent efforts of the Joint Editorial Board for *Standard Methods*—A. E. Greenberg, J. J. Connors, D. Jenkins and the Secretary, J. G. DeBoer, and most especially Mary Ann H. Franson, Managing Editor of the Fifteenth Edition.

The sponsors of *Standard Methods* are pleased to provide this Supplement with the Fifteenth Edition of *Standard Methods* so that analysts can benefit from a single source of analytical methods for the examination of water and wastewater.

OBTAINED FROM JOHN YOUNGERMAN, SWRCB



STATE WATER RESOURCES
CONTROL BOARD
P. O. BOX 100
SACRAMENTO, CA 95801

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¹EPA Methods, March, 1979. See the full title of the Government publication in footnote 2 of TABLE A. Method numbers are those in the Government publication as noted in TABLE A.

²Methods for Uranium available in a recent EPA publication which is not yet referred to in 40 C.F.R. Part 141. See the full title of the Government publication in TABLE A, Footnote 8.

³EPA Methods, 1974. See the full title of the Government publication in footnote 1 of TABLE A. Page references are to the location of the methods in the Government publication as noted in TABLE A.

⁴EPA Interim Methods, September, 1978. See the full title of the Government publication in footnote 3 of TABLE A. Page references are to the location of the methods in the Government publication as noted in TABLES A, B and C.

⁵U.S. Geological Survey water method. See the full title of the Government publication in footnote 5 of TABLE C. Page reference is to the location of the method in the Government publication as noted in Table C.

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3. American Society for
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Those interested in crankcase oil wear and accumulation of piston deposits engine operation, and in particular to crankcase lubricating oils. 94 pages

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1981 ANNUAL BOOK OF ASTM STANDARDS, PART 23, PART 24, PART 25, AND PART 47

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In the serial designations prefixed to the following titles, the number following the dash indicates the year of original issue as tentative or of adoption as standard or, in the case of revision, the year of last revision. Thus, standards adopted or revised during the year 1981 have as their final number 81. A letter following this number indicates more than one revision during that year, that is 81a indicates the second revision in 1981, 81b the third revision, etc. Standards that have been reapproved without change are indicated by the year of last reapproval in parentheses as part of the designation number, for example (1981). A superscript epsilon indicates an editorial change since the last revision or reapproval—e1 for the first change, e2 for the second change, etc.

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¹ Editorially changed.

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Due to the special nature of this method it is of interest to a limited number of users of this book; it is, therefore, not included in this book. It will not be published by the American Society for Testing and Materials but will be published by the American Petroleum Institute. Separate copies will be available from

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1981 ANNUAL BOOK OF ASTM STANDARDS

Part **31** Water



Revision issued annually.

Part 31 of the 1981 Annual Book of ASTM Standards is a 1488 page book with 10 sections dealing with test procedures for water. Each section covers a separate category of conditions for water testing. They include the general principles, the apparatus involved, and the test procedure is discussed in detail. Topics such as sampling, general properties of water, and tests for impurity constituents may be useful for tank monitoring. This reference can be obtained at the California Resources Agency Library.

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X. Water Treatment Materials

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Excerpts from E 380 Standard for Metric P
Abbreviated Test Methods in Water Supply

Following these is a complete subject index
number of each standard referred to in the i

INTRODUCTION

The methods in this volume are under the jurisdiction of Committee D-19 on Water. This committee is concerned with the study of water, the promotion of knowledge thereof, and the standardization of terminology and methods for (1) sampling and analysis of water, water-borne materials and wastes, water-formed deposits; (2) the determination of the structure, function, and condition of communities of indigenous and other aquatic organisms; (3) surface water hydraulics and hydrologic measurements; (4) the determination of the performance of materials used to modify water characteristics; and (5) the determination of the corrosivity or deposit-forming properties of water.

Committee D-19, formed in 1932, has technical activities which are carried forward by more than 750 members working in the following subcommittees:

- D19.01 Statistical Methods
- D19.02 General Specifications and Technical Resources
- D19.03 Hydraulics, Sampling, and Surveillance of Water and Water-Formed Deposits
- D19.04 Methods of Radiochemical Analysis
- D19.05 Inorganic Constituents in Water
- D19.06 Methods of Analysis for Organic Substances in Water
- D19.07 Methods of Testing for Sediments
- D19.08 Water Treatment Materials
- D19.09 Saline and Brackish Waters
- D19.11 Water for Power Generation and Process Use
- D19.21 Effluent Testing
- D19.23 Biological Field Methods
- D19.24 Water Microbiology
- D19.31 Identification of Waterborne Oils
- D19.32 Water for Subsurface Injection
- D19.33 Water Associated with Alternative Fuels Production

Membership is open to all who have an interest in participating in the development of standards in these areas. While Committee D-19 may generally be considered one of the unclassified committees of the Society, Subcommittee D19.08 on Water Treatment Materials is classified for Particulate Ion Exchange Materials. The standards published herein are reviewed by the committee at least once every 5 years. Each committee member is given an opportunity through a written letter ballot to vote on new standards, revisions to standards, the reapproval of standards, and the withdrawal of standards. All negative votes with accompanying reasons must be acted upon within the committee before acceptance of the action.

The designation numeric list is followed by a subject-oriented Table of Contents in which the standards are listed alphabetically according to the subject of the test under the following areas of interest:

- I. Definitions, Specifications, Reagents, and Reporting Results
- II. Sampling and Flow Measurement
- III. General Properties of Water
- IV. Inorganic Constituents
- V. Organic Constituents
- VI. Radioactivity
- VII. Saline and Brackish Waters, Seawaters, and Brines
- VIII. Microbiological Examination

Introduction

- IX. Water-formed Deposits
- X. Water Treatment Materials

At the back of the book, the gray-marked pages include:

- Excerpts from E 380 Standard for Metric Practice
- Abbreviated Test Methods in Water Supplies in the Evaporative Industry Proposed Test Methods

Following these is a complete subject index in alphabetical order including the designation number of each standard referred to in the index.

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5. Association of Official
Analytical Chemists. Official
Methods of Analysis of the
AOAC

ABOUT THE BOOK

Official Methods of Analysis is the major publication of the Association of Official Analytical Chemists.

Chemists, microbiologists, and other scientists in government, industry, and universities depend upon *Official Methods of Analysis of the AOAC*. Reliability of methodology is their major concern. And the reliability and uniformity of each AOAC analytical method has been demonstrated by thorough testing in interlaboratory collaborative studies.

U.S. and Canadian national, state, and provincial laws, regulations, and policy often stipulate the use of AOAC methods, as do commercial specifications. The authority of the methods is further enhanced by the collaboration of such international organizations as the ISO (International Organization for Standardization), IDF (International Dairy Federation), and CIPAC (Collaborative International Pesticides-Analytical Council).

This compendium contains over 1700 methods. Its step-by-step format specifies reagents and apparatus to be used. Alternative methods are often provided to accommodate a wide range of laboratory capabilities. The book is published every five years and is supplemented between editions by four annual updates included in the purchase price.

This edition has been updated to enhance clarity and ease-of-use. Along with 165 additional methods, it offers the following features:

- Method-performance parameters: within-laboratory and between-laboratory standard deviations for each method adopted since publication of the 13th Edition.
- Easy-to-locate references
- Chemical and common names of all drugs and pesticides
- A greatly expanded index
- More-descriptive titles
- Chemical Abstracts Service (CAS) numbers wherever applicable.

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ABOUT THE ASSOCIATION

Founded in 1884 AOAC is an independent international association devoted to the development, testing, validation and publication of methods of analysis for foods, drugs, feeds, fertilizers, pesticides, water, forensic materials and other substances.

AOAC coordinates the development, testing, and validation of these methods and requires an interlaboratory collaborative study before a method can be approved as official. Approval of methods is accomplished by vote of eligible organizations. Approved methods are published in *Official Methods of Analysis*.

The actual work of devising and testing methods and initiating and carrying out collaborative studies is accomplished by a network of hundreds of volunteer-member scientists worldwide. These scientists work in their official and professional capacities as staff scientists in government, university, and industry laboratories.

Other AOAC activities include annual and regional meetings, symposia, courses and training workshops; publishing the *Journal of the AOAC*, manuals, proceedings, and other books, and The Referee, an informative bulletin for members.

About the Members

The AOAC membership is made up of individuals and organizations. Individual members are analytical science professionals: analytical chemists, biologists, microbiologists, biochemists, toxicologists, spectroscopists, and forensic and other scientists in laboratory, administrative, and management positions. Organization or Sustaining Members, are government agencies, and private firms and organizations with an interest in the development and interlaboratory evaluation of analytical methods.

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NOBLE GASES	2	He	4.00260	10	Ne	20.179	18	Ar	39.948	36	Kr
VIIIB	1	H	1.00794	9	F	18.998403	17	Cl	35.453	35	Br
VIB	8	O	15.9994	16	S	32.06	34	Se			
VB	7	N	14.0067	15	P	30.97376	33	As			
IVB	6	C	12.011	14	Si	28.0855	32	Ge			
IIIB	5	B	10.81	13	Al	26.98154	31	Ga			
IIB							30	Zn			
IB							29	Cu			
VIIIA							28	Ni			
VIIA							27	Co			
VIA							26	Fe			
VA							25	Mn			
IVA							24	Cr			
IIIA							23	V			
IIA							22	Ti			
IA							21	Sc			
	1	H	1.00794	3	Li	6.941	11	Na	22.98977	19	K
	4	Be	9.01218	12	Mg	24.305	20	Ca			

The "Official Methods of Analysis" by the Association of Official Analytical Chemists is a comprehensive book for laboratory analysis of any substance related to public health, safety and quality. The book has 52 chapters, each devoted to one particular group of consumer products (drugs, foods, pesticides, etc.). There are 1141 pages. 
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About the Association

PURPOSE AND FUNCTION

The primary objectives of the Association of Official Analytical Chemists (AOAC) are to obtain, improve, develop, test, and adopt uniform, precise, and accurate methods for the analysis of foods, drugs, feeds, fertilizers, pesticides, water, or any other substances affecting public health and safety, economic protection of the consumer, or quality of the environment; to promote uniformity and reliability in the statement of analytical results; to promote, conduct, and encourage research in the analytical sciences related to agriculture and public health and the regulatory control of commodities in these fields; and to afford opportunity for discussion of matters of interest to scientists engaged in relevant pursuits.

AOAC itself maintains no laboratories, conducts no analyses, performs no tests. The actual work of devising and testing methods is done by members of AOAC in their official and professional capacities as staff scientists of federal, state, provincial, and municipal regulatory agencies, experiment stations, colleges and universities, commercial firms, and consulting laboratories.

AOAC coordinates these scientific studies, receives and evaluates the results, gives official sanction to acceptable methods, and publishes and disseminates the methods.

The reliability of methods of analysis is more important than ever before. Regulatory agencies need reliable, reproducible, and practical methods to enforce laws and regulations. Industry needs reliable methods to meet compliance and quality control requirements. Few organizations in the United States are devoted primarily to testing and validating analytical methods through interlaboratory collaborative studies—as is AOAC.

MEETINGS

The Annual International Meeting, held each October, is the focal point of AOAC's yearly work. Here, members have opportunities to exchange ideas with colleagues from all over the world, and to update their technical knowledge at scientific sessions and symposia, exhibits, and short courses.

The Spring Workshop, held in a different city each year, provides practical educational seminars and hands-on training workshops, primarily for the bench analyst.

The regional section program provides AOAC-affiliated local or regional scientific meetings, workshops, short courses, and other activities for laboratory analysts. Each regional section is organized by a local volunteer committee.

COOPERATIVE ACTIVITIES

AOAC has established joint committees, liaison, and representation with numerous scientific organizations worldwide. Thus, methods are often developed in cooperation with other standards-setting bodies. AOAC liaison representatives for contact outside North America are the following: Harold Egan, Laboratory of the Government Chemist, Cornwall House, Stamford St, London, UK SE1 9NQ; telephone +44-1928-7900; and Margreet Tuinstra-Lauwaars, Langhoven 12, 6712 SR Bennekom, Netherlands, telephone +31-8389-8725.

AWARDS

The awards program of AOAC includes the following: The Scholarship Award is given each year to a student intending to do further study or work in an area important to public health or agriculture.

The Fellow of the AOAC Award is given to selected members in recognition of at least 10 years of meritorious service to the Association as referees and/or committee members.

The Harvey W. Wiley Award, honoring the "father" of the U.S. Pure Food and Drug Act and a founder of AOAC, is presented each year to a scientist or group of scientists who have made outstanding contributions to analytical methodology in an area of interest to AOAC. The \$2500 award is supported by the Wiley Fund.

PUBLICATIONS

Official Methods of Analysis includes full details of official methods but no descriptive or interpretative material or tables of data. However, AOAC publishes the *Journal of the AOAC*, which contains research articles and reports of the development, validation, and interpretation of analytical methods; and all collaborative study results. *Journal* contributors and its readers represent the worldwide analytical science community. The *Journal* is a forum for the exchange of information among methods researchers. The *Journal* also records the transactions of the Annual International Meeting, including committee and referee reports, lists of officers, referees, and committee members, and all official actions of the Association, including newly adopted methods. The Association publishes a variety of other books, manuals, and symposium proceedings of interest to analytical scientists.

MEMBERSHIP

The organization of AOAC consists of the members; the Board of Directors, a governing body concerned with administration and policy making; Official Methods Board; Editorial Board; special standing committees and other groups concerned with development of methods and general activities; and the headquarters staff which carries out the publications program and manages the Association.

The AOAC Bylaws provide for 4 classes of membership: Members, Associate Members, Government-Sustaining Members, and Private Sustaining Members. Chemists, microbiologists, and other scientists engaged in analysis or analytical research related to agriculture and public health, and employed by a college or university or by any agency of a local, state, provincial, or national government may be members. Associate members represent firms or industries concerned with commodities or substances of interest to AOAC. Government sustaining members and private sustaining members are government agencies or private industries, respectively, that provide financial support to AOAC.

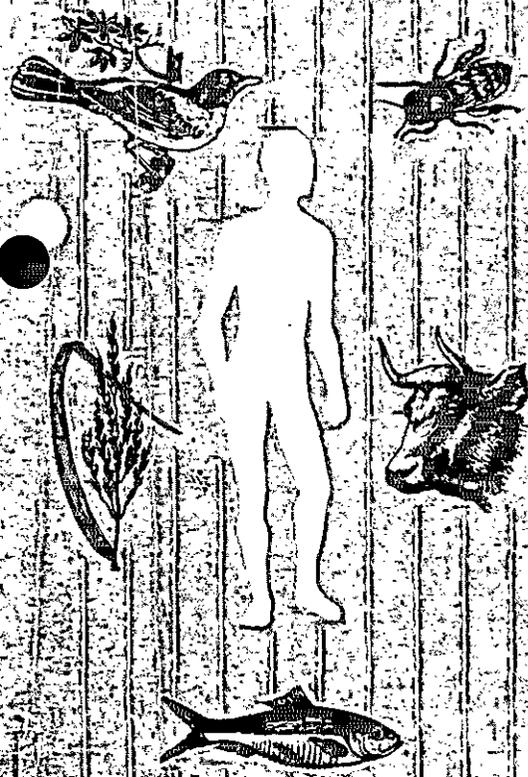
The Referee, published 10 times yearly, is sent free to all members, and contains methods news, collaborative study news, previews and wrap-ups of meetings, news about AOAC people, and Association news. All members also receive the membership directory, issued annually.

6. Federal Working Group on
Pest Management. Guidelines on
Sampling and Statistical
Methodologies for Ambient
Pesticide Monitoring, October
1974

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**GUIDELINES
ON
SAMPLING AND
STATISTICAL METHODOLOGIES
FOR
AMBIENT PESTICIDE MONITORING**



**FEDERAL WORKING GROUP ON PEST MANAGEMENT
WASHINGTON, D.C.
OCTOBER, 1974**

GUIDELINES ON SAMPLING AND STATISTICAL METHODOLOGIES
FOR AMBIENT PESTICIDE MONITORING

MONITORING PANEL

U.S.

FEDERAL WORKING GROUP ON PEST MANAGEMENT

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INTRODUCTION

In the course of revising and updating various aspects of the National Pesticide Monitoring Program, the Monitoring Panel of the Federal Working Group on Pest Management identified a need for a standardized approach to sampling methodologies for the respective environmental components of the Program. Accordingly the Panel set up a task group to undertake this effort.

In preparing this report the task group imposed four restrictions on itself as it applies to the scope of the report. These restrictions were as follows:

1. The report was to be considered as a set of guidelines and not as a manual. The term "manual" implies a series of step-by-step procedures with its inferred inflexibility. The variability encountered in sampling various media from different geographical regions and with different program objectives, precludes the establishment of fixed methodologies, in a manual form.
2. The report was to apply primarily to the type of ambient or trend monitoring as defined in the charter of the Monitoring Panel. Thus, monitoring as included in the National Pesticide Monitoring Program, is defined as the repeated sampling and analysis of components of the environment to produce estimates of pesticide residue levels in these components and the changes in these levels with time.
3. The report was to be designed for use by people with some familiarity with field sampling operations although not necessarily with ambient sampling for pesticide residues. Such people will most likely be associated with a federal or state agency, university or large private contractor involved with an extensive monitoring program.
4. The report was to consider both the statistical aspects of sampling as well as the field sampling procedures necessary to implement a large scale monitoring program as exemplified by the National Pesticide Monitoring Program. This Program is presently designed to include the following components: air, soil, water, estuaries, freshwater fish, birds, food and feed, and human tissues. The guidelines were to be developed around these components.

This report represents a first effort only, and the task group fully recognizes the need for updating and modifying these guidelines as time goes by. The format of the guidelines is designed to facilitate such updating.

ACKNOWLEDGMENT

The preparation of these guidelines was initiated by a task group of the Monitoring Panel, Federal Working Group on Pest Management. The task group was chaired by Dr. G. B. Wiersma, EPA, and included Dr. E. L. Cox, USDA; Mr. R. G. Heath, USDI; Mr. F. P. Kapinos, EPA; and Dr. A. R. Yobs, EPA. Additional help in the initial preparation was provided by Mr. B. L. Berger, USDI; Dr. P. A. Butler, EPA (Fla.); Ms. A. E. Carey, EPA; Mr. D. G. Donahoo, USDI; and Dr. H. Roberts, FDA. The cooperation of these persons and other representatives of the federal agencies comprising the Monitoring Panel, who made suggestions and reviewed the final draft is gratefully acknowledged. Final editing and publication of the document was done by the FWGPM Secretariat.

CHAPTER I - Statistics and Study Design

The concept of "taking a sample" is a familiar one. Loosely, it is implied that a sample is some part, generally small, of a larger entity. The concept of the sample being "representative" in the statistical sense is not so well known. It is through the quality of representativeness that information from samples can be used to make numerical statements characterizing the universe from which they come.

To conform strictly with statistical criteria, procedures for selecting a representative sample require that:

1. The total number of units or amounts of material (universe) that the sample is to represent be clearly and uniquely definable.
2. The sample or samples from the universe be selected by a method which gives all parts of the universe a definable chance of appearing (random selection).
3. More than one sample be taken from each universe under investigation unless the reliability of the sample to be representative has been pre-established.
4. If the reliability of the representativeness is not known, enough samples will be selected from the universe so that a desired level of reliability will be achieved.

It can be noted that there are problems to be solved by sampling which do not require that the samples be representative. Frequently in regulatory work the aim will be to determine the maximum (or possibly minimum) value which can be found in a sampling unit from a given universe. This aim can be met at minimum cost by following principles of random selection and designed search.

A sampling program may be properly designed to provide adequate definition of local conditions or universes. It is generally not possible to consider these local universes as subuniverses of a broader or national universe. Many mistakes have been made by not recognizing this fallacy. If, however, the large universe is considered in the design and the subuniverses are selected by statistical principles then representative samples from these subuniverses can be used in making inferences about the large universe.

A basic premise in statistical thought is that many phenomena are incompletely or inadequately described by a single measure. The average, mean, median, or some other measure of centrality is too often used as an index for description of a set of samples where much of the information in the set reflects the spread around the central value. Statistical usage insists that estimates of at least two parameters be considered for descriptions based on sample information. The two parameters most frequently estimated are known as mean and standard deviation.

Underlying the specification of estimates of two parameters for definitions is the concept of distribution or probability distribution. Even a well defined universe from which a large number of samples can be taken would exhibit for all possible samples an almost continuous spectrum of sample values against probability of attainment of these values. Hence, if enough random samples are taken from a universe, a good definition of the possible values from that universe can be made as well as estimates of the chance that certain specified values will be exceeded.

For example, suppose that the residue level of a pesticide in the eggs produced for human consumption in a state during a given period can be considered as a well defined universe. A well designed program of taking random samples from this universe would provide an approximation of the distribution of these residue levels and from this approximation, the chance that residues exist in excess of any prescribed level can be estimated with an order of reliability dependent on the number of samples used in defining the distribution.

The challenge might be raised that the method described above presents the probability that levels of residues exist which have not been observed in any sample. This is true. For example, a set of samples might contain, no observed residues above 0.1 ppm but the estimation of a distribution to fit the set of samples might imply 1% of all possible samples could be in excess of 0.1 ppm. The examination of the reliability of this estimate might result in the confidence statement "there is a 5% chance that more than 1.3% of all possible samples could have values in excess of 0.1 ppm". If the implications of this result are serious, the estimates and the confidence statement can be improved only by obtaining additional and properly designed sampling information.

The general principles implied here will be basic for obtaining and treating sample information from all components of the natural environment. Certain components will introduce special problems and require special methodology to meet the general principles.

The need for a universe to be well defined has been referred to above. It is easily recognized that the more homogenous a universe is, the number of samples needed to provide an adequate description of that universe will be smaller. Thus, it is generally advantageous to divide a universe, prior to samplings into subunits which are known to be more homogenous within themselves, when this can effectively be done. This valuable concept is called stratification.

As an example, in the national plan for sampling pesticide residues in soils, two strata were defined. These strata were called cropland and noncropland. The names are somewhat self explanatory and the fact that somewhat different pictures are expected of the pesticide residues in the two strata is readily recognized. At the time the project was planned,

subdivisions into many more strata were proposed. These were difficult to define clearly and hence were not considered. The principle was correct but the means for achievement were unavailable.

In planning an investigation to define the levels of some deleterious element in a component of the natural environment on a regional or national basis, it would be advisable to review all the recorded data now in existence. It will generally be found that these data have not come from a program designed according to statistical principles. Hence it will be incorrect to extrapolate from these results knowing that if such an action is tried, no assessment of reliability can be given for the estimates presented. Nevertheless, these data need to be examined to get some feeling as to the type of values that may arise. Also the records will give valuable information for defining strata and estimating numbers of samples needed for a planned investigation. When all available background is considered, a pilot study for some region or stratum should be planned. While the pilot study is being expedited, the planning for an operational program can begin. The latter may need to be modified after the results of the pilot study are assessed. A program for a national study needs frequent points at which the results will be reviewed, and an understanding that modifications will be quickly made when these results suggest that preconceptions may not have been correct. There is a concept very widely held that after a plan for an investigation is presented it should never be altered no matter how badly it works. Many programs have produced less than optimum results through this wrong-headedness. It is just as easy to produce and operate a program which permits feedback and modification when the nature of the findings indicate that changes are desirable.

A caution must be kept in mind in dealing with the type of data that arises from most investigations of residues. Any well designed program is likely to show most of the sample results to be in the "nondetected" category. This means that generally a rather large number of samples must be taken to achieve a reasonable picture of the distribution. A well defined estimate of the mean or other central value is generally difficult to express. The types of summary statements depending on assumptions of the distributional form have not received full acceptance. Unless an acceptable alternative can be proposed, the methods based on a distributional assumption is recommended.

In applying the above principles to the evaluation of pesticide residues in soils by a sampling program, we immediately recognize a potential difference in distribution depending on whether persistent or nonpersistent chemicals are under consideration. The least elaborate program can be designed for the definition of the persistent chemicals. Stratification according to two or more use levels would be in order.

The problem of detecting changes with time can be approached by taking samples at the same locations at intervals of several years if no

additional pesticide is applied in the interval. If the application is yearly, the sampling program needs to be modified accordingly.

In dealing with nonpersistent chemicals, the time since application needs to be considered in providing an appropriate stratification system. Changes with time in terms of years may have little interest but changes by month or even days may be the information desired.

Even if yearly or more frequent applications of a chemical under consideration is the nature of its use, the date of application is an element to be considered in making a meaningful plan for its evaluation. A general plan to provide estimates for both the easy and difficult problems needs to be primarily guided by planning to meet the difficult.

The general evaluation of pesticide residues in water is inherently more difficult than for soils. Thus separation into watershed units neglects consideration of samples from large rivers. A succession of samples along the course of a large river might suggest successive integrations which would permit earlier fractions to be subtracted but the validity of this procedure needs to be established. It has been pointed out that the sampling of waters may be considered not only for estimating the residue load coming from the land but also for estimating the residues headed for lakes or the sea. For many residues, however, a lengthy time of transport may change their character by deposit, chemical reaction, etc., and hence a good definition of upstream waters may not provide a good predictor of the quality further downstream. Experience in the Hudson and Chesapeake estuaries has demonstrated that an integrated sample across the estuary at any time would be a poor indicator of the nature of the waters at some other time. An integrated sample cross channel and over a full tidal cycle is needed for a firm measurement.

The basic geographic stratification for an air sampling program should recognize regions with larger concentrations of populations and/or industry as needing the heaviest sampling rate. These regions should be mapped as larger than standard metropolitan areas. Possibly two additional strata; low and moderate population densities should be considered.

The problem of recognizing classes of prevailing meteorological conditions needs to be met. Certain areas such as southern California and the Great Basin are examples of air masses that have a tendency to be stationary for lengthy periods and which form a recognizable category. There are other areas where such stagnation may exist for only short periods. How these conditions should be considered for planning purposes is uncertain.

The foregoing discussion outlines the range of statistical considerations which a planner must draw upon in setting up any sampling procedures for a monitoring program. Specific choice of statistical methodology and computational details for such methodology are obtainable from several basic texts. A brief list of the more widely used texts is provided.

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CHAPTER II - AIR

Monitoring ambient air for pesticide residues is technically difficult at present because the fundamental technology necessary for such a program is still being developed. The physical-chemical behavior of airborne residues, i. e., duration of vapor stage, factors governing particulate adsorption/absorption and desorption, influence of water vapor, etc. and the pattern of geo-physical effects are all largely unknown and must be defined to optimize sampling efficiency. Ambient air monitoring is also difficult because it is possible that an unlimited range of pesticide residues are present, requiring identification and measurements at microquantity concentrations that vary widely with geography, season, local pesticide usage and altitude. Various nonpesticide air pollutants may also be collected during the sampling process and may subsequently interfere with analysis.

Specific guidelines for air sampling in connection with monitoring pesticide residues in ambient air cover four areas listed below.

PROGRAM DESIGN

Goal Identification: Clear definition of the purpose of the contemplated monitoring program is essential to the success of the program and will direct many of the decisions required in preliminary planning.

Sampling Site Criteria: The criteria for sites will be guided by and are important to attaining the program goal. Criteria must be selected after considering a variety of conditions such as geographic divisions, prevailing weather patterns, pesticide usage patterns, cropping population concentrations, elevation above ground level or above sea level, etc. Service requirements such as power supply and travel time must also be considered. The attributes of sampling sites must be defined before a monitoring design is developed.

Statistical Design: This is most important in assuring that collected data is unbiased and can be treated statistically to determine the significance of findings. The statistical design provides for the selection of sampling sites on a random basis, insuring that equal consideration is given to sites that meet the established criteria.

Nature of Sample: A sample of air may be collected continuously or intermittently depending on restrictions imposed by monitoring goal, program design, sampling equipment capability and analytical factors. The parameters of a sample must therefore be defined in these terms and expressed as a volume of air to be sampled.

Sampling Frequency: Samples may be collected as often as indicated by the established monitoring goal and statistical design so long as this is consistent with available laboratory support.

Ancillary Information: Measurements of such variables as temperature, windspeed and direction, precipitation, etc. along with information about the sampling locality and pesticide usage is helpful in the interpretation of ambient air monitoring results. Need for or value of such ancillary information must be predetermined and arrangements made to obtain this information at the time of sampling.

ANALYTICAL SUPPORT

Sampling and analysis are distinct parts of any monitoring program. They are interdependent, however, since each controls certain aspects of the other. It is necessary to make certain decisions about the analytical phase at this point in program planning because these decisions will control such things as the volume of air to be collected in each sample, the maximum tolerated delay between sample collection and analysis, and sample handling, including transport and storage.

Residues to be Monitored: The variety of pesticides potentially present in ambient air together with the limited number of multi-residue techniques available means that target residues must be carefully selected to meet program needs within available analytical support limitations. This also is important in selection analytical procedures to be used.

Analytical Procedures: These must be of such sensitivity and specificity to permit detection and identification of the desired compounds at the levels at which it is anticipated that they will be present.

Confirmatory Procedures: These are necessary because of the unlimited variety of pesticide residues potentially present. Such procedures are generally less sensitive than the basic analytical procedures and require additional analytical time. The investment of these resources is imperative, however, to substantiate the identification of the residues.

Reporting: Details must be established for reporting analytical findings, including units of reporting (weight per volume of air, particulates, etc.). These should be selected to assure reporting in whole numbers as much as possible.

SAMPLING EQUIPMENT

Sampling Equipment must be selected which can operate within the criteria established for the site.

Construction: Equipment should be constructed for durability in a variety of climatic conditions, yet be light enough to facilitate transportation. It may be constructed of any materials as long as the air stream is not exposed to contaminants or otherwise modified prior to sampling.

Calibration: Each sampler should be tested upon installation in the field to assure that it is working properly and to calibrate the actual air flow air volume sampled.

Pre-testing: Equipment and trapping reagents should be tested with regard to the selected residues for sampling efficiency, and retention at the planned air flow rate.

FIELD OPERATION

Action must be taken to assure field operation by the desired parameters.

Sampler Location: This should be standardized. The intake passage should be as short as possible to decrease residue loss through absorption at the inlet. There should be free access on all sides to ambient air. This should be no less than 5 feet above ground level to avoid surface turbulence. If external power is required, a source must be available.

Servicing: A schedule should be established for regular servicing and preventive maintenance as indicated by the sampling equipment and schedule. Glassware should be cleaned after each sampling interval.

Sample Handling, Storage and Transport: Do not disregard the importance of these in the overall program. They are vital in preserving collected residues for analysis. Collecting reagents should be placed in chemically clean screw top glass containers with aluminum foil or other non-reactive liners and refrigerated. Transport to the laboratory should be by the most rapid practical method.

CHAPTER III - Soil

It is the purpose of this chapter to review techniques of soil sampling capable of application to pesticide residue estimations in soil: the types of sampling equipment, shipping and storage, and soil properties used for correlation with residue levels. Most of the information is drawn from the open literature, as well as from the methodologies of government agencies actively involved in monitoring pesticide residues in soil.

Compared with analysis for soil nutrients, sampling for pesticide residues is relatively new. However, many of the basic concepts which guide sampling for nutrient studies can be utilized in residue monitoring. Cline (1) in his classic work on soil sampling, endorsed the concept that soil should be considered a volume to be sampled, not merely an area. Soil is also a heterogenous medium, i.e., most of the physical and chemical properties are not uniform along all dimensions. However, within a limited spatial area, a soil body can also be considered homogeneous, with respect to soil type, vegetation and cultural practices. Therefore, any good sampling plan must recognize and attempt to minimize these variations in order to obtain a sample which can give an accurate estimate of the parameters under investigation.

GENERAL SOIL SAMPLING CONSIDERATIONS

Sampling Error vs. Analytical Error

Several studies have demonstrated that field error is much greater than analytical error in soils testing (1,2,3,4). Therefore, the field sampling methodology should aim at minimizing this error.

Disturbed vs. Undisturbed Profiles

On cultivated agricultural land, cultivation has mixed the upper horizons of the soil to a fairly homogeneous layer called the plow layer or furrow slice. Organic matter, usually concentrated at the surface is uniformly incorporated. On uncultivated land or forested land, the layer of organic matter is usually present at the surface and acts as an efficient receptor and retainer of many pesticidal compounds. Organic matter is a highly ionic soil fraction and, along with the clay fraction, is responsible for most of the adsorptive capacity of a soil. A large percentage of the pesticides applied to this type of site will be held in the organic layer. Depending on the main objective of sampling, uncultivated lands may be sampled by one of the following methods:

- a. Collecting separate samples of both the organic layer and the mineral soil horizon beneath it.

- b. Collecting a composite sample in which the organic and mineral soil fractions are mixed and treated as the sample.
- c. Removing the organic layer at each core site and sampling only the mineral soil.

Urban Soils

Urban areas present unique problems for soil sampling. Here distinct profiles may be almost non-existent. Practically nothing would be gained by sampling deeper than the top 5-8 cm (2-4 inch). Sampling personnel should be aware that the surface layer of urban soils often contains a number of foreign contaminants, such as broken glass, nails, bricks, etc., which should be eliminated by sieving. For samples contaminated with oil or other non-natural liquids, notation should be made on the sample collection forms so that analytical procedures can be appropriately modified.

Depth of Sampling

For most pesticide sampling situations, collecting soil to a depth of 5-8 cm (2-4 inches) is sufficient. Most of the persistent pesticides and many of the less persistent pesticides remain at or near the surface.

Sampling Horizons vs. Set Depths

If sampling at depths greater than 30 cm (12 inches) must be done (as in monitoring for a water-soluble compound), it is advisable to collect samples at pre-selected depths from the surface rather than attempt to sample a particular soil horizon(s). Most field personnel do not have the necessary expertise in soils to identify particular soil horizons over a variety of soil types and geographical area. In addition, the costs for this type of sampling method would be prohibitive for all but the most limited applications, since a trench must be dug to expose the profile or specialized equipment such as a split-tube sampler or earth-drill-bucket auger combination must be used.

SPECIFIC CONSIDERATIONS FOR PESTICIDE RESIDUES

Contamination - In any sampling program for pesticide residues. Contamination of samples presents a significant source of error. Since soil is an aqueous system and most pesticides are either insoluble or only slightly soluble in water, the probability of carrying residues from one sample site to another on sampling equipment, vehicles and clothing is high. The use of the following proper sanitation procedures cannot be overemphasized:

All tools and equipment used in residue monitoring should be constructed of metal and be easily cleanable. Wood should not be used for constructing equipment. Tools must be thoroughly cleaned immediately after sampling a site. Scrub with a brush and water, then rinse with an organic solvent such as alcohol or acetone.

Sampling tools and equipment ideally should be wrapped in clean cloth bags and subsequently transported or stored in large, heavy-gauge plastic bags, sealed with masking tape or cord. They must not be stored near any pesticides or in a building used for storing pesticides.

Vehicles which have been used to haul pesticides should be avoided for collecting samples if at all possible. Before using any vehicle, it should be thoroughly cleaned inside and out with soap or detergent and hot water and rinsed.

Clothing, gloves and shoes that have been exposed to pesticides should not be worn when sampling unless they have been thoroughly cleaned. Neoprene work gloves can be used in sieving soil but must be washed with alcohol and air dried between samples.

Type of Pesticides - The properties of the particular pesticide or group of pesticides under investigation will determine many aspects of the sampling program and the subsequent handling of the samples. The following should be considered:

Persistent - Samples containing less persistent compounds may have to be collected sooner, given special handling and extracted sooner than samples containing persistent compounds.

Solubility, Volatility, etc. - Water-soluble compounds are likely to be found slightly below the surface rather than right at the surface.

Use - Placement of pesticide in relation to target species or crop affects the spatial distribution of the soil sample.

GENERALIZED SAMPLING METHOD

Statistical Design - Unless a sampling program has a statistical basis, the data generated by it is not likely to be representative of the area sampled and consequently the effort will be wasted. The most advanced analytical methodologies cannot improve upon a poorly taken sample. In general, the sampling sites should represent a percentage of the total areas to be sampled (i.e., one sampling site per specified area of land). Total area sampling is essentially impossible as well as wasteful of both time and money, and the increase in precision cannot justify the resource expenditures.

Site Size and Number of Cores - In general, the number of cores should be enough to adequately sample the variation present within the site. The National Soils Monitoring Program, operated by the Environmental Protection Agency, uses the following site sizes and core numbers:

	<u>SIZE</u>	<u>NO. OF CORES</u>
National program (cropland)	4 ha (10 acres)	50
Urban monitoring	225 sq. m (270 sq yds)	16
Core dimensions:	5 cm (2") in diameter x 8 cm (3.5") in depth.	

The cores should be taken in a grid pattern over the entire site. The grid insures uniform coverage of the site and is easier for nontechnically-trained, field personnel to master.

Compositing - For assessing the residue levels on several sites over a large geographic area, compositing the individual cores from each site to one sample is recommended. It is the most economical method of obtaining the mean residue value. If any statistic other than the mean is desired, the composite sample should not be used.

Sample Preparation - The soil cores taken from the site should be sieved and thoroughly mixed. Although a 10-mesh sieve (2 mm opening) would be preferable, a larger mesh should probably be used to compensate for the wide range of moisture conditions encountered in the field (the National Soils Monitoring Program uses a 3-mesh sieve with 6.3 mm opening). If the sample is too wet to sieve, it should be air dried on aluminum foil until sieving can be accomplished. Sieving removes the coarse soil fractions and undecomposed organic debris. The sieved sample should be sub-sampled as necessary to fill the sample container, sealed and labeled. All sample containers should be clearly labeled as to site location, material class and date. Site locations should be marked on a county map or otherwise recorded. If agricultural land is being sampled, a pesticide use history should be obtained from the landowner or operator. This use history should be sent with the sample to the analytical laboratory.

SAMPLE SHIPPING AND STORAGE

Proper handling and storage of samples after collection is just as important as proper sampling techniques. Careless shipping or storage can lead to sample contamination or degradation of the sample.

Sample Containers - Containers for pesticide monitoring samples should protect the integrity of the sample during transport. There are several kinds available.

Metal - Metal containers offer a rigid structure that can protect the sample during shipping. They should be rinsed in acetone or alcohol and air-dried before using. Metal containers may be more expensive.

sandy soils. Most tube samples tend to be slightly compacted. Open-sided tubes permit observation of the core before removal. The most often used diameters are from 2.5 - 7.6 cm (1-3 inches). A uniform depth of sampling can be maintained by painting a line on the side of the tube at the desired depth or fabricating a metal collar to restrict vertical penetration.

A few types of split-tube samplers can also be either purchased or fabricated. These consist essentially of a tube within a tube. Most are used in connection with a power auger system. After the core is taken, the outer tube is removed and the actual sample used is that contained within the inner tube. This method is very good for minimizing contamination between soil horizons, but is also much more expensive, and time-consuming. Its use for most pesticide monitoring situations is not recommended.

SOIL TESTING

The fate of pesticides in the soil is determined by several factors, including the physical and chemical properties of the medium itself. Most adsorption of pesticides in soil can be correlated to the percent *organic matter and the clay content*. A few simple tests can give a more complete picture of the soil-pesticide complex. The properties most often tested are: percent organic matter, soil texture and pH. Methodologies for all tests are given in many handbooks (5,6)

Percent organic matter - Loss on ignition is the simplest method and requires no special equipment or chemicals. Each sample is weighed, the organic carbon is burned in a muffle furnace, and the sample is weighed again. If large numbers of samples are to be tested, the chromate titration method (Walkley-Black) may be used.

pH - Values for pH can be determined using a pH meter. The determination is relatively quick and simple; it is easily adapted to large numbers of samples.

Soil texture - Texture of soils is expressed in percentages of sand, silt and clay. The hydrometer method is generally the easiest to use.

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CHAPTER IV - THE HYDROLOGIC ENVIRONMENT

Pesticides are distributed throughout the hydrologic environment-- the atmosphere, precipitation, surface water, ground water, suspended and bed sediments, flora, and fauna. Measurements in each component are equally important, and validity begins immediately upon sampling. Irrespective of scrutiny and quality control applied in performing laboratory analyses, reported data are no better than the confidence that can be placed in the representativeness of the sampling (1).

This chapter directs attention to the occurrence of pesticide residues in water and sediments, sampling techniques for obtaining representative samples, and sample handling and preservation.

OCCURRENCE OF PESTICIDE RESIDUES

Pesticide residues have been detected in all components of the dynamic hydrosystem, attesting to the ubiquitous nature of the residues. The occurrence and distribution of residues are as divergent as the components. Concentrations range from the generally accepted lower detection limit of 0.01/ug/l (micrograms per liter) in filtrates to 100,000 times this value in particulate matter separated from the same aqueous samples. The environment ranges from the most humid to the driest. Residues may originate from local applications, industrial or urban discharge, or as fallout transported from remote areas.

Preliminary results of an investigation of pesticide residues in runoff to streams draining different land-use areas in central Pennsylvania indicated that the concentration of the DDT family sometimes is directly correlated with suspended-sediment concentration⁽¹⁾. This is particularly true for the chlorinated hydrocarbon pesticides which are only sparingly soluble in water and tend to sorb on sand and clay particles being transported and/or deposited in the water body.

In the case of the more soluble pesticides, including organophosphate and carbamate insecticides and many of the herbicides, dispersion of the pesticide residues is more dependent on the vertical and lateral mixing within any given cross section of a body of water. The hydrologist collecting the samples must, therefore, not only be familiar with the mixing characteristics of streams and lakes, but also have a good understanding of the role of fluvial-sediment transport and deposition.

SITE SELECTION

Many factors are involved in the proper selection of sampling sites, including the following: objectives of the study; accessibility; flow, mixing, and other physical characteristics of the water body; pesticide source locations; and personnel and facilities available to conduct the study.

Objectives - Different agencies will have different objectives for determining the concentrations of pesticide residues in streams or lakes. Assuming that most water-oriented studies are based on evaluating the effects of overland runoff, ground water inflow and/or waste disposal into our waterways, the study can usually be tied to the physiographic features of the area under consideration. In most cases, the quality of water flowing into a lake or past a particular point along a stream can be related directly to inputs within the drainage basin which includes the entire drainage area upstream of a selected point. Therefore, whether the basic objective for the monitoring program be reconnaissance, long-term trend evaluation, or solving specific problems, the first step in the study is to define the appropriate hydrological boundaries and then establish the sampling site locations above and/or below these boundaries accordingly.

Accessibility - Accessibility to any sampling site is an obvious requirement and can often be directly related to sampling costs. Bridges are normally the first choice for locating a sampling station since they not only provide ready access to a stream but they also permit sampling at any point across the width of the stream. Sampling locations on lakes as well as those on larger rivers may require the use of a boat. Frequently, however, the use of a boat will not only take more time in traversing a stream, it may prove difficult in the manipulation of the sampling equipment.

Physical Characteristics - The ideal sampling station would be a cross section of a stream (or lake) at which samples from all points on the cross section would yield the same concentrations of all constituents, and a sample taken at any time would yield the same concentrations as one taken at any other time (2). This situation never persists in nature for any length of time which points to the need for careful site selection which will, as nearly as possible, provide uniform flow and good mixing conditions. Any uncertainty regarding the uniformity of flow or the completeness of lateral and vertical mixing may be resolved by taking multipoint, depth-integrated samples and compositing the samples prior to analysis.

Availability of streamflow and/or sediment discharge records can be an important consideration in the selection of pesticide sampling sites on streams. Adequate discharge data are essential for estimating the total loads carried by the stream. If a gaging station is not conveniently located on a selected stream, the hydrologist should explore the possibility of obtaining discharge data by direct or indirect means.

Source locations - The hydrologist must be aware of the locations of any point sources of pesticide discharges (such as formulating or manufacturing plants, sewage outfalls, etc.) so that he can select sampling sites which would reflect the conditions set forth in the

objectives. Representative measurements of a pesticide load at a point on the main stream that is close below a source of waste inflow or a tributary stream is highly impractical. The inflow frequently hugs the stream bank with very little lateral mixing for some distance. A solution for avoiding this situation is to select a station site above the waste source or tributary stream, or to move the site far enough downstream to allow for adequate mixing.

Personnel and facilities - The sample collector visits the stream or lake under investigation more than anyone else involved in the study. An experienced, observant, and conscientious fieldman can contribute a great deal to any monitoring study. Therefore, anyone who wishes to achieve good proficiency in the planning and conduct of monitoring programs will be well-advised to spend a reasonable apprenticeship in the job of sample collection.

The fieldman should make all preparations possible before starting on his sampling assignment. This is best accomplished from a centrally located field office where a workshop is available to make any necessary repairs or adjustments to sampling equipment, boats, outboard motors, trucks or cars as appropriate.

SAMPLING TECHNIQUES

Water - Sample collection in the water column varies in degree from the simplest of hand sampling procedures at a single point to the more sophisticated multipoint sampling techniques known as the equal-discharge-increment (EDI) method or the equal-transit-rate (ETR) method (3).

Generally, the number and type of samples to be taken depends on the width, depth, stream discharge, and the suspended sediment being transported. In the sampling of lakes, a number of samples can be collected at selected grid points and then composited or a single sample can be collected near the center of the water mass, depending on the size of the lake. In any case, the larger the number of individual points sampled the more nearly will the composite sample represent the water body.

Water is often sampled by filling a container held just beneath the surface of a body of water. Published data and discussions by investigators reveal that a high percentage of samples have been obtained in this manner (commonly referred to as a dip or grab sample). Using a weighted-bottle holder which allows the bottle to be lowered to any desired depth and returned to the surface improves on this method. If the bottle is lowered to the bottom and raised to the surface at a uniform rate, the resulting sample will roughly approach the collection of what is known as a depth-integrated sample.

A true depth-integrated sample is collected by means of a depth-integrating sampler which integrates discharge as a function of

depth. Sediment is maintained in suspension because of velocity and turbulence. Velocity varies from the water surface to the stream bed, being generally highest near the surface and lowest at the bed. Sediment concentration varies also from the surface to the bed, being lower at the surface and greatest at the bed. Fine sediment (finer than about 0.062 mm) is easily kept in suspension and is distributed relatively uniformly throughout the depth of flow. However, as particle size increases, more energy is required to maintain suspension in a given flow, and the average size of sediment in suspension increases from the surface to the bed. Depth integration is used to collect a water-sediment sample that is weighted according to velocity at each increment of depth. This means that the water-sediment mixture must enter the sample container at the same velocity as the flow passing the intake. If the depth-integrating sampler is lowered from the surface to the bed and back at the same transit rate, each increment of flow in that vertical is sampled proportionately to the velocity.

The open-mouth weighted bottle sampler, therefore, does not collect a truly representative sample in a flowing stream if there are many particles coarser than about 0.062 mm carried in suspension. Another disadvantage in using an open-mouth bottle sampler in flowing streams is that there is no assurance as to when the bottle becomes filled, compounding the uncertainty that the collected sample truly represents the distribution of both dissolved and suspended material in the sampled water column. This method of sampling may be extremely poor for flowing streams but may be used effectively for slow-moving bodies of water such as ponds, lakes, and estuaries.

One sampling technique currently accepted by hydrologists for use in sand-bed streams is the equal-transit-rate (ETR). With this method standard suspended-sediment samplers are used to collect a velocity-weighted sample. Samples are taken at a number of equally spaced verticals in the cross section depending on stream width. The transit rate of the sampler, which is the rate of movement of the sampler from the surface to the bed and back to the surface, is the same at all verticals. Samples collected in each vertical are all composited into a single sample representative of the entire flow in the cross section. In this manner, the composite sample of the water-sediment mixture flowing in the cross section is velocity- and discharge-weighted.

It is recommended that all water samples be collected using depth-integrating methods whether the samplers are hand held or cable-and-reel suspended. The only exception would be in the case of very shallow streams where the depth is insufficient to allow true depth-integration. In such cases dip samples collected at one or more verticals across the stream would be appropriate; however, the sample container should be carefully held beneath the water surface in order to avoid stirring up and entraining bottom sediments.

The number of verticals at each sampling site will usually be decided by the fieldman. For small streams, a depth-integrated sample taken at a single transverse position located at the centroid of flow is usually adequate. Larger streams require selection of several verticals at centroids of equal-discharge-increment (EDI). This method requires that the fieldman have some knowledge of the streamflow distribution in the cross section before sampling verticals can be selected. To make the EDI measurement when prior streamflow data is not available, it is first necessary to determine the total discharge across the stream channel and then subdivide the cross section according to incremental discharges.

The number of verticals required for the equal-transit-rate (ETR) method depends on the streamflow and sediment characteristics at the time of sampling as well as on the desired accuracy of the result. For all but the very wide and shallow streams, twenty verticals are usually sufficient.

Obviously, the multipoint sampling techniques can become very time consuming and, consequently, expensive. An alternate method often used consists of sampling at the quarter points or other equal intervals across the width of the stream. Composite samples obtained from individual samples collected at the quarter points can be fairly representative in most cases, providing that the stream cross section was properly located.

Lakes can be sampled on three-dimensional grids consistent with the shape and depth of the water body; however, small ponds or lakes are usually sampled at a single vertical which should be near the center of the water mass. Distribution of sampling locations in large bodies of water will be largely dependent on manpower and financial restraints.

Bottom Materials -- Bottom sediment samples are usually taken at the same horizontal locations at which water samples are collected. A bottom sediment sample may consist of a single scoop or core, or be a composite of several individual samples in the cross section.

Pesticides sorbed in bottom material, irrespective of the ratio of inorganic to organic composition, may reflect an integration of chemical and biological processes. They serve the indispensable historical role in reflecting input to non-scouring streams, lakes, and estuaries with respect to time, application of pesticides, and land use. Recalling that fluvial materials tend to settle out during periods of low streamflow or of calm conditions in lakes, and are additive to solids that have accumulated on stream beds or in lake bottoms, periodic sampling of water overlying these deposits might not reveal the presence of pesticides, yet they may be found in the solid material which acts as a sink and reservoir.

The loss of low-density deposits must be kept minimal during any sampling process, requiring a bottom-material sampler that is capable of collecting and retaining the "fines" which sometimes contain the highest concentration of pesticide residues.

Few data have appeared in the literature regarding the presence of pesticide residues at the liquid-solid interface or in the hydrosol area. Depending upon ambient physical, biological, and chemical controls, residues may be transformed into metabolites, degraded, or taken into solution. Further study of these processes is an open and challenging field of endeavor. An evaluation of this portion of the hydrosystem is essential to comprehensive assessment of the occurrence and distribution of pesticides.

Sampling Devices - To overcome the problem associated with collecting representative samples, equipment that has been specifically designed and thoroughly tested is favored. In most instances, samples for pesticide residue analysis are best collected with the same equipment and techniques used for the collection of suspended-sediment samples. Several depth-integrating samplers are available and suitable for this purpose. In shallow streams and wetlands that can be waded, the US DH-48 suspended-sediment sampler can be used successfully. The US DH-59 suspended-sediment sampler was designed to be suspended by a hand-held rope in streams too deep to be waded. Both of these samplers are simple and of clean design using a container which is easily inserted into position and held firmly by spring action. The US D-49 suspended-sediment sampler has been used for many years in collecting depth-integrated suspended-sediment samples in the larger streams and rivers. It is provided with a choice of nozzles - 1/8, 3/16, and 1/4-inch in diameter, with which inflow of the water-sediment mixture can be controlled. The D-49 sampler, which weighs about 60 pounds, is suspended on a cable and operated with a reel attached to a boom.

The open-mouth weighted-bottle sampler, which is available in many sizes, is acceptable for use in lakes and slow-moving streams having little suspended sediment. The sample bottle is inserted into a weighted holder to which a rope is attached as a means for suspending the sampler.

Bottom deposits present a more difficult set of sampling conditions than those in the water column in streams or lakes, primarily because of the varying firmness of bed materials. The US BMI-60 bed-material sampler is a 30-pound impact type sampler designed primarily for use in sand-bed streams. However, it works equally well for firm and partially consolidated bottom materials. One man can collect samples with this sampler under most conditions. The bucket takes a bed-material sample that is approximately 2.2 x 5 x 1.7 inches. This sampler can be used in about 75% of the river miles across the United States and also in many small lakes and reservoirs.

In large lakes or estuaries bottom sediment samples are usually collected with various types of dredges including the Ekman, Petersen and Shipek dredges. The Ekman dredge is widely and successfully used for soft bottoms. The Petersen dredge can be used for taking samples on hard bottoms such as sand, gravel, marl and similar materials. The Shipek dredge is a spring loaded sampler for use on all types of bottoms, but is especially useful in collecting and retaining the "fines" obtained from deposits of sand, silt or clay.

Numerous investigators prefer to collect core samples when interest is primarily in obtaining historical data, and provided the bed is sufficiently compacted to be sampled with a coring device. Though value of this type of sample should not be minimized, fresh deposition is of prime importance in a continuous evaluation of the occurrence, distribution and movement of pesticide residues.

Most core samplers lack positive seals to hold a core or moist sample in place as the sampler is withdrawn from the water. The Controlled-Depth Volumetric Bottom Sampler described by Jackson and the Core Sampler For In Situ Freezing of Benthic Sediments designed by Gleason and Ohlmacher are examples of efforts to overcome the drawbacks of the common core sampler and to provide the investigator with reliable equipment (1).

Little progress has been made in developing equipment to collect representative samples at the liquid-solid interface because it is difficult to sample without disturbance. The Gleason core sampler offers an advantage in sampling this interface because it can be used as a point sampler. The Hydrosol Sampler designed by Lawrence may be used in many sampling situations.

SAMPLE HANDLING AND PRESERVATION

Deteriorated samples negate all the efforts and cost expended in obtaining good samples. Cleansed, narrow mouth glass bottles equipped with Teflon-lined screw caps should be used for the water samples collected by the various depth-integrating samplers. Bottom materials containing a high percentage of water and composite water samples can be placed in cleansed, wide mouth glass bottles equipped with Teflon-lined caps. Plastic bottles must not be used since they are known to introduce interference and sorb pesticides. Alternately, solid bed-material samples may be sealed in foil. Sufficient sample should be collected to satisfy the volume requirements of each analysis and also to permit running of duplicate and spiked analyses. Breakage of glass sample bottles is overcome by shipping them in expanded polystyrene containers molded to fit the bottles.

The fieldman should provide the following information in writing for each sample: date, time, location, depth, type of sample, name of sample collector, and any other information that may be helpful in selecting the analytical approach or in interpreting the results. All samples should be kept near freezing, and extractions should be carried out in minimum elapsed time, preferably within 2 days from time of sample collection.

SAMPLING FREQUENCY

In conducting reconnaissance studies, defined here as short-term one-time evaluations, both bottom deposits and the overlying water should be sampled at each site. Monitoring, which consists of repetitive, continuing measurements to define variations and trends at a given location, should include collection of water samples during each of the four seasons, with particular emphasis on the fall and spring collections. Bed-material samples should be collected for analysis of fresh deposits at least once per year at monitoring sites, and preferably during both the spring and fall seasons.

Evaluation of the variability in available pesticide data must precede any decision as to the number of samples and collection frequency required to maintain an effective monitoring program.

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CHAPTER V - ESTUARIES

The decision to monitor an estuary for pesticides may derive from any one or several specific needs. These needs or objectives will largely determine the character and *modus operandi* of the program. Obviously, two pesticide monitoring programs in the same estuary might be entirely different because of the kinds of information sought. Estuarine monitoring objectives may be for the purpose of determining:

1. Background levels of an array of persistent waterborne pesticides by randomized sampling of estuaries in a particular geographical area.
2. The escapement of pesticides in surface run-off from specific use areas in the drainage basin by sampling deltaic sediments.
3. The cause of increased faunal mortalities or lack of species diversity in an otherwise normal appearing estuary.
4. Tissue residue levels of persistent pesticides to ensure that they are within legal tolerance levels for edible fish and shell fish or their products.
5. Pesticide residues in food chain organisms to alert resource management agencies of possible mortalities resulting from trophic magnification.
6. Pesticide residues in pre-spawning gonads of commercially valuable species to identify causes of change in productivity.

The choice of which physical or biological elements are to be monitored in an estuary will be determined by specific program objectives.

Water samples taken at infrequent intervals or at limited points in an estuarine system will usually be of limited value. If the monitoring program objective requires specific knowledge of pesticide residues in the water, the guidelines enumerated in Chapter IV should be followed for such samples as well as for sediment samples.

Sediment samples are useful in detecting persistent pesticides in the estuary. However, interpretation of their analyses requires knowledge of particle size, organic/inorganic composition, station location with reference to current flow and similar data that frequently are not readily available. Sediments in shallow estuaries can be

disturbed by storm conditions and their pollution burden may change drastically in time of flood or drought without reference to pesticide usage in the area. Analysis of stratified estuarine sediments may reveal unusual patterns of pesticide residue accumulation, but our lack of information on aerobic and anaerobic degradation of persistent pesticides complicates the interpretation of such sediment samples. Carefully collected samples at the sediment-water interface along the geographic axis of an estuary may be useful, however, in pinpointing up-stream sources of pesticide pollution.

The choice of a biological sample for monitoring the estuary is determined largely by two factors: is the form to be sampled migratory, and what is its position in the trophic web? Sessile or non-migratory species, representing entire communities present obvious advantages since they reflect pollution levels at specific locations. Their life style usually facilitates age determination and permits some degree of bracketing of the occurrence of the pesticide pollution.

Many non-mobile species, e.g., molluscs and barnacles, are detritus and filter-feeders. Pesticide residues may be biologically retained and magnified in their tissues and reflect the introduction of pollutants into the lowest levels of the food web. Such residues suggest direct contact with pollution sources. Residues in vertebrate carnivores, on the other hand, are more likely to reflect trophic magnification of persistent pesticides. Fish-eating birds or mammals not only concentrate but store for long periods compounds that contaminate their diets.

Plankton offers several advantages as a tool for estimating levels of pesticide pollution. Its small particle size presents a relatively large sorptive surface. The cells are usually high in lipid content and readily take up organochlorine compounds. However, the rapid cell division and growth rates favor dilution of tissue residues. Also the interpretation of data on pesticide residues in plankton may be confused by the facts that plankton is a composite of living and dead materials that contains varying amounts of silt and other inorganic materials, and its moisture content varies widely depending on the components. Plankton samples containing pesticide residues are probably indicative of fairly recent contamination. When samples are taken at frequent intervals, they may be especially useful in identifying pollution sources.

Crustacea, such as commercial shrimp, are generally one of the least satisfactory groups to monitor because of their extreme sensitivity to insecticides. Both organophosphorus and organochlorine insecticides

will kill crustaceans at concentrations in the parts-per-trillion range. Carbamates are somewhat less toxic to them and herbicides generally are not toxic at concentrations likely to be encountered. The net result is that pesticide effects on crustaceans are likely to be an all-or-none affair and crustacean samples may reveal little about relative levels of pesticide pollution in the estuarine environment.

Molluscs (oysters, clams, and mussels) have special merit as bioassay tools because of their sensitivity to synthetic organochlorine pollutants present in the ambient water. They detect and accumulate these persistent pesticides to an astounding extent without being themselves markedly affected by the pollution levels generally encountered in estuaries. Not all molluscs are equally sensitive and, as with other bioassay animals, care must be exercised in comparing pesticide residue levels between individuals and species. Salt-water mussels are especially useful as monitor species because of their wide geographic distribution and their ubiquity over a broad range of salinity regimes.

The chief objection to the use of molluscs lies in their rapid metabolism of pesticide residues. Although they can concentrate pollutants in their tissues by a factor of 50,000 or more, these residues are lost in a matter of days when the ambient water becomes free of contamination. Thus, oysters and mussels are monitor animals of choice when sampling can be done on a monthly or more frequent basis. They are relatively useless in reflecting trends in environment pollution when sampling can be done only once a year.

Fish are often the most convenient group to monitor because of their availability from the commercial catch. They are sometimes sensitive to high pesticide residues in their environment as evidenced by massive fish-kills, but may accumulate relatively large residues and become pesticide-resistant when the concentration of a pollutant is low. Experimental work has shown that they accumulate pesticides directly from the ambient water as well as from their food supply. The interpretation of pesticide residue data in fish is difficult unless their life history is known.

Fish are highly selective in their diet and may accumulate small or large pesticide residues in polluted estuaries, depending on their food supply. Plankton-feeding or herbivorous fish tend to have significantly lower pesticide residues, for example, than carnivorous species that feed on small fish in the same estuary. Populations of even the same species of fish may have quite different diets in two different estuaries. Comparison of pesticide residues in these two populations could be very misleading if their food habits are not known.

Fish store organochlorine residues primarily in tissues having a high lipid content. Such residues accumulate as the fish age but may diminish sharply at spawning or in starvation periods when stored body fats are mobilized. Wide variations in pesticide residues may occur also in fish having presumably similar backgrounds. In one series of analyses of 15 "similar" specimens collected simultaneously from a school of estuarine fish, for example, DDT residues varied by two orders of magnitude.

Fish are most useful as monitors when they are small enough to permit whole body analysis of at least 15 specimens, thus averaging individual variations. If the fish are about 1 year in age or sampled prior to their first spawning, the residues reflect pollution exposure during a known time period.

Sample Preservation - The handling of estuarine samples for pesticide monitoring poses the same types of problems as samples from any other medium. Increased knowledge of the dangers of sample contamination through contact with various kinds of synthetic wraps and containers has demonstrated the necessity for glass and perhaps aluminum foil containers to preserve the integrity of wet samples. Immediate freezing and maintenance of frozen sample until analysis is still the best way to protect samples and prevent degradation or loss of pesticide residues. Freezing, because of its simplicity, is also perhaps the best method for use by unskilled personnel.

The preservation of tissue samples for pesticide analysis at room temperature by the use of desiccants has been used with marked success in estuarine monitoring. Although this method requires a modest amount of personnel training as well as special chemicals, it avoids the loss of frozen samples because of missed airmail schedules and power failure. It has proven especially useful for samples collected long distances from the analytical laboratory. In practice, field samples of plants or animals are chilled, homogenized, and blended with a combination of two desiccants - sodium sulfate and powdered silica. The resulting mixture is a dry, free-flowing powder in which pesticide residues remain intact for 15 days or more at room temperature. This desiccant mixture is compatible with chromatographic procedures for organochlorine, phosphorus, and phenoxy pesticide compounds.

Representative Samples - The collection of representative field samples requires careful planning and pre-supposes a good understanding of estuarine ecology. The introduction of stratification into the selection of sample type, collection frequency, and station location is advisable if the most knowledge is to be gained from samples that are necessarily limited in number and areal coverage.

It has been found in past monitoring programs, that apparent pesticide pollution levels have been grossly altered or misinterpreted because of drought, windstorms, substitution of one species of clam for another, collection of samples on different tidal stages, and by assuming that the diet of a particular species of fish being monitored was the same in two different estuaries. Ultimately, the understanding of field sample analyses is determined by knowledge of the response of similar samples, either organic or inorganic, to pesticide pollution under controlled conditions. Too often, money and effort in environmental monitoring have been largely wasted because of the failure to select samples whose analyses could be meaningfully related to environmental conditions.

CHAPTER VI - FRESH WATER FISH

Monitoring of fish for pesticide residues is carried out because of their wide range of sensitivity to this group of pollutants, often demonstrating residue levels which are many fold greater than those found in water. Another reason for monitoring fish is that they are frequently used for human consumption and must therefore be free of unsafe levels of these contaminants. Except for a few species, however, commercial exploitation of fresh water fish for the market place would not justify the regulatory monitoring of many other species available. Since freshwater fish play a significant role in peoples recreational pursuit and since many other species of desirable wildlife rely on fish as their main food source, a knowledge of the level of pesticide contamination and its possible effects on fish populations is a necessary resource management tool. Thus, because of their widespread distribution, their opportunity for exposure to pesticides, their role in the national economy, and their importance in the web of life, fish are a logical organism for monitoring pesticide residues in the aquatic ecosystem. After determining the major objective for including fish in a monitoring scheme, specific decisions must be made as to how these objectives will be met. The following considerations are presented as a guide in making these decisions. Many of these considerations will be interdependent.

Complete standardization of representative fish species to be used in a monitoring program is difficult. No one species can represent all fishes. The availability of a given species for successive years, geographic location and background history are factors which dictate the selections. Species near the top of the food chains such as largemouth bass, yellow perch, channel catfish, green sunfish, rainbow trout and even carp are some logical choices because of their food habits or availability. Alternate species from the same fish family should be substituted, if necessary.

Where the mode of pesticide action is rapid, fish species should be selected near the top of the food chain so as to reflect maximum residues present. When long-term or chronic subtle effects of pesticides are to be studied, other species of fish and aquatic organisms representing various trophic levels may be included. Other considerations for selecting the species to be monitored have been discussed in the preceeding chapter.

The factors of fish size, age and numbers are considerations to be made. Uniform size and age of a single fish species should produce less variability in residue values. Erroneous residue readings will probably result in analyzing a composite of large, small, young and old, and intermixed species. Extremely large or old fish

should be avoided or should be analyzed as individuals. Fish which are in their first year or have not yet spawned represent the ideal age group for detecting recent contamination and are particularly suited for programs with sampling frequencies of one or more years.

Number of fish to be collected is somewhat arbitrary. Residue variations in the individual fish in a particular situation must be determined and will serve to establish the number of fish needed to constitute a statistically valid test. Availability of fish and costs of analysis will determine the numbers that are used. The National Pesticide Monitoring Program was established using 3-5 uniform sized fish in a replicated composite. Each composite is treated as a single sample. This is considered a minimal number of fish per sample. Ten to twenty individuals would be considered more ideal. Initially, depending on time or available funds, a cursory screening program may be adequate to gather information until refinements can be made.

Fish collections should be made using only electrical or mechanical means such as: seines, gill nets, trap nets, hook and line, electro-shocking equipment, etc. No fish-collecting chemicals are recommended. Fish collections must be made in conformance with state or local regulations and may require special or specific permits from the proper authorities.

A choice must be made whether to analyze whole fish or only the edible portions. Analyzing the whole fish is preferred where biomagnification aspects are concerned, such as in predator-prey relationships. Analysis of edible portions of fish is recommended for determining whether fish intended for human consumption contain unsafe levels of pesticide residues. If specific tissues are to be analysed then each fish must be handled separately, thus increasing time and costs of the program.

All samples should be chilled or frozen immediately for shipping to the laboratory. If whole fish are to be used for analysis then the field preparation of the sample will be minimal. Fish should be wrapped, either individually or as a composite sample, in clean aluminum foil and frozen as quickly as possible. If specific tissues or organ systems (brains, gonads, etc.) are to be analysed separately, they should be removed before such freezing, isolated in vials or other suitable container, labeled and rapidly frozen along with the rest of the sample. Such tissues cannot be removed after thawing without significant deterioration. If whole fish are to be used, all the fish in the sample should be ground up and homogenated and subsamples should be taken as needed. All samples should be protected from contamination after the samples are taken.

CHAPTER VII - WILDLIFE

The environmental circumstances under which monitoring of pesticides in wildlife may be warranted are sufficiently varied to preclude more than guidelines for developing monitoring plans and procedures. Further, with less than a decade of experience in wildlife monitoring, much is yet to be learned about the dynamics of pesticides in a diversity of wildlife populations. Thus the following guidelines are based on intuition as well as experience.

The term "wildlife", as used here, refers primarily to birds or bird parts and occasionally their eggs, but it may logically be extended to mammals and other terrestrial vertebrates. Certain fish or invertebrate species important in avian diets might be monitored as part of a total wildlife program; however, procedures for monitoring such forms are presented elsewhere in the report.

Although the "working" objective in virtually all wildlife monitoring is to assess body levels and trends of pesticides and related chemicals in given wildlife populations, both in time and space, specific objectives will vary among situations. Any optimal monitoring plan, including selection of the species to be monitored, will depend upon the predetermined need for monitoring and the specific objectives to be met. Clearly, an optimal plan cannot be formulated without first a precise statement of objectives and priorities.

A concept helpful in planning is to consider wildlife monitoring as being either species-oriented, region- or ecosystem-oriented, or perhaps a combination of such approaches. At times interest in the welfare of a particular species may justify its monitoring, in which case the survey design should be oriented toward sampling that population rather than specific areas or ecosystems. If the species of interest is too valuable to be sampled or for some reason is not readily available, a closely-associated "indicator" species might be substituted provided one can be found whose residue levels bear a strong relationship to the original species.

When regions or specific ecosystems rather than species are of primary importance, the species should be selected as an effective indicator of the relative degree of contamination of wildlife associated with the given environment. The species itself may or may not be of particular importance and, in fact, may advantageously be an expendable nuisance species (5,6).

SPECIES SELECTION

Selection of a "best" species for monitoring is seldom a simple matter, and at least the following factors, some more obvious than others, should

be considered in attempting to meet monitoring objectives:

Availability -- A species must be available in numbers sufficient to provide statistically adequate sample sizes. When animals must be sacrificed in monitoring -- the usual case -- availability infers: sufficient abundance to insure no harm to the population; expendability in that a highly desirable species is not used in lieu of a less valuable but fully suitable substitute; the species is sufficiently easy to capture to be practical.

If sacrifice is not prerequisite, as would be the case if blood samples could be used for residue analysis, then one need be concerned principally with ease of capture. The subject of sample size is discussed in detail in the chapter on statistics and study design. We stress at this time only that there is no fixed or quick answer to what constitutes an adequate sample. One must first specify the magnitude of the smallest difference relative to the mean he wishes to detect; the probability that he will detect such a difference if it exists (power); and the probability that his sample will erroneously indicate a difference when, in fact, none exists (type I error). He must also, from previous sampling, have an adequate estimate of the variance of the residue data to be encountered and the expected form of its statistical distribution.

Distribution -- If the primary interest is in monitoring residue trends on a regional basis rather than in a particular species, it is highly preferable that a candidate species occur throughout that region. Assuming only one species is to be used, any part of the region permanently devoid of that species cannot be considered as being included in the survey. When an otherwise suitable species is not available throughout an entire region, it may be possible to substitute an alternate species in those areas devoid of the principal species provided one can be found whose tendencies to accumulate residues are relatively similar. This procedure should be undertaken cautiously, however, and in no event should the two species be considered equivalent and their residue data indiscriminately combined.

Mobility -- The mobility of a species or, more precisely, the size of its home range, is a necessary consideration in determining if the species will serve to meet the objectives of a survey. One must consider the extent of daily and seasonal movements, and if a migratory species, the timing and pattern of migration as well as the extent of movement at either end of the migration route. If the monitoring objective is to estimate residue tendencies over a rather broad area, one may utilize a more mobile species than if he wishes to associate residues with specific areas. Use of migratory species to associate residues with particular areas obviously poses special problems, and if a suitable resident species is available, the latter will in all likelihood be the better choice. Any attempt to use a migratory species should be undertaken cautiously and with adequate knowledge of migration patterns and rates of residue accumulation in that species.

Diet -- Food habits are a primary consideration in selection of a species, since the principal route of pesticidal exposure in the wild is undoubtedly through the diet. Because persistent pesticides tend to become progressively concentrated through successive levels of food chains, a species' food habits must be representative of the segment of the environment at which the monitoring is primarily directed. Because of food chain concentration, or "biological magnification", herbivorous species in a given ecosystem will tend to be exposed to lower levels of pesticides than will omnivorous species, and they, in turn, will be exposed to lower levels than carnivorous ones. In particular, fish-eating animals will be exposed to the highest residues because of eventual translocation and buildup of persistent residues in aquatic systems. With reference to the factor of mobility, there is a decided tendency for carnivorous species to range more widely in search of food than do herbivorous species. Thus, if the investigator wishes to monitor a species with a restricted home range, his choice may be limited to herbivorous animals with restricted exposure to environmental residues. In such instances, some compromise between food habits and size of home range may be necessary.

Habitat -- The habitat preference of a species is an obvious factor to be considered and little elaboration here seems necessary. Clearly, if the intent of monitoring is to evaluate residues in a wetland ecosystem, the investigator does not select an upland species. In practice, however, the habitat factor may involve something more than a simple dichotomy and require greater scrutiny.

Physiology -- The physiology of a species must be considered with regard to its propensity to acquire and retain residues of those pesticides to be monitored. Such information may be available in the literature, otherwise, experimentation prior to operational monitoring is strongly recommended. A species uniquely able to rid itself of given residues may not be satisfactory for monitoring.

THE MONITORING PLAN

Following the selection of species, a detailed monitoring plan must be developed that conforms with limitations of budget, personnel, and operation logistics. The plan must be based on statistically sound sampling procedures if data interpretation is to be meaningful. It must also include such details as frequency of sampling, required sample size, method(s) of capture or collection to be used, and instructions for handling specimens from time of collection through chemical analysis. Careful consideration should be given to the type(s) of statistical analysis to be employed so that there is compatibility with the sampling protocol.

Randomization -- To obtain, from a given animal population, a sample that is known to be absolutely random is perhaps an "impossible dream". Nonetheless, the investigator must strive, to the best of his ability, to achieve randomness in his sampling. Certainly he should keep his sampling methods consistent from period to period, so that any bias due to sampling should remain relatively constant among periods and thus have little effect on measurements of trends in residue levels.

Sampling Approaches -- Basically, there are two approaches to obtaining specimens for monitoring: Specimens may be collected in the field specifically for monitoring; or they may be sampled from some collection unrelated to monitoring, such as the hunting bag. When sampling from the field, it is the sampling site that must be chosen at random as it is virtually impossible to select the individual animal at random. It should be emphasized that even though more than one specimen be taken from a site, it is the site, not the specimen, that is the primary sampling unit; and degrees of freedom for estimating survey precision are based on total sites, not total specimens. When sampling from a collection of specimens unrelated to monitoring, one can sample only the collection at random and thus obtain unbiased estimates of residues in the collection. Since the collection itself is not likely to be random, it must be assumed that future collections will be made in a similar manner and that any biases will be relatively constant among collections.

When an objective for monitoring is to estimate residue levels and trends for specific subdivisions of populations, stratified random sampling is called for. The subject of stratified sampling is too extensive to be more than mentioned in this section, except to point out that strata must be established before actual sampling has occurred; one may not construct strata after the fact.

Sex and Age Differences -- An important consideration in wildlife monitoring design is whether a species' capacity to accumulate certain residues differs according to sex and/or age of the animal. For example, fall levels of DDE in wings of mallards and black ducks have been shown to be higher for adult than for immature birds (1). There is evidence that wings of adult male mallards and black ducks may develop higher residues of DDE than adult females (4), possibly because of partial purging of the chemical via the egg during laying. In experiments with bobwhite, mirex was shown to be readily eliminated via the egg to an extent that after eight weeks of laying, carcass residues in male breeders were about twelve times as high as those in the females (3). If sex or age differences in residue levels are likely to be meaningful, either the particular groups should be sampled separately, or the sample size should be sufficiently large to insure the likelihood that all groups are properly represented.

Frequency of Sampling -- The frequency with which monitoring should be repeated to meet objectives most efficiently is best determined uniquely for each program. Monitoring is not an inexpensive operation, and frequency should obviously be kept to the essential minimum. At times the expectation of seasonal differences in residue levels may be of sufficient importance to justify monitoring more frequently than once a year. Conversely, it is conceivable that trends would be sufficiently gradual to require monitoring only once every two or three years. Perhaps the soundest approach is to monitor, at the onset, as frequently as might be necessary and fiscally possible, and then reduce the schedule to the frequency found to be sufficient.

Methods of Capture -- Wild specimens may be collected in the field using a variety of techniques, which may be categorized basically as shooting, live- or kill-trapping, netting, or capture with drugs. A detailed account of such techniques and further references may be found in "Wild-Life Management Techniques, Third Edition" (7). Wildlife collections must be made in conformance with all applicable laws and regulations and may require special or specific permits from the proper federal, state or local authorities.

To be satisfactory, a capture technique must be practical, it must not contaminate the specimen with any substance that might interfere with pesticide analysis, and it must not introduce sampling bias in being more selective of one segment of a population than another. If, for example, one sex or age group is more readily captured than another and groups are not stratified, or if there is a correlation between body residue burden and ease of capture, then a biased sample is the inevitable result. There is seldom a ready means of determining whether a particular capture technique will be biased under given conditions, and perhaps the best one can do is to combine experience and the literature with the best logic he can muster to minimize the likelihood of this bias.

Constructing the Tissue Sample -- The manipulation of specimens following collection constitutes an important phase of the monitoring plan. For example, is it advantageous to quantify residues in the whole body, in the skinned, eviscerated carcass, or in some particular organ or tissue? Is it most efficient to analyze specimens individually, to "pool" the specified tissues of several animals and analyze the homogenized tissue-pool, or is it best to use a combination of both approaches? There are no ready answers to these questions: each will depend on the species being sampled, specific monitoring objectives, and perhaps budgetary limitations.

In estimating environmental trends, a reasonable approach is to analyze the whole body, less visceral contents, and thus quantify the total body burden. A further refinement might be to remove feathers or hair and skeletal protuberance such as the beak and feet of birds. An alternative to the tedious job of plucking birds is to skin them; however, skin is high in lipid material which may contain significant amounts of fat-soluble pesticides. For monitoring some chemicals, it may be advantageous to analyze specific

organs rather than entire carcasses if such organs are known to be foci of residue accumulation.

When the only realistic way to monitor a species is to use body parts, such as wings or legs of animals bagged by hunters, it is essential that residue levels in such parts be highly correlated with residues in the total body. The literature may contain such information for a few species; but most often, tests must be conducted prior to monitoring to determine whether or not a satisfactory relationship exists.

Pooling Specimens for Analysis -- When the primary objective in monitoring is to measure trends in mean residue levels, as is generally the case, a given level of precision may be obtained at a reduced cost by pooling specimens for chemical analysis. If, for example, an investigator collects 10 specimens from a given site, he might analyse each specimen individually (10 analyses) or he might first chop and blend the 10 specimens into a single homogenate and make a single analysis of the homogenate. In both instances he is estimating a mean residue level in a sample comprising 10 specimens, but he does so at about one-tenth the cost by pooling. Assuming random sampling from a given population, the variance of mean residue levels in pools of ten specimens should be one-tenth the variance of ten individual specimens.

The disadvantage to pooling is that little if anything can be learned about the frequency distribution of residue levels in the population. Pooling, at best, offers only partial answers to questions such as: Is the distribution skewed to the right, as is frequently the case, and, if so, how badly? What are the extreme levels in the sample, and are they sufficiently high to be detrimental? A reasonable compromise is to analyze a sufficient number of specimens individually to examine residue distributions and a sufficient number of pools to estimate mean residue levels with adequate precision.

THE NEED FOR TRIAL MONITORING

Because of the number of variables and probable unknowns to be encountered in establishing a monitoring program, there is much to be said for testing proposed procedures with a trial program (2). The scale of the trial need only be large enough for an adequate test of procedures and will probably depend more on the extent of uncertainties than on the size of the proposed program. In the extreme, trial monitoring may show the proposed program to be untenable, with resultant savings of significant magnitude. Most often the trial will permit adjustments of procedures and sample size determinations that should justify the expense of the trial.

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CHAPTER VIII - FOODS AND FEEDS

This chapter is intended to provide a brief overview of the principals of sampling, the form of resulting data and the statistical aspects of data analysis relative to pesticide residues in foods and feeds. General observations are also made relative to computer support and to field sampling procedures.

The general types of food and feed sampling include:

Regulatory (or selective) sampling to prevent the introduction of over-tolerance products, both domestic and imported, into the food supply.

Surveillance (or objective) sampling to identify suspect shipments and emerging problems which should be subjected to regulatory sampling, and to derive a data base on the occurrence of pesticides in individual food and feed commodities.

Trend sampling (FDA total diet or market basket studies) to identify shifts or other trends in food pesticide levels relative to existing dietary intake patterns. These data are derived from food prepared for the dinner table.

Products subject to pesticide sampling range from raw agricultural commodities to processed and packaged foods and feeds. Two general types of sampling procedures are normally involved, those for bulk sampling and those for unit package sampling.

GENERAL SAMPLING PRINCIPLES

There are several basic considerations in sampling that apply to the problem of pesticides in food and feeds.

Statement of Objectives

A precise statement of the objectives desired from the sampling program must be derived. For example: the objective might entail coming to a well founded decision relative to regulatory action or in another case merely to identify gross trends in pesticide levels. Sampling results in one situation may not be adequate for the objectives of a different situation.

Definition of the Population

The term, population, refers to the aggregate of units about which a decision is to be made or an inference is drawn. In some cases the population will be readily identifiable physical collection of units (e.g., a production lot in a warehouse consisting of a specific

number of units such as bags, cans, or other units). In other cases the units may have to be defined in the problem context (e.g., the number of grams of food product consumed daily during a one week period by an individual). Sometimes the target population cannot readily be sampled and a somewhat different actual population must be used (e.g., units of food product consumed might have to be approximated by units of food products purchased). When the target population cannot be sampled directly it is important to recognize this fact and adjust inferences from the sample data accordingly.

Required Data Definition

Careful definition of the required data can result in sampling economies as well as in attaining program objectives. If information is desired only relative to the occurrence of units with pesticide levels in excess of tolerance levels less effort is required than would be if more detailed data are required.

Derivation of Required Sampling Precision

Inferences about pesticides in the population to be sampled depend on the type of sample, sample size and pesticide level variability. Therefore the precision required for the inferences sought are dictated by these sampling factors. In estimating a population parameter the precision required can be stated in terms of an acceptable degree of error and desired level of confidence (e.g., estimating the average pesticide level in a production lot within 1% of its true value with 95% confidence). For hypothesis testing situations (e.g., is regulatory action indicated) precision can be defined in terms of the producer's risk (Type I error) and consumer's risk (Type II error). Acceptable levels of these risks must be established during the planning stage.

Definition of Measurement Methods

Sample data are useful only within the limits of the measurement methods employed. In some cases, the most accurate pesticide analytical methodology may be required for individual population units whereas in others a gross screening method on composited units may suffice. The pesticide analytical methodology alternatives should be carefully assessed relative to precision, accuracy, time and cost and decision made consistent with program objective.

Construction of the Frame

As indicated above, the population definition is dependent in turn on the definition of the units making up the population. The frame is the identified list of sampling units. In production lots of packaged products this will be merely the individual containers, a small set of containers or perhaps a case of containers. However, in bulk sampling of foods (e.g., a car load of wheat) the sampling

units may well be dictated by the mechanical device used to collect the sample (e.g., the contents of a grain probe). Construction of the frame is essential to the application of random sampling procedures.

Sample Collection Requirements

With the preceding problem defined it is possible to specify to some degree the sample size and the type of sample required. Consideration of the time and costs for the sample collection may then dictate some modification of the problem objective.

Conduct of a Pretest

It is often of considerable use to conduct a preliminary small scale sampling exercise. Such a pretest will yield, for example, estimates of pesticide variability which will permit more accurate determination of sample size requirements. A pretest can often also identify problems in field interpretations, analytical methodology and other facets which can be resolved before the overall exercise is initiated.

Description of Field Procedures

Careful thought (and if possible a pretest) should be devoted to the field instructions relative to sampling site, physical collection of the sample, sample unit identification, preservation of the sample, packaging and shipping, etc. If pesticide analyses are to be made in field laboratories, detailed methodology instructions (method, equipment, sample handling, data recording, etc.) must be provided. Preferably specially designed data reporting forms should be used, which will facilitate data analysis and resolution of any questionable selection of the sample units.

Analysis of the Data

If the survey or sampling program is properly planned, procedures for the analysis of the data will have been detailed ahead of time. Analysis should first involve a review of the raw data for omissions, recording errors or other inconsistencies. Pesticide levels in foods and feeds will in general be highly variable depending on the food product involved, source, geography, degree of processing, etc. Distributional forms of pesticide residue levels in a given situation will usually be quite definitely skewed (i.e., most values very small with the frequency of occurrence decreasing rapidly as the values increase numerically). Analytical treatment of such findings can be made by using the lognormal distribution as the reference model. For the usual statistical tests of significance or estimation problems, observed pesticide data can be transformed by taking logarithms of the values and treating the transformed data in accord with normal (Gaussian) distribution theory.

The types of statistical techniques that will find use in pesticide problems include acceptance sampling (e.g., for regulatory decisions relative to domestic and import sampling) or analysis of variance (for identifying differences in pesticide levels as a function of various factors such as source, type or level of processing, brands, style, etc.). Trend analysis and related correlation/regression techniques will apply in those situations where relationship of time or other factors to pesticide levels are of interest.

A most important consideration in the analysis of food/feed pesticide data is the variability in the sample data. Variability arises from two major sources (1) sampling error and (2) method error. Sampling error arises from the fact that we have access only to data from a portion of the population and of course different samples from the same population will yield differing numerical values. Method error refers to the less than perfect capability of the analytical procedure to provide the true pesticide level. Any analytical method should then have associated with it statistical measures of its accuracy and precision. Estimates of variation associated with the method as supplied by different laboratories and different technicians have been derived through collaborative studies for several analytical methods.

Sampling errors will automatically be included in the statistical procedure (e.g., identification of the probability of getting a violative sample from a non-violate lot in acceptance sampling). However, special provision must be made for analytical error in many cases (e.g., a violative pesticide value may in fact be non-violative when method error is taken into account) such as in regulatory activity. In other situations it will be less important (e.g., a relative comparison of pesticide levels between two populations).

Computer Support

In most surveys or surveillance problems of food pesticide levels, sufficient data will be generated so that analysis is facilitated by computer treatment. It is also considered of value to retain data from past surveys. Access to such data is facilitated by computer treatment. Normally agencies concerned with pesticide problems associated with food will have access to medium to largescale computers. Therefore, equipment exists for convenient treatment but the program for storage and retrieval and for analysis will probably have to be developed or adapted in each case.

CHAPTER IX - HUMAN TISSUES

This discussion will be limited to the monitoring of humans for pesticides. It is recognized that many of the points discussed must be common to any program monitoring humans for other chemical, physical, or infectious agents. While human monitoring is similar in many respects to other environmental monitoring, it is quite different in a number of both technical and ethical aspects. Indeed, human monitoring may be the most difficult to perform meaningfully.

The following questions must be answered as the first step in planning a human monitoring program:

1. What use will be made of the collected data? By whom?
2. What population will be studied? How is it distributed geographically, by age, sex, race, health condition, occupation, cultural mores, etc.? What is the total potential population for study?
3. What other information is available concerning the group to be studied and how much of it will be coordinated with the monitoring data?
4. How often will samples be collected from the same individuals?
5. What chemicals including metabolites, are to be studied? Are analytical procedures available which are adequately sensitive and specific for the study requirements?
6. What laboratory support is available? What is its work capacity, technical competence, and quality control program?
7. What time interval can be tolerated between sample collection and data availability?

Clearly the answers to these questions will shape the final program plans.

Man is monitored in order to estimate his total exposure to one or more pesticide chemicals. This is a much simpler approach than is the direct measurement of exposure by all routes, and it is the only approach which permits survey of a sizable population group.

The problems of ambient monitoring are quite different from those of occupation-linked monitoring with regard to almost all of the preceding questions. In general, occupational monitoring is easier to perform since the potential study group is usually limited by sex, age and health condition, and to some extent, geographically and socio-economically. Such a group is exposed to occupationally encountered

pesticides and may also be exposed through avocational activities to the same or different pesticides.

Ambient monitoring is generally concerned with minute traces and may produce negative results unless carefully planned as to chemicals to be studied, materials to be analyzed and sample collection procedures. Unlike sampling other environmental substrates, consideration must be given not only to the technology of the actual sample collection but also to the legality and ethics of sample collection as well as to the inherent limitation on the size of sample which it is feasible to obtain.

In order for ambient human sampling to reflect the condition of the population, the sample group must reflect the demographics of the population, i.e. sex, race, age and geographic distribution. Definition of the study population may restrict it in a number of specific parameters thereby increasing the standardization of the group. This definition must be done carefully in order to avoid biasing the entire study. Furthermore, in presenting and interpreting data from the study, the definition of the study population must be clearly reiterated in order to avoid unjustified and potentially erroneous extrapolation. Census data can be most helpful in identifying age, sex, race and geographic demographics by city, county, state, region or nation and should be reviewed before designing the study.

The necessity of monitoring a biologic creature further complicates the problem, requiring careful selection of the tissue or fluid to be sampled. Some pesticide chemicals and/or their metabolites are stored in the tissues of the body at different concentrations for long periods of time, others are rapidly metabolized and excreted a short time after exposure as unique products or as products indistinguishable from those of normal metabolic processes. Since the original level of exposure is usually quite low in the general population, the stored or excreted levels must also be low. Normal body components or other materials to which there has been exposure may also complicate analysis. Analytical technology does not permit the measurement of all pesticide chemicals and metabolites in a single sample of tissue or fluid, therefore, more than one tissue may be required from each individual.

Samples from the human body, whether tissues, blood or excreta, are not easily obtained. The question of informed consent must be resolved for each individual.

Sample identification and handling are other areas which require pre-planning decisions. Usually a small amount of information is desirable about the sample donor, but this should be kept to a minimum, being limited to those facts for which there is a demonstrated need. The donor's identity must remain anonymous when the data is

evaluated. Sample container, sampling technique and sample storage and transport are important in preventing the introduction of extraneous and interfering materials which further complicate the interpretation of analytical results and in preserving chemicals within the sample. Details of these procedures must be verified with the supporting laboratory before sample collection is initiated. At the same time the reporting terms and format should be finalized for each type sample collected in units, total sample or extracted weight basis, before or following adjustment of osmolality, hematocrit or pH, etc. Confirmatory tests to be used should be preselected since this will be important in determining the size of each sample collected.

Within this context, the following guidelines are offered for ambient human monitoring within any geographic subdivision:

1. Identify the intended use of data from the study
2. Identify the geographic area of the study
3. Define the study population by size, geographic distribution, age, sex, race, occupation, ethnic customs, etc.
4. Develop statistical design based on study population parameters to assure the collection of representative samples on a random basis. This should provide confidence levels and define acceptable margins of variation.
5. Determine pesticide residues to be monitored and materials to be collected and analyzed, also amount of material required for "a sample."
6. Select identifying information to accompany each sample.
7. Define sample collection, handling, storage and transport procedures, including procedures for assuring use of uncontaminated sample containers.
8. Identify sampled tissues.
9. Identify sampling locations geographically and make appropriate contacts. Informed consent procedures must be worked out with each sample provider.

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June 1980

ANALYSIS OF PESTICIDE RESIDUES IN HUMAN AND ENVIRONMENTAL SAMPLES

A COMPILATION OF METHODS
SELECTED FOR USE IN
PESTICIDE MONITORING PROGRAMS

REVISIONS BY

THE ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS

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The "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples" is owned by the SWRCB, and can be purchased through NTIS. There are 554 pages in the book.

FOREWARD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory participates in the development and revision of air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

This manual provides methodology useful in determining the extent of environmental contamination and human exposure to pesticides and related industrial chemicals. It has been compiled and produced in an effort to promote general acceptance and adoption of uniform chemical methodology of utmost reproducibility and accuracy and to ensure that analytical results can be correlated and directly compared between laboratories. This standardization of data collection will greatly increase our knowledge and understanding of the extent of environmental contamination by pesticides.

F. G. Hueter, Ph. D.
Director
Health Effects Research Laboratory

Revised

ABSTRACT

This manual provides the pesticide chemist with methodology useful in determining human exposure to pesticides and related industrial chemicals. Methods are also presented for measuring the extent of environmental contamination with these compounds. This manual has been compiled and produced in an effort to promote general acceptance and adoption of uniform chemical methodology of utmost reproducibility and accuracy and to ensure that analytical results can be correlated and directly compared between laboratories. Methods contained in this manual have generally been developed and/or evaluated by this laboratory within the Environmental Toxicology Division.

The analytical methodology compiled herein consists of both multi-residue and specific residue procedures. Included also, are miscellaneous topics treating a number of important activities such as the cleaning of laboratory glassware, the preparation of analytical reference standards, and the calibration and maintenance of the gas chromatograph. Several of the methods have been subjected to collaborative studies and have thereby been proved to produce acceptable interlaboratory precision and accuracy. These methods are designated by stars placed at the left of the title in the TABLE OF CONTENTS. Other methods presented are thought to be acceptable but have not been validated by formal interlaboratory collaboration.

Revised 12/15/79

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INTRODUCTION

The analytical methodology collected in this manual was primarily intended for use by EPA Laboratories conducting analyses of pesticides in various sectors of the environment and by laboratories under contract with EPA to conduct community studies and the monitoring of concentrations of pesticides in the human population.

One of the primary objectives of the Epidemiologic Studies and Monitoring Laboratory program was to establish and maintain, in collaboration with other federal agencies, a broad surveillance and evaluation program concerned with the extent and significance of the contamination of man and his environment by pesticides and their metabolites. To accomplish this goal, data have been continuously obtained on the levels of pesticides and their metabolites in the human population and various elements of the environment. It is important that uniform chemical methodology of utmost reproducibility and accuracy be used by participating laboratories to ensure that analytical results can be correlated and directly compared between laboratories.

A prime responsibility of the Environmental Toxicology Division is to make new and improved analytical procedures available to EPA and related laboratories and to those of state and local agencies working to assess pesticide residues in people and/or environmental media. Thus, the Division serves as a primary facility to provide (1) high purity analytical reference standards, (2) information on analytical quality control, (3) instrumental troubleshooting and calibration, and further (4) to conduct research on analytical methodology for the measurement of residues of pesticides and other toxic residues in human and environmental media.

The analytical methodology compiled herein consists of both multi-residue and specific residue procedures. Included also are miscellaneous topics treating a number of important activities such as the cleaning of laboratory glassware, the preparation of analytical reference standards, and the calibration and maintenance of the gas chromatograph. Several of the methods have been subjected to collaborative studies and have thereby been proved to produce acceptable interlaboratory precision and accuracy. These methods are designated by plus signs placed at the left of the title in the TABLE OF CONTENTS. Other methods presented are thought to be acceptable but have not been validated by formal interlaboratory collaboration.

A numbering system is used in this manual whereby each page bears a date and numbers and/or letters designating the identity of the section and subsection. Additions, deletions and revisions will be distributed to manual holders as they are made available, with each such issuance bearing appropriate section identification and revision date.

Revised 12/2/75

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The cooperation of scientists using this manual is solicited in helping to improve and update the material. Suggestions and comments based on user's experience will be welcomed. Such suggestions or requests for additional copies of the manual should be directed to:

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Research Triangle Park, NC 27711

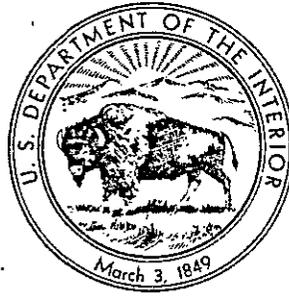
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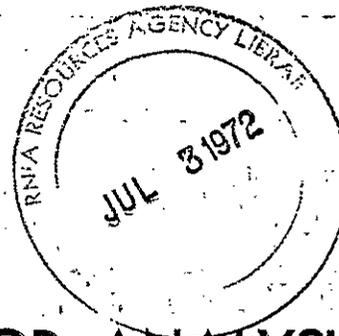
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Techniques of Water-Resources Investigations
of the United States Geological Survey



METHODS FOR ANALYSIS OF
ORGANIC SUBSTANCES IN WATER

BOOK 5
CHAPTER A3



Techniques of Water-Resources Investigations
of the United States Geological Survey

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↳ **METHODS FOR ANALYSIS OF
ORGANIC SUBSTANCES IN WATER**

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Book 5

LABORATORY ANALYSIS

PREFACE

The series of manuals on techniques describes procedures for planning and executing specialized work in water-resources investigations. The material is grouped under major subject headings called books and further subdivided into sections and chapters. The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises. Section A of Book 5 presents techniques used in water analysis.

Provisional drafts of chapters are distributed to field offices of the U.S. Geological Survey for their use. These drafts are subject to revision because of experience in use or because of advancement in knowledge, techniques, or equipment. After the technique described in a chapter is sufficiently developed, the chapter is published and is for sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

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METHODS FOR ANALYSIS OF ORGANIC SUBSTANCES IN WATER

By Donald F. Goerlitz and Eugene Brown

Abstract

This manual contains methods used by the U.S. Geological Survey for the determination of organic substances in water. Procedures are included for the following categories of organic substances: Organic carbon, chlorophylls, color, detergents, nitrogen, oils and waxes, oxygen demand (chemical), phenolic materials, herbicides, and insecticides. Procedures are also given for the determination of chlorinated hydrocarbon insecticides, as well as chlorinated phenoxy acid herbicides, in sediment and bottom materials.

Introduction

The yellow or brown color commonly associated with natural water is often the result of the decomposition of naturally occurring organic matter. The most abundant sources of this material include decaying vegetation, algae, and microscopic organisms. These substances are produced mostly on land and during runoff are flushed into the water, where complex biological processes continue. The role of natural organic substances in water processes is not very well understood. These compounds are known to aid in transporting and solubilizing many trace elements and are important in weathering. Further, natural organic substances interact with both organic and inorganic pollutants.

In addition to organic matter from natural sources, increasing amounts are entering water as a direct and (or) indirect result of man's activities. Leading sources of this material are industrial and domestic waste, agriculture, urban runoff, mining, and watercraft. Foaming detergents have been observed in water supplies. Fish kills have been caused by toxic chemicals and have been linked to nutrient-induced algae blooms, which deplete the dissolved oxygen.

Because of the myriad of sources from both pollution and natural processes, organic matter is present in almost all surface and ground waters and directly influences the water quality.

In reviewing water-quality reports, one may observe that although color, oxygen consumed (chemical oxygen demand), and other criteria for the analysis of organic substances are described in the introductory remarks, seldom are such data included in the tables of the report. These data are noticeably absent from past reports because such crude measurements did not appear to serve any meaningful purpose in explaining most water processes. The value of even the most primitive measurements of organic substances in water is apparent, considering the general awareness of man's effect on the environment and the implementation of programs to stem the tide of water pollution, lake eutrophication, and similar problems.

The purpose of this manual is to provide directions for collection and analysis of water samples containing organic substances as required by the Geological Survey in making water-quality investigations. This manual is an updating and compositing of the organic analytical methods contained in Geological Survey Water-Supply Paper 1454, "Methods for Collection and Analysis of Water Samples" (Rainwater and Thatcher, 1960). The intense activity in the field of organic analysis is providing new and improved methods, and as appropriate methods become available they will be added to this manual. All methods as written may be subjected to revision from time to time. Methods labeled as tentative are assumed to be adequate but need further testing before final acceptance.

Part I. Sampling

Refer to Part I, Chapter A1 of Book 5, for information on site selection, frequency, field safety, and first aid. Before a proper sampling program can be initiated, the nature of the organic compounds sought must be considered. As a general rule, organic compounds having less than six carbon atoms are water soluble, whereas compounds with more than six carbons are not. This generalization must be applied with care, however, because the presence of hydroxyl or other polar sites on a molecule increases its solubility. Even very soluble compounds, however, may prefer to reside on organic-layered sediment. Further, some insoluble compounds may be suspended on the water surface. In summary, organic matter in a body of water may be distributed on the surface, in suspension, adsorbed on suspended sediment, in bed materials, and (or) in solution.

Because of this wide and generally unpredictable distribution of organic material in a body of water, the collection of a truly representative sample requires a great deal of care and often requires the use of specialized sampling equipment. In most instances, samples for organic analysis are best collected with the same equipment and technique used for the collection of samples for suspended-sediment measurements. The technique and equipment used in such measurements have been extensively studied, and they are discussed at length in one of a series of reports by the Inter-Agency Committee on Water Resources (1963) and, more recently, in a report by Guy and Norman (1970). When more elaborate equipment is not available, a simple weighted bottle may often be used for sampling wells, lakes, and slow-moving streams with little suspended sediment. Other available samplers have rubber gaskets and valving arrangements that may either contaminate the sample or remove organics from the water by adsorption. Such devices as the DH-48, D-49, or the P-46 samplers, which are specially designed to collect suspended-sediment samples from fast-moving streams at water velocity, must be modified for organic sample collection. Most importantly, all the neoprene gaskets must be replaced by inert plastic material, such as teflon, and oil must be eliminated from valves.

Organic substances on the water surface or incorporated in the bed material present very difficult sampling problems. Surface films may appear chronically or intermittently and most often come from accidental spills or seepage. Samples taken from the surface of a body of water, especially moving water, are almost impossible to evaluate. Quite often the samples must be related to the total volume of water, surface area, film area, and film thickness. At present, no universally acceptable surface samplers are available, and investigators are required to fabricate their own. Floating hoops or rectangles covered with clean metal foil which delineate an area and allow skimming a surface sample from calm water have been used with limited success. Other methods for collecting films and slicks from surface waters, such as "dustpan skimmers," absorbent cloths, and floor mops, have been used, but none have been satisfactory for general application. The method most often used for describing a problem area when surface films are involved is identification of the material, locating the source, and then estimating the amount entering the water.

A rational approach to site selection for sampling stream bottoms is also difficult. Fortunately, bed-material samplers are available. Ideally, bottom material, including that which is moving by saltation, rolling, or otherwise drifting along the streambed, should be included. It is also desirable to collect the water from the 3 or 4 inches of flow immediately above the stream bottom. This is commonly called the "unsampled zone," because it is not sampled by suspended-sediment samplers or most other water-sampling devices because of mechanical limitations.

Bed-material and suspended-sediment samplers may be obtained through the Federal Inter-Agency Project, U.S. Army Engineer District, St. Paul, Minn. One of these is the piston-type bed-material hand sampler BMH-53 for shallow water, and the other is the BM-54 or BM-60 bed-material sampler for deeper water. Both of these are constructed to prevent sample washout when raised to the surface. Bed-material samplers to sample at the interface are now under development and should be available soon.

Most investigations are not concerned with surface or bottom material, but rather with that within the body of the water. Most of samples are

collected from just beneath the surface of the stream to as near the bottom as the sampling apparatus will allow. Accurate samples are taken either by depth integration or at a number of points in a transverse cross section. For small streams, a depth-integrated sample or a point sample taken at a single transverse position located at the centroid of flow is usually adequate. Larger streams require selection of several verticals at centroids of equal flow after careful and often extensive measurement. Depth-integrated samples may also be taken by the ETR (equal transit rate) method, at equally spaced points across the stream cross section. In collecting these samples, the sampler is lowered and raised at each sampling point in the same length of time (Guy and Norman, 1970). Lakes are sampled on three-dimensional grids consistent with the shape and depth of the water body. Wells may be sampled from the pump, provided the oils from the mechanism do not contaminate the sample, otherwise a bottle sampler should be used. Compositing samples in the field is not recommended. Individual samples for compositing should be taken to the laboratory, where careful control can be maintained. Organic sediments and soils tend to cling to sample containers, and special precaution must be taken to avoid improper handling.

Glass bottles are the most acceptable containers for collecting, transporting, and storing samples for organic analysis. Glass appears to be inert relative to organic materials and can withstand a rigorous cleaning procedure. Because organic materials are so plentiful in the environment, it is extremely difficult to collect samples free from extraneous contamination. Apparatus for sampling or processing samples must be scrupulously clean. Sample bottles, especially, must be free of contaminating materials. Boston round glass bottles of 1-liter capacity with sloping shoulders and narrow mouths are satisfactory for most applications. The closure should be metal, preferably inert, and lined with teflon. This plastic is the only organic material that should be allowed to contact the sample.

All sample bottles, whether new or used, must be cleaned before collecting organic samples, and the following procedure is recommended: After washing in hot detergent solution and rinsing in warm tapwater, the bottles are rinsed in dilute

hydrochloric acid. Following a rinse in distilled water, the glass containers are put into an oven and heated at 300°C (Celsius) overnight. The teflon cap liners and the metal closures are washed in detergent. After rinsing with distilled water, the caps are set aside to air-dry. The liners are rinsed in dilute hydrochloric acid and then soaked in redistilled acetone for several hours and heated at 200°C overnight. When the heat treatments are completed, the bottles are removed from the oven and capped with the closure and teflon liner. The clean bottles are usually stored or shipped in a "duo-pak" container—a form-fitting expanded polystyrene case in a corrugated cardboard carton.

In actuality, the analysis begins with the collection of the sample. The sample must represent the body of water from which it was collected at the time it was taken. The importance of the sample to the final result cannot be over-emphasized. If possible, an analyst or a person directly concerned with the particular study should collect the samples. Inexperienced personnel should never be allowed to collect samples unless they are very closely supervised. If possible, the principal investigator should give personal instruction on sample collection. In all instances, detailed printed instructions should accompany each set of sample bottles. The sample containers should always be sent from the laboratory directly to the person taking the samples just before sampling. Extra or spare sample bottles should be actively inventoried and remain under the control of the laboratory.

Sample preservation

Most water samples for organic analysis must be protected from degradation. Provisions for refrigerating or otherwise preserving the sample should be available. Icing is the most acceptable method of preserving a sample, but it is not always possible. Timing of collection should be arranged so that the sample can reach the laboratory in a minimum of time. There is no single preservative that may be added to a sample for all forms of organic analysis, but each sample must be treated according to the analytical procedure to be performed. For the determinations in this manual, the following general methods

of sample preservation should be used:

Oxygen demand, chemical: Add concentrated H_2SO_4 (sp gr 1.84) at a rate of 2 milliliters (ml) per liter of sample.

Carbon, inorganic: Refrigerate at 4°C.

Carbon, organic: Add concentrated H_2SO_4 at a rate of 2 ml per liter of sample and refrigerate at 4°C.

Chlorophylls: Refrigerate at 4°C.

Color: Refrigerate at 4°C.

Oils and waxes: Add concentrated H_2SO_4 until the pH of the sample is below 3.0. Generally, 5 ml per liter will be sufficient.

Surfactants: Refrigerate at 4°C.

Nitrogen: Add 40 milligrams (mg) of $HgCl_2$ per liter of sample and refrigerate at 4°C.

Phenolic material: Acidify sample to pH 4.0 with H_3PO_4 , add 1.0 gram (g) $CuSO_4 \cdot 5H_2O$ per liter of sample, and refrigerate at 4°C.

Herbicides: Acidify with concentrated H_2SO_4 at a rate of 2 ml per liter of sample and refrigerate at 4°C.

Insecticides: None required for chlorinated compounds.

References

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Part II. Analysis of samples

Carbon, all forms

The procedure given affords an accurate determination of carbon in water in solution as well as in suspended matter. Both organic and inorganic carbon can be selectively measured. The organic carbon determination gives a much truer measure of the organic matter present in aqueous solution and (or) suspension than does

the chemical oxygen demand determination. This technique is not hampered by the presence of reducing substances or affected by the type of organic material being oxidized. It cannot, however, be used to replace the biological oxygen demand determination.

1. Summary of method

Using a microsyringe, a fraction of a milliliter of sample is injected into a combustion tube under a sweep of oxygen gas. All the carbon in the sample is converted to carbon dioxide and measured by use of a nondispersive infrared analyzer (Van Hall and others, 1963).

2. Application

Water containing carbon from about 1.0 mg/l (milligram per liter) to 1,000 mg/l may be analyzed directly. For a more sensitive procedure, the analyst is referred to the work of Menzel and Vaccaro (1964). Higher carbon concentrations must be diluted. Water containing organic particulate matter may be analyzed directly provided the largest particle diameter is $\frac{1}{6}$ – $\frac{1}{8}$ the syringe needle diameter. Otherwise, the particles must be reduced in size by homogenizing or blending, and the resulting suspension must be fairly uniform and stable.

Depending on the sample treatment, results should be reported as follows:

2.1 Total carbon: Sample analyzed without filtration or acidification.

2.2 Total organic carbon: Sample analyzed without filtration, but acidified and purged with inert gas to remove inorganic carbon.

2.3 Dissolved carbon: Sample analyzed after filtration, but without acidification.

2.4 Dissolved organic carbon: Sample analyzed after filtration and acidification and purging to remove inorganic carbon.

In addition to these reporting forms, concentrations of inorganic carbon (dissolved and suspended) and suspended carbon (organic and inorganic) may be computed by differences from the above measurements.

3. Interferences

Strongly acidic solutions and some brines interfere with this technique by producing infrared-absorbing fogs. Very volatile carbon

compounds may be lost during carbonate elimination. Injections in excess of 0.08 ml result in incomplete combustion owing to the large volume increase associated with the water vaporization.

4. Apparatus

4.1 *Carbonaceous analyzer*, Beckman Model 115-A, Model 915, or equivalent.

4.2 *Microliter syringe*, 100- μ l (microliter) capacity with large-bore needle.

4.3 *Microfiltration apparatus*: Use only silver metal filters having 0.45 μ m (micrometer) maximum pore size, obtainable from Selas Flotronics. Filters should be heated at 300°C overnight to remove organic matter.

5. Reagents

All reagents must be checked for organic contamination.

5.1 *Carbonate-bicarbonate standard solution*, 1.00 ml=1.00 mg carbon: Dissolve 3.500 g sodium bicarbonate and 4.418 g sodium carbonate, both dried at 105°C for 1 hr (hour), in carbon-free distilled water and dilute to 1,000 ml.

5.2 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.3 *Nitrogen gas*, free of carbon dioxide and organic impurities.

5.4 *Oxygen gas*, free of carbon dioxide and organic impurities.

5.5 *Potassium hydrogen phthalate standard solution*, 1.00 ml=1.00 mg carbon: Dissolve 2.128 g potassium hydrogen phthalate, primary standard grade, which has been dried at 105°C for 1 hr, in carbon-free distilled water and dilute to 1,000 ml.

6. Procedure

6.A Instrument standardization

6.A.1 *Single-channel analyzer*, Beckman Model 115-A, or equivalent.

6.A.1.1 Prepare a series of standards containing 5, 10, 20, 40, 60, and 80 mg/l of carbon by dilution of the potassium hydrogen phthalate standard stock solution.

6.A.1.2 Successively introduce 20- μ l samples of the 20-mg/l standard into the carbonaceous analyzer until the response is reproducible. Allow the recorder to return to the original

baseline between injections. Run duplicate determinations, at the least, for each standard and plot the milligrams per liter of carbon versus peak height measured from baseline on the recorder.

6.A.2 *Dual-channel analyzer*, Beckman Model 915, or equivalent.

6.A.2.1 Prepare a standard curve for the organic carbon channel of the analyzer as in step 6.A.1 above.

6.A.2.2 Prepare a standard curve for the inorganic channel of the analyzer, using the same technique, by injection of standards prepared by dilution of the carbonate-bicarbonate stock standard.

6.B Analysis of samples

6.B.1 Single-channel analyzer

6.B.1.1 Depending on how the results are to be reported, the sample may be filtered and (or) acidified. If the sample is to be filtered through the metal membrane filter, the filtration must be done before acidification. Only enough filtrate for the determination need be collected.

6.B.1.2 Adjust the pH of the sample to 2 or below, using concentrated hydrochloric acid, and slowly bubble nitrogen gas through the solution for 3-5 min (minutes) to purge carbon dioxide.

6.B.1.3 Mix the sample well. Inject 20-80 μ l of the sample into the combustion tube, using the same technique as for the standards. Record the peak heights from at least two determinations for each sample.

6.B.1.4 Prepare a blank from carbon-free distilled water and all the reagents used, and analyze the blank as the sample. If more than 1 percent of salts is present in the sample, the blank should be prepared similarly.

6.B.2 Dual-channel analyzer

6.B.2.1 Depending on whether results are desired for total or dissolved carbon, the sample may be injected untreated, or filtered through the 0.45- μ m silver filter, but *not* acidified.

6.B.2.2 Make duplicate 20- μ l injections of each sample into each channel of the analyzer, using the same technique as in the preparation of the standard curves.

7. Calculations

7.A Single-channel analyzer

7.A.1 Concentrations of carbon, in milligrams per liter, are obtained directly from ap-

propriate standard curves, depending on the sample treatment used.

7.B Dual-channel analyzer

7.B.1 Concentrations of inorganic and inorganic-plus-organic carbon, in milligrams per liter, in each sample are obtained from the appropriate standard curves.

7.B.2 By difference, compute the concentration of organic carbon, in milligrams per liter. When this difference is small and the determined values are large, results should be verified. This may be done by injecting an acidified, nitrogen-purged sample into the high-temperature furnace to obtain a direct measure of organic carbon.

8. Report

Carbon concentrations are reported as follows: Less than 10 mg/l, one significant figure; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available, but results are believed reproducible within ± 1 mg/l at the 100-mg/l level.

References

- Beckman Instruments, Inc., 1966, Laboratory carbonaceous analyzer: Beckman Instructions 137879, Fullerton, Calif., 27 p.
- 1968, Total organic carbon analyzer: Beckman Instructions 81706-B, Fullerton, Calif., 34 p.
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Chlorophylls

The concentrations of photosynthetic pigments in natural waters vary with time and with changing aquatic conditions. Chlorophyll *a*, *b*, and *c* concentrations are used to estimate the biomass and the photosynthetic capacity of phytoplankton. Ratios between the different forms of chlorophyll are thought to indicate the taxonomic composition or the physiological state of the algal community.

Extractive spectrophotometric method

1. Summary of method

Individual chlorophylls are determined simultaneously without elaborate separation. The sample is filtered, and the cells retained on the filter are mechanically disrupted to facilitate extraction of pigments into a solvent composed of 90 percent acetone and 10 percent water (volume per volume). The concentrations of chlorophylls are calculated from measurements of absorbance of the extract at 4 wavelengths, corrected for the 90-percent acetone blank.

2. Application

The method is suitable for all natural waters. The volume of water filtered should contain less than 10 μ g (micrograms) chlorophyll *a*. (See step 6.1.)

3. Interferences

Large amounts of inorganic sediment in the sample may clog the filter. Erroneously high values may result from the presence of fragments of tree leaves or other terrestrial plant material.

The presence of phaeopigments, the decomposition products of chlorophyll, results in overestimates of chlorophylls (Yentsch, 1965, 1969; Lorenzen, 1965, 1967).

4. Apparatus

4.1 *Filtration equipment*: Filter holder assembly, Millipore XX63 001 20, or equivalent, and a source of vacuum.

4.2 *Glass pestle-type tissue homogenizer* (grinder), 15-ml capacity, Corning 7725, or equivalent. Motor drive with low-torque clutch to operate at about 500 rpm (revolutions per minute).

4.3 *Membrane filter*, Millipore HAWP 047 00 type, HA 0.45- μ m mean pore size, white, plain, 47-mm (millimeter) diameter, or equivalent.

4.4 *Swing-out centrifuge*, 4,000-5,000 gravity, with stoppered 15-ml graduated centrifuge tubes. Saveguard centrifuge, Model CT-1140, or equivalent.

4.5 *Spectrophotometer* (Beckman Model DU, or equivalent), with a bandwidth of 3 nm (nanometers) or less, allowing absorbance to be read to ± 0.001 units. Use cells with a light-path of from

1 to 10 cm (centimeters). If only chlorophyll *a* is determined, instruments with interference filters with not more than 5–10 nm (Beckman Model B, or equivalent) half-bandwidth may be used.

4.6 *Vacuum-pressure pump*, Millipore XX60 000 00, or equivalent.

5. Reagents

5.1 *Acetone solution*: To 900 ml acetone, add 100 ml distilled water.

5.2 *Magnesium carbonate*, powdered.

6. Procedure

6.1 Collect a sample of water which contains less than 10 μg , and preferably about 1 μg , of chlorophyll *a*. A sample of 0.5–1.0 liter may be adequate for fresh or estuarine waters; 4–5 liters of ocean water may be required. Samples must be refrigerated at 4°C until time of analysis.

6.2 Cover the surface of a 0.45- μm membrane filter with finely powdered MgCO_3 , using about 10 mg/cm² of filter area (about 170 mg for the 47-mm-diameter filter).

6.3 Filter the sample at no more than two-thirds atm (atmosphere).

6.4 Fold the filter with the plankton on the inside and proceed immediately with the extraction and measurement steps. If the sample must be stored, dry the filter in a silica gel desiccator in the dark at 1°C or less. Dry ice is recommended for storing samples in the field.

6.5 Place the filter in a glass homogenizer. Add 2 to 3 ml acetone solution. Grind 1 min (minute) at about 500 rpm.

6.6 Transfer to a graduated centrifuge tube and wash the pestle and homogenizer two or three times with acetone solution. Adjust the total volume to some convenient value, such as 5 or 10 ml ± 0.1 ml. Keep 10 min in the *dark* at room temperature.

6.7 Centrifuge for 10 min at 4,000 to 5,000 gravity.

6.8 Carefully pour or pipet the supernatant into the spectrophotometer cell. Do not disturb the precipitate. If extract is turbid, try to clear by adding a little 100-percent acetone or distilled water, or by recentrifuging.

6.9 Read the absorbance at 750, 663, 645, and 630 nm against an acetone-solution blank. (Dilute with acetone solution if the absorbance is

greater than 0.8.) If the 750-nm reading is greater than 0.005/cm light-path, reduce the turbidity as mentioned in step 6.8.

7. Calculations

Subtract the absorbance at 750 nm from the absorbance at 663, 645, and 630 nm. Divide the difference by the light-path of the cells, in centimeters. The concentrations of chlorophylls in the extract, as $\mu\text{g}/\text{ml}$ (micrograms per milliliter), are given by the following equations:

$$\begin{aligned} \text{chlorophyll } a, \text{ in } \mu\text{g}/\text{ml} &= 11.64e_{663} - 2.16e_{645} + 0.10e_{630} \\ \text{chlorophyll } b, \text{ in } \mu\text{g}/\text{ml} &= -3.94e_{663} + 20.97e_{645} - 3.66e_{630} \\ \text{chlorophyll } c, \text{ in } \mu\text{g}/\text{ml} &= -5.53e_{663} - 14.81e_{645} + 54.22e_{630} \end{aligned}$$

where:

$$e_{663} = \frac{\text{absorbance at 663 nm} - \text{absorbance at 750 nm}}{\text{light-path, in cm}}$$

$$e_{645} = \frac{\text{absorbance at 645 nm} - \text{absorbance at 750 nm}}{\text{light-path, in cm}}$$

$$e_{630} = \frac{\text{absorbance at 630 nm} - \text{absorbance at 750 nm}}{\text{light-path, in cm}}$$

$$\begin{aligned} \text{chlorophyll } a, \text{ in } \mu\text{g}/\text{l} &= \text{chlorophyll } a \text{ in } \mu\text{g}/\text{ml} \\ &\times \frac{\text{extract volume, in ml}}{\text{sample volume, in liters}} \end{aligned}$$

8. Report

Report chlorophyll concentrations as follows: Less than 1.0 $\mu\text{g}/\text{l}$ (micrograms per liter), one decimal; 1.0 $\mu\text{g}/\text{l}$ and above, two significant figures.

9. Precision

The precision of chlorophyll determinations is influenced by the volume of water filtered, the range of chlorophyll values encountered, the volume of extraction solvent, and the light-path of the spectrophotometer cells.

The precision for chlorophyll *a* determination at the 5- μ g level was reported to be ± 5 percent in one study (Strickland and Parsons, 1960). The UNESCO (1966) report recommended that precision be determined by each analyst.

References

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- 1967, Determination of chlorophyll and phaeopigments: Spectrophotometric equations: *Limnology and Oceanography*, v. 12, p. 343-346.
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Color

The color of water as considered herein is that due only to substances in solution. Color in water may be of natural mineral, animal, or vegetable origin. It may be caused by metallic substances, humus material, peat, algae, weeds, or protozoa. Industrial wastes may also color water. Color may range from zero to several hundred units.

In domestic water, any noticeable color is undesirable. Color-imparting solutes may dull clothes or stain food and fixtures. The U.S. Public Health Service (1962) stated that the color shall not exceed 15 units in drinking and culinary water on carriers subject to Federal quarantine regulations. Color is undesirable in water for many industries, particularly food processing, laundering, ice manufacturing, bottled beverage, photographic, and textile (California State Water Quality Control Board, 1963).

Comparison method

1. Summary of method

The color of the water is compared with that of colored glass disks which have been calibrated

to correspond to the platinum-cobalt scale of Hazen (1892). The unit of color is that produced by 1 mg of platinum per liter. A small amount of cobalt is added to aid in color matching. The Hazen scale is satisfactory for most waters, but the hues and shades of some waters may not easily be compared with standards. If the hue of the water does not compare with that of the standard, there is very little that can be done, other than to visually compare the optical densities of the sample and standard. Highly colored waters should not be diluted more than necessary because the color of the diluted sample often is not proportional to the dilution. The colored glass disks should be recalibrated at frequent intervals against platinum-cobalt standards, as their color may fade with time.

2. Application

This method may be used to measure the color of samples whose colors reasonably match the Hazen scale and which contain no excessive amount of suspended matter.

3. Interferences

Turbidity generally causes the observed color to be higher than the true color, but there is some disagreement as to the magnitude of the effect of turbidity. The removal of turbidity is a recurrent problem in the determination of color. Color is removed by adsorption on suspended material. Filtration of samples to remove turbidity frequently removes some of the color-imparting solutes, possibly by adsorption on the sediments or on the filter medium. Centrifuging is preferable to filtration and is the only recommended method for the removal of suspended matter.

4. Apparatus

Color comparator, with standard color disks covering the range 0-500 color units.

5. Reagents

None.

6. Procedure

6.1 Remove turbidity by centrifuging the sample.

6.2 Fill one instrument tube with the sample of water, level the tube, insert the glass plug,

making sure that no air bubbles are trapped, and insert the tube into the comparator.

6.3 Use distilled or demineralized water in the second tube as a blank.

6.4 The color comparison is made by revolving the disk until the colors of the two tubes match.

7. Calculations

The color is read directly from the matching color standard, and the proper dilution factor is applied.

8. Report

Report color as follows:

Color unit	Record units to nearest
1-50.....	1
51-100.....	5
101-250.....	10
251-500.....	20

9. Precision

Because of the many complicating factors involved, the measurement of color is not a precise determination. No statements on the reproducibility of the tests can be made.

References

- California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 168.
 Hazen, Allen, 1892, A new color standard for natural waters: Am. Chem. Soc. Jour., v. 12, p. 427.
 U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 6.

Extractable organic matter

Oils and waxes

Oils and waxes in natural waters most likely come from vegetation and aquatic life. Oils or fats and waxes from plants and animals are, for the most part, of the ester type—that is, the combination of an alcohol with an organic acid. Petroleum oils and tars, otherwise known as mineral oils, are almost exclusively hydrocarbon in composition. Petroleum oils, on occasion, can enter the water from natural seeps but most often result from industrial pollution and accidental

spills (Dept. of Interior, Office of Secretary, 1968). Most oils are insoluble in water but may be dispersed by natural and waste chemicals such as soaps and detergents. Ester-type compounds can hydrolyze to become soluble, form soaps, and further aid dispersion of the insoluble material. Oils, greases, fats, and waxes can severely damage water quality by (1) producing a visible film on the surface, (2) imparting an odor to the water and causing a noxious taste, (3) coating the banks and bottoms of the water body by adsorbing on sediment, and (4) destroying aquatic life (Federal Water Pollution Control Administration, 1968).

1. Summary of method

Oils and waxes are removed from the water by extraction with organic solvents and are determined gravimetrically. This method is similar in principle to that found in "Standard Methods," 12th edition (Am. Public Health Assoc., 1965). For characterization, and for volatile substances, the analyst is referred to the papers by Kawahara (1969) and Maehler and Greenber (1968).

2. Application

The extraction method is applicable to the analysis of waters containing oil, fat, grease, wax, and other solvent-soluble substances.

3. Interferences

Organic solvents vary considerably in their ability to dissolve not only oily substances but other organic matter as well. The ester-type oils and waxes may be decomposed to alcohols and acids or soaps. Glycerine, the alcohol from animal or vegetable fats and oils which are known as triglycerides, defies extraction by this technique. Soaps must be acidified to release the organic part of the molecule. Storage of the sample must be avoided because many oils are utilized by micro-organisms. Volatile compounds (boiling point <100°C) cannot be accurately determined by this method.

4. Apparatus

4.1 *Kuderna-Danish concentration apparatus*, 250-ml capacity. Use an ungraduated receiver and a 1-ball Snyder column.

4.2 *Separatory funnel*, 1-liter capacity, with unlubricated glass or teflon stopcock.

5. Reagents

5.1 *Chloroform*, boiling range 61°–62°C, distilled in glass.

5.2 *Petroleum ether*, boiling range 30°–60°C, distilled in glass.

5.3 *Sodium sulfate*, anhydrous, ACS reagent, granular.

5.4 *Sulfuric acid*, 1:1 solution: Mix a volume of sulfuric acid (sp gr 1.84) with an equal volume of distilled water.

6. Procedure

Surface samples must be taken with great care. (See p. 2.) The relationship of the affected surface to the body of water should be well documented. A complete written description of the sampling technique should be made for future reference. Samples of the water beneath the surface should be collected according to the recommended practice for organic samples. Usually 1-liter samples are sufficient for subsurface sampling.

6.1 Weigh the water and sample container with the cap removed. Pour the sample into the separatory funnel. Weigh the drained sample bottle and record the weight of the sample to three significant figures. (If an oil separation is observed, the weight of water may be obtained after a preliminary petroleum ether extraction before acidification.)

6.2 Rinse the sample bottle with 15 ml of petroleum ether and pour the washings into the separatory funnel. Rinse the sample bottle again with another 15 ml of petroleum ether and pour the washings into the separatory funnel.

6.3 Acidify the sample by the addition of 5.0 ml of 1:1 H₂SO₄ per liter of sample.

6.4 Shake the separatory funnel vigorously for 1–2 min, stopping to vent the pressure after the first few shakes. Allow the layers to separate for about 10 min. Draw off the water layer into the sample container and pour the solvent into a 125-ml erlenmeyer flask containing about 0.5 g anhydrous sodium sulfate. Difficult emulsions may be broken by shaking the funnel vigorously after most of the water has been withdrawn. Beware of excessive pressure buildup in the funnel at this step.

6.5 Pour the sample back into the separatory funnel. Rinse the sample bottle with 15 ml of

chloroform and add the washings to the separatory funnel. Pour an additional 15 ml of chloroform into the separatory funnel and shake 1–2 min. Allow the layers to separate. Collect the chloroform layer in the 125-ml erlenmeyer flask containing the petroleum ether extract.

6.6 Filter the extract through a plug of extracted glass wool into a Kuderna-Danish apparatus fitted with a tared (including a small boiling stone) receiver tube. Use liberal washings of petroleum ether to complete the transfer.

6.7 Remove the solvent by distillation on a steam bath and take nearly to dryness. As the last of the solvent is vaporizing, remove the apparatus from the heat and allow the vapor to condense and wash down the sides of the flask. After cooling, remove the receiver and volatilize the last of the solvent with a gentle stream of air or nitrogen gas.

6.8 Wipe the sides of the receiver tube with a moist tissue and allow to dry in the room for 30 min. Place the receiver in a desiccator for 30 min and then determine the weight of the sample.

7. Calculations

The concentration of material in the sample is calculated as follows:

Extractable organic matter (mg/l)

$$= \frac{A-B}{C} \times 1,000,$$

where

A = total weight (receiver + extract), in grams,
B = receiver tare, in grams, and
C = water sample volume, in liters.

The amount of material found in a surface sample may be related to an affected area provided the film is uniform. The weight of material per square meter of surface may be calculated as follows:

$$\text{Extractable organic matter (mg/m}^2\text{)} = \frac{1}{A} \times B,$$

where

A = area sampled, in square meters (m²), and
B = weight of extracted material, in milligrams.

8. Report

Concentrations of extractable organic matter are reported to two significant figures for values in excess of 10 mg/l, or to the nearest whole milligram.

9. Precision

The precision between samples depends upon the homogeneity of the dispersion and the volatility of the material. Duplicate results varying less than 5 percent from the mean have been obtained on prepared samples. Results from poorly dispersed material and surface film samples vary greatly.

References

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Methylene blue active substances

Synthetic anionic detergents

Methylene blue active substances (MBAS), synthetic detergents or surfactants, occur in natural waters almost exclusively as a result of pollution. Detergents in natural water can drastically alter the normal regimen. As surface-active agents, they disrupt the stability at the interface between water and other substances. In the presence of surfactants, normally insoluble organic compounds may be dispersed, and the function of vital membranes of aquatic organisms may be altered. Because they are water soluble, detergents can disperse toxic organic compounds normally incorporated in bottom muds, adsorbed

on sediment, or floating on the surface. In addition to acting synergistically to compound pollution problems, some detergents are toxic to certain aquatic life. According to the report of the Federal Water Pollution Control Administration (1968) levels of LAS (linear alkylate sulfonates) exceeding 0.2 mg/l may be harmful to aquatic life.

Three types of surface-active agents are in general use. They are classified by their chemical characteristics as anionic or cationic, indicating the charge of the active ions, and as nonionic hydrophilic organic compounds. Fortunately, anionic detergents react with cationic detergents to precipitate. Production of anionic detergents has greatly exceeded the other two, and, consequently, greater amounts of anionic detergents may be expected in waste water. Owing to this excess, cationic detergents are almost always effectively precipitated and seldom appear in solution in sewage treatment facilities. Synthetic nonionic detergents, alkyl or aryl polyols, have not caused much concern because their use has been limited principally to industrial applications and as a minor additive in household detergents for foam control.

Until 1965, ABS (alkyl benzene sulfonates) anionic detergents were the most common surfactants on the market. Because ABS resist biological degradation, they are not easily removed by waste treatment and were often found in water supplies, even drinking water. Since then, LAS (linear alkyl sulfonates), for the most part, have replaced ABS in detergent formulation because LAS surfactants are biodegradable and may be removed from waste water by ordinary treatment.

Both ABS and LAS are methylene blue active substances but are not identical in color production for spectrophotometric determination. Owing to this, methylene blue active substances are measured in units relative to an ABS standard.

1. Summary of method

Methylene blue reacts with anionic surfactants, both ABS and LAS, to form a blue-colored dye complex. The complex is extracted in chloroform, and the methylene blue active substances are determined spectrophotometrically. This method is similar in substance to "Standard Methods," 12th edition (Am. Public Health Assoc., 1965).

2. Application

This method is applicable to the analysis of waters containing 0.025–100 mg/l MBAS (methylene blue active substances relative to ABS standard).

3. Interferences

Phenols, proteins, and inorganic chlorides, cyanates, nitrates, and thiocyanates will complex methylene blue and give positive interference in the determination. With ABS concentrations from 0.0 to 1.0 mg/l, tests have shown no interference from the following individual constituents: 10 mg/l NO_2 , 25 mg/l NO_3 , 5 mg/l phenol, and 1 mg/l H_2S . Organic compounds having amine groups cause low results.

4. Apparatus

4.1 *Separatory funnels*, 500-ml, unlubricated glass or teflon stopcock.

4.2 *Spectrophotometer*, Beckman Model B, or equivalent.

With this instrument the following conditions have been used:

Wavelength.....	635 nm.
Cells.....	10 mm.
Phototube.....	Red-sensitive.
Initial sensitivity setting.....	2.
Slit width.....	0.2 mm.
Blank.....	CHCl_3 .

With these operating conditions, the following absorbances have been observed:

MBAS (as ABS) (mg)	Absorbance
0.01.....	0.052
.02.....	.150
.05.....	.438
.10.....	.870

5. Reagents

5.1 *Chloroform*, spectrophotometric grade.

5.2 *Detergent* (ABS) standard solution I: Dissolve 1.030 g 97.1-percent-purity ABS powder (obtained from Association American Soap and Glycerine Producers, Inc., 295 Madison Ave., New York, N. Y. 10010, and dried over H_2SO_4 for 1 week) in 500 ml distilled water in a 1,000-ml volumetric flask with gentle swirling. Allow the foam to break and dilute to volume. Refrigerate during storage.

5.3 *Detergent* standard solution II, 1.00 ml=0.010 mg ABS: Dilute 10.0 ml detergent standard solution I to 1,000 ml. Prepare fresh weekly.

5.4 *Methylene blue* reagent: Dissolve 0.35 g methylene blue in 0.01N sulfuric acid and dilute to 1,000 ml with same.

5.5 *Sulfuric acid* solution, 5N: Mix 245 ml concentrated H_2SO_4 (sp gr 1.84) in 500 ml water and, after cooling, dilute to 1,000 ml.

6. Procedure

Samples should be collected according to the recommended practice for organic analysis. Usually a 1-liter sample is adequate. LAS detergents are biodegradable; therefore samples should be analyzed as soon as possible after collection. All glassware should be rinsed with dilute hydrochloric acid after washing. As a further precaution, sample bottles, separatory funnels, and beakers may be heat treated at 300°C overnight to remove organic matter.

6.1 Measure a volume of sample containing less than 0.10 mg MBAS and not to exceed 100 ml into separatory funnel. Dilute to 100 ml if necessary. Prepare a blank and detergent standards in the same manner.

6.2 Adjust the pH of the sample to near neutral if necessary. To the sample, blank, and standard solution, add 1.0 ml 5N H_2SO_4 , mix, then add 5.0 ml methylene blue solution. Mix thoroughly.

6.3 Add 25.0 ml chloroform and shake the contents of the separatory funnel for 1 min. Allow the layers to separate.

6.4 Drain the lower chloroform layer through a layer of absorbent cotton contained in a small filtering funnel into 1.0-cm cells and measure the absorbance of the sample and standards against the blank at a wavelength of 655 nm.

7. Calculations

Determine the amount of detergent contained in the sample, minus the blank, from the standard curve. Calculate the amount of MBAS in the sample using the following equation:

MBAS (relative to ABS standard) mg/l

$$= \frac{\text{mg MBAS}}{\text{ml sample}} \times 1,000.$$

8. Report

Report synthetic anionic detergents concentrations as follows: Less than 1 mg/l, two decimals; greater than 1 mg/l, two significant figures.

9. Precision

Deviation of ± 10 percent may be expected in the range of 1-5 mg/l in surface water.

References

- American Public Health Association, 1965, Standard methods for the examination of water and wastewater [12th ed.]: New York, Am. Public Health Assoc., Inc., 769 p.
 [U.S.] Federal Water Pollution Control Administration, 1968, Report of the committee on water-quality criteria: Washington, U.S. Govt. Printing Office, 234 p.

Nitrogen, ammonia

Ammonia nitrogen includes nitrogen in the forms of NH_3 and NH_4^+ . As a component of the nitrogen cycle, it is often present in water, but usually in only small amounts. Ammonia is used in some water-treatment processes. More than 0.1 mg/l usually indicates organic pollution (Rudolph, 1931).

There is no evidence that ammonia nitrogen in water is physiologically significant to man or livestock. Fish, however, cannot tolerate large quantities. The toxicity to fish is directly related to the amount of free ammonia in solution; hence, the toxicity is dependent on the pH of the water. Ammonia decreases the ability of hemoglobin to combine with oxygen, and the fish suffocate. Although the tolerances of fish differ, 2.5 ml/l of ammonia nitrogen is considered harmful in the 7.4-8.5 pH range (Ellis and others, 1948).

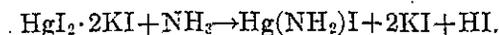
The low concentrations of ammonia in natural waters are of little industrial significance, except that ammonium salts are destructive to concrete.

Distillation method

1. Summary of method

The sample is buffered to a pH of 9.5 to minimize hydrolysis of organic nitrogen compounds. Ammonia is distilled from the buffered solution,

and an aliquot of the distillate is then Nesslerized. Essentially, Nesslerization is the reaction between potassium mercuric iodide and ammonia which forms a red-brown complex of mercuric ammono-basic iodide:



Concentrations of ammonia are then determined by standard spectrophotometric measurements. Alternatively, the distillate may be titrated with standard sulfuric acid solution.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 633) and by Blaedel and Meloche (1963).

2. Application

This method is recommended for analysis of samples containing less than 2 mg of ammonia and ammonium ion per liter. Higher concentrations may be determined by the alternate titration procedure provided.

3. Interferences

Calcium, magnesium, iron, and sulfide interfere with the Nesslerization, but the interference of the metals is eliminated by the distillation, and sulfide can be precipitated in the distillation flask with a little lead carbonate.

Some organic compounds may distill over with the ammonia and form colors with Nessler reagent which cannot be satisfactorily read with the spectrophotometer. Under such conditions, the sample should be distilled into H_3BO_3 and titrated with standard H_2SO_4 .

4. Apparatus

4.1 *Kjeldahl distillation apparatus*, 1,000-ml flasks.

4.2 *Spectrophotometer*, Beckman Model B, or equivalent.

With this instrument, the following operating conditions have been used:

Wavelength.....	425 nm.
Cells.....	40 mm.
Phototube.....	Blue-sensitive.
Initial sensitivity setting.....	1.
Slit width.....	0.3 mm.
Blank.....	Ammonia-free water plus reagents.

With these operating conditions, the following absorbances have been observed:

Nitrogen (mg)	Absorbance
0.02-----	0.24
.04-----	.47
.06-----	.70
.10-----	1.16

5. Reagents

5.1 *Ammonium chloride* standard solution I, 1.00 ml=1.00 mg N: Dissolve 3.819 g NH_4Cl , dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 ml.

5.2 *Ammonium chloride* standard solution II, 1.00 ml=0.010 mg N: Dilute 10.00 ml ammonium chloride standard solution I to 1,000 ml with ammonia-free water. Prepare fresh.

5.3 *Borate* buffer solution: Dissolve 9.54 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in ammonia-free water. Adjust the pH to 9.5 with 1M NaOH (approx 15 ml) and dilute to 1 liter with ammonia-free water.

5.4 *Boric acid* solution: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to 1 liter.

5.5 *Methyl red* indicator solution: Dissolve 0.1 g methyl red indicator in 100 ml ethanol.

5.6 *Nessler* reagent (CAUTION: HgI_2 is a deadly poison, and the reagent must be so marked): Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 ml ammonia-free water and dilute to 1 liter. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.7 *Sodium carbonate* solution, 0.0357N: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide free water and dilute to 1,000 ml.

5.8 *Sodium hydroxide* solution, 1M: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

5.9 *Sulfuric acid* standard solution, 0.0357N, 1.00 ml=0.5 mg N: Mix 1.3 ml concentrated H_2SO_4 (sp gr 1.84) with demineralized water and dilute to 950 ml before standardization. Standardize by titrating 25.0 ml 0.0357N Na_2CO_3 to pH 4.5.

6. Procedure

If acid has been added to the sample as a preservative at the time of collection, this must

be neutralized with NaOH solution before proceeding with the analysis. All glassware should be rinsed with ammonia-free water, prepared by passing distilled water through a mixed-bed ion-exchange resin.

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using Nessler reagent (CAUTION: Deadly poison).

6.2 Measure a volume of sample containing less than 1.0 mg ammonia nitrogen (500 ml maximum) into a 600-ml beaker, and adjust the volume to approximately 500 ml with ammonia-free water.

6.3 Add 25 ml borate buffer solution and adjust the pH to 9.5 with 1M NaOH, if necessary.

6.4 Immediately transfer the solution into the distillation flask and distill at a rate of 6-10 ml per minute; catch the distillate in a 500-ml volumetric flask containing 50 ml boric acid solution. The tip of the delivery tube must be below the surface of the boric acid.

6.5 Collect approximately 250 ml of distillate, dilute to 500 ml with ammonia-free water, and mix.

6.6.A Nesslerization procedure

6.6.A.1 Pipet an aliquot of distillate containing less than 0.1 mg ammonia nitrogen (50.00 ml maximum) into a graduate, and adjust the volume to 50.0 ml with ammonia-free water.

6.6.A.2 Prepare a blank of ammonia-free water and sufficient standards. Add 5 ml boric acid solution to each, and adjust the volumes to 50.0 ml.

6.6.A.3 Add 1.0 ml Nessler reagent (CAUTION: Deadly poison), and mix.

6.6.A.4 Allow the solutions to stand at least 10 min, but not over 30 min.

6.6.A.5 Determine absorbance of test sample and standards against the blank.

6.6.B Titration procedure

6.6.B.1 To the distillate, and an ammonia-free water blank containing the same volume of H_3BO_3 , add 3 drops methyl red indicator solution, and titrate with sulfuric acid standard solution.

7. Calculations

7.A Nesslerization procedure

7.A.1 Determine mg N in aliquot from a plot of absorbances of standards.

7.A.2 Ammonia nitrogen as N, in mg/l

$$= \frac{1,000}{\text{ml sample}} \times \frac{500}{\text{ml aliquot}} \times \text{mg N in aliquot.}$$

7.B Titration procedure

7.B.1 Ammonia nitrogen as N, in mg/l

$$= \frac{V_a \times N_a \times 14,000}{V_s},$$

where

V_a = ml standard H_2SO_4 used in titration of sample minus ml used to titrate blank,

N_a = normality of standard H_2SO_4 , and

V_s = ml of original sample used for distillation.

7.C Ammonia nitrogen as NH_4^{+} , in mg/l = mg/l as $\text{N} \times 1.288$. Ammonia nitrogen as free NH_3 , in mg/l = mg/l as $\text{N} \times 1.216$.

8. Report

Report ammonia nitrogen concentrations as follows: Less than 1 mg/l, two decimals; 1 mg/l and above, two significant figures.

9. Precision

No precision data are available.

References

- Blaedel, W. J., and Meloche, V. W., 1963, *Elementary quantitative analysis—Theory and practice* [2d ed.]: New York, Harper & Row, 826 p.
- Ellis, M. M., Westfall, B. A., and Ellis, M. D., 1948, *Determination of water quality*: U.S. Fish Wildlife Service Research Rept. 9, 122 p.
- Kolthoff, I. M., and Sandell, E. B., 1952, *Textbook of quantitative inorganic analysis* [3d ed.]: New York, Macmillan Co., 759 p.
- Rudolph, Z., 1931, Principles of the determination of the physical and chemical standards of water for drinking, industrial, and domestic purposes: *Water Pollution Abs.* 4 [March].

Nitrogen, nitrate

Nitrate is usually the most prevalent form of nitrogen in water because it is the end product of the aerobic decomposition of organic nitrogen. Nitrate from natural sources is attributed to the oxidation of nitrogen of the air by bacteria and to the decomposition of organic material in the soil. Fertilizers may add nitrate directly to water resources. Nitrate concentrations range from a

few tenths to several hundred milligrams per liter, but in unpolluted water they seldom exceed 10 mg/l. Nitrate and chloride are major components of human and animal wastes, and abnormally high concentrations of both suggest pollution.

Cyanosis due to methemoglobinemia may occur in infants whose drinking or formula water contains a high concentration of nitrates. The nitrates, when ingested, are converted to nitrites in the digestive system of some infants. The nitrite ion oxidizes hemoglobin to methemoglobin and thereby causes cyanosis. It is widely recommended that water containing more than 10–20 mg/l of nitrate nitrogen should not be used in infant feeding (Comly, 1945).

Nitrates in large amounts are injurious to the dyeing of wool and silk and are undesirable in fermentation processes (California State Water Quality Control Board, 1963). At least 2 mg/l of nitrate prevents intercrystalline cracking of steel in steam boilers.

Brucine method

1. Summary of method

The reaction between the alkaloid, brucine, and nitrate in acid medium produces a yellow color that may be measured by standard spectrophotometric procedures. Close attention must be given to procedural technique if accuracy and precision are to be obtained. The procedure is similar to that of Jenkins and Medsker (1964).

2. Application

This method may be applied to essentially colorless water containing up to 5.0 mg of nitrate per liter. Any significant amount of color should be removed. Samples containing higher concentrations must be diluted.

3. Interferences

Organic color, nitrite ion, and all strong oxidizing and reducing agents interfere. The interference by residual chlorine up to 5 mg/l may be eliminated by addition of sodium arsenite, and interference of up to 1 mg/l of nitrite eliminated by use of sulfanilic acid. The interference by chloride is effectively masked by the addition of a large amount of chloride ion to the reaction mixture.

4. Apparatus

4.1 *Water bath*, boiling.

4.2 *Spectrophotometer*, Beckman Model B, or equivalent.

With this instrument, the following operating conditions have been used:

Wavelength.....	410 nm.
Cells.....	23 mm.
Phototube.....	Blue-sensitive.
Initial sensitivity setting.....	2.
Slit width (approximate).....	0.10 mm.

With these operating conditions, the following absorbances have been observed:

NO ₃ (mg)	Absorbance
0.005.....	0.115
.010.....	.220
.020.....	.440
.030.....	.640
.040.....	.800
.050.....	.950

5. Reagents

5.1 *Brucine-sulfanilic acid* reagent: Dissolve 1 g brucine sulfate (CAUTION: Very poisonous) and 0.1 g sulfanilic acid in 70 ml hot demineralized water. Add 3 ml concentrated HCl (sp gr 1.19), cool, and dilute to 100 ml. This solution is stable for several months. The pink color that develops does not affect its usefulness.

5.2 *Nitrate* standard solution I, 1.00 ml = 1.00 mg NO₃: Dissolve 1.631 g KNO₃, dried overnight over concentrated H₂SO₄, in demineralized water and dilute to 1,000 ml.

5.3 *Nitrate* standard solution II, 1.00 ml = 0.010 mg NO₃: Dilute 10.0 ml nitrate standard solution I to 1,000 ml with demineralized water.

5.4 *Sodium chloride* solution: Dissolve 300 g NaCl in 1 liter demineralized water.

5.5 *Sulfuric acid*, 29N: Add 500 ml concentrated H₂SO₄ (sp gr 1.84) to 125 ml demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.05 mg NO₃ (10.0 ml maximum) into a 23-mm absorption cell and dilute to 10.0 ml.

6.2 Prepare a demineralized-water blank and sufficient standards and adjust the volume of each to 10.0 ml.

6.3 Add 2.0 ml sodium chloride solution, and mix well by swirling.

6.4 Place the absorption tubes into a cold-water bath (15°–20°C) and add 10.0 ml 29N H₂SO₄. Mix well by swirling, return to cold-water bath, and allow the contents of the tubes to cool to water-bath temperature.

6.5 Add 0.5 ml brucine-sulfanilic acid solution and mix thoroughly.

NOTE.—If a deep-pink color forms immediately upon addition of the brucine-sulfanilic acid reagent, it is an indication of a high nitrate concentration—exceeding the range of the method. Such sample aliquots must be discarded at this point and the samples reanalyzed, using a smaller aliquot.

6.6 Remove the rack of tubes from the cold-water bath and place in a boiling-water bath for 20 min. The water bath must be sufficiently large so that boiling does not cease when the tubes are placed in it. This step is critical. All tubes must be heated uniformly.

6.7 Remove the tubes from the boiling-water bath and immerse them in the cold-water bath. Allow to cool before proceeding. This inhibits any further color change. The cold-water bath must be sufficiently large to cool all tubes uniformly. Circulation of water in the bath is desirable.

6.8 Determine the absorbance of the sample and standards against the blank within 1 hr.

7. Calculations

7.1 Determine the mg NO₃ in the sample from a plot of absorbances of standards.

$$7.2 \text{ NO}_3 \text{ in mg/l} = \frac{1,000}{\text{ml sample}} \times \text{mg NO}_3 \text{ in}$$

sample.

7.3 To convert NO₃ to N, multiply by 0.2259.

8. Report

Report NO₃ concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Single-laboratory analysis of two test samples resulted in mean values of 0.9 and 2.9 mg/l, and standard deviations of 0.09 and 0.11 mg/l, respectively.

Reduction method

Samples containing more than 30 mg/l of NO_3^- may be analyzed by reduction using Devarda's alloy, distillation of the resulting NH_3 , and titration with standard H_2SO_4 solution. Details of the procedure are given by Blaedel and Meloche (1963) and by Kolthoff and Sandell (1952). For high concentrations of nitrate, the method yields results which are comparable in accuracy to those obtained by the brucine method.

References

- Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis—Theory and practice [2d ed.]: New York, Harper & Row, 826 p.
- California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 226.
- Comly, H. H., 1945, Cyanosis in infants caused by nitrates in well water: Am. Med. Assoc. Jour., v. 129.
- Jenkins, D., and Medsker, L. L., 1964, Brucine method for determination of nitrate in ocean, estuarine, and fresh waters: Anal. Chemistry, v. 36, p. 610.
- Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co., 759 p.

Nitrogen, nitrite

Nitrite is unstable in the presence of oxygen and is, therefore, absent or present in only minute quantities in most natural waters under aerobic conditions. The presence of nitrite in water is sometimes an indication of organic pollution.

Recommended tolerances of nitrite in domestic water supplies differ widely. A generally accepted limit is 2 mg/l, but as little as 0.1 mg/l has been proposed (California State Water Quality Control Board, 1963). Nitrite is undesirable in water used in dyeing wool and silk and in brewing.

Diazotization method

1. Summary of method

Nitrite is diazotized with sulfanilamide, and the resulting diazo compound is coupled with 1-naphthylethylenediamine dihydrochloride to form an intensely colored red dye (Rider and Mellon, 1945). The absorbance of the dye is proportional to the amount of nitrite present (Fishman and others, 1964).

2. Application

This method may be applied to samples containing less than 4 mg nitrite per liter. Samples containing higher concentrations must first be diluted.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Spectrophotometer, Beckman Model B, or equivalent.

With this instrument, the following operating conditions have been used:

Wavelength.....	535 nm.
Cells.....	10 mm.
Phototube.....	Blue-sensitive.
Initial sensitivity setting.....	2.
Slit width.....	0.08 mm.

With these operating conditions, the following absorbances have been observed.

NO_2 (mg)	Absorbance
0.05.....	0.53
.10.....	1.06
.15.....	1.59
.20.....	2.04

5. Reagents

5.1 *Formic acid*, 87–90 percent.

5.2 *1-naphthylethylenediamine dihydrochloride* solution: Dissolve 0.5 g 1-naphthylethylenediamine dihydrochloride in 100 ml demineralized water. Store in refrigerator.

5.3 *Nitrite* standard solution I, 1.00 ml = 1.00 mg NO_2 : Dissolve 1.850 KNO_2 in demineralized water and dilute to 1,000 ml.

5.4 *Nitrite* standard solution II, 1.00 ml = 0.010 mg NO_2 : Dilute 10.0 ml nitrite standard solution I to 1,000 ml with demineralized water.

5.5 *Sulfanilamide* solution: Dissolve 0.5 g sulfanilamide in 100 ml demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.20 mg NO_2 (50.0 ml maximum) into a 100-ml volumetric flask and adjust the volume to 50 ml with demineralized water.

6.2 In a similar manner, prepare a blank and sufficient standards containing 0.00–0.20 mg NO₂, and adjust the volume of each to 50 ml with demineralized water. Place in ice bath and allow to cool for about 2 min.

6.3 Add successively, while in the ice bath, and mixing thoroughly after each addition: 1.0 ml sulfanilamide solution, 4.0 ml formic acid, and 1.0 ml 1-naphthylethylenediamine dihydrochloride solution.

6.4 Remove the flasks from the ice bath and allow at least 15 min for maximum color development. Adjust each to exact volume with demineralized water. Mix thoroughly and measure the absorbance of samples and standards against the blank.

7. Calculations

7.1 Determine the mg NO₂ in the test samples from a plot of absorbances of standards.

$$7.2 \text{ NO}_2 \text{ in mg/l} = \frac{1,000}{\text{ml aliquot}} \times \text{mg NO}_2 \text{ in}$$

sample.

7.3 To convert NO₂ to N, multiply by 0.3043.

8. Report

Report NO₂ concentrations as follows: Less than 1.0 mg/l, two decimals; 1.0 mg/l and above, two significant figures.

9. Precision

No precision data are available.

References

- California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 226.
 Fishman, M. J., Skougstad, M. W., and Scarbro, G. F., 1964, Diazotization method for nitrate and nitrite: Am. Water Works Assoc. Jour., v. 56, p. 633.
 Rider, B. F., and Mellon, M. G., 1945, Colorimetric determination of nitrites: Indus. Eng. Chemistry, Anal. Ed., v. 18, p. 76.

Nitrogen, organic

Organic nitrogen includes all nitrogenous organic compounds, such as amino acid, polypeptides, and proteins. It is present naturally in all surface waters as the result of inflow of nitrogenous products from the watershed and the normal biological life of the stream. Effluents of sewage

and waste from slaughter houses and chemical plants often contain nitrogen in varying combinations. Organic nitrogen in unpolluted ground water is usually very low.

Organic nitrogen is not pathologically significant but is sometimes an indication of pollution. Organic nitrogen is important to considerations involving aquatic biology.

Kjeldahl method

1. Summary of method

Organic nitrogen is degraded to the ammonium ion by digestion with sulfuric acid in the presence of copper sulfate, which acts as a catalyst. The solution is made alkaline with sodium hydroxide, and the free ammonia is distilled off and Nesslerized. The color developed is proportional to the organic nitrogen content.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 537).

2. Application

This method may be applied to most natural water containing less than 2 mg of nitrogen per liter. Higher concentrations must be reduced by dilution.

3. Interferences

Nitrate and nitrite do not interfere. The effect of ammonium ions and ammonia is strictly additive. Therefore, the organic nitrogen is normally determined on the residue of the ammonia nitrogen determination.

Calcium, magnesium, iron, and sulfide interfere with the Nesslerization, but the interference of the metals is eliminated by the distillation. Sulfides interfere and must be precipitated in the distillation flask with a little lead carbonate before addition of sodium hydroxide.

Some organic compounds may distill over with the ammonia and form colors with Nessler reagent which cannot be satisfactorily read with the spectrophotometer. Under such conditions, the sample should be distilled into H₃BO₃ and titrated with standard H₂SO₄.

4. Apparatus

4.1 *Kjeldahl distillation apparatus*, 1,000-ml flasks.

4.2 *Spectrophotometer*, Beckman Model B, or equivalent.

With this instrument, the following operating conditions have been used:

Wavelength.....	425 nm.
Cells.....	40 mm.
Phototube.....	Blue-sensitive.
Blank.....	Ammonia-free water plus reagents.
Initial sensitivity setting.....	1.
Slit width (approximate).....	0.3 mm.

With these operating conditions, the following absorbances have been observed:

N (mg)	Absorbance
0.02.....	0.24
.04.....	.47
.06.....	.70
.10.....	1.16

5. Reagents

5.1 *Ammonium chloride* standard solution I, 1.00 ml = 1.00 mg N: Dissolve 3.819 g NH_4Cl , dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 ml.

5.2 *Ammonium chloride* standard solution II, 1.00 ml = 0.010 mg N: Dilute 10.00 ml NH_4Cl standard solution I to 1,000 ml with ammonia-free water. Prepare fresh.

5.3 *Borate* buffer solution: Dissolve 9.54 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in ammonia-free water. Adjust the pH to 9.5 with 1M NaOH (approx 15 ml) and dilute to 1 liter with ammonia-free water.

5.4 *Boric acid* solution: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to 1 liter.

5.5 *Copper sulfate* solution: Dissolve 10 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in ammonia-free water and dilute to 100 ml.

5.6 *Nessler* reagent (CAUTION: HgI_2 is a deadly poison, and the reagent must be so marked): Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 ml ammonia-free water and dilute to 1 liter. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.7 *Sodium hydroxide* solution, 10N: Dissolve 400 g NaOH in ammonia-free water and dilute to 1 liter.

5.8 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

All glassware should be rinsed with ammonia-free water.

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using Nessler reagent (CAUTION: Deadly poison).

6.2 The residue from the ammonia nitrogen determination may be used for this determination. Alternatively, buffer a volume of sample containing less than 1.0 mg organic nitrogen (500.0 ml maximum) to pH 9.5 with borate buffer solution and evaporate to approximately 20 percent of original volume to drive off ammonia.

6.3 Cool; add 10 ml concentrated H_2SO_4 and 1 ml CuSO_4 solution.

6.4 Digest under a hood until copious fumes are given off and the liquid becomes colorless or pale yellow.

6.5 Cool and dilute to approximately 300 ml with ammonia-free water.

6.6 Add 50 ml 10N NaOH cautiously down the side of the flask.

6.7 Immediately connect the flask to the distillation apparatus, and cautiously mix the contents by swirling gently.

6.8 Distill at a rate of no more than 10 ml nor less than 6 ml per minute; catch the distillate in a 500-ml volumetric flask containing 50 ml boric acid solution. The tip of the delivery tube must be below the surface of the boric acid.

6.9 Collect approximately 250 ml distillate, dilute to 500 ml with ammonia-free water, and mix.

6.9.A *Nesslerization procedure*. Proceed as directed in "Nitrogen, Ammonia," steps 6.6.A.1-6.6.A.5.

6.9.B *Titration procedure*. Proceed as directed in "Nitrogen, Ammonia," step 6.6.B.1.

7. Calculations

7.A *Nesslerization procedure*

7.A.1 Determine a reagent blank for each new batch of H_2SO_4 by taking 300 ml ammonia-free water through the entire procedure:

$$\text{mg reagent blank} = \text{mg N per 10 ml H}_2\text{SO}_4$$

$$\times \frac{\text{ml aliquot}}{\text{ml distillate}}$$

7.A.2 Determine the mg N in the aliquot from a plot of absorbances of standards.

7.A.3

Organic nitrogen as N, in mg/l

$$= \frac{1,000}{\text{ml sample}} \times \frac{500}{\text{ml aliquot}}$$

$\times [(\text{mg N in aliquot}) - (\text{mg reagent blank})]$.

7.B *Titration procedure*

7.B.1 Ammonia nitrogen as N, in mg/l

$$= \frac{V_a \times N_a \times 14,000}{V_s}$$

where

V_a = ml standard H_2SO_4 used in titration of sample minus ml used to titrate blank,

N_a = normality of standard H_2SO_4 , and

V_s = ml of original sample used for distillation.

7.C Ammonia nitrogen as NH_4^{+1} , in mg/l = mg/l as N $\times 1.288$.

Ammonia nitrogen as free NH_3 , in mg/l = mg/l as N $\times 1.216$.

8. Report

Report organic nitrogen concentrations as follows: Less than 1.0 mg/l, two decimals; 1 mg/l and above, two significant figures.

9. Precision

No precision data are available.

Reference

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co., 759 p.

Oxygen demand, chemical (COD)

The oxygen-demand determination is a measure of the readily oxidizable material in the water, and it furnishes an approximation of the minimum amount of organic and reducing material present. In reality, the term "chemical oxygen demand" is defined by the method used for its determination. In the method given below it is defined as the amount of oxygen used by the sample when refluxed 2 hr with an excess of acid-potassium dichromate solution. The determined value may correlate with natural-water color or with car-

bonaceous organic pollution from sewage or industrial wastes.

Normal, unpolluted river waters generally have a COD from about 10 to 30 mg/l; mildly polluted river waters, 25 to 50 mg/l; and domestic sewage about 250 mg/l (R. C. Kroner, written commun., 1970).

Tolerances for oxygen-demand values in feed water for low- and high-pressure boilers are 15 and 3 mg/l, respectively. Wash water containing more than 8 mg/l has been reported to impart a bad odor to textiles; concentrations for water used in beverages and brewing range from 0.5 to 5.0 mg/l (California State Water Quality Control Board, 1963).

Dichromate oxidation method

1. Summary of method

Organic and other oxidizable material is oxidized by refluxing with standard acid-dichromate solution in the presence of silver sulfate catalyst. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as indicator (American Society for Testing and Materials, 1968).

2. Application

This method can be used for analysis of natural waters and industrial wastes containing less than 2,000 mg/l chloride ion and more than 50 mg/l chemical oxygen demand (COD). Samples containing less than this amount should be analyzed as directed in step 6.9. COD values for waters containing more than 2,000 mg/l of chloride ion should be corrected as indicated in step 6.10.

3. Interferences

Reducing substances such as ferrous iron and chlorides interfere since they are oxidized. Chlorides constitute by far the largest and most common interference, being quantitatively oxidized by dichromate in acid solution. One mg/l Cl^{-1} is equivalent to 0.226 mg/l COD. To eliminate chloride interference, mercuric sulfate is added to the sample to form a soluble mercuric chloride complex.

Care should be taken to prevent heating of the sample during addition of reagents to minimize loss of volatile constituents.

4. Apparatus

4.1 *Reflux* apparatus consisting of a 500-ml erlenmeyer flask and water-cooled condenser, with ground-glass joints and made of heat-resistant glass.

4.2 *Hot plate* or heating mantle.

5. Reagents

5.1 *Ferrous ammonium sulfate* standard solution, 0.2500*N*: Dissolve 98.0 g $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in demineralized water. Add 20 ml concentrated H_2SO_4 , cool, and dilute to 1 liter. To standardize, dilute 25.0 ml standard 0.2500*N* $\text{K}_2\text{Cr}_2\text{O}_7$ solution to 250 ml. Add 20 ml concentrated H_2SO_4 and cool. Titrate with the ferrous ammonium sulfate solution, using 8–10 drops Ferrouin indicator. The solution must be standardized daily, or before use.

5.2 *Mercuric sulfate*, powdered HgSO_4 .

5.3 *Orthophenanthroline ferrous sulfate (Ferrouin) indicator* solution: Dissolve 1.48 g 1,10-(ortho)-phenanthroline monohydrate and 0.70 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml of water. The prepared indicator is available commercially.

5.4 *Potassium dichromate* standard solution, 0.2500*N*: Dissolve 12.259 g $\text{K}_2\text{Cr}_2\text{O}_7$ primary standard, dried for 2 hr at 100°C, in demineralized water and dilute to 1,000 ml.

5.5 *Silver sulfate*, powder.

5.6 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Pipet 50.0 ml of sample or a smaller aliquot diluted to 50.0 ml into the reflux flask and add slowly, over a period of 2–3 min, 1 g HgSO_4 ; allow to stand 5 min, swirling frequently.

6.2 Add 1 g Ag_2SO_4 and a few glass beads that have been ignited at 600°C for 1 hr.

6.3 Cool in ice water and add 75 ml concentrated H_2SO_4 , slowly enough, with mixing, to present appreciable solution heating with the consequent loss of volatile constituents.

6.4 Add 25.0 ml 0.2500*N* $\text{K}_2\text{Cr}_2\text{O}_7$ solution and mix thoroughly by swirling.

6.5 Attach flask to condenser, start water flow, and reflux for 2 hr.

NOTE.—If contents are not well mixed, superheating may result, and the contents of the flask may be blown out of the open end of the condenser.

6.6 Allow flask to cool, and wash down condenser with 25 ml water.

6.7 Dilute to 300 ml with demineralized water, cool to room temperature, and titrate the excess dichromate with 0.2500*N* ferrous ammonium sulfate solution, using 8–10 drops Ferrouin indicator solution. The end point is a sharp change from blue green to reddish brown.

6.8 A demineralized-water blank is carried through all steps of the procedure with each group of samples.

6.9 Samples containing less than 50.0 mg/l COD should be reanalyzed, using 0.025*N* solutions of potassium dichromate and ferrous ammonium sulfate. A sample size should be selected so that no more than half the dichromate is reduced. A further increase in sensitivity may be obtained by evaporating a larger sample to 150 ml in the presence of all reagents. A blank should be treated in a similar manner.

6.10 To obtain more accurate COD values for samples containing more than 2,000 mg/l of chloride ion, the following procedure may be used (Burns and Marshall, 1965). A series of chloride solutions are analyzed by the procedure indicated above, except that 10 mg of HgSO_4 is added to each solution for each milligram of chloride ion present instead of a constant 1-g quantity. The chloride concentrations should range from 2,000 mg/l to 20,000 mg/l, with the concentration interval not exceeding 4,000 mg/l. Plot the COD values obtained versus milligrams per liter chloride. From this curve, COD values may be obtained for any desired chloride concentration. This value is subtracted as a correction factor to obtain the COD value of a sample.

7. Calculations

Calculate the COD in each sample as follows:

7.1 For samples not requiring chloride correction:

$$\text{COD, in mg/l} = \frac{(a-b)c \times 8,000}{\text{ml sample}};$$

7.2 For samples requiring chloride correction:

$$\text{COD, in mg/l} = \left[\frac{(a-b)c \times 8,000}{\text{ml sample}} \right] - d \times 1.20,$$

where:

- COD = chemical oxygen demand from dichromate,
 a = ml ferrous ammonium sulfate for blank,
 b = ml ferrous ammonium sulfate for sample,
 c = normality ferrous ammonium sulfate,
 d = chloride correction value from graph of chloride concentration versus COD, and
 1.20 = empirical compensation factor.

8. Report

Report COD as follows: Less than 10 mg/l, whole numbers; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available. The general precision of COD determinations has been reviewed by the Analytical Reference Service of the U.S. Public Health Service (1965).

References

- American Society for Testing and Materials, 1968, Water; atmospheric analysis, pt. 23 of 1968 Book of standards: Philadelphia, Am. Soc. Testing Materials, p. 244.
 Burns, E. R., and Marshall, C., 1965, Correction for chloride interference in the chemical oxygen demand test: Water Pollution Control Federation Jour., v. 37, p. 1716.
 California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 233.
 U.S. Public Health Service, 1965, Water oxygen demand no. 2: Public Health Service Study 21, Pub. 999-WP-26.

Phenolic material

Phenolic material in water resources is usually a result of pollution from oil refineries, coke plants, and from chemical manufacture. Mixed phenolic wastes at 0.02–0.15 mg/l levels in water cause tainting of fish flesh. Low concentrations of phenol impart a very disagreeable taste to drinking water. Reported thresholds of taste and odor range from 0.01 to 0.1 $\mu\text{g/l}$. Chlorination produces an even more disagreeable taste and odor by reacting with the phenols to form chlorophenols. Concentrations of phenolic material up to 1,000 $\mu\text{g/l}$ are not believed toxic to animals, but 5.0

$\mu\text{g/l}$ is harmful to many fish (Federal Water Pollution Control Administration, 1968).

1. Summary of method

The steam-distillable phenols react with 4-aminoantipyrine at pH 10.0 ± 0.2 in the presence of potassium ferricyanide to form a colored anti-pyrine dye. This dye is extracted from aqueous solution with chloroform, and the absorbance is measured at a wavelength of 460 nm. The concentration of phenolic compounds is expressed as micrograms per liter of phenol ($\text{C}_6\text{H}_5\text{OH}$). This method is similar in principle to, but different in detail from, ASTM Method D 1783-62 (1969, p. 515-521).

2. Application

This method may be used to analyze waters containing from 0.0 to 1,000 $\mu\text{g/l}$ of phenolic material.

3. Interferences

Other phenolic compounds, as determined by this method, may produce less color than an equivalent amount of phenol itself. The introduction of substituent groups to the benzene nucleus of phenol lowers the sensitivity of the particular compound to color formation. The composition of various phenolic compounds which may be present in a given water sample is unpredictable. Phenol itself, therefore, has been selected as the standard for reference. Using this basis, the amount of phenol determined represents the minimum concentration of phenolic compounds present in the sample.

Certain bacteria, oxidizing and reducing substances, and highly alkaline waste waters may interfere with this method. Information for removal of major interference may be found in ASTM Method D 1783-62 (1969, p. 515-521).

4. Apparatus

4.1 *Distillation apparatus*, all glass, consisting of a 1-liter Pyrex distilling apparatus and a water-cooled condenser.

4.2 *Funnels*, Buchner type with fritted-glass disk (15-ml Corning 36060, or equivalent).

4.3 *Photometer*, spectrophotometer or filter photometer suitable for use at a wavelength setting to 460 nm, and accommodating cells having light paths of 1.0 and 10 cm.

4.4 *pH* meter, glass electrode.

4.5 *Separatory funnels*, 1-liter capacity, Squibb type, with unlubricated glass or teflon stopcock.

5. Reagents

All reagents must be prepared with phenol-free distilled water. De-ionized water is usually not satisfactory.

5.1 *Aminoantipyrine* solution: Dissolve 2.0 g 4-aminoantipyrine in distilled water and dilute to 100 ml. This solution is not stable for storage and should be prepared each day of use.

5.2 *Ammonium chloride* solution: Dissolve 20 g of reagent-grade ammonium chloride in water and dilute to 1 liter.

5.3 *Ammonium hydroxide*, concentrated (sp gr 0.90), ACS reagent grade.

5.4 *Chloroform*, spectrophotometric grade.

5.5 *Copper sulfate* solution: Dissolve 100 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water and dilute to 1 liter.

5.6 *Phenol* standard solution, 1.00 ml = 1.00 mg phenol: Dissolve 1.00 g analytical reagent phenol in 1,000 ml freshly boiled and cooled distilled water. Solution may be used for up to 1 month.

5.7 *Phosphoric acid* solution: Dilute 10 ml 85-percent H_3PO_4 to 100 ml with distilled water.

5.8 *Potassium ferricyanide* solution: Dissolve 8.0 g $\text{K}_3\text{Fe}(\text{CN})_6$ in water, dilute to 100 ml, and filter. This solution is not stable and should be prepared each day of use.

5.9 *Sodium sulfate*, anhydrous, ACS reagent grade, granular.

6. Procedure

Samples should be collected according to the recommended practice for organic samples. Samples must be preserved with 10 ml of copper sulfate and 2 ml of phosphoric acid solution. A sealed glass ampoule of the preservative, with instructions, should accompany the sample container. A 1-liter sample should be collected for each analysis. Samples should be protected from light and analyzed as soon as possible. The analyst is referred to "Standard Methods," 12th edition (Am. Public Health Assoc., 1965), for the analysis of very alkaline or highly polluted water.

6.1 Measure 500 ml of the sample into a beaker. Determine the pH and adjust below 4.0

if necessary. (Add 5.0 ml of copper sulfate solution if for any reason it was not added at sampling.) Transfer the solution to the distillation apparatus, add boiling stones, and set for distillation. Collect 450 ml of distillate and stop. Add 50 ml of distilled water to the residue and proceed with the distillation until 500 ml of distillate is collected.

6.2 Prepare a 500-ml distilled-water blank. Also prepare 500-ml standards containing 5, 10, 20, 30, 40, and 50 μg of phenol, using the standard phenol solution.

6.3 Treat the sample, blank, and standards as follows: Add 10.00 ml ammonium chloride solution and adjust the pH to 10.0 ± 0.2 with concentrated ammonium hydroxide. Transfer the solution to a 1-liter separatory funnel, add 3.00 ml of aminoantipyrine solution, mix, add 3.00 ml of potassium ferricyanide solution, and again mix. Allow the color to develop for 3 min, and a clear to light-yellow solution should result.

6.4 Add 25.0 ml chloroform for 1- and 5-cm cells and 50.0 ml for 10-cm cells. Shake the separatory funnel vigorously for 1 min. Allow the layers to separate and repeat the shaking.

6.5 After the layers have separated, draw off the lower chloroform layer and filter through a 5-g layer of sodium sulfate, using the sintered glass funnel, directly into the appropriate absorption cell. Avoid working in a draft to reduce evaporation of the solvent.

6.6 Measure the absorbance of the sample and standards against the blank at a wavelength of 460 nm. Prepare a calibration curve plotting absorbance against micrograms of phenol.

7. Calculations

$$\text{Phenol } (\mu\text{g/l}) = \frac{A}{B} \times 1,000,$$

where

A = μg phenol measured, and

B = ml of the original sample used.

8. Report

Report phenolic material concentration for less than 100 $\mu\text{g/l}$ to the nearest whole microgram, and greater than 100 $\mu\text{g/l}$ to two significant figures.

9. Precision

Precision at 5 mg/l for phenol only is ± 5 percent but is variable for other phenolic materials.

Because of interferences and because it is only a relative measure, the result should be considered as a minimum value.

References

- American Public Health Association, 1965, Standard methods for the examination of water and wastewater [12th ed.]: New York, Am. Public Health Assoc., Inc., 769 p.
- American Society for Testing and Materials, 1969, Water; atmospheric analysis, pt. 23 of 1969 Book of standards: Philadelphia, 1032 p.
- [U.S.] Federal Water Pollution Control Administration, 1968, Report of the committee on water-quality criteria: Washington, U.S. Govt. Printing Office, 234 p.

Pesticides—Gas chromatographic analysis

The term "pesticide" encompasses a broad class of toxicants used to control insects, mites, fungi, weeds, aquatic plants, and undesirable animals. More specific designations include such terms as insecticides, miticides, fungicides, herbicides, and rodenticides.

Synthetic organic pesticides have introduced a far-reaching technological advance in the control of pests. Although the compound DDT (dichlorodiphenyltrichloroethane) was first synthesized in 1874, its insecticidal properties were not discovered until 60 years later. Since the introduction of synthetic chemical pesticides in the United States, annual production has reached 1 billion pounds. There are almost 60,000 pesticides formulations registered, and each contains at least one of approximately 800 different pesticide compounds (Simmons, 1969).

With the increased concern by noted world ecologists over the effects of toxic pesticides on the environment, efforts are being made to substitute more specific, fast-acting, and easily degradable compounds for the chlorinated hydrocarbon pesticides. These pesticides were developed for general application and have proved to be very resistant to environmental degradation.

1. Summary of method

Prepared extracts of water or sediment are analyzed for pesticides by gas chromatography.

The technique of gas chromatography is most useful for qualitative and quantitative analysis of multicomponent mixtures. Small volumes of extract, as little as 1 μ l, are injected into the gas chromatograph, where the components are separated and detected. The separation of vaporized material takes place in the chromatographic column as it is carried along by a flow of inert gas. Actual separations occur as the component vapors partition between the vapor phase and a non-volatile stationary liquid incorporated in the column. Each component, according to its physical and chemical properties, enters and leaves the stationary liquid at a unique rate. Because this partitioning is occurring between a moving vapor and a stationary liquid, components injected at one end of a column emerge from the other end at different times.

Several different devices are available for detecting and measuring pesticides as they emerge from the column. The electron-capture detector is highly sensitive, responding to as little as 0.1 pg (picogram) of lindane, and is used extensively for detecting the presence of pesticides in water. Other somewhat less sensitive detectors, such as microcoulometric and flame photometric, are used in pesticide analysis because they respond only to specific elements incorporated in the pesticide molecules, and thus aid identification. There are numerous books and papers on the analysis of pesticides by gas chromatography. One such treatment is "Pesticide Residue Analysis Handbook" (Bonelli, 1965). The book, "A Programmed Introduction to Gas-liquid Chromatography" (Pattison, 1969), is a good source for beginning gas chromatographers.

2. Application

Organic insecticides and herbicides which are volatile or can be made volatile for gas chromatographic purposes may be analyzed by this technique.

3. Interferences

The most seriously interfering substances for chlorinated pesticide analysis are halogenated organic compounds, such as "polychlorinated biphenyls" from industrial waste. Any compound or compounds having chemical properties similar to the pesticides of interest may cause inter-

ference. The electron-capture detector is extremely sensitive but much less specific than the other detectors mentioned above and, as a result, is much less reliable when interfering substances are present. Special precautions are necessary to avoid contamination during sample handling and to remove extraneous material from the sample extract.

4. Apparatus

4.1 *Electron-capture gas chromatograph*: A gas chromatograph having an electron-capture detector which, for an injection of 0.1 ng (nanogram) of aldrin, gives 100 mv-sec (millivolt-seconds) of response is adequate. A Varian-Aerograph Model 600-D, or equivalent, may be used. (A radioisotope-byproduct-material license is required for electron-capture detectors employing H^3 or Ni^{63} sources.)

4.2 *Flame-photometric gas chromatograph*: A gas chromatograph equipped with a Melpar flame-photometric detector having filters for the specific detection of phosphorus or sulfur. Such an instrument is the Micro-Tek Model MT-220 flame-photometric gas chromatograph. A provision for venting solvent effluent between the column and the detector should be specified.

4.3 *Microcoulometric-titrating gas chromatograph*: A gas chromatograph connected to a Dohrmann microcoulometer detection system. The system employs a Model S-200 sample-combustion unit, a Model C-200 coulometer-amplifier, and a choice of titration cells, namely: for halides, the T-300-S cell; for sulfur, the T-300-P cell; and for nitrogen, the T-400-H cell. This unit may be used with the Micro-Tek Model MT-200 gas chromatograph, or equivalent.

4.4 *Gas chromatographic columns*: The gas chromatographic columns are fabricated from 1.5-m (meter) lengths of Pyrex glass tubing. For electron capture, 1.8-mm ID (inside diameter) tubing is used preferably, whereas for other modes of detection either 1.8-mm ID or 4-mm ID glass tubing may be used. The smaller bore columns accept injection volumes up to 10 μ l and the larger bore columns will accept volumes up to 80 μ l.

Gas Chrom Q support, 60/80 mesh, is used for the preparation of two different column packings as follows: (1) With 5 percent by weight DC-200

silicone oil (viscosity 12,500 centistokes) and 0.5 percent by weight Carbowax 20 M; and (2) with 5 percent by weight QF-1 fluorinated silicone oil (also designated FS-1265) and 0.5 percent by weight Carbowax 20 M. The support should be coated with the liquid phase by the "frontal analysis" technique (Smith, 1960). The packing materials are loaded in the glass columns using vibration and a vacuum to settle. The packing is held in place by small plugs of "silanized" glass wool.

The columns are installed in the gas chromatograph and are conditioned as follows: (1) Purge the columns for 30 min with inert carrier gas. (2) Turn off carrier gas flow and heat the columns to 250°C for 2 hr. (3) Reduce the temperature to 210°C and allow temperature to equilibrate for 30 min. (4) Turn on carrier gas flow to about 30 ml/min (milliliters per minute) and continue heating the column at 210°C for 12 hr. The column should not be connected to the detector during column conditioning.

After conditioning, the columns are ready for use. Performance and retention-time characteristics must be determined for each column by use of standards. Retention data in tables 1, 2,

Table 1.—Retention values for chlorinated hydrocarbon insecticides, relative to aldrin¹

Columns..... 1.8-m long \times 1.8-mm ID
Carrier gas flow..... 30 ml/min nitrogen.
Column temperature..... 185°C.
Electron-capture detector.

Insecticides	Relative retention time	
	5 percent DC-200	5 percent QF-1
Lindane.....	0.46	0.80
Heptachlor.....	.79	.87
Aldrin ¹	1.00	1.00
Isodrin.....	1.18	1.34
Heptachlor epoxide.....	1.28	2.06
Dieldrin.....	1.92	3.31
<i>p,p'</i> -DDE.....	1.98	2.30
Endrin.....	2.15	3.93
<i>p,p'</i> -DDD.....	2.53	4.24
<i>o,p'</i> -DDT.....	2.69	3.01
<i>p,p'</i> -DDT.....	3.41	4.69
Methoxychlor.....	5.36	7.96

¹ Aldrin retention times: DC-200, 4.18 min; QF-1, 2.60 min.

Table 2.—Retention values for phosphorothioate insecticides, relative to parathion

Insecticides	Relative retention time	
	5 percent DC-200	5 percent QF-1
Columns.....	1.8-m long × 4.0-mm ID	
Carrier gas flow.....	75 ml/min nitrogen.	
Column temperature.....	185°C.	
Flame-photometric detector.		
Dioxathion.....	0.50	0.40
Diazinon.....	.55	.22
VC-13.....	.71	.34
Methyl Parathion.....	.72	1.04
Malathion.....	.93	.79
Parathion ¹	1.00	1.00
Methyl Trithion.....	2.2	2.7
Ethion.....	2.6	1.84
Carbophenothion.....	2.9	2.48

¹ Parathion retention times: DC-200, 3.82 min; QF-1, 4.55 min.

and 3 may be used as a guide for evaluating the columns. Column efficiency is measured by employing the following equation:

$$n = 16 \left(\frac{tr}{\Delta t} \right)^2$$

where

- n = number of theoretical plates,
 tr = uncorrected retention time of peak, and
 Δt = peak retention width (length of baseline cut by the two tangents of the peak at the half-height points).

Using a *p,p'*-DDT standard to test the column efficiency, a value of no less than 1,500 theoretical plates for a 1.8-m column is considered acceptable for pesticide analysis.

4.5 *Microliter capillary pipets*: Volumetric micropipets in 1, 5, 10, and 25 μ l sizes; the disposable types are satisfactory.

4.6 *Microliter syringes*: Three microsyringes having capacities of 10, 50, and 100 μ l, respectively, are used. The syringe needle should be about 2 inches long and have a point shaped to prevent punching out a core when penetrating the injection septum.

4.7 *Compressed gases*: Use only the gases recommended by the vendor for the particular instrument system being used. Also, select pre-

purified grade or better, furnished in size 1A high-pressure cylinders. (CAUTION: Never use oxygen regulators for other gases.)

4.8 *Microbalance*: A Cahn Gram Electrobalance, or equivalent.

4.9 *Volumetric glassware*: Class A volumetric flasks in 5, 10, and 25 ml sizes. The stoppers should fit well because volatile organic solvents are used for dilutions. Volumetric ware such as supplied by Kontes Glass Co., or equivalent, is acceptable.

4.10 *Integrating equipment*: A compensating polar planimeter readable to the nearest 0.01 square inch is acceptable. Other instruments or methods of integration demonstrating greater accuracy may be used.

4.11 *Recorder*: A 1-mv (millivolt) full-scale response, 1-sec (second) pen speed, strip-chart recorder. Such a recorder having a fixed or selectable chart speed of one-half inch per minute is acceptable.

5. Reagents

Solvents and reagents are specified for the particular isolation technique used. Recommendations of the manufacturer should be followed for special reagents to be used with a particular gas chromatographic system.

5.1 *Benzene*, pesticide-analysis quality: Nanograde, distilled in glass, or equivalent. Benzene is usually the solvent of choice for preparation of concentrated standard solution because it is relatively nonvolatile and the pesticide solution can be stored for long periods in a safety refrigerator.

Table 3.—Retention values for methyl esters of chlorinated phenoxy acid herbicides, relative to 2,4-D

Herbicides	Relative retention time	
	5 percent DC-200	5 percent QF-1
Columns.....	1.8-m long × 1.8-mm ID	
Carrier gas flow.....	30 ml/min nitrogen.	
Column temperature.....	145°C.	
Electron-capture detector.		
2,4-D ¹	1.00	1.00
Silvex.....	1.42	1.22
2,4,5-T.....	1.91	1.80

¹ 2,4-D retention times: DC-200, 3.92 min; QF-1, 3.05 min.

5.2 *Pesticide standards*: Reference or analytical-grade pesticide chemicals may be obtained from gas chromatography specialty suppliers and often also by written request from the manufacturer. It is desirable to obtain a particular pesticide from at least two different suppliers. The pesticide standards should be refrigerated during prolonged storage, and appropriate hazard warnings should be posted on the refrigerator.

6. Procedure

6.1 Standardization

Each gas chromatographic system must be calibrated to reference standards at the operating conditions to be used for analysis.

6.1.1 *Picogram standards*: Weigh 1.00 mg of pesticide on the microbalance and transfer into a 10.00-ml volumetric flask. Dilute to volume with benzene and mix thoroughly. Prepare a series of required picogram standards from this solution. (Example: Take 1.00 μl of the above pesticide solution and dilute to 10.00 ml with the solvent to be used in the analysis. The concentration of pesticide in the resulting solution is 10×10^{-12} g/ μl (grams per microliter), or 10 pg/ μl (picograms per microliter).)

6.1.2 *Nanogram standards*: Weigh 5.00 mg of reference pesticide into a 5.00-ml volumetric flask and dilute to volume with benzene. Make a series of appropriate nanogram standards from this solution. (Example: Take 10.0 μl and dilute to 10.00 ml with the solvent to be used in the analysis. The concentration of pesticide in the resulting solution is 1.0×10^{-9} g/ μl , or 1.0 ng/ μl (nanogram per microliter).)

6.1.3 *Calibration*: The picogram standards are used for electron-capture gas chromatography, and the nanogram standards are used for flame-photometric and microcoulometric gas chromatography. A 5.0- μl volume of each of the appropriate standard solutions is injected into the gas chromatograph. The concentration of pesticide in the series of standard solutions should be such to calibrate either the full range of linear detector response or the range of anticipated pesticide concentration in the sample, whichever is less. The injection should be made so that the solution enters the injection port in a single volume and in a reproducible manner. The volume injected should be measured by reading the syringe before and after injection. All information pertinent to

the standardization should be written directly on the recorder chart. Calibration should be performed on both the DC-200 and the QF-1 columns.

6.2 Sample analysis

The sample extracts are analyzed in the same manner as the standards and under the same operating conditions.

6.2.1 The first analysis is performed by electron-capture gas chromatography using the DC-200 column. Concentration or dilution of the extract may be required to allow a 5.0- μl injection. Proceed with the analysis by injecting 5.0 μl of the sample into the chromatograph, recording the extract volume and the volume injected. Do not make any subsequent injections until the last compound has eluted and the baseline has returned to normal.

6.2.2 Run a calibration-retention-time standard and a reagent blank as an analysis check. Should a pesticide be detected in the sample, a standard containing the same pesticide at nearly the same concentration is also analyzed just after the sample.

6.2.3 Pesticides detected in concentrations ranging from 0.01 $\mu\text{g}/\text{l}$ to 1.0 $\mu\text{g}/\text{l}$ for water samples, or from 0.10 $\mu\text{g}/\text{kg}$ (microgram per kilogram) to 1.0 $\mu\text{g}/\text{kg}$ for sediment, must be analyzed a second time by electron-capture gas chromatography, on the QF-1 column, for confirmation.

6.2.4 The presence of pesticides at concentrations greater than 1.0 $\mu\text{g}/\text{l}$ in water or 1.0 $\mu\text{g}/\text{kg}$ in sediment samples must be confirmed by microcoulometric or flame-photometric gas chromatography on both the DC-200 and QF-1 columns. This requirement is not intended to restrict the use of specific detectors but rather to indicate concentrations above which they must be used. Specific detection should always be used whenever practical. Volumes of extract up to 10 μl for the smaller diameter columns and up to 80 μl for the larger diameter columns may be injected. In this instance, a check standard at nearly the same concentration should also be run.

7. Calculations

Each gas chromatographic system must be calibrated with standards. The response of the gas chromatographic detector is usually the display of an analog signal on a strip-chart recorder.

The signal is recorded as a differential curve or peak. The area inscribed beneath the peak is proportional to the amount of material passing through the gas chromatographic detector. The time elapsed from the introduction of the sample to the differential curve maximum is designated as the retention time for a particular component. The retention time for a compound on a specified column is nearly unique and is used for qualitative analysis. Also, the retention time relative to another selected compound is often used because this expression reduces variation usually found in day to day operation. The response of the chromatograph must be standardized at optimum conditions and enough determinations made so that the data may be treated by the method of least squares. During analysis, the standard curve must be checked by running at least two standards at different concentrations so corrections can be made for day to day fluctuations.

7.1 Qualitative analysis

Directly comparing the retention times of a sample component and a reference standard on both DC-200 and QF-1 columns is the method used for qualitative identification. Additionally, specific detection is employed to further confirm the presence of a particular component at levels greater than 1.0 $\mu\text{g}/\text{l}$ for water samples and 1.0 $\mu\text{g}/\text{kg}$ for sediment. Relative retention time, the ratio of the retention time of an unknown to that of a selected standard, may be used to determine which reference standard to choose for comparison. The pesticides selected for this purpose are: Aldrin for the chlorinated hydrocarbon insecticides, parathion for the phosphorothioate insecticides, and the methyl ester of 2,4-D for the chlorinated phenoxy acid herbicides. The following equation is used in qualitative identification:

$$RRT \text{ (relative retention time)} = \frac{RT_u}{RT_r}$$

where

RT_u = retention time of the unknown compound, and

RT_r = retention time of the reference compound.

7.2 Quantitative analysis

Measurement of gas chromatogram peak areas

by use of a planimeter or by any method of equal or greater accuracy is acceptable. If a planimeter is used, the average of at least two measurements is taken as the peak area.

Interpretation of the chromatogram is very important to the precision of area measurement. Reliable interpretation comes with experience and much can be gained by careful study of the elution patterns and peak shapes of individual mixed standards. In general, peaks may appear in four different ways, which are: (1) A single peak, (2) two or more discrete peaks not completely separated, (3) a small peak or shoulder on the leading or trailing edge of a relatively large peak, and (4) two or more peaks perfectly overlapping one another. The presentation of a single peak is ideal and allows precise area measurement. Peaks not completely resolved are graphically separated by drawing a line from the valley point between two adjacent peaks down to the baseline. It is very difficult to isolate a shoulder from the larger peak in a reproducible manner. Also the retention time is biased toward the larger component. In this situation a line is drawn to conform with the shape of the major peak. Although the area under the larger peak is usually quite reliable, that of the shoulder is not. Other steps should be taken, such as gas chromatography using a different column or techniques of column or thin-layer chromatography, to isolate the shoulder compound for quantitative determination. The same consideration must be given to overlapping peaks. Components eluting at nearly the same time to form a single peak are easily misinterpreted. Correlation of retention times and peak areas on both the DC-200 and QF-1 columns is extremely important in this instance. To obtain reliable qualitative and quantitative analysis, other isolation techniques may have to be employed whenever this occurs (Federal Water Pollution Control Administration, 1969).

7.2.1 Standard curve

Using log-log graph paper, plot area of response, in square inches (in^2), against nanograms of pesticide injected. If six or more values fall in the linear response region of the detector, the equation of the line may be found by the method of least squares, as follows:

$$m = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}$$

and

$$b = \frac{\sum x^2 \sum y - \sum x \sum xy}{n \sum x^2 - (\sum x)^2}$$

where

x = injection amounts (ng),
 y = area response values (in²),
 b = y intercept,
 m = slope, and
 n = number of points selected.

For the equation of the straight line,

$$y = mx + b,$$

the value for b , the y intercept, is an indication of whether any experimental bias exists. It is usually small enough to be insignificant so that the equation of the standard curve may be expressed as:

$$y = mx.$$

The two or more daily response check standards are used to correct the slope of the standard curve, as follows:

$$C = \frac{A_s}{A_c}$$

where

C = correction factor,
 A_c = area of check standard obtained from the standard curve, and
 A_s = area obtained from chromatogram of the check standard.

The slope of the standard curve is corrected by multiplying it by the correction factor.

7.2.2 Calculations for samples

The concentration of pesticides in water samples may be determined using the following equation:

$$\begin{aligned} \text{Concentration of pesticide } (\mu\text{g/l}) \\ = A \times \frac{1}{Cm} \times \frac{V_{ext}}{V_{inj}} \times \frac{1}{V_s}, \end{aligned}$$

where

A = area of component (in²),
 Cm = corrected slope (in²/ng),
 V_{ext} = volume of extract (ml),
 V_{inj} = volume injected (ml), and
 V_s = volume of water sample (liters).

This equation may be used to calculate the concentration of pesticides in sediment or soil by

substituting the weight of sample in kilograms for the sample volume (V_s) with the resulting concentration expressed as $\mu\text{g/kg}$.

8. Report

Pesticides found in water samples are reported as follows: At concentrations of less than 1.0 $\mu\text{g/l}$, two decimals and report less than 0.005 $\mu\text{g/l}$ as 0.00 $\mu\text{g/l}$; at concentrations of 1.0 $\mu\text{g/l}$ and greater, two significant figures. Pesticides in sediment and soil samples are reported as follows: Less than 1.0 $\mu\text{g/kg}$ to one decimal; 1.0 $\mu\text{g/kg}$ and above, two significant figures. The identities of pesticides found in concentrations greater than 0.01 $\mu\text{g/l}$ in water or 0.1 $\mu\text{g/kg}$ in sediment must be confirmed by two-column gas chromatography. For concentrations greater than 1.0 $\mu\text{g/l}$ in water and 10 $\mu\text{g/kg}$ in sediment, specific detection must be employed. Identities of compounds in concentrations greater than 10 $\mu\text{g/l}$ in water and 100 $\mu\text{g/kg}$ in sediment must be confirmed by mass spectrometry.

9. Precision

Precision of the gas chromatographic technique is variable for multicomponent analysis. The response of one component may be considerably greater or less than that of another. Peaks of compounds having longer retention times are affected more by instrumental noise and drift. Under ideal conditions repetitive analysis of a single component may be determined to a precision of ± 3 percent.

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Insecticides in water

Gas chromatographic method

1. Summary of method

The insecticides are extracted directly from the water sample with n-hexane. After drying and removing the bulk of the solvent, the insecticides are isolated from extraneous material by micro-column adsorption chromatography. The insecticides are then analyzed by gas chromatography. This method is a modification and extension of the procedures developed by Lamar, Goerlitz, and Law (1965, 1966). For the analysis of insecticides in waters that are grossly polluted by organic compounds other than pesticides, the analyst is referred to the high-capacity cleanup procedure detailed in Federal Water Pollution Control Administration "Method for Chlorinated Hydrocarbon Pesticides in Water and Wastewater" (1969).

2. Application

This method is usable for the analysis of water only. The insecticides and associated chemicals (aldrin, *p,p'*-DDD, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, isodrin, lindane (BHC), and methoxychlor) may be determined to 0.005 µg/l in 1-liter water samples. The insecticides carbophenothion, chlordan, dioxathion, diazinon, ethion, malathion, methyl parathion, Methyl Trithion, parathion, toxaphene, and VC-13 may be determined when present to higher levels (method for organophosphorus pesticides similar to that of Zweig and Devine, 1969). Also, the chemicals chlordene, hexachlorobicycloheptadiene, and hexachlorocyclopentadiene, which are pesticide manufacturing precursors, may be analyzed by this method.

3. Interferences

Any compound or compounds having chemical and physical properties similar to the pesticide of interest may cause interference. The procedure incorporates a column chromatographic technique which eliminates most extraneous material. Special precautions are necessary to avoid contamination during sampling and analysis.

4. Apparatus

See step 4, "Gas Chromatographic Analysis of Pesticides."

4.1 *Concentrating apparatus*: A Kuderna-Danish concentrator, 250-ml capacity with a 1-ball Snyder column, is used for the initial concentration step. Final concentration is performed in the receiver using a 1-ball Snyder micro-column. A calibrated 4.00-ml receiver tube is used with the concentration apparatus.

4.2 *Cleanup microcolumns*: Disposable Pasteur pipets, 14-cm long and 5-mm ID, are used for the chromatographic cleanup columns. The pipets are washed in warm detergent solution, thoroughly rinsed with dilute hydrochloric acid and organic-free distilled water, then heated to 300°C overnight to remove any traces of organic matter. A column is prepared by plugging the pipet with a small amount of specially cleaned glass wool, adding enough deactivated alumina through a microfunnel to fill 3 cm of the column, followed by another 0.5 cm of anhydrous sodium sulfate.

4.3 *Sandbath*, fluidized, Tecam, or equivalent.

4.4 *Separatory funnels*, Squibb form, 1- or 2-liter capacity. No lubricant is used on the stopcocks.

5. Reagents

5.1 *Alumina*, neutral aluminum oxide, activity grade I, Woelm. Weigh 19 g activated alumina into a 50-ml glass-stoppered erlenmeyer flask and quickly add 1.0 ml distilled water. Stopper the flask and mix the contents thoroughly by tumbling. Allow 2 hr before use. The deactivated alumina may be used for 1 week.

5.2 *Benzene*, distilled in glass, pesticide-analysis quality.

5.3 *n-Hexane*, distilled in glass, pesticide-analysis quality.

5.4 *Sodium sulfate*, anhydrous, granular. Prepare by heating at 300°C overnight and store at 130°C.

5.5 *Water*, distilled, obtained from a high-purity tin-lined still. The feed water is passed through an activated carbon filter. The distillate is collected in a tin-silver-lined storage tank, and the water is constantly irradiated with ultraviolet

light during storage. A gravity delivery system is used, and no plastic material other than teflon is allowed to contact the distilled water.

6. Procedure

Samples should be collected according to the recommended practice for the collection of samples for organic analysis. A 1-liter bottle of water should be collected for each sample. No preservative is used. Samples should be shipped promptly. Unless analyzed within a few days, the water should be protected from light and refrigerated. If the sample contains sediment, then the sediment must be analyzed separately. Remove the sediment by centrifugation or filtration through a metal membrane filter. See step 6.1, "Chlorinated Hydrocarbon Insecticides in Suspended Sediment and Bottom Material."

All glassware, except volumetric flasks, should be washed in the usual manner, rinsed in dilute hydrochloric acid and distilled water, and heat treated at 300°C overnight. Instead of heat treating, the volumetric ware may be solvent rinsed or steamed to remove organic matter. A reagent and glassware blank should accompany each analysis.

6.1 Water samples (800–900 ml) are extracted with n-hexane in such a manner that the water and the container itself are exposed to the solvent. Weigh the uncapped bottle of water on a triple-beam balance and pour the sample into a 1-liter separatory funnel. Allow the bottle to drain for a few minutes, weigh again, and record the weight of water to three significant figures.

6.2 Add 25 ml n-hexane to the empty sample bottle and gently swirl to wash the sides of the container with the solvent. Pour the contents of the sample bottle into the separatory funnel containing the water. Stopper and shake the separatory funnel vigorously for 1 full min, venting the pressure often. Allow the contents to separate for 10 min and draw off the aqueous layer into the original sample bottle. If the hexane layer emulsifies, separate as much water as possible, then shake the contents of the funnel very vigorously so that the liquids contact the entire inside surface of the vessel. (CAUTION: Vent often!) Allow the layers to separate and add approximately 5 ml distilled water to aid the separation, if necessary. Remove the water and

pour the extract from the top of the separatory funnel into a 125-ml erlenmeyer flask containing about 0.5 g anhydrous sodium sulfate.

6.3 Repeat a second and third extraction of the water sample in the same manner using 25 ml n-hexane each time, and collect the extracts in the 125-ml erlenmeyer flask containing the drying agent. Cover the flask containing the extract with foil and set aside for 30 min.

6.4 Filter the dried extract through glass wool into the Kuderna-Danish apparatus. Add a sand-sized boiling stone and remove most of the hexane by heating on a fluidized sandbath at 100°C in a hood. When the ball in the Snyder column just stops bouncing, remove the apparatus from the heat and allow to cool. Add another small boiling stone, fit the receiver with a Snyder microcolumn and reduce the volume to between 0.4 and 0.5 ml on the sandbath. Set aside to cool. When changing columns, sand must be cleared from the glass joint before opening.

6.5 Quantitatively transfer the contents of the Kuderna-Danish receiver (0.4–0.5 ml) to the top of a deactivated alumina cleanup microcolumn. Use a disposable pipet to transfer. Not more than 0.1–0.2 ml hexane should be needed for washing. Using hexane, elute the extract from the column to a volume of 8.5 ml in a calibrated 10.00-ml receiver. Add only enough hexane so that the solvent level enters the column packing just as the 8.5-ml elution level is reached. Change receivers and continue the elution using 1:1 benzene-hexane solvent. Collect 8.5 ml of eluate in a second receiver. The first fraction of eluate should contain all the chlorinated hydrocarbon insecticides, and carbophenthion, Methyl Trithion, and VC-13. The remaining phosphorus-containing pesticides are eluted in the benzene-hexane fraction. Reduce the volume of each eluate to 1.00 ml using a Kuderna-Danish microapparatus on the sandbath.

NOTE.—The insecticides are separated chromatographically in a predictable order on the microcolumn, and this may be used to augment gas chromatographic analysis. Although alumina is the adsorbent of choice for the majority of water and sediment samples, occasionally a second pass through a different column is needed for more difficult samples. The analyst is referred to the work of Law and Goerlitz (1970) for a more

Table 4.—Insecticides in water: recovery of compounds added to surface-water samples

Sample No.	Insecticide and amount added ($\mu\text{g}/\text{l}$)											
	Aldrin 0.019	<i>p,p'</i> - DDD 0.080	<i>p,p'</i> - DDE 0.040	<i>p,p'</i> - DDT 0.081	Dieldrin 0.019	Endrin 0.040	Hepta- chlor 0.018	Hepta- chlor epoxide 0.021	Lindane 0.021	Mala- thion 0.181	Methyl para- thion 0.082	Para- thion 0.076
1	82.0	92.5	86.5	95.0	98.8	95.1	88.8	94.0	90.7	92.9	75.1	99.0
2	113	89.1	94.3	97.0	104	98.0	98.7	94.9	101	106	94.6	96.0
3	90.1	96.0	93.5	103	99.6	86.0	95.2	99.2	99.0	120	89.8	110
4	92.1	95.5	92.1	101	104	81.9	96.3	98.1	107	89.3	81.0	86.0
5	97.0	95.0	93.2	98.0	106	81.1	99.6	103	97.5	105	87.8	107
6	89.5	90.5	92.1	96.0	97.7	83.4	95.5	94.2	109	99.3	86.3	84.1
7	91.2	105	95.6	99.0	104	86.6	95.7	99.1	103	107	81.5	103
8	96.1	99.5	96.8	99.0	105	85.0	103	101	115	109	97.1	118
9	95.7	94.0	99.0	102	103	83.3	100	98.3	101	115	91.7	97.9
10	85.0	94.0	98.3	98.0	103	83.3	93.7	98.5	111	103	99.0	101
11	89.9	93.5	95.6	97.5	99.4	90.0	93.3	92.1	99.8	97.8	96.6	85.7
12	86.5	93.0	89.2	92.6	94.9	83.3	90.0	91.7	94.5	101	83.4	87.8
13	91.9	87.6	87.4	93.6	99.3	89.9	99.2	95.4	94.4	106	86.8	124
14	95.3	89.6	90.7	93.1	105	88.2	97.8	100	98.5	89.0	95.1	86.7
15	85.9	86.6	92.8	93.1	104	89.0	88.1	93.4	108	99.6	86.8	88.4
16	96.4	85.6	92.1	88.6	102	90.6	98.1	97.6	102	105	93.7	89.4
17	96.4	84.1	86.5	92.6	104	92.4	99.8	100	101	100	92.1	95.6
18	84.2	98.5	107	104	110	82.5	88.5	90.6	117	107	121	110
Mean	92.1	92.8	93.4	96.7	102	87.2	95.5	96.7	103	103	91	98.3
Variance	49.3	27.9	24.9	17.1	12.9	23.0	21.5	12.5	51.1	63.4	96.5	139.7
Std. dev.	7.02	5.28	4.99	4.14	3.59	4.80	4.64	3.54	7.15	7.96	9.82	11.8
Mean error	-7.9	-7.2	-6.6	-3.3	+2.0	-13	-4.5	-3.3	+3.0	+3.0	-9.0	-1.7
Total error ¹	22	18	13	12	9.2	22	14	10	17	19	29	25

¹ McFarren, E. F., Liska, R. J., and Parker, J. H., 1970, Criterion for judging the acceptability of analytical methods: *Anal. Chemistry*, v. 42, p. 355-358.

comprehensive treatment of the cleanup procedure.

6.6 Analyze the eluates by gas chromatography under conditions optimized for the particular gas chromatographic system being used. Run the first analysis on the electron-capture gas chromatograph using the DC-200 column. For components in concentrations ranging from 0.01 $\mu\text{g}/\text{l}$ to 1.0 $\mu\text{g}/\text{l}$, a second analysis by electron capture on the QF-1 column is required. Pesticides in concentrations greater than 1.0 $\mu\text{g}/\text{l}$ must be analyzed by microcoulometric or flame-photometric gas chromatography on both the DC-200 and the QF-1 columns.

7. Calculations

See step 7, "Gas Chromatographic Analysis."

8. Report

The pesticide concentrations in water samples are reported as follows: Less than 1.0 $\mu\text{g}/\text{l}$, two decimals and report less than 0.005 $\mu\text{g}/\text{l}$ as 0.00 $\mu\text{g}/\text{l}$; 1.0 $\mu\text{g}/\text{l}$ and above, to two significant figures. If more than one column or gas chromatographic system is used, report the lowest value.

9. Precision

The results may vary as much as ± 15 percent for compounds in the 0.01- to 0.10- $\mu\text{g}/\text{l}$ concentration range. Recovery and precision data are given in table 4.

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Chlorinated hydrocarbon insecticides in suspended sediment and bottom material

Gas chromatographic method

1. Summary of method

The insecticides are extracted from the sediment or soil using acetone and *n*-hexane. The solid is dispersed first in acetone, and then hexane is added to recover the acetone together with the desorbed insecticides. The extract is washed with distilled water and dried over sodium sulfate. A preliminary gas chromatographic analysis is performed before concentration and cleanup. Following this, the volume is reduced and extraneous material is removed by microcolumn adsorption chromatography. The insecticides are determined by gas chromatography.

2. Application

Sediment and bed material may be analyzed by this method. Water samples containing suspended sediment may also be analyzed by this technique. The insecticides aldrin, *p,p'*-DDD, *p,p'*-DDE, *o,p*-DDT, *p,p'*-DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, isodrin, lindane, and methoxychlor, may be determined down to 0.20 $\mu\text{g}/\text{kg}$ for a 50.0-g sample, on a dry-weight basis. The pesticide chemicals chlordane, chlordene, hexachlorobicycloheptadiene, hexachlorocyclopentadiene, and toxaphene may also be determined by this method.

3. Interferences

As in the analysis of water for pesticides, chlorinated hydrocarbon compounds similar to pesticide chemicals give the most interference. Organic coextractives, occurring naturally in sediments and soils, are usually adequately removed from extracts by the cleanup microcolumn. Sulfur compounds present in some bottom muds often hinder electron-capture chromatography but do not appear to interfere with microcoulometric gas chromatography.

4. Apparatus

See step 4, "Gas Chromatographic Analysis of Pesticides."

4.1 *Centrifuge*: A medium-speed centrifuge with a head capable of accepting large-volume glass centrifuge bottles and tubes is adequate.

4.2 *Concentrating apparatus*: A Kuderna-Danish concentrator, 500-ml capacity with a 1-ball Snyder column.

4.3 *Erlenmeyer flasks*, 250-ml and 500-ml, having ground-glass stoppers, and having spring clips for securing the stoppers.

4.4 *Microfiltration apparatus*: Use only silver metal filters having 0.45 μm maximum pore size, obtainable from Selas Flotronics. Filters should be rinsed with acetone and heated to 300°C overnight to reduce interfering substances.

4.5 *Shaker table*, or combination shaker table and wrist-action shaker having a 12-container capacity.

5. Reagents

5.1 *Acetone*, distilled in glass, pesticide-analysis quality.

5.2 *n-hexane*, distilled in glass, pesticide-analysis quality.

5.3 *Sodium sulfate*, anhydrous, granular. Prepare by heating at 300°C overnight and store at 130°C.

5.4 *Water*, distilled water obtained from a high-purity tin-lined still. The feed water is passed through an activated carbon filter. The distillate is collected in a tin-silver-lined storage tank, and the water is constantly irradiated with ultraviolet light during storage. A gravity system is used, and no plastic material other than teflon is allowed to contact the distilled water.

6. Procedure

Samples should be collected according to the recommended practice for suspended sediment and bed materials. Special care should be taken to avoid contaminating the sample with oil from the sampling device. Rubber gaskets should be replaced with teflon. Two suspended-sediment samples should be taken, one for insecticide analysis and the other for determining the sediment concentration and particle-size distribution. A 1-liter suspended sediment sample is needed for the insecticide determination.

At least 150 g of material should be collected for each sample when only solids are to be analyzed. All samples must be kept in watertight

glass containers to prevent water loss and contamination. No preservative is added. Unless analyzed within a few days of collection, the samples should be refrigerated and protected from light.

6.1 *Procedure for water samples having suspended sediment.* A reagent blank must accompany the analysis.

6.1.1 Allow the water-sediment sample to remain undisturbed until the sediment has settled. Weigh the uncapped bottles on a balance to three significant figures and carefully decant the water into a separatory funnel of appropriate size. (Separate by centrifugation as in 6.2.2 below and (or) filtration through metal membrane filters if necessary.)

6.1.2 Measure 10 ml acetone or a volume approximately half the equivalent volume of solid, whichever is greater, into the sample bottle containing the sediment. Replace the cap and gently mix the contents of the bottle on a shaker table for 20 min. Add 25 ml n-hexane and mix the contents for an additional 10 min. Decant the extract into the separatory funnel containing the water from the sample. Repeat the extraction of the sediment in the same manner two more times, using fresh acetone and hexane each time.

NOTE.—Additional hexane may be needed to recover the acetone extract from the sediment. Also, the extract may have to be filtered through a plug of glass wool. Anhydrous sodium sulfate may be added to aid in separating the solvent from the sediment. Add the sodium sulfate slowly and mix to the desired consistency. A quantity of sodium sulfate equal to the amount of sediment may be added if necessary.

6.1.3 Shake the combined extracts with the water from the sample for 1 min. Rinse the sediment from the sample bottle with distilled water and collect the water from the sample in the sample bottle. The sediment may be discarded. Decant the extract from the top of the separatory funnel into a 250-ml erlenmeyer flask.

6.1.4 Extract the water from the sample with an additional 25 ml hexane and discard the water. Weigh the sample bottle to determine the weight of the sample.

6.1.5 Combine the extracts in the separatory funnel and wash two times with 500 ml distilled water each time. Collect the extract in the 250-ml erlenmeyer flask containing approximately 0.5 g

Na_2SO_4 , and continue the analysis as in the procedure, beginning step 6.4, "Insecticides in Water."

6.2 *Analysis of sediment, soil, and bed-material samples.* A reagent blank must accompany the analysis.

6.2.1 Desiccated samples, such as bed material from dry streams, should be moistened with distilled water (to about 15 percent by weight). Samples to which water is added are first pulverized, then mixed with the water, and then kept in an airtight glass container. A minimum of 2 hr should be allowed for equilibration. Start the analysis of homogeneous samples at step 6.2.3, below.

6.2.2 Excessive water in sediment and bottom-mud samples must be separated from the solids in order to obtain a homogeneous fraction of the sample. A proportionate amount of this water is used later so that any suspended material is included in the analysis. This technique may also be used whenever water and solids are to be analyzed separately. Weigh the container and contents and transfer the sample to centrifuge bottles. Spin the solids at a relative centrifuge force of 500–1,000 times gravity. Use the supernatant water to complete the transfer and repeat the centrifugation as necessary. Decant the separated water into the empty tared sample container. (See step 6.2.5.) Calculate the weight of the solid by difference.

6.2.3 Thoroughly mix the moist solid until homogeneous and then weigh 50.0 g into a 250-ml erlenmeyer flask having a ground-glass stopper. Also at this time, weigh an additional 10.00 g of the solid into a tared 50-ml beaker to be heated at 130°C overnight for moisture determination.

6.2.4 Measure 40 ml acetone into the erlenmeyer flask containing the sample and clamp the stopper in place. (If the sediment is sandy, use 20 ml acetone instead.) Mix the contents of the flask for 20 min using a wrist-action shaker. Add 80 ml hexane and shake again for 10 min. Decant the extract into a separatory funnel containing 500 ml distilled water. Add 20 ml acetone to the erlenmeyer flask and shake 20 min. Again add 80 ml hexane, shake 10 min, and decant the extract into the separatory funnel. Repeat as in the second extraction one more time.

NOTE.—If the sediment is not wet enough to agglomerate when the hexane is added, add water,

by drops, while swirling the flask and observe if this helps. Very sandy material may remain dispersed. Extremely wet, mucky sediments may be better handled by the addition of anhydrous sodium sulfate. Add sodium sulfate, in small quantities, until the desired consistency is attained or until the amount added approximates the weight of the sediment. The extract volume recovered should be measured at each extraction to insure that 75 percent or more is regained. If not, additional extractions are necessary to obtain quantitative removal of the insecticides.

6.2.5 If any water was separated in step 6.2.2 above, mix thoroughly and weigh out an aliquot equivalent to the fraction of solid taken for analysis. Transfer the aliquot of water into the separatory funnel containing the sample extract and distilled water.

6.2.6 Gently mix the contents of the separatory funnel for about 1 min and allow the layers to separate. Collect the water in a clean beaker and decant the extract into a 500-ml erlenmeyer flask. Back-extract the water wash with 25 ml hexane. Combine the solvent layers and wash with fresh 500-ml quantities of distilled water two more times. Discard the water layers and collect the washed extract in the 500-ml erlenmeyer flask to which has been added about 0.5 g anhydrous sodium sulfate.

NOTE.—A preliminary gas chromatographic analysis at this point is helpful for determining the volume reduction necessary.

Proceed with the analysis beginning at step 6.4, "Insecticides in Water."

7. Calculations

See step 7, "Gas Chromatographic Analysis of Pesticides."

8. Report

The pesticide concentrations in water-sediment mixtures should be reported as in step 8, "Insecticides in Water," and the sediment concentration should accompany the report. The concentration of pesticides in sediment, soil, and bed material is reported on a dry-weight basis as follows: Less than 1.0 $\mu\text{g}/\text{kg}$ to one decimal; 1.0 $\mu\text{g}/\text{kg}$ and greater to two significant figures. Because negative bias exists in the extraction procedure, insecticides found in sediments and solids are considered minimum amounts.

9. Precision

The recovery of pesticides from sediments and soils is mainly dependent on two factors: (1) the ability of the solvent to remove the pesticide from the solid, and (2) the amount of solvent reclaimed at each extraction step. Comparative studies of single and exhaustive extractions of soil samples taken from contaminated fields showed that the extraction technique described removed 90–95 percent of the chlorinated pesticides. Dehydrated clay soils, however, proved slow to yield the pesticides unless they were premoistened. Apparently, the collapsed layers of certain dehydrated clays and the resulting agglomerates entrap the pesticides, and the addition of water prior to analysis helps to open the layers and separate the aggregation. It is imperative that sufficient solvent be reclaimed at each extraction to avoid low results. Removal of 90–95 percent of the desorbed pesticides may be expected if at least 75 percent of the solvent is recovered at each extraction step.

Chlorinated phenoxy acid herbicides in water

Gas chromatographic method

1. Summary of method

Chlorinated phenoxy acids and their esters are extracted from the acidified water sample with ethyl ether. The extracts are hydrolyzed, and extraneous materials are removed with a solvent wash. The acids are converted to their methyl esters and are further cleaned up on an adsorption microcolumn. The esters are determined by gas chromatography. This method is a modification and extension of the procedure developed by Goerlitz and Lamar (1967).

2. Application

The method is usable for the analysis of esters and salts of 2,4-D (2,4-dichlorophenoxyacetic acid), silvex [2-(2,4,5-trichlorophenoxy) propionic acid], 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), and similar herbicides found in water. Concentrations as low as 0.02 $\mu\text{g}/\text{l}$ of 2,4-D and 0.005 $\mu\text{g}/\text{l}$ of silvex and 2,4,5-T in 1 liter of water may be determined.

3. Interferences

Halogenated organic acids and their salts and esters cause interference when BF_3 -methanol esterification is used, and both the acids and halogenated phenols interfere when diazomethane is used for esterification.

4. Apparatus

See step 4, "Gas Chromatographic Analysis of Pesticides."

4.1 *Concentrating apparatus.* A Kuderna-Danish concentrator, 250-ml capacity, with a 1-ball Snyder column is used for the initial concentration step. Final concentration is performed in the receiver using a 1-ball Snyder micro-column. A 4.00-ml graduated receiver tube is used for the diazomethane esterification, and a 5.00-ml volumetric flask receiver is utilized for the boron trifluoride-methanol esterification.

4.2 *Erlenmeyer flasks,* 250 ml and 500 ml, having ground-glass stoppers.

4.3 *Pasteur pipets,* disposable, 14-cm long and 5-mm inside diameter.

4.4 *Sandbath,* fluidized, Tecam, or equivalent.

4.5 *Separatory funnels,* Squibb form, some of 1-, or 2-liter capacity and others of 60-ml capacity. No lubricant is used on the stopcocks.

5. Reagents

All reagents must be checked for purity as reagent blanks using the gas chromatographic procedure. Effort is saved by selecting high-quality reagents that do not require further preparation. However, some purification of reagents may be necessary as outlined below.

5.1 *Boron trifluoride-methanol,* esterification reagent: Dissolve 14.0 g BF_3 gas in 86.0 g anhydrous methanol.

5.2 *Benzene,* distilled in glass, pesticide-residue quality, such as Nanograde, or equivalent.

5.3 *2-(2-Ethoxyethoxy) ethanol,* high purity, n_D^{20} 1.4068.

5.4 *Ethyl ether,* reagent grade, redistilled from an all-glass packed-column still, after refluxing over granulated sodium-lead alloy for 8 hr. Purity is checked by gas chromatography after a part is evaporated to one-tenth the original volume. The purified ether should be distilled as needed and should never be stored for more than 1 month. Explosive peroxides readily

form in redistilled ether, making it hazardous for storage and subsequent use.

5.5 *Florasil adsorbent,* Florisil, PR grade, commercially activated at 650°C and stored at 130°C in a glass-stoppered bottle.

5.6 *Herbicides,* chlorinated phenoxy acids, reference grade: 2,4-D mp (melting point) 138°–139°C; silvex, mp 181°–182°C; and 2,4,5-T, mp 154°–155°C. The methyl esters of the herbicides may be obtained from commercial sources. The methyl esters may also be prepared by reacting 0.5–1.0 g herbicide acid with 50 ml BF_3 -methanol reagent at reflux for 1 hr. The methyl ester is extracted in ether, washed with 5-percent Na_2CO_3 solution, and finally washed with distilled water. The ether extract is dried over anhydrous Na_2CO_3 , and the ester is isolated by removing the ether under vacuum.

5.7 *Methanol,* reagent grade, redistilled from an all-glass packed-column still after reacting with 5 g of magnesium lathe turnings per liter of solvent.

5.8 *N-methyl-N-nitroso-p-toluenesulfonamide,* mp 60°–62°C.

5.9 *Potassium hydroxide reagent,* 7M solution: Prepare by dissolving 78 g KOH reagent-grade pellets in 200 ml carbon-dioxide-free distilled water. Reflux for 8 hr to reduce interfering substances. A calcium chloride tube filled with Ascarite is used at the top of the reflux condenser to exclude carbon dioxide.

5.10 *Silicic acid,* chromatographic grade, 100/200 mesh, heated at 300°C overnight and stored at 130°C in a glass-stoppered bottle.

5.11 *Sodium sulfate,* reagent grade, anhydrous, granular; heat-treated at 300°C for 24 hr. The heat-treated material is divided, and one part is labeled "neutral sodium sulfate" and stored at 130°C in a glass-stoppered bottle. The other part is slurried with enough ether to cover the crystals and acidified to pH 4 by adding a few drops of purified sulfuric acid. (To determine the pH, a small quantity of the slurry is removed, the ether evaporated, water added to cover the crystals, and the pH is measured on a pH meter.) The ether is removed by vacuum, and the treated material is labeled "acidified sodium sulfate" and stored at 130°C in a glass-stoppered bottle.

5.12 *Sodium sulfate solution,* 0.35M: Prepare by dissolving 50 g neutral sodium sulfate in 1.0 liter distilled water.

5.13 *Sulfuric acid*, reagent grade (sp gr 1.84), purified by distilling off water until a constant boiling solution remains. The acid is refluxed for about 4 hr.

6. Procedure

Water samples for herbicide analysis should be collected according to the procedure described for the collection of organic water samples. The samples may be preserved with sulfuric acid at the collection site only if the acid is supplied with the sampling package. Regardless of whether preserved or not, the samples must be iced or refrigerated in the dark within 4 to 5 hr of collection. Samples must reach the laboratory within 24 hr of collection if not acidified. A 1-liter sample should be collected for each analysis.

6.1 Immediately upon receipt in the laboratory, the samples are acidified to pH 2 or lower with the specially prepared sulfuric acid. If more than 24 hr is required for shipment, then the samples must be acidified at the collection site. For this purpose, 5 ml of 1:1 diluted sulfuric acid, sealed in a prescored glass ampoule must accompany each empty sample container. Detailed instructions for proper addition should also be included. After adding the acid the bottles should be loosely capped for 5 min or so before closing tightly. Refrigerate the sample until analysis.

6.2 Weigh the opened bottle containing the sample. Pour the sample into a 1- or 2-liter separatory funnel. Allow the bottle to drain for a few minutes and then weigh. Record the sample weight to three significant figures. Add 150 ml ethyl ether to the sample bottle, rinse the sides thoroughly, and pour the solvent into the funnel. Shake the mixture vigorously for 1 min. Allow the contents to separate for at least 10 min. Occasionally, emulsions prevent adequate separation. In this event, draw off the clear aqueous layer, invert the separatory funnel and shake. (CAUTION: Vent the funnel frequently to prevent forming excessive pressure.) Addition of small volumes of distilled water often aids removal of sediment from the ether layer. Small amounts of water included in the extract do not interfere with the analysis. Collect the extract in a 250-ml ground-glass erlenmeyer flask containing 2 ml 7*M* potassium hydroxide solution. Extract

the sample two more times, using 50 ml ether each time, and then combine the extracts in the 250-ml erlenmeyer flask.

6.3 Add 15 ml distilled water and a boiling chip to the extract and fit the flask with a 1-ball Snyder column. Remove the ether on a steam bath in a hood and continue heating for a total of 90 min.

6.4 Allow to cool and transfer the water to a 60-ml separatory funnel. Extract the basic solution once with 20 ml and two more times each with 10 ml of ether and discard the ether layers. The herbicides remain in the aqueous phase. Add 2 ml cold (4°C) dilute sulfuric acid (1 part concentrated H₂SO₄ (sp gr 1.84) diluted to 4 parts with distilled water) to the contents of the funnel to bring the pH to 2 or below, and extract the herbicides once with 20 ml and two times each with 10 ml of ether. Collect the extracts in a 125-ml erlenmeyer flask containing about 0.5 g acidified anhydrous sodium sulfate. Cover the flask with foil and allow the extract to remain in contact with the sodium sulfate, preferably in an explosion-proof refrigerator, for at least 2 hr. (Refer to steps 6.6 and 6.7, below, before continuing.)

6.5 Transfer the ether solution into the Kuderna-Danish apparatus through glass wool in a funnel. Use liberal washings of ether and break up the hardened sodium sulfate to obtain quantitative transfer. Concentrate the extract to about 0.5 ml on the fluidized sandbath heated to 60°–70°C. Under no circumstances allow the extract to evaporate completely to dryness. Clear sand from the glass joints before opening.

6.6 *Esterification with diazomethane*. A 4.00-ml graduated receiver tube is used with the Kuderna-Danish apparatus when the sample is to be esterified with diazomethane. Add a volume of anhydrous methanol equal to 0.1 of the volume of the concentrated extract. Connect two 20- by 150-mm test tubes in series with glass tubing through neoprene stoppers so that incoming nitrogen bubbles through the liquid in the tubes. At the outlet, position a piece of glass tubing having a right-angle bend and a drawn-out tip so that the gas can be bubbled through the sample. Add about 5 ml ether to the first test tube. To the second test tube, add 0.7 ml ether, 0.7 ml 2-(2-ethoxyethoxy) ethanol, 1.0 ml 7*M* potassium hydroxide solution, and 0.1–0.2 g

N-methyl-N-nitroso-p-toluenesulfonamide. Immediately position the second test tube and adjust the nitrogen flow through the apparatus to about 10 ml per minute. (CAUTION: Diazomethane is a toxic and explosive gas. The use of a good fume hood is absolutely necessary.) Place the Kuderna-Danish receiver so that the gas bubbles through the sample. Allow the reaction to proceed for about 10 min, or less if the yellow color of diazomethane can be observed to persist in the sample tube. Remove the tube containing the sample, stopper, and allow to stand in the hood for about 30 min. Carefully discard all waste from the reaction. Add about 0.1–0.2 g silicic acid to the sample solution to destroy excess diazomethane. After evolution of nitrogen has subsided, pass the solution through a disposable pipet plugged with glass wool and packed with 1.5 cm neutral anhydrous sodium sulfate over 1.5 cm Florisil adsorbent. The eluate is collected in a graduated receiver tube. The transfer is completed by washing the receiver tube several times with small quantities of ether to a final volume of 2.00 ml. The tube is stoppered and the contents thoroughly mixed and analyzed by gas chromatography.

6.7 *Esterification with boron trifluoride-methanol.* A 5.00-ml volumetric receiver flask is used with the Kuderna-Danish apparatus when the sample is to be esterified with boron trifluoride-methanol reagent. Prior to the initial concentration step described previously (see step 6.5, above), 0.5 ml benzene is added to the extract in the Kuderna-Danish apparatus. The extract is concentrated to less than 1 ml, and the walls of the flask are washed down with a small amount of ether. Sand adhering to the joint is cleared off with an air gun or brush, and the receiver is fitted with a 1-ball Snyder microcolumn. The liquid volume is further reduced to 0.5 ml in the sandbath. After the benzene solution in the receiver has cooled, 0.5 ml boron trifluoride-methanol reagent is added. The Snyder column is used as an air-cooled condenser, and the contents of the receiver are held at 50°C for 30 min in a sandbath. The reaction mixture is allowed to cool to room temperature. About 4.5 ml of the sodium sulfate solution is added to the reaction mixture so that the benzene-water interface is observed in the constricted neck of the receiver flask. The flask is stoppered with a glass plug and vigorously shaken for about 1 min. Allow to stand

for about 3 min for phase separation. Twirling the flask between the palms of the hands from time to time aids separation. The benzene layer is pipetted from the receiver and passed through a small cleanup column prepared by plugging a disposable pipet with glass wool and packing with 2.0 cm neutral anhydrous sodium sulfate over 1.5 cm Florisil adsorbent. The eluate is collected in a graduated receiver. The transfer is completed by repeating the extraction step with small quantities of benzene until a final volume of 2.00 ml is attained. Add a few crystals of neutral anhydrous sodium sulfate to the benzene solution and thoroughly mix for gas chromatographic analysis.

6.8 Analyze the extract by gas chromatography under conditions optimized for the particular gas chromatographic system being used. Run the first analysis on the electron-capture chromatograph using the DC-200 column. For components in concentrations ranging from 0.01 $\mu\text{g/l}$ to 1.0 $\mu\text{g/l}$, a second analysis by electron capture on the QF-1 column is required. Pesticides in concentrations greater than 1.0 $\mu\text{g/l}$ must be analyzed using microcoulometric detection on both the DC-200 and QF-1 columns.

7. Calculations

See step 7, "Gas Chromatographic Analysis of Pesticides."

Each gas chromatographic system must be calibrated with standards. Methyl ester standards of the herbicides must be converted to the acid equivalent. During analysis, at least two standards should be run so that the standard curve can be corrected for day-to-day instrumental fluctuation.

8. Report

The pesticide concentrations are reported as follows: Less than 1.0 $\mu\text{g/l}$, two decimals, and report less than 0.005 $\mu\text{g/l}$ as 0.00 $\mu\text{g/l}$; 1.0 $\mu\text{g/l}$ and above, two significant figures. If more than one column or gas chromatographic system is used, report the lowest value found.

9. Precision

The results vary ± 20 percent for 2,4-D at the 0.10- $\mu\text{g/l}$ level and ± 10 percent at 1.0- $\mu\text{g/l}$ concentration.

Reference

Goerlitz, D. F., and Lamar, W. L., 1967, Determination of phenoxy acid herbicides in water by electron-capture and microcoulometric gas chromatography: U.S. Geol. Survey Water-Supply Paper 1817-C, 21 p.

Chlorinated phenoxy acid herbicides in sediment (tentative)

Gas chromatographic method

1. Summary of method

Chlorinated phenoxy acids and their salts and esters are extracted from an acidified slurry of sediment and water with acetone and ether. The extract is hydrolyzed, and extraneous materials are removed with a solvent wash. The acids are converted to their methyl esters and are further cleaned up on an adsorption microcolumn. The esters are determined by gas chromatography.

2. Application

This method may be used for the analysis of esters and salts of 2,4-D (2,4-dichlorophenoxyacetic acid), silvex [2-(2,4,5-trichlorophenoxy) propionic acid], and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), and similar herbicides found in sediments.

3. Interferences

Halogenated organic acids having properties similar to the herbicides cause interference when BF_3 -methanol esterification is used, and both the extraneous acids and halogenated phenols interfere when diazomethane is used for esterification.

4. Apparatus

See steps 4, "Gas Chromatographic Analysis of Pesticides" and "Chlorinated Phenoxy Acid Herbicides in Water."

4.1 *Shaker table*, or combination shaker table and wrist-action shaker having a 12-container capacity.

5. Reagents

See step 5, "Chlorinated Phenoxy Acid Herbicides in Water."

5.1 *Acetone*, distilled in glass, pesticide-

analysis quality, such as Nanograde, or equivalent.

5.2 *Hydrochloric acid*, concentrated (sp gr 1.18), ACS reagent grade.

5.3 *Sodium sulfate* solution, 0.35M: Prepare by dissolving 50 g neutral sodium sulfate in 1.0 liter distilled water.

6. Procedure

Samples should be collected according to the recommended practice for suspended sediment or bed materials. The samples must be iced or refrigerated. The analysis should begin as soon as possible because the herbicides, particularly 2,4-D, may decompose significantly in a few hours. Samples should be kept in tightly closed glass containers to prevent water loss and contamination. A reagent blank must accompany the analysis.

6.1 Excess water is separated from the sediment as described in steps 6.1 and 6.2, "Chlorinated Hydrocarbon Insecticides in Suspended Sediment and Bottom Material." The water from suspended sediment samples is analyzed as in the procedure, "Chlorinated Phenoxy Acid Herbicides in Water," using proportionally less ether for smaller amounts of water. Water separated from bed material is included in step 6.5, below.

6.2 Thoroughly mix the moist solid until homogeneous and weigh 50.0 g into a 250-ml erlenmeyer flask having a ground-glass stopper. Also at this time, weigh an additional 10.00 g of sample into a tared 50-ml beaker to be heated at 130°C overnight for moisture determination.

6.3 While stirring, slowly add water to the sample in the erlenmeyer flask until the mixture has the consistency of paste, or until water begins to separate. Acidify the slurry to pH 2 or below by the addition, by drops, of concentrated hydrochloric acid. Allow to stand with occasional stirring for 15 min, and insure that the pH remains below 2. Add more acid if necessary and until stabilized.

6.4 Measure 40 ml acetone into the erlenmeyer flask containing the acidified sample and clamp the stopper in place. Mix the contents of the flask for 20 min using the wrist-action shaker. Add 80 ml ether and shake again for 10 min. Decant the extract into an appropriate-sized separatory funnel containing 250 ml 0.35M sodium sulfate.

NOTE.—If the sediment does not settle to allow decanting the solvent, add anhydrous sodium sulfate in small amounts until the mixture separates. A quantity of sodium sulfate equal to the amount of sample may be added if necessary. To ensure adequate recovery, measure the volume of extract at each decanting step.

Add 20 ml acetone to the erlenmeyer flask and shake 20 min. Again, add 80 ml ether, shake 10 min, and decant the extract into the separatory funnel. Repeat the process as in the second extraction one more time, and collect the acetone-ether extract in the separatory funnel containing the 0.35M sodium sulfate solution.

6.5 If any water was separated in step 6.1 above, mix thoroughly and weigh out an aliquot equivalent to the fraction of solid taken for analysis. Transfer the aliquot of water to the separatory funnel containing the sample extract and the sodium sulfate solution.

6.6 Gently mix the contents of the separatory funnel for about 1 min and allow the layers to separate. Collect the aqueous layer in a clean beaker and collect the extract in a 500-ml ground-glass erlenmeyer flask. Back-extract the water wash with 25 ml ether. Separate the aqueous layer and discard. Pour the ether layer into the erlenmeyer flask containing the sample extract.

6.7 Add 5 ml 7M aqueous potassium hy-

droxide and 15 ml distilled water to the extract in the 500-ml erlenmeyer flask. Add a boiling chip and fit the flask with a 1-ball Snyder column. Evaporate the ether on a steam bath in a hood and continue the heating for a total of 90 min. Continue the analysis, beginning at step 6.4, "Chlorinated Phenoxy Acid Herbicides in Water."

7. Calculations

See step 7, "Gas Chromatographic Analysis of Pesticides."

Each gas chromatographic system must be calibrated with standards. Methyl ester standards of the herbicides must be converted to the acid equivalent. During analysis, at least two standards should be run so that the detector response curve can be corrected for day-to-day instrumental fluctuation.

8. Report

Pesticide concentrations in sediment are reported as follows: Less than 1.0 $\mu\text{g}/\text{kg}$, two decimals; 1.0 $\mu\text{g}/\text{kg}$ and above, to two significant figures. If more than one column or the gas chromatographic system is used, report the lowest value found.

9. Precision

No precision data are available at this time.

17. U. S. Geological Survey
"Methods for Determination of
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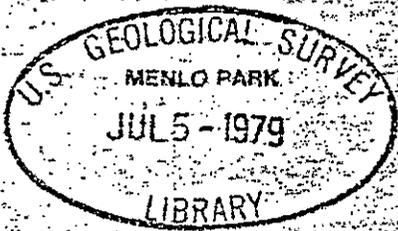


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U.S. GEOLOGICAL SURVEY

Techniques of Water-Resources Investigations
of the United States Geological Survey

**METHODS FOR DETERMINATION
OF INORGANIC SUBSTANCES
IN WATER
AND FLUVIAL SEDIMENTS**



BOOK 5
CHAPTER A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin W. Skougstad, Marvin J. Fishman, Linda C. Friedman, David E. Erdmann, and Suandra S. Duncan, editors

Abstract

Chapter A1 of the laboratory manual contains methods used by the Geological Survey to analyze samples of water, suspended sediments, and bottom material for their content of inorganic constituents. Included are methods for determining dissolved, total recoverable, and total concentrations of constituents in water-saturated sediment samples, and recoverable and total constituents in samples of bottom material. Essential definitions are included in the introduction to the manual, along with a brief discussion of the use of significant figures in calculating and reporting analytical results. Quality control in the water-analysis laboratory is discussed, including accuracy and precision of analyses, the use of standard reference water samples, and the operation of an effective quality assurance program. Methods for sample preparation and pretreatment are given also.

The analytical methods are arranged according to the analytical technique employed for the determination: atomic absorption spectrometric, calculation, colorimetric, electrometric, gravimetric, and titrimetric methods. More than 200 methods are given for the determination of 69 different inorganic constituents and physical properties of water, suspended sediment, and bottom material, and many of the methods given are identical except for the preparation step, which varies with the particular type of sample that is taken for analysis. Included in the manual are many automated methods, particularly the colorimetric methods that make use of the Technicon AutoAnalyzer system to automate the determination from sample introduction to final concentration readout.

A brief discussion of the principles of the analytical technique involved and its particular application to water analysis precedes each group of analytical methods. For each method given, the general topics covered are application, principle of the method, interferences, apparatus and reagents required, a detailed description of the analytical procedure, reporting results, units and significant figures, and analytical precision data, when available.

Methods for the following determinations are included in the manual:

Dissolved constituents and physical properties

Acidity	Arsenic
Alkalinity	Barium
Aluminum	Beryllium
Antimony	Boron

Dissolved constituents and physical properties

Bromide	Oxygen, dissolved
Cadmium	pH
Calcium	Phosphorus
Carbon dioxide	Phosphorus, hydrolyzable
Chloride	Phosphorus, organic
Chromium	Phosphorus, orthophosphate
Chromium(VI)	Potassium
Cobalt	Selenium
Copper	Silica
Cyanide	Silver
Fluoride	Sodium
Hardness	Sodium adsorption ratio
Hardness, noncarbonate	Sodium, percent
Iodide	Solids, sum of constituents
Iron	Solids, nonvolatile on ignition
Iron(II)	Solids, volatile on ignition
Lead	Solids, residue on evaporation, at 105°C
Lithium	Solids, residue on evaporation, at 180°C
Magnesium	Specific conductance
Manganese	Strontium
Mercury	Sulfate
Molybdenum	Tin
Nickel	Vanadium
Nitrogen, ammonia plus organic	Zinc
Nitrogen, ammonia	
Nitrogen, nitrate	
Nitrogen, nitrite	
Nitrogen, nitrite plus nitrate	

Suspended constituents

Solids, nonvolatile on ignition
 Solids, suspended, residue at 105°C
 Solids, volatile on ignition

Total recoverable constituents and physical property

Aluminum	Copper
Barium	Iron
Beryllium	Lead
Boron	Lithium
Cadmium	Magnesium
Calcium	Manganese
Chromium	Mercury
Cobalt	Molybdenum
Color	Nickel

Total recoverable constituents and physical property

Potassium	Strontium
Silver	Tin
Sodium	Zinc

Total constituents and physical properties

Antimony	Phosphorus
Arsenic	Phosphorus, hydrolyzable
Cyanide	Phosphorus, organic
Density	Phosphorus, orthophosphate
Fluoride	Selenium
Nitrogen, ammonia	Solids, nonvolatile on ignition
Nitrogen, ammonia plus organic	Solids, residue on evaporation, at 105°C
Nitrogen, nitrite	Solids, volatile on ignition
Nitrogen, nitrite plus nitrate	Sulfide
Oxygen demand, biochemical	Turbidity
Oxygen demand, chemical	

Constituents recoverable from bottom material

Aluminum	Lithium
Barium	Magnesium
Beryllium	Manganese
Boron	Mercury
Cadmium	Molybdenum
Calcium	Nickel
Chromium	Potassium
Cobalt	Sodium
Copper	Strontium
Iron	Zinc
Lead	

Total constituents in bottom material

Antimony	Nitrogen, nitrite plus nitrate
Arsenic	Oxygen demand, chemical
Boron	Phosphorus
Cyanide	Selenium
Nitrogen	Solids, volatile on ignition
Nitrogen, ammonia	
Nitrogen, ammonia plus organic	

Introduction

The Department of the Interior has a basic responsibility for the appraisal, conservation, and efficient utilization of the Nation's natural resources—including water as a resource as well as water involved in the use and development of other resources. As one of several Interior agencies, the Geological Survey's primary function in relation to water is to assess its availability and utility as a national resource for all uses. The Geological Survey's responsibility for water appraisal includes not only assessments of the lo-

cation, quantity, and availability of water, but also determinations of water quality. Inherent in this responsibility is the need for extensive water-quality studies related to the physical, chemical, and biological adequacy of natural and developed surface- and ground-water supplies. Included, also, is a need for supporting research to increase the effectiveness of these studies.

As part of its mission the Geological Survey is responsible for generating a large part of the water-quality data for rivers, lakes, and ground water that is used by planners, developers, water-quality managers, and pollution-control agencies. A high degree of reliability and standardization of these data is paramount.

This manual is one of a series prepared to document and make available data collection and analysis procedures used by the Geological Survey. The series describes procedures for planning and executing specialized work in water-resources investigations. The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises. For convenience the chapters on methods for water-quality analysis are grouped into the following categories:

- Inorganic substances
- Minor elements by emission spectroscopy
- Organic substances
- Aquatic biological and microbiological samples
- Radioactive substances

Provisional drafts of new or revised analytical methods are distributed to field offices of the Geological Survey for their use. These drafts are subject to revision based on use or because of advancement in knowledge, techniques, or equipment. After a method is sufficiently developed and confirmed, it is incorporated in a supplement to the manual or a new edition of the manual and is then available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

Purpose

Rapid changes in technology are constantly providing new and improved methods for the study of water-quality characteristics. It is, therefore, necessary that methods manuals be updated frequently in order to gain the advantages of improved technology. The purpose of

this chapter is to record and disseminate methods used by the Geological Survey to analyze samples of water, suspended sediment, and bottom material collected in connection with ongoing water-quality investigations. The manual is an update and enlargement of Techniques of Water-Resources Investigations (TWRI) of the U.S. Geological Survey, Book 5, Chapter A1, "Methods for collection and analysis of water samples for dissolved minerals and gases," by Brown, Skougstad, and Fishman, published in 1970. Of special note is the fact that this manual includes methods for analyzing samples of water-suspended sediment mixtures and of bottom material collected from streams, lakes, and reservoirs.

Although excellent and authoritative manuals on water analysis are available (American Public Health Association and others, 1976; American Society for Testing and Materials, 1966), most of them emphasize primarily either municipal, industrial, or agricultural water utilization. No single reference or combination meets all requirements as a guide to the broader phases of water-quality investigations conducted by the Geological Survey. These investigations are intended to define the chemical, physical, and biological characteristics of the Nation's surface- and ground-water resources, as well as to indicate the suitability of these resources for various beneficial uses.

Scope

This chapter includes techniques and procedures found to be suitable for the analysis of representative samples of water and fluvial sediments. The methods are grouped according to the analytical techniques involved and include—

- Sample preparation and pretreatment
- Atomic absorption spectrometry
- Calculation methods
- Colorimetry
- Electrometry
- Gravimetry
- Titrimetry

Most of the groups are introduced by a brief description of the chemical or instrumental principles of the technique involved, followed, where appropriate, by a discussion of the types of analytical operations that may be required, the sensitivity that may be expected from the tech-

nique, interferences, applications of the technique, and general references. Each section also includes a detailed description of all methods in which that technique is used, first as they may apply to the determination of constituents in solution (dissolved), then to the determination of total or total recoverable constituents (substances both in solution and adsorbed on or a part of suspended sediment) and finally to the determination of total or recoverable constituents from samples of bottom material.

Each method has a single identifying four-digit number preceded by a letter. The letter prefix designates whether the method applies to a physical characteristic (P), an inorganic substance (I), an organic substance (O), a radioactive substance (R), a biological characteristic or determination (B), an element determined by emission spectrographic method (E), or a sediment characteristic (S). The first digit of the identifying number indicates the type of determination (or procedure) for which the method is suitable, according to the following:

- 0 ----- Sample preparation.
- 1 ----- Manual method for dissolved constituents.
- 2 ----- Automated method for dissolved constituents.
- 3 ----- Manual method for analyzing water-suspended sediment mixtures.
- 4 ----- Automated method for analyzing water-suspended sediment mixtures.
- 5 ----- Manual method for analyzing samples of bottom material.
- 6 ----- Automated method for analyzing samples of bottom material.
- 7 ----- Method for suspended constituents.

The last three digits are unique to each method. Additionally, each method number has an appended two-digit number designating the year of last approval of that method. If revisions of a method are issued within the calendar year of last approval, suffixes A, B, . . . are added to the year designation to identify such a subsequent revision. This numbering system simplifies unequivocal identification of each method and also simplifies updating of the chapter as new or revised methods are introduced.

Definitions

Reporting the results of analyses of water and fluvial sediment samples requires the use of a number of terms that are based on the combination of physical phases sampled (water or sedi-

ments) and analytical methods used. These terms are defined below.

Dissolved. Pertaining to the material in a representative water sample which passes through a 0.45- μ m membrane filter. This is a convenient operational definition used by Federal agencies that collect water data. Determinations of "dissolved" constituents are made on subsamples of the filtrate.

Suspended, recoverable. The amount of a given constituent that is in solution after the part of a representative water-suspended sediment sample that is retained on a 0.45- μ m membrane filter has been digested by a method (usually using a dilute acid solution) that results in dissolution of only readily soluble substances. Complete dissolution of all the particulate matter is not achieved by the digestion treatment, and thus the determination represents something less than the "total" amount (that is, less than 95 percent) of the constituent present in the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses, because different digestion procedures are likely to produce different analytical results.

Determinations of "suspended, recoverable" constituents are made either by analyzing portions of the material collected on the filter or, more commonly, by difference, based on determinations of (1) *dissolved* and (2) *total recoverable* concentrations of the constituent.

Suspended, total. The total amount of a given constituent in the part of a representative water-suspended sediment sample that is retained on a 0.45- μ m membrane filter. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent determined. A knowledge of the expected form of the constituent in the sample, as well as the analytical methodology used, is required to determine when the results should be reported as "suspended, total."

Determinations of "suspended, total" constituents are made either by analyzing portions of the material collected on the filter or, more commonly, by difference, based on determinations of (1) *dissolved* and (2) *total* concentrations of the constituent.

Total, recoverable. The amount of a given constituent that is in solution after a representative water-suspended sediment sample has been digested by a method (usually using a dilute acid solution) that results in dissolution of only readily soluble substances. Complete dissolution of all particulate matter is not achieved by the digestion treatment, and thus the determination represents something less than the "total" amount (that is, less than 95 percent) of the constituent present in the dissolved and suspended phases of the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses, because different digestion procedures are likely to produce different analytical results.

Total. The total amount of a given constituent in a representative water-suspended sediment sample, regardless of the constituent's physical or chemical form. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent present in both the dissolved and suspended phases of the sample. A knowledge of the expected form of the constituent in the sample, as well as the analytical methodology used, is required to judge when the results should be reported as "total." (Note that the word "total" does double duty here, indicating both that the sample consists of a water-suspended sediment mixture and that the analytical method determines all of the constituent in the sample.)

Recoverable from bottom material. The amount of a given constituent that is in solution after a representative sample of bottom material has been digested by a method (usually using an acid or mixture of acids) that results in dissolution of only readily soluble substances. Complete dissolution of all bottom material is not achieved by the digestion treatment and thus the determination represents less than the total amount (that is, less than 95 percent) of the constituent in the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses because different digestion procedures are likely to produce different analytical results.

Total in bottom material. The total amount of a given constituent in a representative sample of bottom material. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent determined. A knowledge of the expected form of the constituent in the sample, as well as the analytical methodology used, is required to judge when the results should be reported as "total in bottom material."

In describing an analytical method, it is necessary to compare the result obtained by the method to the value that is sought, normally the true concentration of the chemical substance in the sample. Definitions of terms that are used for this purpose are given below.

Accuracy. A measure of the degree of conformity of the values generated by a specific method or procedure with the true value. The concept of accuracy includes both bias (systematic error) and precision (random error).

Bias. A persistent positive or negative deviation of the values generated by a specific method or procedure from the true value; expressed as the difference between the true value and the mean value obtained by repetitive testing of the homogeneous sample.

Precision. The degree of agreement of repeated measurements by a specific method or procedure, expressed in terms of dispersion of the values generated about the mean value obtained by repetitive testing of a homogeneous sample.

Significant figures

The significant figures used by the Geological Survey in reporting the results of analysis in milligrams or micrograms per liter are the result of a compromise between precision of the measurement, importance of this precision to the use of the analytical data, and obvious advantages of some semblance of uniformity in tabulations of analytical data. One of the commonly used methods, which applies only to the expression of the

TABLE 1.—Factors for converting milligrams per liter to milliequivalents per liter

[1975 atomic weights]					
Ion	Sum of atomic weights	Conversion factor	Ion	Sum of atomic weights	Conversion factor
Ag ⁺¹	107.868	0.00927	I ⁻¹	126.9045	0.00788
Al ⁺³	26.9815	.11119	K ⁺¹	39.0983	.02558
As ⁺³	74.9216	.04004	Li ⁺¹	6.941	.14407
AsO ₄ ⁻³	138.9192	.02160	Mg ⁺²	24.305	.08229
Ba ⁺²	137.33	.01456	Mn ⁺²	54.9380	.03640
Be ⁺²	9.01218	.22192	Mn ⁺⁴	54.9380	.07281
BO ₃ ⁻³	58.5082	.05101	Mo ⁺³	95.94	.03127
Br ⁻¹	79.904	.01252	Na ⁺¹	22.9898	.04350
Ca ⁺²	40.08	.04990	NH ₄ ⁺¹	18.0383	.05544
Cd ⁺²	112.41	.01779	Ni ⁺²	58.70	.03407
Cl ⁻¹	35.453	.02821	NO ₂ ⁻¹	46.0055	.02174
Co ⁺²	58.9332	.03394	NO ₃ ⁻¹	62.0049	.01613
CO ₃ ⁻²	60.0092	.03333	OH ⁻¹	17.0073	.05860
Cr ⁺³	51.996	.03770	Pb ⁺²	207.2	.00965
CrO ₄ ⁻²	115.9936	.01724	PO ₄ ⁻³	94.97136	.03159
Cu ⁺²	26.0177	.03644	S ⁻²	32.06	.06238
F ⁻¹	63.546	.03147	SeO ₄ ⁻²	142.9576	.01399
Fe ⁺²	18.9984	.05264	Sn ⁺²	118.69	.01665
Fe ⁺³	55.847	.03581	Sn ⁺⁴	118.69	.03370
Fe ⁺³	55.847	.05372	SO ₄ ⁻²	96.0676	.02082
H ⁺¹	1.0079	.99216	S ⁺²	87.62	.02283
Hg ⁺²	200.59	.00997	V ⁺²	50.9414	.03926
HCO ₃ ⁻¹	61.0171	.01639	VO ⁺²	66.9408	.02968
HPO ₄ ⁻²	95.97926	.02084	VO ₃ ⁻¹	98.9396	.01011
H ₂ PO ₄ ⁻¹	96.98716	.01031	Zn ⁺²	65.38	.03059

precision of a determination, is to include all digits known with certainty and the first (and only the first) doubtful digit. This method has one obvious disadvantage: published data so reported may not be interpreted to mean the same thing by all users of the data.

Chemical milliequivalents per liter are computed by multiplying the reported concentration of the individual constituents, in milligrams per liter, by the reciprocal of their equivalent weights. The factors for the conversion of milligrams per liter to milliequivalents per liter for the more commonly determined constituents are given in table 1.

Milliequivalents per liter as reported by the Geological Survey are numerical expressions of milligrams per liter and for uniformity are carried to three decimal places regardless of the magnitude of the milligrams-per-liter value; the significant figures shown in no way reflect the precision of the measurement as do the milligrams-per-liter values.

"Methods for Determination of Inorganic Substances in Water and Fluvial Sediments" can be loaned out by the U.S. Geological Survey library in Menlo Park (415-323-8111).

The book has 626 pages of more than 200 methods used to determine 69 different inorganic substances and physical properties of water.

The book as a whole may be useful for determining if ground water has been contaminated, depending upon the circumstances involved.

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