USGS
science for a changing world

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

Chapter A3

METHODS FOR THE DETERMINATION OF ORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

**Edited by R. L. Wershaw, M. J. Fishman,
R. R. Grabbe, and L. E. Lowe**

This manual is a revision of "Methods for Analysis of Organic Substances in Water," by Donald F. Goerlitz and Eugene Brown, Book 5, Chapter A3, published in 1972.

Book 5
LABORATORY ANALYSIS

DEPARTMENT OF THE INTERIOR
DONALD PAUL HODEL, *Secretary*

U.S. GEOLOGICAL SURVEY
Dallas L. Peck, *Director*

UNITED STATES GOVERNMENT PRINTING OFFFICE, WASHINGTON: 1987

For sale by the Books and Open-File Reports Section, U.S. Geological Survey,
Federal Center, Box 25425, Denver, CO 80225

PREFACE

This series of manuals on techniques describes methods used by the U.S. Geological Survey for planning and executing water-resources investigations. The material is grouped under major subject headings called books and is further subdivided into sections and chapters. Book 5 is on laboratory analyses. Section A is on water. The unit of publication, the chapter, is limited to a narrow field of subject matter. "Methods for the Determination of Organic Substances in Water and Fluvial Sediments" is the third chapter to be published under Section A of Book 5. The chapter number includes the letter of the section.

This manual was prepared by many chemists and hydrologists of the U.S. Geological Survey and provides accurate and precise methods for the analysis of water, water–suspended-sediment mixtures, and bottom-material samples. Supplements, to be prepared as the need arises, will be issued as they become available.

Reference to trade names, commercial products, manufacturers, or distributors does not constitute endorsement by the U.S. Geological Survey or recommendation for use.

This manual is a revision of "Methods for Analysis of Organic Substances in Water" by D.F. Goerlitz and Eugene Brown (U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A3, 1972).

TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS OF THE U.S. GEOLOGICAL SURVEY

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The manuals published to date are listed below and may be ordered by mail from the **U.S. Geological Survey, Books and Open-File Reports, Federal Center, Building 810, Box 25425, Denver, Colorado 80225** an authorized agent of the Superintendent of Documents, Government Printing Office).

Prepayment is required. Remittance should be sent by check or money order payable to U.S. Geological Survey. Prices are not included in the listing below as they are subject to change. **Current prices can be obtained** by writing to the USGS, Books and Open File Reports. Prices include cost of domestic surface transportation. For transmittal outside the U.S.A. (except to Canada and Mexico) a surcharge of 25 percent of the net bill should be included to cover surface transportation. When ordering any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations."

TWI 1-D1. Water temperature—influential factors, field measurement, and data presentation, by H. H. Stevens, Jr., J. F. Ficke, and G. F. Smoot, 1975, 65 pages.
TWI 1-D2. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents, by W. W. Wood. 1976. 24 pages.
TWI 2-D1. Application of surface geophysics to ground water investigations, by A. A. R. Zohdy, G. P. Eaton, and D. R. Mabey. 1974. 116 pages.
TWI 2-E1. Application of borehole geophysics to water-resources investigations, by W. S. Keys and L. M. MacCary. 1971. 126 pages.
TWI 3-A1. General field and office procedures for indirect discharge measurement, by M. A. Benson and Tate Dalrymple. 1967. 30 pages.
TWI 3-A2. Measurement of peak discharge by the slope-area method, by Tate Dalrymple and M. A. Benson. 1967. 12 pages.
TWI 3-A3. Measurement of peak discharge at culverts by indirect methods, by G. L. Bodhaine. 1968. 60 pages.
TWI 3-A4. Measurement of peak discharge at width contractions by indirect methods, by H. F. Matthai. 1967. 44 pages.
TWI 3-A5. Measurement of peak discharge at dams by indirect methods, by Harry Hulsing. 1967. 29 pages.
TWI 3-A6. General procedure for gaging streams, by R. W. Carter and Jacob Davidian. 1968. 13 pages.
TWI 3-A7. Stage measurements at gaging stations, by T. J. Buchanan and W. P. Somers. 1968. 28 pages.
TWI 3-A8. Discharge measurements at gaging stations, by T. J. Buchanan and W. P. Somers. 1969. 65 pages.
TWI 3-A9. Measurement of time of travel and dispersion in streams by dye tracing, by E. P. Hubbard, F. A. Kilpatrick, L. A. Martens, and J. F. Wilson, Jr. 1982. 44 pages.
TWI 3-A11. Measurement of discharge by moving-boat method, by G. F. Smoot and C. C. Novak. 1969. 22 pages.
TWI 3-A12. Fluorometric procedures for dye tracing, Revised, by James F. Wilson, Jr., Ernest D. Cobb, and Frederick A. Kilpatrick. 1986. 41 pages.
TWI 3-A13. Computation of continuous records of streamflow, by Edward J. Kennedy. 1983. 53 pages.
TWI 3-A14. Use of flumes in measuring discharge, by F. A. Kilpatrick, and V. R. Schneider. 1983. 46 pages.
TWI 3-A15. Computation of water-surface profiles in open channels, by Jacob Davidian. 1984. 48 pages.
TWI 3-B1. Aquifer-test design, observation, and data analysis, by R. W. Stallman. 1971. 26 pages.
TWI 3-B2. Introduction to ground-water hydraulics, a programmed text for self-instruction, by G. D. Bennett. 1976. 172 pages.
TWI 3-B3. Type curves for selected problems of flow to wells in confined aquifers, by J. E. Reed. 1980. 106 p.
TWI 3-C1. Fluvial sediment concepts, by H. P. Guy. 1970. 55 pages.
TWI 3-C2. Field methods of measurement of fluvial sediment, by H. P. Guy and V. W. Norman. 1970. 59 pages.
TWI 3-C3. Computation of fluvial-sediment discharge, by George Porterfield. 1972. 66 pages.
TWI 4-A1. Some statistical tools in hydrology, by H. C. Riggs. 1968. 39 pages.
TWI 4-A2. Frequency curves, by H. C. Riggs, 1968. 15 pages.
TWI 4-B1. Low-flow investigations, by H. C. Riggs. 1972. 18 pages.
TWI 4-B2. Storage analyses for water supply, by H. C. Riggs and C. H. Hardison. 1973. 20 pages.
TWI 4-B3. Regional analyses of streamflow characteristics, by H. C. Riggs. 1973. 15 pages.
TWI 4-D1. Computation of rate and volume of stream depletion by wells, by C. T. Jenkins. 1970. 17 pages.
TWI 5-A1. Methods for determination of inorganic substances in water and fluvial sediments, by M. W. Skougstad and others, editors. 1979. 626 pages.
TWI 5-A2. Determination of minor elements in water by emission spectroscopy, by P. R. Barnett and E. C. Mallory, Jr. 1971. 31 pages.
TWI 5-A3. Methods for the determination of organic substances in water and fluvial sediments, edited by R. L. Wershaw, M. J. Fishman, R. R. Grabbe, and L. E. Lowe. 1987. 80 pages.
TWI 5-A4. Methods for collection and analysis of aquatic biological and microbiological samples, edited by P. E. Greeson, T. A. Ehlke, G. A. Irwin, B. W. Lium, and K. V. Slack. 1977. 332 pages.
TWI 5-A5. Methods for determination of radioactive substances in water and fluvial sediments, by L. L. Thatcher, V. J. Janzer, and K. W. Edwards. 1977. 95 pages.
TWI 5-A6. Quality assurance practices for the chemical and biological analyses of water and fluvial sediments, by L. C. Friedman and D. E. Erdmann. 1982. 181 pages.

TWI 5-C1. Laboratory theory and methods for sediment analysis, by H. P. Guy. 1969. 58 pages.
TWI 7-C1. Finite difference model for aquifer simulation in two dimensions with results of numerical experiments, by P. C. Trescott, G. F. Pinder, and S. P. Larson. 1976. 116 pages.
TWI 7-C2. Computer model of two-dimensional solute transport and dispersion in ground water, by L. F. Konikow and J. D. Bredehoeft. 1978. 90 pages.
TWI 7-C3. A model for simulation of flow in singular and interconnected channels, by R. W. Schaffranek, R. A. Baltzer, and D. E. Goldberg. 1981. 110 pages.
TWI 8-A1. Methods of measuring water levels in deep wells, by M. S. Garber and F. C. Koopman. 1968. 23 pages.
TWI 8-A2. Installation and service manual for U.S. Geological Survey monometers, by J. D. Craig. 1983. 57 pages.
TWI 8-B2. Calibration and maintenance of vertical-axis type current meters, by G. F. Smoot and C. E. Novak. 1968. 15 pages.

CONTRIBUTORS

Charlene W. Bayer
Michael G. Brooks
Rosalyn Carter
Marvin J. Fishman
Linda C. Friedman
Rolland R. Grabbe
Robert J. Keck
Jerry A. Leenheer
James A. Lewis
Luis E. Lowe
Bernard A. Malo
Douglas B. Manigold
Janice L. O'Byrne
Mary C. Olson
Deanna L. Peterson
Janet B. Pruitt
Paul K. Roscio
Michael P. Schroeder
Thomas R. Steinheimer
Marguerite B. Sweny
Ronald S. Torbet
John D. Vaupotic
Dorothy M. Walker
Robert L. Wershaw
William R. White
Marvin L. Yates

CONTENTS

	Page
Preface	III
Abstract	1
Introduction	1
Purpose	2
Scope	2
Definitions	3
Significant figures	4
Recovery correction	5
Quality control	5
Qualification of the analyst	5
Reagents and standards	5
Equipment	5
Analytical procedure	5
Use and documentation of standard laboratory procedures	6
Approved methods	6
Official methods	6
Provisional methods	6
Special methods	7
Sample collection	7
Preparation of the samplers	7
Sample handling and preservation	7
Extraction, fractionation, and identification	8
Extraction	8
Batch extraction	8
Continuous extraction	9
Fractionation	9
Liquid chromatography	9
Adsorption	9
Liquid-liquid partition	10
Ion exchange	10
Gel permeation	11
Gas-liquid chromatography	11
Identification	11
Thermal-conductivity detector	12
Flame-ionization detector	12
Electron-capture detector	12
Mass spectrometer	12
Other detectors	12
Spectrophotometer	12
Quantitative analysis	12
Qualitative analysis	13
Ancilliary methods of confirmation	13
Selected references	13
Analytical methods	14
Carbon, organic, dissolved, wet oxidation (0–1100–83)	14
Carbon, organic, total, wet oxidation (0-3100-83)	15
Carbon, organic, suspended, wet oxidation (0–7100–83)	16
Carbon, inorganic plus organic, total in bottom material, dry weight, induction furnace (0–5101–83)	17
Carbon, inorganic, total in bottom material, modified Van Slyke (0–5102–83)	19
Analytical methods—Continued	
Carbon, organic, dissolved, fractionation (0–1103–83)	23
Organochlorine and organophosphorous compounds, total recoverable (0–3104–83) and dissolved (0–1104–83), gas chromatographic	27
Organochlorine and organophosphorous compounds, recoverable from bottom material (0–5104–83) and recoverable from suspended sediment (0–7104–83), gas chromatographic	31
Organochlorine compounds, recoverable from fish tissue, gas chromatographic (0–9104–83)	35
Chlorophenoxy acids, total recoverable (0–3105–83) and dissolved (0–1105–83), gas chromatographic	40
Chlorophenoxy acids, recoverable from bottom material (0–5105–83) and recoverable from suspended sediment (0–7105–83), gas chromatographic	43
Triazines, total recoverable, gas chromatographic (0–3106–83)	46
Carbamate pesticides, total recoverable, high-performance liquid chromatographic (0–3107–83)	49
Oil and grease, extractable, extraction-gravimetric (0–3108–83)	51
Oil and grease, extractable from bottom material, extraction-gravimetric (0-5108–83)	53
Fuel oils, light, total recoverable, gas chromatographic (O–3109–83)	54
Phenols, total recoverable, colorimetric, 4-aminoantipyrine (0–3110–83)	55
Methylene blue active substances, total recoverable, colorimetric (0–3111–83)	57
TNT, RDX, and picric acid, total recoverable, high-performance liquid chromatographic (0–3112–83)	58
Polynuclear aromatic hydrocarbons (PNA), total recoverable, high-performance liquid chromatographic (O–3113–83)	60
Ethylene and propane, total recoverable, gas chromatographic, purge and trap (0–3114–83)	63
Purgeable organic compounds, total recoverable, gas chromatographic/mass spectrometric, purge and trap (0–3115–83)	67
Acid extraction compounds, total recoverable, gas chromatographic/mass spectrometric (0–3117–83)	71
Base/neutral extractable compounds, total recoverable, gas chromatographic/mass spectrometric (0–3118–83)	76

FIGURES

Page

1. Diagram of apparatus for the manometric determination of carbon dioxide ---- 20
2. Flow chart showing dissolved organic carbon fractionation analytical scheme ---- 24

3, 4. Diagrams of:

3. Purge vessel ---- 64
4. Stripping and gas chromatographic system in the stripping mode ---- 66

TABLES

Page

1. Concentrations of pesticides and PCB's in mixed standard solutions used for gas chromatograph calibration of water and water-suspended sediment ---- 29
2. Column fractionation scheme for silica gel column for organochlorine insecticides, PCB's, and PCN's ---- 29
3. Column fractionation scheme for alumina and silica columns for insecticides, PCB's, and PCN's in bottom material and suspended sediment ---- 32
4. Concentrations of pesticides and PCB's in mixed standard solutions used for gas chromatograph calibration of bottom material ---- 33
5. Column fractionation scheme for alumina and silica columns for organochlorine insecticides, PCB's, and PCN's in fish ---- 36
6. Concentrations of pesticides and PCB's in mixed standard solutions used for gas chromatograph calibration of fish tissue ---- 37
7. Concentration of herbicides in mixed standard solutions used for gas chromatograph calibration of water and water-suspended sediment ---- 41
8. Concentration of herbicides in mixed standard solutions used for gas chromatograph calibration of bottom material ---- 44
9. Concentration of triazines in mixed standard solutions used for gas chromatograph calibration - 47
10. Concentration of carbamates in mixed standard solutions used for liquid chromatograph calibration ---- 50

METHODS FOR THE DETERMINATION OF ORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

Edited by R.L. Wershaw, M.J. Fishman,
R.R. Grabbe, and L.E. Lowe

Abstract

This manual describes analytical methods used by the U.S. Geological Survey to determine organic substances in water, water–suspended-sediment mixtures, and bottom material. Some of the analytical procedures yield determinations for specific compounds, whereas others provide a measure of the quantity of groups of compounds present in the sample. Examples of the first category are procedures for the organochlorine and organophosphate insecticides, chlorophenoxy acid and triazine herbicides, and specific substituted phenols. Examples of the second category are the various organic carbon analyses and the polychlorinated biphenyl methods. The analytical methods are presented in a standard format; topics covered include conditions for application of the method, a summary of the method, interferences, required apparatus and reagents, analytical procedures, calculations, reporting of results, and estimation of precision.

Introduction

The U.S. Department of the Interior has a basic responsibility for the appraisal, conservation, and efficient use 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 Department of Interior agencies, the U.S. 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 location, quantity, and availability of water, but also determinations of water quality. Inherent in this responsibility is a 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 are 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 chapter in 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. This format permits flexibility in revision and publication as the need arises. For convenience, the chapters on methods of 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, and quality assurance.

Provisional drafts describing 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 described in a supplement to the chapter

or in a new edition of the chapter, and the publication is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

Purpose

The purpose of this manual is to record and disseminate methods used by the U.S. Geological Survey to analyze samples of water, water–suspended-sediment mixtures, and bottom material collected in connection with ongoing water-quality investigations. The manual is an update and enlargement of Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3, "Methods for Analysis of Organic Substances in Water," by D.F. Goerlitz and Eugene Brown, published in 1972. Of special note is the present manual's inclusion of 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, most of them emphasize either municipal, industrial, or agricultural water use. No single reference or combination of references is adequate to serve as a comprehensive guide to the broader phases of water-quality investigations conducted by the U.S. 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.

Rapid changes in technology are constantly providing new and improved methods of studying water-quality characteristics. Methods manuals must be revised more frequently than before so as to gain the advantages of improved technology and to obtain water-quality data in the most efficient manner possible, with a high degree of quality control to ensure nationwide uniformity and standardization of data.

Scope

This manual describes techniques and procedures found to be suitable for analyzing representative samples of water and fluvial sediments for dissolved and sorbed organic constituents. Because of the typically low concentration and complex matrices of samples, the procedures include pretreatment steps to increase concentration and to remove interfering substances. The techniques involving laboratory equipment represent the current state of technology.

For each method, the following topics are covered: application, principles of the method, interferences, apparatus and reagents required, details of the analytical procedure, calculations, reporting of results (units and significant figures), and analytical precision data, when available. Each method, where applicable, applies to the determination of constituents in solution (dissolved), the determination of total or total recoverable constituents (substances both in solution and adsorbed on or a part of suspended sediment), and, finally, the determination of total or recoverable constituents from samples of bottom material.

Associated with each method is one or more four-digit identifying numbers preceded by the letter "O." The letter indicates that the method applies to an organic substance; identifying numbers in other chapters in this series are preceded, for example, by "P" (for physical characteristic), "I" (for an inorganic substance), "R" (for a radioactive substance), or "B" (for a biological characteristic or determination). The first digit of the identifying number indicates the type of determination (or procedure) for which the method is suitable, as follows:

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.
9------Method for fish and other materials.

The second, third, and fourth digits are unique to each method.

Following each identifying number is a two-digit number that indicates the year of last approval of the method. If revisions of a method are issued within the calendar year of last approval, suffixes A, B, and so forth are added to the year designation to identify such subsequent revisions. This numbering

system simplifies unequivocal identification of each method and also simplifies updating of the manual 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 sediments) and analytical methods used. These terms are defined below.

Dissolved.—Pertains to the constituents in a representative water sample that pass through a 0.45-micrometer 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.—Pertains to the constituents extracted from the suspended sediment that is retained on a 0.45-micrometer membrane filter. Complete extraction is generally not achieved, and thus the determination represents something less than the "total" amount (that is, less than 95 percent) of the constituent present in the suspended phase of the sample. To achieve comparability of analytical data, all laboratories performing such analyses would have to use equivalent extraction procedures, because different extraction 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 computing the difference between (1) dissolved and (2) total recoverable concentrations of the constituent.

Suspended, total.—Pertains to the constituents of the suspended sediment that is retained on a 0.45-micrometer membrane filter. This term is used only when the analytical procedure ensures measurement of at least 95 percent of the constituent determined. Knowledge of the expected form of the constituent in the sample, as well as of 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 computing the difference between (1) dissolved and (2) total concentrations of the constituent.

Total, recoverable.—Pertains to the constituents in solution after a representative water–suspended-sediment sample is digested (usually using a dilute acid solution). Complete dissolution of all particulate matter is often 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, all laboratories performing such analyses would have to use equivalent digestion procedures, because different digestion procedures are likely to produce different analytical results.

Total, recoverable also pertains to the constituents extracted from a representative water–suspended-sediment sample. Complete extraction generally is not achieved, 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, all laboratories performing such analyses would have to use equivalent extraction procedures, because different extraction procedures are likely to produce different analytical results.

Total.—Pertains to the constituents in a representative water–suspended-sediment sample. This term is used only when the analytical procedure ensures measurement of at least 95 percent of the constituent present in both the dissolved and suspended phases of the sample. Knowledge of the expected form of the constituent in the sample, as well as of 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.—Pertains to the constituents extracted from a representative sample of bottom material. Complete extraction is generally not achieved, and thus the determination often represents less than the total amount (that is, less than 95 percent) of the constituent in the sample. To achieve comparability of analytical

data, all laboratories performing such analyses would have to use equivalent extraction procedures, because different extraction procedures are likely to produce different analytical results.

Total in bottom material.—Pertains to constituents in a representative sample of bottom material. This term is used only when the analytical procedure ensures measurement of at least 95 percent of the constituent determined. Knowledge of the expected form of the constituent in the sample, as well as of 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 with 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.

Limit of detection.—The minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing analyte.

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.

Definitions of other terms used in this manual are given below.

External standard.—A mixture of compounds of interest (analytes to be determined) prepared in a suitable organic solvent and diluted to approximate environmental residue concentrations; used for calibrating and checking detector response prior to instrumental analysis. External standards establish response and retention factors necessary for quantitative analysis when internal standard or standard addition methods are not used.

Internal standard.—A compound similar in physical and chemical properties to the analyte in the sample; added to the final extract just prior to instrumental analysis. Internal standard responses are incorporated into quantitative analysis calculations, thus serving to normalize all data to a known amount of a common reference. Internal standard materials must be chosen carefully; they must exhibit proper chromatographic behavior and yet must not occur either naturally or as a result of pollution. When using mass sensitive detectors, internal standards may be chosen from stable heavy isotope analogs of analytes of interest. Other types of gas and liquid chromatographic detectors require other kinds of compounds. An internal standard will correct for the biases associated with the instrumental determinative step in an analytical procedure.

Spike.—Spikes result from the addition of a known amount of one or more of the compounds of interest to the sample prior to analysis. Analysis yields accuracy data (from a synthetic matrix) or recovery data (from an authentic matrix). Accuracy reflects the best results that can be expected, and recovery reflects the degree of influence of matrix effects on accuracy.

Surrogate.—A compound similar in physical and chemical properties to the analytes of interest; added to the sample upon receipt in the laboratory (or, ideally, at the time of field sampling). A surrogate is not used as an internal standard for quantitative measurement purposes. Surrogates may be added to every sample to provide quality control by monitoring for matrix effects and gross sample-processing errors. They should not occur naturally or be present in polluted water samples. Also called "surrogate spike."

Significant figures

The number of significant figures to which the results of analysis, in milligrams or micrograms per liter, are reported by the Geological Survey reflects a compromise between precision of measurement and a desire for a degree of uniformity in tabulations of analytical data. One of the commonly used methods, which applies only to the expression of the 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.

Recovery correction

Values reported by Geological Survey laboratories are not corrected for the percentage of constituent recovered. Therefore, almost all of the data for determinations of specific compounds such as pesticides, are biased to the low side. Average recoveries are always less than 100 percent.

Quality Control

Quality control includes the acquisition and documentation of information on personnel, reagents and standards, equipment, and analytical procedures. The principles discussed in this section apply to all analytical procedures described in this manual and represent the minimum level of analytical quality control required to produce acceptable data. This section supplements the practices described in Book 5, Chapter A6 of the Techniques of Water-Resources Investigations series of the U.S. Geological Survey.

Qualification of the analyst

Before performing any analyses, the analyst must demonstrate the ability to produce data of acceptable accuracy and precision using the method by successfully analyzing replicate aliquots of reference materials over the range of the method. To be considered successful, results obtained must fall within two standard deviations of the expected values for each constituent measured.

Reagents and standards

The purity of each reagent must be verified by analysis employing the analytical method at the lowest detection limit that will be reported. The frequency of verification is a function of the stability of each reagent. All reagents and adsorbents must be free of interfering contaminants. The presence of an interfering contaminant requires remedial action and reanalysis to verify reagent purity.

Before processing any samples, the analyst must demonstrate, through analysis of an aliquot of reagent water equivalent in volume to a sample aliquot, that all glassware and reagent interferences are under control. A reagent water blank must be analyzed each time a set of samples is analyzed or there is a change in reagents.

Stock standard solutions need to be prepared from materials of highest available purity. All data concerning the preparation must be recorded in a notebook reserved for standard-solution data. Prior to use, individual component standards need to be analyzed to ensure the concentration and component response. Solutions of individual standards also need to be analyzed by an independent laboratory, or by a second analyst in the preparing laboratory, to confirm the results. All differences must be resolved before a standard solution is used.

As specified in the analytical method, one to seven standard solutions in the concentration range of the procedure need to be analyzed with each sample set, and the results must agree with expected values before sample results can be reported.

Equipment

A notebook containing all information on repair, maintenance, and daily operating conditions should be maintained and available at each instrument work station.

Analytical procedure

The analytical procedures described in this manual must be followed exactly. Whenever possible, method performance must be demonstrated with each sample by the use of surrogate spikes. Appropriate surrogates are listed for each analytical method along with applicable acceptance criteria. For analytical procedures for which appropriate surrogates are unavailable, the laboratory must arrange to receive at least 10 percent of samples in duplicate. One portion of each of these samples will be spiked with a mixture of the compounds of interest and analyzed by the analytical method. If the recovery for any constituent does not fall within control limits for method performance, the results reported for that constituent in all samples processed as part of the same set must be qualified as "suspect." The laboratory must monitor the frequency of suspect data to ensure that it remains below 5 percent. For those samples (sediment, soil, and core material) for which the use of spikes is not appropriate, an estimate of analytical precision must

be obtained and reported by analyzing in duplicate at least 10 percent of the samples in each set.

Because of the rapid advances in analytical technology, the analyst is permitted certain options to improve separations or to lower the cost of measurement. Such modification of methods, however, must conform to the following section, "Use and Documentation of Standard Laboratory Procedures."

Use and Documentation of Standard Laboratory Procedures

The Water Resources Division (WRD) of the U.S. Geological Survey recognizes two types of water-quality analytical methods—approved methods and special methods. Definitions of the two types of methods and requirements for approval of analytical methods are given for the guidance of users of this manual who provide data to or evaluate data from WRD programs.

Approved methods

Two categories of approved analytical methods have been formally established—official methods, and provisional methods. A description of methods in each category and requirements for their approval are given below.

Official methods

Methods in this category are considered the official water-quality analytical methods of the WRD. They are published in the Techniques of Water-Resources Investigations (TWI) series. Data collected by these methods may be stored in the national data file, WATSTORE, and published in the annual basic data reports of the WRD. Requirements for approval are as follows:

1. Submission of documentation of the proposed method or modification of a presently used method, in TWI format, to the Chief, Quality of Water Branch.
2. Submission to and approval by the Quality of Water Branch of a method-development report giving information and supporting data on the following:
   a. applicable range, detection limit, and sensitivity of the method;
   b. known and possible interferences;
   c. precision and bias of the method; these data should, at a minimum, include results of single-laboratory and multiple-operator tests, including at least 10 replicate analyses each of pure solutions, natural water, and spiked natural waters at three concentrations covering the applicable range of the method; and
   d. production rates compared with other methods, when possible.
3. Submission of statements describing hazardous chemical reactions and (or) reagents that are involved in the method, sample-preservation requirements, and level of skill and (or) special training needed by personnel using the method.
4. In addition to the minimum requirements for approval listed above, if it is determined that the proposed method will be used in the Central Laboratories System, the Quality of Water Branch will initiate plans to obtain technical reviews of the method-documentation and method-development report by at least two colleagues, one of whom must be outside the author's laboratory. Further, if the method is developed in one of the Central Laboratories, the other Central Laboratory will be expected, if equipment is available, to confirm the precision and bias of the method and to compare results with present methodology, if a method exists. These requirements must be met within 30 days. Approval of the method will depend on obtaining the reviews and additional data. The Quality of Water Branch may give provisional approval, as outlined below, during the period of review.

Provisional methods

Provisional methods are those believed to produce data comparable to data obtainable from official methods but likely to be used by WRD to such a limited extent that they have not received extensive in-house testing by WRD personnel. Many of the methods published in such reliable compendia as "Standard Methods," "Environmental Protection Agency Methods for Chemical Analysis of Water and Wastes," and "The American Society for Testing and Materials Book of Standards" and used by in-house, cooperator, or contractor laboratories in support of WRD programs would be accepted for approval in this category. These methods will not be published in the TWI series. Data collected by these methods may be stored in WATSTORE if a parame-

ter code exists, and the data may be published in the annual basic data reports. Requirements for acceptance of methods in this category are as follows:

1. Submission of a description of the method to the Chief, Quality of Water Branch, with an explanation of why approval of the method is desired.
2. Provision of the same type of information on precision and bias as is required for "Official Methods" approval, with the exception that data obtained by other than WRD personnel will be accepted for consideration.

Special methods

In contrast to the two categories of approved analytical methods, there are some methods that have specialized or limited application and, therefore, need not be submitted to the Chief, Quality of Water Branch, for approval. These include methods used in support of research, experimental or developmental methods used by a Central Laboratory, and screening methods used in the field or in the laboratory. Data collected by these methods are *not* stored in WATSTORE or published in the annual basic data reports. However, the data may be published in interpretive reports or project data reports, provided the method is fully described or an appropriate reference is cited to provide a basis for peer evaluation of analytical results. Defense of the validity of such a method is, therefore, the responsibility of the individual reporting the data.

Ordinarily, only approved methods are used in the Central Laboratories unless a special method is requested and concurrence in its use is obtained from the individual responsible for analytical technology transfer in the Office of the Analytical Services Coordinator. *Analysts are not to use a modification of an approved method without satisfying all previously stated requirements for an approved method.* Furthermore, when a laboratory uses an alternate method to satisfy a specific analytical request because of technical or management considerations, the analytical method used must have been previously shown, to the satisfaction of the individual responsible for analytical technology transfer, to have equivalent or better sensitivity, precision, and bias compared with the method requested. If these conditions are not met, the requester must be notified promptly and must approve the change in method prior to analysis.

Sample Collection

Collection and preservation of a representative sample of a natural water body is the first and most important task in the determination of any substance in water. If the sampling procedure or preservation procedure is faulty, the entire determination will be of doubtful validity, at best. It is, therefore, important that each step in the collection and preservation of a sample be carried out with utmost care.

The sampling techniques used will depend on the compound or group of compounds to be analyzed. Some organic compounds are associated mainly with suspended or bottom sediments, others are generally found as a surface film floating on water, and still others are dissolved in water.

One must be careful to avoid contamination of a sample. This is particularly difficult when a sample is being taken for trace-level organic determinations, in which case it is necessary to prevent the sample from contacting the myriad of plastics, oils, and greases that are in common use today. Not only do these materials introduce contamination into the sample, but also, in many instances, they sorb the compounds of interest.

Bed-sediment and suspended-sediment samples pose special problems which must be dealt with in a carefully prescribed way.

Preparation of the samplers

The sampler should be completely disassembled and then (1) washed thoroughly with an Alconox solution and a stiff brush, (2) rinsed with tapwater, (3) rinsed with acetone, and (4) rinsed with tapwater. The sampler should then be reassembled and rinsed again. Immediately prior to its use in the field, it should be thoroughly rinsed with native water.

Sample handling and preservation

The samples in general should be collected in specially cleaned sample bottles that have been baked at 300–350°C overnight. Immediately after the samples have been collected, they should be chilled in ice water. After chilling, the sample container should be placed in an insulated shipping container with sufficient ice to keep the sample cold until it reaches the laboratory for analysis. Glass bottles

must be packed in such a way that they will not break during shipping.

There is no single preservative that may be added to a sample for all forms of organic analysis; each sample must be treated according to the analytical procedure to be followed. For the determinations described in this manual, the following general methods of sample preservation should be used in addition to chilling at 4 °C.

- *Ethylene and propane*: Collect samples in vials containing 1 mL of formalin in a manner that precludes headspace formation.
- *Herbicides*: Acidify with concentrated H_2SO_4 at a rate of 2 mL per liter of sample in the laboratory.
- *Oil and grease*: Add concentrated H_2SO_4 until the pH of the sample is below 3.0. Generally, 5 mL per liter of sample will be sufficient.
- *Phenolic material*: Acidify the sample to pH 4.0 with H_3PO_4, and add 1 g of $CuSO_4 \cdot 5H_2O$ per liter of sample.

Samples collected for dissolved-constituent determinations must be filtered immediately at the collection site using either pressure or vacuum filtration apparatus and a 0.45-micrometer silver membrane filter. Samples collected for specific compound determinations, such as pesticides, should be shipped immediately to the laboratory, where they are filtered through an approximately 0.3-micrometer mean pore size glass fiber filter.

Sample bottles used for collecting purgeable organic compound samples must be filled so that a meniscus forms at the mouth of the sample bottle. Then the cap should be attached so that no bubble or headspace is present. Any sample that has a bubble or headspace at the collection site must be discarded and a new sample collected.

Extraction, Fractionation, and Identification

The determination of a specific organic compound generally requires that the compound be isolated from some or all of the other components in the sample. This is true whether the sample is a natural water being analyzed for a particular pesticide or a biological fluid being analyzed for a particular amino acid. The problem is further complicated if the sample consists of more than one phase, with the desired component distributed between the phases. This distribution of a component between two or more phases is either a dynamic equilibrium process, in which the component will redistribute itself between the phases if the concentration in one phase is changed, or a nonequilibrium process, in which the component is irreversibly bound by one or more of the phases in the system. Consider, for example, a stream in which the running water is carrying a suspended-sediment load. Each of the mineral components in the sediment is a separate phase; if a surface film of an insoluble oil is present, it constitutes another phase; colloidal particles of organic polymers such as humic material constitute still another phase. Organic analysis in a natural water system therefore requires that the organic compounds first be isolated from the other components of the stream (extraction) and then separated one from another (fractionation) prior to measurement of the amount of each compound present in the sample.

Extraction

Two different types of liquid-extraction techniques are commonly used to extract organic solutes from waters and sediments: batch extraction and continuous extraction.

Batch extraction

Extraction of an organic compound or a group of compounds from a water sample is generally done by shaking the sample with an immiscible solvent in a separatory funnel. All of the compounds that are soluble in the two liquid phases (designated phases 1 and 2) will distribute themselves between the phases. It can be shown thermodynamically that the concentrations of solutes in the two phases are related to one another at equilibrium by the distribution coefficient

$$K = \frac{m_A^{(1)}}{m_A^{(2)}},$$

where

$m_A^{(1)}$ is the concentration of solute A in phase 1 and

$m_A^{(2)}$ is the concentration of solute A in phase 2.

Therefore, if the concentration of solute A in phase 1 and K are known, the concentration of solute A in phase 2 can be calculated. In an extraction procedure, the distribution coefficients need to be

measured for the various possible extraction solvents in order to choose a solvent that will provide high recovery of the desired solute after a reasonable number of repetitions (generally three or fewer).

Continuous extraction

In the various continuous-extraction procedures, fresh solvent, free of solute, is continually introduced into the extraction chamber in which the sample to be extracted is contained. Continuous-extraction equipment has been devised for extraction of both solid and liquid samples. In some of the continuous-extraction devices for liquid samples, the sample also moves through the device and it is possible to extract a large volume of liquid with a relatively small extractor.

Fractionation

Chromatography has been defined by Denny (1976) as follows: " * * * any separative process in which a mixture carried in a moving phase (either liquid or gas) is separated as a result of differential distribution of the solutes between the mobile phase and a stationary liquid or solid phase around or over which the mobile phase is passing. The systems to which this definition applies include all chromatographic processes, from paper chromatography to ion exchange and gel permeation."

The stationary phase is a solid, or a solid on which is adsorbed liquid that is insoluble in the mobile phase, which may be either a gas or a liquid. If the mobile phase is a gas, we shall refer to the process as gas chromatography, and if it is liquid, we shall refer to it as liquid chromatography.

Liquid chromatography

Liquid chromatography was developed before gas chromatography. The pioneering work was done during the first decade of the 20th century in the United States by David Talbot Day of the U.S. Geological Survey and in Russia by Mikhail Tswett.

At least four different types of interactions have been found to take place between the solutes and stationary phases, the type that occurs depending on the physical and chemical properties of the solutes and the stationary phases, and these have, in turn, given rise to four different types of liquid chromatography. These four types of interactions are

- adsorption,
- liquid–liquid partition,
- ion exchange, and
- gel permeation.

In some systems, more than one type of interaction occurs. It is instructive to consider briefly each type of interaction.

Adsorption

Adsorption of molecules by the surface of an adsorbent occurs because of weak physical forces, such as London forces or electrostatic forces, between the molecules and the adsorbent molecules or because of weak chemical bonds, such as charge transfer or hydrogen bonds, between the molecules. If a chromatographic fractionation is based on adsorption, the adsorption must be reversible. Therefore, only reversible adsorption is considered here; however, it should be noted that many adsorption processes are not reversible. Although discussion of irreversible adsorption is beyond the scope of this paper, it should be pointed out that irreversible adsorption often prevents the complete recovery of organic pollutants from sediments.

The most common theory of adsorption of a solute from a solvent onto an adsorbent surface is an extension of a theory derived for the adsorption of gases by adsorbent surfaces. Langmuir (1918) derived a model for adsorption that is based on the following assumptions:

- The adsorbed molecules form a monolayer on the surface of the adsorbent.
- All of the adsorption sites on the adsorbent surface are equivalent,
- There is no interaction between the adsorbed molecules.

Because some of the assumptions that have been made in the derivation of the equations of the Langmuir model do not hold in all systems, other, more complex adsorption equations have been derived. These are generally empirical relationships that have been found to work for some systems.

The behavior of particular solutions in an adsorption system will, in general, be a function of the surface properties of the adsorbent and the physical/chemical properties of both the solute and the solvent.

All sorbent surfaces are made up of functional groups that can interact with other molecules and bind them. The capacity of a surface to bind molecules depends on the number and distribution of the

active functional groups. In general, the particles of adsorbent that are packed into a chromatographic column do not provide uniform surface for adsorption. Some of the surface is on the outside of the particles, and some of the surface is contained in voids within the particle. If the solute molecules are too large, they will not enter the voids and therefore will be excluded from part of the surface of the particles. In some adsorbents, the active functional groups are not uniformly distributed over the surface, and in some instances some of the groups may be sterically hindered so that they cannot interact with solute molecules. Part of the surface may be deactivated by the presence of a strongly adsorbed molecule. For example, water will strongly adhere to the active sites on the surface of silica gel, effectively removing the affected sites from participating in other adsorption reactions.

The active functional groups on an adsorbent surface may be classified into two groups: polar and nonpolar. In general, polar groups are those that can participate in hydrogen bonding. Nonpolar groups bind mainly by London dispersion forces.

From the above discussion, it follows that the behavior of a solute in a chromatographic system that consists of a solute, a solvent, and an adsorbent surface will be a function of the following:

- the polarity of the solute molecule,
- the size of the solute molecule,
- the distribution of the active sites on the adsorbent,
- the polarity of the adsorbent sites,
- the affinity of the adsorbent surface for the solvent molecules, and
- the polarity of the solvent.

It is therefore possible, by proper manipulation, to achieve a wide variety of different separations.

Liquid–liquid partition

In partition chromatography, two immiscible liquid phases and a stationary phase are used. One of the liquid phases is bound to the stationary phase by adsorption or, in some instances, by chemical bonding, and the other liquid phase moves freely through the column. We shall call the liquid phase that is free to move the mobile phase. The solutes that are to be fractionated are placed in the column dissolved in the mobile phase. The solutes then distribute themselves between the two liquid phases. After the solutes have been placed on the column, they are eluted by the addition of solvent at the head of the column. In this way, a continuous partitioning process takes place on the column and the various solutes are separated one from another. This process was first elucidated by Martin and Synge (1941). Although other theories of partition chromatography have been developed since the work of Martin and Synge, their work contains the basic principles and is the one that is most widely used. In their work they have developed the concept of "height equivalent to one theoretical plate" (HETP) by drawing an analogy between the mode of operation of a chromatographic column and a distillation column. They have defined HETP as "the thickness of the layer such that the solution issuing from it is in equilibrium with the mean concentration of solute in the non-mobile phase throughout the layers." They have assumed that diffusion of solute from one plate to another is negligible and that at equilibrium the distribution ratio of one solute between the two liquid phases is independent of the concentration of the solute and of the presence of other solutes. The equations they derived for partition chromatography may be extended to adsorption chromatography.

Martin and Synge have shown that the movement of the position of the band of maximum concentration of a solute in a partition chromatographic column will be a function of the partition coefficient of the solute, K, between the two liquid phases. Because the K values will be different for different solutes, fractionation of the solutes will occur and the amount of separation between the bands of maximum concentration of the solutes will be a function of the total number of plates in the column.

The HETP is a function of the rate of diffusion of the solute and of the rate of flow of the solvent. There is an optimum flow rate that minimizes the effect of diffusion. The smaller the HETP, the more efficient the column will be for separation. In general, columns made up of smaller particles give smaller HETP values than do columns composed of larger particles. However, columns composed of small particles require high pressures to force the solvent through the column.

Ion exchange

In ion-exchange chromatography, a resin which consists of either anionic or cationic sites attached to a cross-linked polymeric backbone is used. The resin, which is insoluble in water, is formed into beads for packing into a chromatographic column. When buff-

er is added to the column, the beads swell. Ions can then migrate in and out of the beads interacting with the charged sites on the polymer. Ions having charges opposite the charges of the fixed sites on the polymer will be bound to the polymer. In ion-exchange chromatography, the electrolyte molecules to be fractionated are added to a buffer solution and placed on the column of ion-exchange resin. After all of the solute to be fractionated has migrated onto the column, more buffer solution is added to the head of the column to elute the solute fractions. The solute ions to be fractionated compete for the fixed charged sites on the polymer with the salt ions in the buffer. Because, in general, the strengths of the interactions of the various ions with the fixed charged sites are different, fractionation of the solute ions will take place on the column.

Gel permeation

Gel-permeation chromatography is normally used to obtain a molecular size fractionation of a mixture of similar compounds. In principle, gel-permeation chromatography is a relatively simple process; however, as discussed below, the process can be complicated by adsorption and by ion-exchange effects.

In gel-permeation chromatography, the stationary phase generally consists of porous polymer beads which are insoluble in the mobile phase. The manufacturer of the beads attempts to make the dimensions of the pores in the beads uniform. Solute molecules that are larger than the largest pores in the beads do not penetrate the beads but pass through the column and are eluted from the column first. Smaller molecules can penetrate into the pores of the beads and are thereby retarded in their flow through the column. Within limits, the smaller the molecule the more retardation takes place and the longer it takes for the molecule to be eluted from the column. Thus, molecules are eluted from the column in decreasing order of molecular size.

In a classical gel-permeation experiment, it is assumed that the stationary phase is completely inert to the solute molecules, that the process of fractionation is brought about purely by differential penetration of the solute molecules into the pores of the beads, and that molecular forces between the solute molecules and the stationary phase are negligible. In many instances, however, this is not the case and interactions such as adsorption and ion exchange can take place.

Gas–liquid chromatography

In 1952, James and Martin introduced a gas–liquid "detector" (chromatograph) using a design first suggested by Martin and Synge (1941). This separation principle is similar to that discussed in the section on "Liquid–Liquid Partition." In the stationary phase, normally a fairly high boiling polymer is bound to support material by adsorption. The support material can be almost any inert material having a large surface area and good structural strength. Diatomaceous earth is the most commonly used support, and organosilicone oils are the most widely used liquid phases. Recently, very high resolution columns have been constructed by coating the liquid phase directly onto the walls of synthetic fused silica capillary tubing.

An inert gas such as He or N_2 is normally used as a mobile phase (carrier gas) to move the sample from an injection port to a detector. As in partition chromatography, the solutes distribute themselves between the stationary phase and the mobile phase.

The concept of HETP also applies to gas–liquid chromatography and gives an indication of the efficiency of a gas chromatographic column. A rather simple method of calculating the number of theoretical plates is given by McNair and Bonelli (1969) and is quite useful for measuring the efficiency of different columns of the same length and materials.

Identification

The U.S. Geological Survey laboratories perform all gas chromatographic pesticide determinations on two columns of dissimilar polarity such as methyl silicone and 50 percent trifluoropropyl-methyl silicone. An analyte must have the proper retention time on both columns in order to be considered identified. If peaks with the proper retention time on both columns are found but the peak areas are different, one usually calculates the quantity of the analyte based on the smaller peak because almost all interferent compounds produce positive peak areas.

A large variety of detectors have been used over the years, the most successful being the thermal-conductivity and flame-ionization detectors, both of which respond to virtually all compounds. More recently, the electron-capture detector has gained widespread use; it is somewhat more selective in its response.

Thermal-conductivity detector

A thermal-conductivity detector employs a wire filament whose electrical resistance varies with temperature. A constant current is passed through the filament, which is enclosed in a detector block. Carrier gas, usually He, at a constant flow rate will conduct heat away from the filament at a constant rate, establishing a baseline. Any change in carrier gas composition, such as occurs when a sample is introduced, causes a change in filament temperature, with a corresponding change in resistance. This is detected by a wheatstone bridge, and the resulting signal is recorded on a strip chart recorder.

Flame-ionization detector

A flame-ionization detector uses a hydrogen flame to burn and ionize organic compounds. A cathode-anode electrode system with a fixed potential between the electrodes monitors the flame. When a compound is ionized in the flame, the resulting change across the electrode gap is measured by an electrometer and is displayed on a strip chart recorder.

Electron-capture detector

Electron-capture detectors have been used extensively to detect chlorinated pesticides by gas–liquid chromatography. This type of detector is probably the most sensitive available for these compounds; for example, as little as 1 pg (picogram) of lindane can be detected. Its use, however, is limited to compounds that have a significant electron-capture cross section. An electron-capture detector is a relatively simple device; it consists of a two-electrode ion chamber, an internal radiation source, and associated electronic circuitry for measuring the ion current between the electrodes in the chamber.

Mass spectrometer

A mass spectrometer as a detector uses an ionization chamber to ionize atoms and molecules eluting from the GC column. The ions are segregated according to their mass-to-charge ratio, and a plot of intensity versus mass-to-charge ratio is the mass spectrum, which usually provides a great deal of information about the molecular weight and structure of the compound. Special techniques, such as single or multiple ion monitoring, greatly increase the sensitivity of the mass spectrometer so that a few picograms of a compound can be detected. If a data system is used with the gas chromatograph–mass spectrometer system, the system becomes a powerful qualitative and quantitative tool. Computerized library searches can be conducted in an attempt to identify components by comparing their spectra with thousands of library spectra. There are software packages to perform automated quantitation and identification routines.

Other detectors

Other less sensitive detectors such as microcoulometric, flame photometric, photoionization, and electrolyte conductivity detectors are sometimes used in gas chromatography because they respond to only specific elements incorporated into the molecules and this aids in molecular identification.

Spectrophotometer

When electromagnetic radiation impinges upon a material, the radiation interacts with the molecules of the material and, in general, some of the radiant energy is absorbed. The amount of radiation of a given wavelength (or frequency) that is absorbed is a function of the atomic or molecular structure of the material being irradiated. Radiation is absorbed by a molecule when the frequency of the radiation corresponds to the energy of a quantum transition from one electronic vibrational state to another, from one nuclear vibrational state to another, or from one molecular vibrational or rotational state to another. The electronic vibrational transitions cause absorption in the visible and ultraviolet regions of the spectrum (200 to 780 nm), nuclear and molecular vibrational transitions in the infrared region (0.78 μm to 30 μm), and rotational transitions in the far infrared and microwave regions (30 μm to 1 m).

Absorption spectrophotometry may be used for both quantitative and qualitative analysis.

Quantitative analysis

The amount of monochromatic radiation that is absorbed by the substance is a function of the thickness of the sample and of the concentration of the substance in the sample. Thus

$$A_\lambda = \log \frac{I_{\lambda_0}}{I_\lambda} = abc,$$

where A_λ is the absorbance of radiation of wavelength λ, I_{λ_0} is the intensity of the incident radiation of wavelength λ, I_λ is the intensity of the transmitted radiation of wavelength λ, a is the extinction coefficient at the given wavelength, b is the sample thickness, and c is the concentration of the substance. The relationship $A_\lambda = abc$ is Beer's law. From it we see that in order to analyze a solution for a given compound, it is necessary to measure the path length of the light through the sample and to evaluate the extinction coefficient for the compound in the solvent. In practice, this is accomplished by measuring the absorbances of the sample solution and a group of suitable standards in a cell of known path length. A plot of the absorbances of the standards versus concentration is then prepared, and the concentration of the unknown sample is determined from the analytical curve.

For most dilute solutions, Beer's law will hold; however, departures from Beer's law do occur in which concentration is not directly proportional to absorbance. These departures are caused by light scattering, fluorescence, decomposition, saturation, hydrogen bonding, ion pair formation, molecular aggregation or disaggregation, solvation, and chemical reactions. Therefore, to avoid inaccurate results it is imperative in quantitative analysis that standards that closely approximate the sample in concentration and substrate composition be used.

Qualitative analysis

In general, the electronic, nuclear, and molecular energy transitions in any given molecular species will be different from those in any other molecular species, and therefore the absorption spectrum of a pure substance, that is, a plot of absorbance versus wavelength of the sample, will be unique and will allow one in theory to identify the substance. Unfortunately, in practice it may not be possible to obtain sufficient sample to obtain a suitable spectrum.

Within any class of chemical compounds that are characterized by particular structural elements there will be a characteristic group of absorption bands in the absorption spectra. Even if it is not possible to assign a given spectrum to a particular compound, it should be possible to determine the class of compounds. Normally, most diagnostic absorption bands occur in the infrared region of the spectrum; however, for some species the ultraviolet and visible regions also contain useful information.

Ancillary methods of confirmation

In addition to the two-column gas chromatographic procedures used for the pesticides methods, other confirmation procedures may be used, such as gas chromatography employing (1) a mass spectrometer detector monitoring at least three major ions or (2) an element specific detector such as the Hall electrolytic conductivity detector operating in the halogen, sulfur, or nitrogen mode. These supplemental confirmation techniques are normally used when the concentrations of pesticides exceed 2 µg/L in water for a minimum sample size of 1 L or 20 µg/kg in bed materials for a minimum sample size of 50 g dry weight equivalent.

Selected references

Alford, A., 1975, Environmental applications of mass spectrometry: Biomedical Mass Spectrometry v.2, p. 229–253.

Budzikiewicz, A., Djerassi, C., and Williams, D.H., 1967, Mass spectrometry of organic compounds: San Francisco, Holden-Day, 690 p.

Burlingame, A.L., Kimble, B.J., and Derrik, P.J., 1976, Mass spectrometry: Analytical Chemistry, v.48, p. 368R–403R.

Cram, S.P., and Juvet, R.S., Jr., 1976, Gas chromatography: Analytical Chemistry, v.48, p. 411R–442R.

Denny, R.C., 1976, A dictionary of chromatography: New York, Wiley, 191 p.

Guy, H.P., and Norman, V.W., 1970, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 3, Chapter C2, 59 p.

James, A.T., and Martin, A.J.P., 1952, Gas-liquid partition chromatography: The separation and microestimation of volatile fatty acids from formic acid to dodecanoic acid: Biochemical Journal, v. 50, p. 679–690.

Langmuir, Irving, 1918, The adsorption of gas on plane surfaces of glass, mica and platinum: Journal of the American Chemical Society, v.40, p. 1361–1402.

Martin, A.J.P., and Synge, R.L.M., 1941, A new form of chromatogram employing two liquid phases. I. A theory of chromatography. II. Application to the microdetermination of the higher monoamino acids in proteins: Biochemical Journal, v. 35, p. 1358–1368.

McFadden, W.H., ed., 1973, Techniques of combined gas liquid chromatography/mass spectrometry: Applications in organic analysis: New York, Wiley, 463 p.

McLafferty, F.W., 1967, Interpretation of mass spectra: New York, Benjamin, 229 p.

McNair, H.M., and Bonelli, E.J., 1969, Basic gas chromatography: Berkeley, Calif., Consolidated Printers, 306 p.

Oswald, E.O., Albro, P.W., and McKinney, J.D., 1974, Utilization of gas–liquid chromatography coupled with chemical ionization of potentially hazardous environmental agents and their metabolites: Journal of Chromatography, v. 98, p. 363–448.

Safe, Stephen, and Hutzinger, Otto, 1973, Mass spectrometry of pesticides and pollutants: Cleveland, Ohio, CRC Press, 220 p.

Analytical Methods

Carbon, organic, dissolved, wet oxidation (O–1100–83)

Parameter	*Code*
Carbon, organic, dissolved, (mg/L as C)	00681

1. Application

This method is suitable for the analysis of water, water–suspended-sediment mixtures, brines, and waste waters containing at least 0.1 mg/L of dissolved organic carbon (DOC). The method is not suitable for the determination of volatile organic constituents.

2. Summary of method

The sample is acidified, purged to remove inorganic forms of carbon, and oxidized with persulfate in an autoclave at 116–130°C. The resultant carbon dioxide is measured by nondispersive infrared spectrometry.

3. Interferences

3.1 Inorganic forms of carbon usually present in most waters are readily converted to carbon dioxide when acidified but will interfere if the sample is not purged adequately. Purgeable organic compounds are lost during this step.

3.2 Water samples containing large concentrations of reducing agents will interfere by decomposing the persulfate oxidant.

4. Apparatus

4.1 *Ampules,* precombusted, 10 mL, glass, Oceanography International, or equivalent.

4.2 *Ampule purging and sealing unit,* Oceanography International, or equivalent.

4.3 *Autoclave,* Oceanography International 0512AU, or equivalent.

4.4 *Carbon analyzer,* Oceanography International, or equivalent.

5. Reagents

Carbon-free reagent water is required. All reagents should be analyzed to determine carbon content, and any reagent that yields a significant blank value should be rejected.

5.1 *Carbon standard solution,* 1.00 mL = 1.00 mg C (carbon): Dissolve 2.1254 g potassium hydrogen phthalate (primary standard grade, dried at 105°C for 1 h) in reagent water and dilute to 1,000 mL. Store at 4°C.

5.2 *Phosphoric acid solution,* 1.2 *N*: Add 83 mL H_3PO_4 (85 percent) to reagent water and dilute to 1 L with reagent water. Store in a tightly stoppered bottle.

5.3 *Potassium persulfate,* reagent grade, granular: Finely divided forms of this reagent should be avoided.

6. Procedure

6.1 Add 0.2 g potassium persulfate (a dipper calibrated to deliver 0.2 g may be used) and 0.5 mL 1.2 *N* phosphoric acid solution to precombusted ampules.

6.2 Pipet (class A pipets are recommended) a volume of water sample (10.0 mL maximum) into an ampule and adjust the volume to 10 mL with reagent water. If the sample contains precipitated material, it should be homogenized to ensure accurate and reproducible subsampling.

6.3 Prepare one reagent blank (10 mL reagent water plus acid and oxidant) for every 15 to 20 water samples.

6.4 Prepare standards to cover the range 0.1 to 40 mg C/L by dilution of the carbon standard solution (1.00 mL = 1.00 mg C).

6.5 Immediately place the filled ampules on the purging and sealing unit and purge them at 60 mL/min for 6 min with purified oxygen.

6.6 Seal the ampules according to instructions in the manufacturer's manual.

6.7 Place the sealed samples, blanks, and a set of standards in ampule racks inside an autoclave and digest for 4 h at 116–130°C.

6.8 Set the sensitivity range of the carbon analyzer unit by adjusting the zero and span controls in accordance with instructions in the manufacturer's manual.

6.9 Break the combusted ampules in the cutter assembly of the carbon analyzer, sweep the carbon dioxide into the infrared cell with nitrogen gas, and record the area of each carbon dioxide peak. CAUTION: Combusted ampules are under positive pressure and should be handled with care to prevent them from exploding.

7. Calculations

7.1 Prepare an analytical curve by plotting the peak area of each standard versus the concentration (mg/L) of the organic carbon standards.

7.2 The relationship between peak area and carbon concentration is curvilinear. Operating

curves must be defined each day the samples are analyzed.

7.3 Determine the concentration of dissolved organic carbon in each sample by comparing its peak area with the analytical curve.

7.4 Multiply the result of step 7.3 by the appropriate dilution factor.

8. Report

Report dissolved organic carbon concentration (DOC) as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Multiple determinations of four different concentrations of aqueous potassium acid phthalate samples at 2.00, 5.00, 10.0, and 40.0 mg/L of carbon resulted in mean values of 2.2, 5.3, 9.9, and 38 mg/L and standard deviations of 0.13, 0.15, 0.11, and 1.4, respectively.

9.2 The precision may also be expressed in terms of percent relative standard deviation, as follows:

Number of replicates	*Mean (mg/L)*	*Relative standard deviation (percent)*
9	2.2	5.9
10	5.3	2.8
10	9.9	1.1
10	38	3.7

Selected references

Fredericks, A.D., 1968, Concentration of organic carbon in the Gulf of Mexico: Office of Naval Research, Report 68-27T, 65p.

Oceanography International Corporation, 1970, The total carbon system operating manual: College Station, Tex., 51 p.

Carbon, organic, total, wet oxidation (O-3100-83)

Parameter	*Code*
Carbon, organic, total (mg/L as C)	00680

1. Application

This method is suitable for the analysis of water, water-suspended-sediment mixtures, brines, and waste waters containing at least 0.1 mg/L of total organic carbon (TOC). The method is not suitable for the determination of volatile organic constituents.

2. Summary of method

The sample is acidified, purged to remove inorganic forms of carbon, and oxidized with persulfate in an autoclave at 116–130°C. The resultant carbon dioxide is measured by nondispersive infrared spectrometry.

3. Interferences

3.1 Inorganic forms of carbon usually present in most waters are readily converted to carbon dioxide when acidified but will interfere if the sample is not purged adequately. Purgeable organic compounds are lost during this step.

3.2 Water samples containing large concentrations of reducing agents interfere by decomposing the persulfate oxidant.

4. Apparatus

4.1 *Ampules,* precombusted, 10 mL, glass, Oceanography International, or equivalent.

4.2 *Ampule purging and sealing unit,* Oceanography International, or equivalent.

4.3 *Autoclave,* Oceanography International 0512AU, or equivalent.

4.4 *Carbon analyzer,* Oceanography International, or equivalent.

4.5 *Homogenizer,* Willems Polytron PT-10ST, Brinkman Instruments, or equivalent.

5. Reagents

Carbon-free reagent water is required. All reagents should be analyzed to determine carbon content, and any reagent that yields a significant blank value should be rejected.

5.1 *Carbon standard solution,* 1.00 mL = 1.00 mg C (carbon): Dissolve 2.1254 g potassium hydrogen phthalate (primary standard grade, dried at 105°C for 1 h in reagent water and dilute to 1,000 mL. Store at 4°C.

5.2 *Phosphoric acid solution,* 1.2 *N:* Add 83 mL H_3PO_4 (85 percent) to reagent water and dilute to 1 L with reagent water. Store in a tightly stoppered glass bottle.

5.3 *Potassium persulfate,* reagent grade, granular: Finely divided forms of this reagent should be avoided.

6. Procedure

6.1 Add 0.2 g potassium persulfate (a dipper calibrated to deliver 0.2 g may be used) and 0.5 mL of 1.2 *N* phosphoric acid solution to precombusted ampules.

6.2 Homogenize the sample until it is uniformly suspended. Rinse the homogenizer with distilled water after each use.

6.3 Pipet (class A pipets are recommended) a volume of water sample (10.0 mL maximum) into an ampule and adjust the volume to 10 mL with reagent water.

6.4 Prepare one reagent blank (10 mL reagent water plus acid and oxidant) for every 15 to 20 water samples.

6.5 Prepare standards to cover the range 0.1 to 40 mg C/L by dilution of the carbon standard solution (1.00 mL = 1.00 mg C).

6.6 Immediately place the filled ampules on the purging and sealing unit and purge them at 60 mL/min for 6 min with purified oxygen.

6.7 Seal the ampules according to instructions in the manufacturer's manual.

6.8 Place the sealed samples, blanks, and a set of standards in ampule racks, place the racks in an autoclave, and digest for 4 h at 116–130°C.

6.9 Set the sensitivity range of the carbon analyzer by adjusting the zero and span controls in accordance with instructions in the manufacturer's manual.

6.10 Break the combusted ampules in the cutter assembly of the carbon analyzer, sweep the carbon dioxide into the infrared cell with nitrogen gas, and record the area of each carbon dioxide peak. CAUTION: Combusted ampules are under positive pressure and should be handled with care to prevent them from exploding.

7. Calculations

7.1 Prepare an analytical curve by plotting the peak area of each standard versus the concentration (mg/L) of the organic carbon standards.

7.2 The relationship between peak area and carbon concentration is curvilinear. Operating curves must be defined each day the samples are analyzed.

7.3 Determine the concentration of total organic carbon in each sample by comparing its peak area with the analytical curve.

7.4 Multiply the result of step 7.3 by the appropriate dilution factor.

8. Report

Report total organic carbon concentration (TOC) as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for total organic carbon will be greater than that reported for dissolved organic carbon (method O–1100).

Selected references

Fredericks, A.D., 1968, Concentration of organic carbon in the Gulf of Mexico: Office of Naval Research, Report 68–27T, 65 p.

Oceanography International Corporation, 1970, The total carbon system operating manual: College Station, Tex., 51 p.

Carbon, organic, suspended, wet oxidation (O–7100–83)

Parameter	*Code*
Carbon, organic, suspended (mg/L as C)	00689

1. Application

This method is suitable for the analysis of suspended organic carbon (SOC) constituents found in natural waters, brines, and waste waters. The method is not suitable for the determination of volatile organic constituents.

2. Summary of method

The sample is collected on a silver filter, acidified, purged to remove inorganic carbon, and oxidized with persulfate in an autoclave at 116–130°C. The resultant carbon dioxide is measured by nondispersive infrared spectrometry.

3. Interferences

3.1 Inorganic forms of carbon usually present in most waters are readily converted to carbon dioxide when acidified but will interfere if the sample is not purged adequately. Purgeable organic compounds are lost during this step.

3.2 Water samples containing large concentrations of reducing agents will interfere by decomposing the persulfate oxidant.

4. Apparatus

4.1 *Ampules*, precombusted, 10 mL, glass, Oceanography International, or equivalent.

4.2 *Ampule purging and sealing unit*, Oceanography International, or equivalent.

4.3 *Autoclave*, Oceanography International 0512AU, or equivalent.

4.4 *Carbon analyzer*, Oceanography International, or equivalent.

5. Reagents

Carbon-free reagent water is required. All reagents should be analyzed to determine carbon content, and any reagent that yields a significant blank value should be rejected.

5.1 *Carbon standard solution,* 1.00 mL = 1.00 mg C (carbon): Dissolve 2.1254 g potassium hydrogen phthalate (primary standard grade, dried at 105°C for 1 h in reagent water and dilute to 1,000 mL. Store at 4°C.

5.2 *Phosphoric acid,* 14.7 *N* (85 percent), reagent grade.

5.3 *Potassium persulfate,* reagent grade, granular: Finely divided forms of this reagent should be avoided.

6. Procedure

6.1 Carefully remove the silver filter from its container with forceps and coil it into a roll about ⅛ inch in diameter using a steel or glass mandril.

6.2 Drop the coiled filter into a precombusted glass ampule. Add 0.5 mL of 14.7 *N* (85 percent) phosphoric acid and 8 mL reagent water.

6.3 Repeat steps 6.1 and 6.2 using the blank filter supplied by field personnel.

6.4 Cover the top of the ampule with aluminum foil and heat on a steam bath for 12 to 24 h.

6.5 Prepare standards to cover the range 0.1 to 40 mg C/L by dilution of the carbon standard solution (1.00 mL = 1.00 mg C). Pipet 10.0 mL of each standard into precombusted glass ampules containing 0.5 mL of 14.7 *N* phosphoric acid.

6.6 Introduce 0.2 g potassium persulfate (a dipper calibrated to deliver 0.2 g may be used) and rinse down any solid adhering to the neck of the ampule with 2 mL of reagent water.

6.7 Immediately place the filled ampules on the purging and sealing unit and purge them at 60 mL/min for 6 min with purified oxygen.

6.8 Seal the ampules according to instructions in the manufacturer's manual.

6.9 Place the sealed samples, blanks, and a set of standards in ampule racks inside an autoclave and digest for 4 h at 116–130°C.

6.10 Set the sensitivity range of the carbon analyzer unit by adjusting the zero and span controls in accordance with instructions in the manufacturer's manual.

6.11 Break the combusted ampules in the cutter assembly of the carbon analyzer, sweep the carbon dioxide into the infrared cell with nitrogen gas, and record the area of each carbon dioxide peak. CAUTION: Combusted ampules are under positive pressure and should be handled with care to prevent them from exploding.

7. Calculations

7.1 Prepare an analytical curve by plotting the peak area of each standard versus the concentration (mg/L) of the organic carbon standards.

7.2 The relationship between peak area and carbon concentration is curvilinear. Operating curves must be defined each day the samples are analyzed.

7.3 Calculate the concentration of suspended organic carbon in the original water sample from the equation

$$\text{Carbon, suspended organic (mg/L)} = \frac{S-B}{V},$$

where

S = apparent carbon concentration of sample, in mg/L,

B = apparent carbon concentration of blank, in mg/L,

V = number of liters of water filtered (in field).

8. Report

Report suspended organic carbon concentrations (SOC) as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for suspended organic carbon will be greater than that reported for dissolved organic carbon (method O–1100).

Selected references

Menzel, D.W., and Vacaro, F.F., 1964, The measurement of dissolved organic and particulate carbon in seawater: Limnology and Oceanography, v. 9, p. 138–142.

Oceanography International Corporation, 1970, The total carbon system operating manual: College Station, Tex., 51 p.

Carbon, inorganic plus organic, total in bottom material, dry weight, induction furnace (O–5101–83)

Parameter	*Code*
Carbon, total in bottom material dry weight (g/kg as C)	00693

1. Application

This method is suitable for the determination of total carbon in bottom material at concentrations of 0.1 g/kg and above.

2. Summary of method

A sample is oxidized, in the presence of oxygen and a catalyst, in a crucible in an induction furnace. The carbon dioxide evolved is measured by thermal conductivity.

3. Interferences

Sulfur, halides, and water vapor can interfere but are eliminated by traps. Carbon impurities in the reagents can interfere.

4. Apparatus

4.1 *Carbon determinator*, Leco WR-12, or equivalent, consisting of an oxygen purification system, an induction furnace, dust traps, moisture traps, a halide trap, a sulfur trap, a catalytic furnace, and thermistor cells.

4.2 *Combustion crucibles*, carbon-free, disposable, Leco 528-018, or equivalent.

4.3 *Dryer-balance*, consisting of a Mettler LP 15 dryer, a Mettler PC 440 balance, and a Mettler GC 301 application input device, or equivalents.

4.4 *Glass reagent scoops*, Leco 501-032, or equivalent.

4.5 *Grinder*, Torsion MG 2 electric mortar grinder, or equivalent.

4.6 *Sieves*, U.S. No. 18 (2-mm opening) and U.S. No. 60 (0.25-mm opening).

5. Reagents

5.1 *Carbon standards*, 1 g steel rings containing known amounts of carbon C.

5.1.1 High standard, ca. 0.8 percent C, Leco 501-506.

5.1.2 Low standard, ca. 0.1 percent C, Leco 501-502.

5.2 *Catalytic furnace reagent*, platinum on silica, Leco 501-587.

5.3 *Combustion accelerators*

5.3.1 Copper accelerator, Leco 501-263, or equivalent.

5.3.2 Iron chip accelerator, Leco 501-077, or equivalent.

5.4 *Oxygen*, commercial grade.

5.5 *Sodium carbonate*, anhydrous, reagent grade.

5.6 *Trap reagents*

5.6.1 Anhydrone, Leco 501-171, or equivalent, for moisture trap.

5.6.2 Antimony, Leco 769-608, or equivalent, for halide trap.

5.6.3 Ascarite, Leco 183-001, or equivalent, for oxygen purification system.

5.6.4 Manganese dioxide, Leco 501-587, or equivalent, for sulfur trap.

6. Procedure

6.1 Sieve the wet sample through a 2-mm sieve. Place the sieved sample in an aluminum pan that has been fired at 550°C for 1 h and dry the material at 40°C overnight.

6.2 Grind the dried material in an electric grinder, to a powder that passes a No. 60 sieve.

6.3 To determine the percent of dry material, the initial powder must be weighed before drying. Dry an accurately weighed amount of the powder (approximately 1 g) in a combination dryer-balance at 105°C to a constant weight. Determine the percent of dry material.

6.4 Follow the instructions in the manufacturer's manual to leak-test, blank, and calibrate the carbon determinator.

6.5 Place a new combustion crucible on an analytical balance and add 1 g (maximum) of the sample (obtained in step 6.2). Record the sample weight to three significant figures.

6.6 Add a scoopful of iron chip accelerator, spreading it evenly over the sample.

6.7 Add a scoopful of copper accelerator in a similar manner.

6.8 Combust the sample in the determinator and record the reading of percent carbon for the sample.

6.9 Repeat the determination using a smaller sample, if the reading is higher than 5.000 percent C.

7. Calculations

7.1 Calculate the weight of dry bottom material in the sample from the equation

$$W = \frac{S \times D}{100},$$

where

W = weight of dry bottom material in sample, in g,

S = weight of sample, from step 6.5, in g, and

D = percent of dry material in sample, from step 6.3.

7.2 Calculate the concentration of carbon in the bottom material from the equation

$$C\ (\text{g/kg}) = \frac{10 \times DVM \times C_s}{W},$$

where

DVM = direct readout of percent carbon for sample weight as set on compensator,

W = weight of dry bottom material in sample, obtained in step 7.1, in g, and

C_s = compensator setting, in g.

8. Report

Report total carbon concentrations in bottom material as follows: less than 1 g/kg, one decimal; 1 g/kg and above, two significant figures.

9. Precision

Single-operator precision data for carbon steel standards for each standard (10 replicates each) is as follows:

Carbon steel (percent)	*Mean determined (percent)*	*Relative standard deviation (percent)*
0.0440	0.0442	3.6
0.166	0.166	2.1
0.941	0.943	0.86

Selected reference

Leco Corporation, Instruction manual, WR-12, Carbon determinator, model 761-100, 1976: 3000 Lakeview Ave., St. Joseph, MI 49085.

Carbon, inorganic, total in bottom material, modified Van Slyke (O-5102-83)

Parameter	*Code*
Carbon, inorganic, total in bottom material, dry weight (g/kg as C)	00686

1. Application

This method is suitable for the determination of inorganic carbon in bottom material at concentrations of 0.1 g/kg and above.

2. Summary of method

A dry bottom-material sample is placed in a modified Van Slyke apparatus and treated with aqueous hydrochloric acid. The sample is heated, and the amount of carbon dioxide evolved is measured manometrically.

3. Interferences

Sulfides and sulfites form gaseous hydrogen sulfide and sulfur dioxide, respectively, in the presence of acid and heat. These gases are evolved from the sample along with the carbon dioxide and give a positive error.

4. Apparatus

Numbers in parentheses refer to figure 1.

4.1 *Addition tube* (1), 25 mm od (outside diameter)×30 cm, with 19/22 ground-glass fitting and a 120°three-way stopcock (see item 4.15), custom-fitted to the condenser (4).

4.2 *Auto-bubbler gas absorption pipet* (2), Burrell, part 40-105-10 or equivalent.

4.3 *Bunsen burner* (3).

4.4 *Condenser* (4), custom-made, 200 mm long with an expansion bulb (23 mm od). The condenser is fitted to the addition tube (1), as shown in figure 1.

4.5 *Constant-temperature bath and circulator* (5), Forma Scientific 2006, or equivalent.

4.6 *Dryer-balance*, consisting of a Mettler LP 15 dryer, a Mettler PC 440 balance, and a Mettler GC 301 application input device, or equivalents.

4.7 *Funnel* (6), custom-made, 100-mL or greater capacity, with a 19/22 ground-glass joint.

4.8 *Gas buret* (7), 100-mL capacity, Kimax 30025-A, or equivalent, fitted to stopcock (13) (see item 4.15).

4.9 *Gas buret cooling jacket* (8), 25 mm od× 30 cm, custom-made to encase the buret (7).

4.10 *Grinder*, Torsion MG 2 electric mortar grinder, or equivalent.

4.11 *Leveling bulb reservoirs A* (9) *and B* (10), 250-mL capacity, Corning 2080, or equivalent.

4.12 *Rubber stopper* (11), size 6, one hole.

4.13 *Sample vial* (12), custom-made, 25 mL capacity, 25 mm id (inside diameter)×85 mm round-bottom Pyrex tube, flanged to fit tightly around the rubber stopper (12).

4.14 *Sieves*, metal, U.S. No. 18 (2-mm opening), 15 cm id, and U.S. No. 60 (0.25-mm opening), 18.7 cm id.

4.15 *Stopcocks A* (13) and *B* (14) three-way, 120°, narrow bore, Kimax 4160F, or equivalent.

4.16 *Tygon tubing* (15), ¼ in id, 1/16 in wall, used to make connections in the apparatus.

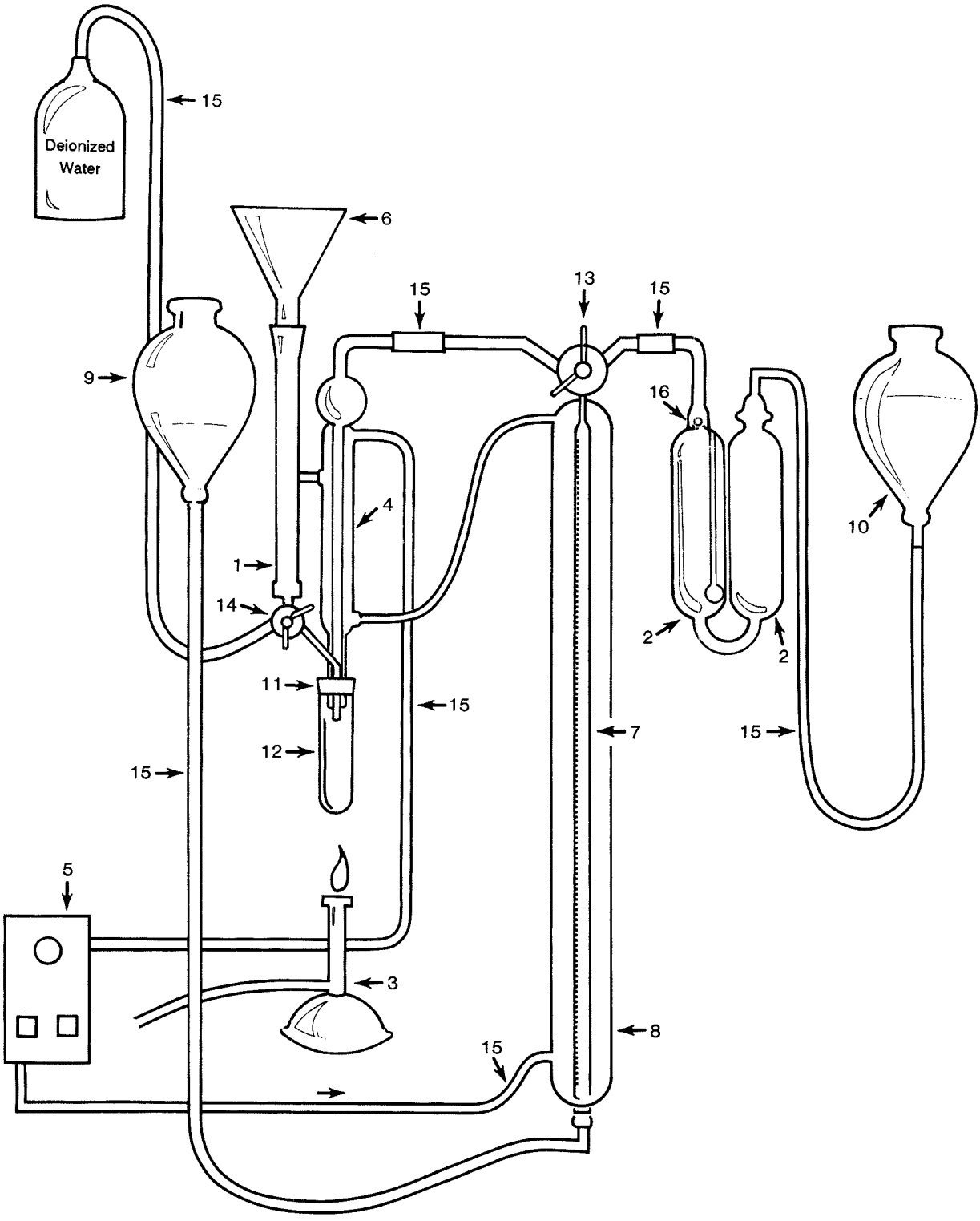

Figure 1.—Apparatus for the manometric determination of carbon dioxide.

5. Reagents

5.1 *Hydrochloric acid*, 3.2 *N*: Add 270 mL concentrated HCl (sp. gr. 1.19) to 500 mL deionized water. CAUTION: Add the acid slowly with stirring. Allow to cool to room temperature and dilute to 1L with deionized water.

5.2 *Sodium carbonate*, anhydrous, reagent grade: Dry the material at 105°C for at least 1 h and store in a desiccator.

5.3 *Sodium hydroxide*, 10 *N*: Dissolve 400 g NaOH in 500 mL deionized water. CAUTION: Add the pellets slowly with stirring. Allow to cool to room temperature and dilute to 1 L.

5.4 *Sulfuric acid*, 7.2 *N*: Add 200 mL concentrated H_2SO_4 (sp. gr. 1.84) to 500 mL deionized water. CAUTION: Add the acid slowly with stirring. Allow to cool to room temperature and dilute to 1 L. Add 5 mg of methyl red indicator.

6. Procedure

6.1 Set up the apparatus as follows:

6.1.1 Assemble the apparatus as in figure 1.

6.1.2 Add 7.2 *N* H_2SO_4 to leveling bulb A (9) and the gas buret as follows:

6.1.2.1 Turn stopcock A (13) to the position that connects the left arm with the gas buret.

6.1.2.2 Add 200 mL of 7.2 *N* H_2SO_4 to leveling bulb A (9) and fill the gas buret by raising the leveling bulb until the buret is filled just to stopcock A (13).

6.1.2.3 Close stopcock A (13). Lower leveling bulb A (9) and place it in a ring support. The support must be positioned approximately 50 cm below stopcock A (13).

6.1.3 Add 10 *N* NaOH solution to leveling bulb B (10) and to the auto-bubbler (2) as follows:

6.1.3.1 Turn stopcock A (13) to the position that connects both arms.

6.1.3.2 Mark a line about 1 cm above the check valve (16) of the auto-bubbler (2).

6.1.3.3 Fill the auto-bubbler (2) to the mark (step 6.1.3.2) by adding 200 mL of 10 *N* NaOH solution to leveling bulb B (10) and raising the bulb.

6.2 Circulate tapwater through the apparatus until a constant temperature is achieved. Record the temperature to the nearest 0.1°C.

6.3 Record the atmospheric pressure to the nearest mm of mercury.

6.4 Calibrate the system as follows:

6.4.1 Weigh 50 to 80 mg sodium carbonate on an analytical balance. Record the weight to the nearest 0.1 mg.

6.4.2 Transfer the sodium carbonate to a sample vial. Add two boiling chips, and secure the vial to the rubber stopper (11) by applying an upward, twisting motion.

6.4.3 Close stopcock B (14).

6.4.4 Turn stopcock A (13) to the position that connects the left arm with the gas buret.

6.4.5 Pour approximately 20 mL of 3.2 *N* HCl into the funnel (6).

6.4.6 Open stopcock B (14) to the position that connects the addition tube (1) with the sample vial. Allow 15 mL of 3.2 *N* HCl to flow into the vial. CAUTION: Add the acid slowly. Do not allow the acid level in the addition tube to reach stopcock B (14).

6.4.7 Heat the bottom of the vial for at least 2 min until no more gas is evolved. This can be determined by watching the liquid level in the buret.

6.4.8 Turn off the burner and fill the addition tube (1) and the funnel (6) with water.

6.4.9 Open stopcock B (14) to the position that connects the addition tube (1) with the sample vial and flood the path from the sample vial to stopcock A (13). Close stopcock A (13).

6.4.10 Move leveling bulb A (9) next to the buret and position it so that the liquid in the bulb and in the buret are at the same level.

6.4.11 Read and record the volume of gas in the buret, to the nearest 0.1 mL.

6.4.12 Raise leveling bulb A (9) and turn stopcock A (13) to the position that connects the buret with the auto-bubbler (2). Push the gas from the buret into the auto-bubbler by raising leveling bulb A (9) until the H_2SO_4 in the buret reaches stopcock A (13).

6.4.13 Lower leveling bulb A (9) until the NaOH level in the auto-bubbler (2) reaches its original level (step 6.1.3.2).

6.4.14 Raise and lower leveling bulb A (9) as in steps 6.4.12 and 6.4.13, two more times. Finish with the NaOH at its original level.

6.4.15 Close stopcock A (13) and position leveling bulb A (9) as in step 6.4.10.

6.4.16 Read and record the volume of gas in the buret, to the nearest 0.1 mL.

6.4.17 Calculate (see steps 7.1–7.3) the concentration of carbon in the Na_2CO_3. If recovery is

at least 95 percent, proceed to step 6.5. If recovery is less than 95 percent, check for leaks and ensure that the pH of the NaOH is no less than 14. Correct any problems and repeat the analysis (steps 6.4.1–6.4.16) until a recovery of at least 95 percent is attained.

6.5 Prepare for the next determination by returning leveling bulb A (9) to a position above stopcock A (13), removing the vial, opening stopcock A (13) and allowing the liquid above the vial to empty into a waste container.

6.6 Close stopcock A (13) when the H_2SO_4 level reaches the stopcock.

6.7 Prepare the sample for analysis as follows:

6.7.1 Sieve the wet sample through a 2-mm sieve. Place the sample in an aluminum pan that has been fired at 550°C for 1 h. Dry the material at 40°C overnight.

6.7.2 Grind the dried material in an electric grinder to a powder that passes a No. 60 sieve.

6.7.3 Dry an accurately weighed amount of the powder (approximately 1 g) in a combination dryer-balance at 105°C to a constant weight. Determine the percent of dry material.

6.8 Analyze the sample as follows:

6.8.1 Weigh approximately 2 g of sample obtained in step 6.7.2, to the nearest mg.

6.8.2 Transfer the sample to a sample vial using a small funnel. Add two boiling chips, and secure the vial to the rubber stopper by applying a slight upward, twisting motion.

6.8.3 Place leveling bulb A (9) in a position approximately 50 cm below stopcock A (13) and repeat steps 6.4.3–6.4.16, 6.5, and 6.6.

6.8.4 Repeat the analysis with a smaller sample if the volume of evolved carbon dioxide exceeds the volume measurable in the system (approximately 20 mL).

7. Calculations

7.1 Calculate the weight of dry bottom material in the sample from the equation

$$W = \frac{S \times D}{100},$$

where

W = weight of dry bottom material in sample, in g,

S = weight of sample, from step 6.8.1, in g, and

D = percent of dry material in sample, from step 6.7.3.

7.2 Calculate the volume of carbon dioxide evolved from the sample from the equation

$$V = V_i - V_f$$

where

V = volume of carbon dioxide evolved from sample, in mL,

V_i = volume reading from step 6.4.11, in mL, and

V_f = volume reading from step 6.4.16, in mL.

7.3 Calculate the inorganic carbon concentration in the original sample from the equation

$$C\,(\text{g/kg}) = \frac{V}{W} \times \frac{273°C}{273°C + t} \times \frac{P_{atm} - P_{water}}{760\ \text{mm}} \times \frac{12.0}{22.4},$$

where

V = volume of carbon dioxide evolved from sample, from step 7.2, in mL,

W = weight of dry bottom material in sample, from step 7.1, in g,

t = temperature of carbon dioxide, from step 6.2, in °C

P_{atm} = atmospheric pressure determined in step 6.3, in mm of mercury, and

P_{water} = vapor pressure of water at temperature t, from a reference source, in mm of mercury.

8. Report

Report inorganic carbon in bottom material as follows: less than 10 g/kg, one decimal; 10 g/kg and above, two significant figures.

9. Precision

Precision data are not available.

Selected references

Rader, L.F., and Grimaldi, F.S., 1961, Chemical analyses for selected minor elements in Pierre shale: U.S. Geological Survey Professional Paper 391–A, 45 p.

Van Slyke, D.D., and Folch, J., 1940, Manometric carbon determination: Journal of Biological Chemistry, v. 136, p. 509–541.

Carbon, organic, dissolved, fractionation (O–1103–83)

Parameter — *Code*

Carbon, organic, dissolved, fractionation --- None assigned.

1. Application

Dissolved organic carbon fractionation analysis can be applied to water samples whose DOC concentrations range between 5 and 25 mg/L and whose specific conductance is less than 2,000 µmhos/cm at 25°C. Water samples whose DOC is less than 5 mg/L can be freeze-concentrated to the specific conductance limit. DOC concentrations greater than 25 mg/L need to be diluted with organic carbon-free reagent water to approximately 25 mg/L DOC prior to analysis. DOC that is sufficiently volatile to be lost during a 6 min gas purge of an acidified sample is not included in the fractionation.

2. Summary of method

A flow chart of the analytical scheme of DOC fractionation analysis is given in figure 2.

2.1 Dissolved organic carbon is first fractionated and classified as hydrophobic or hydrophilic organic solute on the basis of the solute's capability for physical adsorption. Hydrophobic organic solutes are separated from hydrophilic organic solutes by physical adsorption of hydrophobic solutes upon Amberlite–XAD–8 resin. Both the hydrophobic and hydrophilic organic solute classes are secondarily fractionated into acid, base, and neutral compound classes, thus giving a total of six characteristic DOC fractions. The procedure requires 2 days to complete.

2.2 Hydrophobic acids and bases are selectively desorbed from XAD–8 resin with aqueous alkali and acid, respectively. Hydrophobic neutral solutes are not desorbed with aqueous solvents. After removal of the hydrophobic solutes from solution by adsorption upon XAD–8 resin, the hydrophilic solutes are fractionated by selectively adsorbing hydrophilic bases as cations on a cation-exchange resin, followed by selective adsorption of the anionic hydrophilic acids upon an anion exchange resin. Hydrophilic neutral organic solutes are not adsorbed by any of the adsorbents. The fractionation is based on an organic carbon materials balance using DOC as the quantifying parameter.

3. Interferences

3.1 Water samples whose specific conductance exceed 2,000 µmhos/cm contain inorganic ionic salts in concentrations that exceed the capacity of the ion-exchange resins. These samples can be analyzed if the DOC exceeds 5 mg/L after the sample is diluted with reagent water to a specific conductance of 2,000 µmhos/cm.

3.2 A few samples will form organic precipitates when they are acidified to pH 2 in the analytical fractionation scheme. Care should be taken to suspend these precipitates by stirring, so that they are incorporated into the column containing XAD–8 resin.

3.3 Colloidal clay will foul the resin adsorbents. All samples should be field-filtered prior to analysis to remove particulate and colloidal material.

3.4 All reagents must be tested for contamination by running reagent blanks.

4. Apparatus

4.1 *Carbon analyzers*

4.1.1 *Beckman 915*, or equivalent.

4.1.2 *Oceanography International*, or equivalent.

4.2 *Clamps*: Size 18 pinch clamps with compression screw for ball-and-socket joints.

4.3 *Columns*: All columns are custom-prepared from 11 mm od (outside diameter)×7 mm id (inside diameter) Pyrex glass tubing, and are connected with 18/7 ball-and-socket ground-glass joints.

4.3.1 *Anion-exchange columns*: Two columns are needed. They are 18 cm long between the base of the socket joint at the top of the column and the 6 mm od×2 mm id glass nipple at the bottom of the column. Column capacity is approximately 6 mL.

4.3.2 *Cation-exchange column*: The column is 10 cm long between the base of the socket joint on the top and the four indentations used to hold the glass-wool plug above the ball joint on the bottom. Column capacity is approximately 2.5 mL. Indentations are 1 cm from the ball joint.

4.3.3 *XAD–8 column*: The column is 8 cm long between the four indentations at the ends of the column. Ball joints are fused to both ends of the column above and below the indentations. Column capacity is approximately 3 mL. Indentations are 1 cm from the ball joints.

4.3.4 *Tubing-column adaptors*: Two socket-joint and two ball-joint fittings fused to 6 mm od×2 mm id glass nipples are adaptors, which enable connection of the Teflon tubing to the columns.

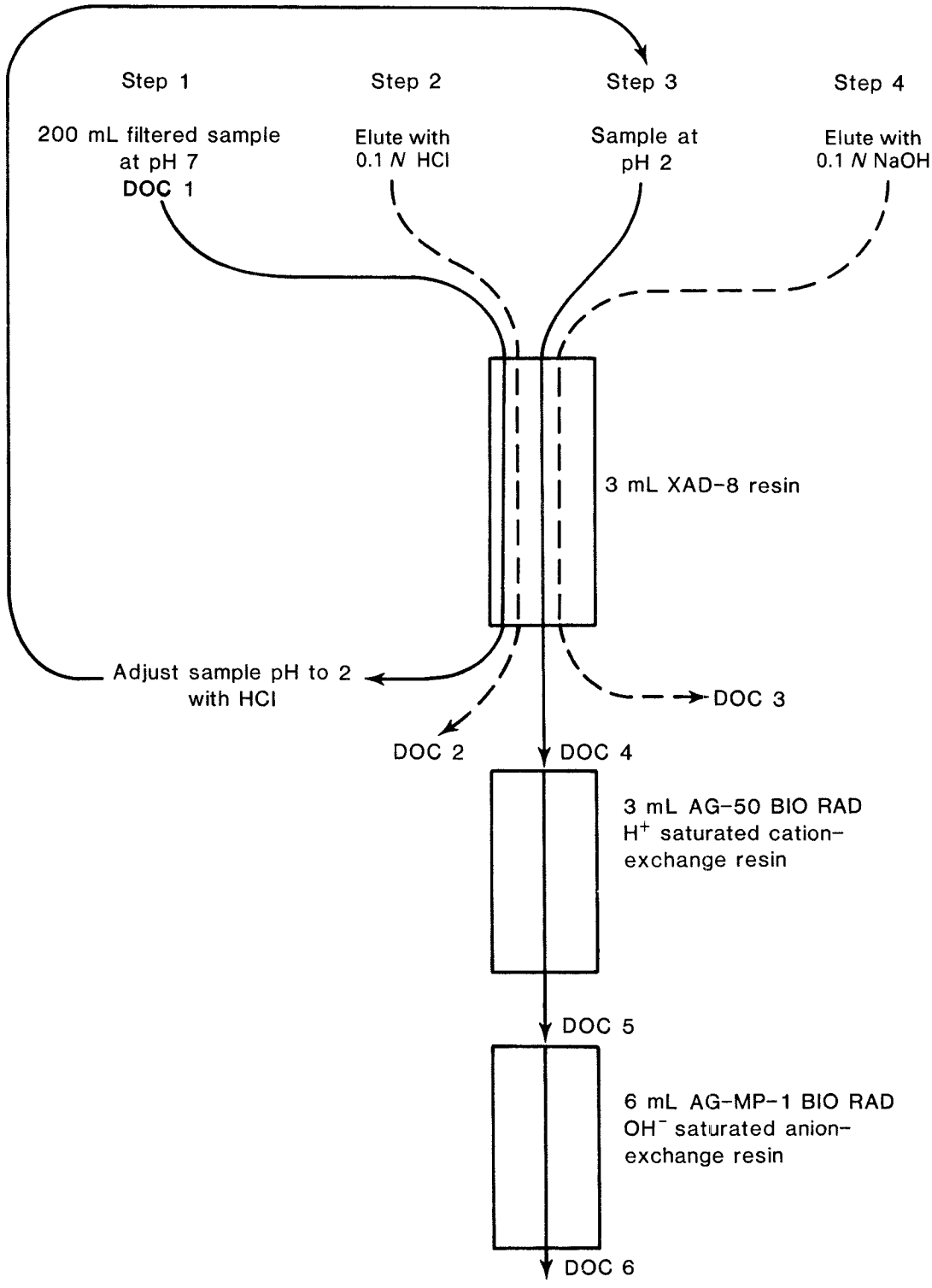

Figure 2. — Dissolved organic carbon fractionation analytical scheme.

4.4 *Extraction apparatus, Soxhlet*: 145 mL thimble capacity, 300 mL flask capacity.

4.5 *Graduate cylinders*: One 200 mL capacity and five 25 mL capacity, with ground-glass stoppers.

4.6 *Pump*: Cole Palmer Masterflex with silicone-rubber tubing (1–5 mL/min), or equivalent.

4.7 *Tubing, Teflon*: ⅛ in od×.085 in id (32 mm od ×22 mm id).

4.8 *Silver membrane filter*: 0.45 μm porosity.

5. Reagents

5.1 *Acetonitrile*: Reagent grade.

5.2 *Diethyl ether*: Reagent grade.

5.3 *Glass wool*: Fine fiber. Clean by Soxhlet extraction with methanol for 24 h.

5.4 *Hydrochloric acid*, 1.0 *N* and 0.1 *N*: Prepared by diluting 82.9 and 8.29 mL of concentrated HCl (sp. gr. 1.19) to 1 L, respectively, in carbon-free distilled water.

5.5 *Methanol*: Reagent grade.

5.6 *Resin adsorbents*: All adsorbents must be extensively cleaned before use.

5.6.1 *Anion-exchange resin*: BioRad AG–MP–1, 20–50 mesh, chloride-saturated. Clean by Soxhlet extraction with methanol for 24 h. Store in methanol.

5.6.2 *Cation-exchange resin*: BioRad AG–MP–50, 20–50 mesh, hydrogen-saturated. Clean by Soxhlet extraction with methanol for 24 h. Store in methanol.

5.6.3 *XAD–8 resin*: Available from Rohm and Hass, 20–50 mesh. Clean the XAD–8 resin by first slurrying with 0.1 *N* NaOH, and then decanting off the fines, and store in 0.1 *N* NaOH for 24 h. Decant the sodium hydroxide, slurry in methanol, and decant off the fines with the methanol. Perform sequential 24-h Soxhlet extractions with methanol, acetonitrile, and diethylether. Store resin in methanol.

5.7 *Sodium hydroxide*, 2 *N*, 1 *N*, 0.1 *N*: Prepared by dissolving 80 g, 40 g, and 4 g, respectively, of analytical reagent-grade sodium hydroxide in 1 L of carbon-free distilled water. Purify by passing through OH-saturated AG–MP–1 anion-exchange resin.

5.8 *Water, carbon-free*: Prepare by double distillation of tapwater in a glass still. Prepare bulk quantities of 50 L or more per batch and store in clean glass containers. Water blank should be ≤0.2 mg/L DOC.

6. Procedure

6.1 Samples need to be collected in organic-free glass containers. Filter 200 mL of sample on-site through a silver membrane filter of 0.45μm porosity. Chill on ice (recommended method of sample preservation).

6.2 *Initial parameters*: Before preparing the columns, take two 10-mL aliquots of sample for DOC analysis (DOC 1 in fig. 2). Take a third 10-mL aliquot and determine pH and specific conductance. If the pH is less than 6.5, carefully adjust the pH of the sample to 7.0 by dropwise addition of 1.0 *N* NaOH. Once the DOC and specific conductance parameters are known, dilute or concentrate the sample as specified in the section on "Application."

6.3 *Column packing and final resin purification*: The final tasks in the resin purification procedure are done after the columns are packed with the resin adsorbents. All three columns should be packed at the same time so the reagent solutions used to prepare the columns can be pumped through the columns simultaneously. All resin adsorbents are used only once.

6.3.1 *Anion-exchange column*: Place a small glass-wool plug in the bottom of the anion-exchange column. Pack a 6-mL bed of purified AG–MP–1 resin by pouring the resin slurried in methanol into the column. Do not let the column run dry during the packing procedure. Always keep methanol or water above the resin bed in the column. Pack two columns. Connect the packed columns in series to the transfer tubing and pump; then pass 100 mL of reagent water, 100 mL of 1.0 *N* HCl, 100 mL of 2 *N* NaOH, and 50 mL of reagent water through the two columns at 4 mL/min. Disconnect the columns and discard the resin in the first column of the series. The first column serves as a pre-column to adsorb reagent contaminants which are usually present in the sodium hydroxide. The second column is used in the analysis. For best results, use the prepared anion-exchange column immediately, as the hydroxide-saturated resin is unstable over time and the blank organic carbon values increase during storage.

6.3.2 *Cation exchange column*: Place a glass-wool plug at the four indentations at the bottom of the cation-exchange column. Pack a 3-mL

bed of purified AG–MP–50 resin using the procedure specified in step 6.3.1. Connect the packed column to the transfer tubing and pump; then pass 100 mL of reagent water, 100 mL of 1.0 *N* NaOH, 100 mL of 1.0 *N* HCl, and 50 mL of reagent water through the column at 4 mL/min. Do not let the column run dry after it is prepared.

6.3.3. *XAD–8 column*: Place a glass-wool plug at the four indentations at one end of the column. Pack a 3-mL bed of purified XAD–8 resin using the procedure specified in step 6.3.1, and place a second glass-wool plug at the four indentations above the resin bed. Connect the packed column to the transfer tubing and pump; then pass 500 mL of reagent water, 50 mL of 0.1 *N* HCl, 50 mL of methanol, and 100 mL of reagent water through the column at 4 mL/min. Do not let the column run dry after it is prepared.

6.4 After the three columns are packed and prepared, clamp the three columns together in the following series: XAD–8 column first, cation-exchange column second, anion-exchange column third. Connect the column series to the transfer tubing and pump, and pass reagent water through the columns at 4 mL/min until the DOC in the effluent is 1.0 mg/L or less, as monitored by the Beckman 915 organic carbon analyzer. The volume of water needed to rinse the residual methanol from the columns varies between 1 and 2 L. This is the best point in the 2-day analytical procedure for the overnight pause.

6.5 Just before the sample is analyzed, disconnect the XAD–8 column and pump 50 mL of 0.1 *N* NaOH, followed by 100 mL of reagent water, at 4 mL/min through the XAD–8 column, to desorb any hydrophobic acid contaminants that may have been previously adsorbed from the reagent purification solvents.

6.6 Pump the water sample through the XAD–8 column at 2 mL/min and collect precisely 160 mL of eluent in a 200-mL glass-stoppered graduate cylinder. Follow the sample with a 20-mL wash of reagent water so that a total of 180 mL are collected.

6.7 Pump 0.1 *N* HCl through the XAD–8 column at 1 mL/min until 23 mL are collected. Collect 23 mL of 0.1 *N* HCl in a 25-mL graduate cylinder having a glass stopper. This fraction is used to determine DOC 2 (see fig. 2).

6.8 Carefully adjust the pH of the sample eluent from 6.6 to 2.0 by dropwise addition of concentrated HCl, while stirring the sample.

6.9 Reconnect the XAD–8 column as given in step 6.4, pump the 180 mL of acidified sample through the column series, and take aliquots for DOC determination in the following sequence:

6.9.1 Discard the first 50 mL of sample eluate. This volume is diluted with reagent water from the dead volume in the three columns.

6.9.2 Collect the next 23 mL of eluate in 25-mL glass-stoppered graduate cylinder. This fraction is used to determine DOC 6 (see fig. 2).

6.9.3 Disconnect the anion-exchange column and collect 23 mL of eluate from the cation-exchange column in a 25-mL glass-stoppered graduate cylinder. This fraction is used to determine DOC 5 (fig. 2).

6.9.4 Disconnect the cation-exchange column and collect 23 mL of eluate from the XAD–8 column in a 25-mL glass-stoppered cylinder. This fraction is used to determine DOC 4 (fig. 2).

6.9.5 Pump the remainder of the sample through the XAD–8 column. Desorb the hydrophobic acids by pumping 0.1 *N* NaOH through the column at 1 mL/min. Collect 23 mL of eluate in a glass-stoppered 25-mL graduate cylinder. This fraction is used to determine DOC 3 (fig. 2).

6.10 Thoroughly shake and mix each of the collected fractions in the graduate cylinders before taking aliquots for DOC determination. For samples with low DOC values, the Oceanography International system of carbon determination must be used. The Beckman 915 analyzer can be satisfactorily used if sample DOC is 15–25 mg/L. Analyze each fraction for DOC using the above methodology specified.

6.11 Run a complete DOC fractionation of reagent water blank for each set of samples, and correct each DOC fraction value with the respective blank value obtained.

7. Calculations

Refer to figure 2 and the procedural description for definition of terms and sample fractions. All DOC fractions need to be reported in mg/L units calculated for the concentration in the original water sample prior to dilution or concentration. Following is the list of parameters and the computation formulas:

7.1 Total hydrophobic DOC (mg/L) = mg/L DOC 1 − (1.125 × mg/L DOC 4) (1.125 is a dilution coefficient equal to total volume divided by sample volume).

7.2 Total hydrophilic DOC (mg/L) = 1.125× mg/L DOC 4.

7.3 Hydrophobic base DOC (mg/L) = (mg/L DOC 2 × 0.023)/0.160 (0.023 is the fraction volume, in liters; 0.160 is the sample volume, in liters).

7.4 Hydrophobic acid DOC (mg/L) = (mg/L DOC 3×0.023)/0.160.

7.5 Hydrophobic neutral DOC (mg/L) = total hydrophobic mg/L DOC − hydrophobic base mg/L DOC − hydrophobic acid mg/L DOC.

7.6 Hydrophilic base DOC (mg/L) = 1.125× (mg/L DOC 4 − mg/L DOC 5).

7.7 Hydrophilic acid DOC (mg/L) = 1.125× (mg/L DOC 5 − mg/L DOC 6).

7.8 Hydrophilic neutral DOC (mg/L) = 1.125 × mg/L DOC 6.

Subtract the respective blank DOC values from the equivalent sample DOC fractions.

8. Report

Report all fraction DOC concentrations to two significant figures, in mg/L.

9. Precision

9.1 Two factors influence precision: the variability of the reagent blank DOC that elutes from the columns, and the variability of the DOC determination. The maximum average deviation for duplicate DOC determinations is about 5 percent of the DOC mean and, therefore, also 5 percent of the DOC value of each fraction. The total precision is the sum of the two factors.

9.2 The average deviations in the reaction blank for dissolved organic carbon fractionation analysis are as follows:

Fraction	*Average deviation (mg/L)*
Total hydrophobic DOC	0.2
Total hydrophilic DOC	.2
Hydrophobic base DOC	.1
Hydrophobic acid DOC	.1
Hydrophobic neutral DOC	.4
Hydrophilic acid DOC	.5
Hydrophilic base DOC	.5
Hydrophilic neutral DOC	.3

Selected references

Leenheer, J.A., and Huffman, E.W.D., Jr., 1976, Classification of organic solutes in water by using macroreticular resins: U.S. Geological Survey Journal of Research, v. 4, no. 6, p. 737–751.

Stuber, H.A., and Leenheer, J.A., 1978, Fractionation of organic solutes in oil shale retort waters for sorption studies on processed shale: Preprints, American Chemical Society, Division Fuel Chemistry, v. 23, no. 2, p. 105–174.

Thurman, E.M., Aiken, G.R., and Malcolm, R.L., 1978, The use of macroreticular nonionic resins to preconcentrate trace organic acids from water: Joint Conference on Sensing of Environmental Pollutants, American Chemical Society, 4th, 1977, New Orleans, Proceedings, p. 630–634.

Thurman, E.M., Malcolm, R.L., and Aiken, G.R., 1978, Prediction of capacity factors for aqueous organic solutes adsorbed on a porous acrylic resin: Analytical Chemistry, v. 50, no. 6, p. 775–779.

Organochlorine and organophosphorous compounds, total recoverable (O-3104-83) and dissolved (O-1104-83), gas chromatographic

Parameter	*Code* *Total recoverable*	*Dissolved*
Aldrin	39330	39331
Chlordane	39350	39352
DDD	39360	39361
DDE	39365	39366
DDT	39370	39371
Diazinon	39570	39572
Dieldrin	39380	39381
Endosulfan	39388	82354
Endrin	39390	39391
Ethion	39398	82346
Polychlorinated biphenyls	39516	39517
Polychlorinated naphthalenes	39250	82360
Heptachlor	39410	39411
Heptachlor epoxide	39420	39421
Lindane	39340	39341
Malathion	39530	39532
Methoxychlor	39480	82350
Methyl parathion	39600	39602
Methyl trithion	39790	82344
Mirex	39755	39756
Parathion	39540	39542
Perthane	39034	82348
Toxaphene	39400	39401
Trithion	39786	82342

1. Application

This method is suitable for the determination of organochlorine insecticides, polychlorinated biphenyls (PCB's), polychlorinated naphthalenes (PCN's), and organophosphorous insecticides in water and water–suspended-sediment mixtures containing at least 0.01 µg/L of the analyte.

2. Summary of method

Organochlorine and organophosphorous compounds are extracted from water and water–

suspended-sediment mixtures with hexane. Organophosphorous compounds are determined on a gas chromatograph with flame-photometric detectors. The extracts are then purified using adsorption chromatography on an alumina column. If PCB's, PCN's, and toxaphene are present, the extracts are further purified using a silica gel column. The organochlorine compounds are then determined by gas chromatography using electron-capture detectors.

3. Interferences

Compounds having chemical and physical properties similar to the compound of interest may cause interference. Sulfur and organosulfur compounds will interfere, but these substances can be removed by treating the final extracts with mercury; however, the mercury treatment will also remove organophosphorous compounds.

4. Apparatus

4.1 *Alumina column*: Plug a disposable pipet with glass wool. Fill to a depth of 3 cm with alumina; then add 0.5 cm anhydrous sodium sulfate.

4.2 *Boiling chips*, micro, granules, Hengar H–1366C, or equivalent: Rinse with hexane, air dry, and heat overnight at 300°C.

4.3 *Concentrator, Kuderna-Danish (K-D)*, 250-mL flask, 5.0-mL receiver, and one-ball Snyder column.

4.4 *Evaporative concentrator*, Organomation N–Evap, or equivalent.

4.5 *Gas chromatograph*, Tracor 560, or equivalent.

4.5.1 The following conditions are recommended for organochlorine compounds:

Columns, borosilicate glass, 1.8 m × 2 mm id (inside diameter) operated at 200°C: Column packing materials are (1) 3 percent SP 2100 on 100/120 mesh Supelcoport, or equivalent; and (2) 1.5 percent SP 2250 + 1.95 percent SP 2401 on 100/120 mesh Supelcoport, or equivalent.

Detectors, electron capture, operated at 345°C.

Injection port temperature, 220°C.

Carrier gas, nitrogen or 5 percent methane in argon, flow rate 30 mL/min.

4.5.2 The following conditions are recommended for organophosphorous pesticides:

Columns, borosilicate glass, 1.8 m×2 mm id operated at 175°C: Column packing materials are (1) 5 percent SP 2100 on 100/120 mesh Supelcoport, or equivalent; and (2) 2 percent SE–30 + 3 percent OV–210 on 100/120 mesh chromosorb HP, or equivalent.

Detectors, flame photometric, Melpar, or equivalent, operated at 210°C.

Injection port temperature, 210°C.

Carrier gas, helium or nitrogen, flow rate 30 mL/min.

4.6 *Glass filters*, 142 mm, 0.3 μm mean pore size, Gelman, or equivalent: Prepare the filters by rinsing with acetone and hexane, evaporating the solvent, and heating overnight at 300°C.

4.7 *Silica column*; to a 130 mm × 10 mm id glass tube having a coarse-porosity fritted disc, add 1 cm anhydrous sodium sulfate, 10 cm silica, and 1 cm anhydrous sodium sulfate.

5. Reagents

5.1 *Alumina adsorbent*, Woelm neutral aluminum oxide, or equivalent: Prepare deactivated adsorbent by adding 8 g deionized water to 92 g alumina and shake for at least 2 h on a wrist-action shaker. The alumina is tested for required deactivation by attempting to elute the organochlorine compounds of interest from a test column with 10 mL hexane. If the test compounds do not elute with 10 mL hexane, further deactivation is required.

5.2 *Mercury*, metallic, reagent grade.

5.3 *Pesticide mixed standards*, analytical reference grade, EPA analytical reference standards, or equivalent: Prepare individual stock solutions by weighing about 10 mg of each compound to at least three significant figures and quantitatively transfer each compound to a 25.0-mL volumetric flask. Dilute to volume with benzene and mix thoroughly. Aliquots are removed and diluted to volume with iso-octane to obtain the final concentrations listed in table 1.

5.4 *Silica adsorbent*, Woelm silica, 70–150 mesh, or equivalent: Prepare deactivated adsorbent by adding 0.2 g deionized water to 99.8 g silica and shake for at least 2 h on a wrist-action shaker. The deactivation is evaluated by attempting to reproduce the elution scheme in table 2. If the test compounds do not elute with 25 mL of hexane from the first silica fraction, additional deactivation is required.

5.5 *Sodium sulfate*, granular, anhydrous: Heat overnight at 300°C and store in a covered beaker at 130°C.

5.6 *Solvents*, benzene, hexane, and iso-octane, pesticide residue quality, distilled in glass, Burdick and Jackson, or equivalent.

Table 1. Concentrations of pesticides and PCB's in mixed standard solutions used for gas chromatograph calibration of water and water-suspended sediment

[Micrograms per microliter]

Mixture number	Compound	High standard concentration	Low standard concentration
1	----Lindane	40	20
	Heptachlor	40	20
	Aldrin	40	20
	DDE	40	20
	DDD	40	20
	Mirex	40	20
	Methoxychlor	70	35
2	----Aldrin	40	20
	Heptachlor epoxide	40	20
	Dieldrin	40	20
	Endrin	40	20
3	----Chlordane	200	100
4	----Aldrin	40	20
	Endosulfan	40	20
	Perthane	40	20
	DDT	40	20
5	----Toxaphene	600	300
6	----p,p-DDE	40	20
	o,p-DDD	40	20
	o,p-DDT	40	20
7	----Aroclor 1016 (a PCB)	300	150
8	----Aroclor 1254 (a PCB)	400	200
9	----Aroclor 1260 (a PCB)	300	150
10	----Diazinon	100	50
	Malathion	130	65
	Dursban	100	50
	DEF	100	50
	Ethion	100	50
11	----Methyl parathion	100	50
	Ethyl parathion	100	50
	Methyl trithion	200	100
	Trithion	200	100

6. Procedure

All glassware must be washed in warm detergent solution, rinsed with organic-free water, and heated at 300°C overnight. Immediately before use, all glassware is rinsed with the solvent. Do not use stopcock grease on any ground-glass joints. For the determination of dissolved components, filter the sample through a glass fiber filter. Pour the filtrate into the original sample bottle and continue with the procedure.

6.1 A blank must accompany each group of samples. For each sample, rinse a 1,000-mL separatory funnel and a 125-mL Erlenmeyer flask with hexane.

6.2 Weigh the sample bottle plus the sample and record the weight to three significant figures.

6.3 Pour the sample into the separatory funnel and allow the bottle to drain completely. Weigh the empty bottle and cap, and record the weight to three significant figures. Calculate and record the sample weight.

Table 2. Column fractionation scheme for silica gel column for organochlorine insecticides, PCB's, and PCN's

Fraction 1 (20 mL hexane eluate)	Fraction 2 (30 mL benzene eluate)
Heptachlor 70	Heptachlor 30
percent	percent
DDE 85 percent	DDE 15 percent
Endosulfan	Lindane
Mirex	Perthane
PCB's	DDD
PCN's	DDT
	Methoxychlor
	Heptachlor epoxide
	Endrin
	Dieldrin
	Chlordane

6.4 Add 25 mL hexane to the sample bottle, rinse the sides thoroughly, and pour the solvent into the separatory funnel. The Teflon-lined cap is not rinsed because of the potential for contamination from solvent that has contacted the threads and surface beneath the Teflon liner. Shake the funnel vigorously for at least 1 min, venting often. Allow the layers to separate, and drain the aqueous layer. Pour the hexane extract into the Erlenmeyer flask. Extract the sample twice more, using 25 mL hexane each time, and collect the extracts in the Erlenmeyer flask. Add about 0.5 g anhydrous sodium sulfate to the flask, cover with foil, and set aside for at least 2 h or refrigerate until analysis can continue.

6.5 Quantitatively transfer the extract with hexane to the K-D apparatus, add a boiling chip, and attach a Snyder column. Concentrate the extract to about 5 mL on a water bath maintained at about 90°C. Remove the K-D apparatus from the water bath, dry the joints with a towel, rinse the lower joint with hexane as the receiver is disconnected, and place the receiver on an evaporative concentrator to reduce the volume to about 0.5 mL. Rinse the walls of the receiver two or three times with a few drops of hexane during the final concentration. Dilute the extract to 1.0 mL and analyze the extract by gas chromatography using flame-photometric detectors for the determination of organophosphorous insecticides.

6.6 Prepare gas chromatograph calibration curves daily with the mixed standards (table 1). Operating conditions must be identical to those used for sample analysis. Calibrate both analytical columns. Record the volume of the standard injected and the retention time and integrated peak area of each component in the standard.

6.7 Inject an aliquot of sample extract into the gas chromatograph. Record the volume injected. Identify peaks by retention time. The identification must be made on both analytical columns. Record the retention time and integrated area of any identified peak. Dilute any extract containing an identifiable component above the highest standard (see table 1) to bring it within that range. Identified compounds may be quantitated using the calculations described below.

6.8 Following analysis for organophosphorous insecticides, transfer the extract to an alumina column. Elute with hexane and collect 10 mL. Add 1.0 mL iso-octane to the eluate and reduce the volume to 1.0 mL on an evaporative concentrator, rinsing the sides of the receiver two or three times with iso-octane during the concentration. Analyze the concentrated eluate by gas chromatography as described in steps 6.6 and 6.7 using electron-capture detectors for organochlorine compounds.

6.9 If the extract contains multiple component mixtures such as PCB's, PCN's, toxaphene, or interferences, it might be necessary to perform the silica gel cleanup to obtain the fractionation shown in table 2.

7. Calculations

7.1 Calculate the response factor of each identified component in the calibration standard using the equation

$$RF = \frac{A_1}{C_s \times V_1},$$

where

RF = response factor of identified component in calibration standard, in area/pg,
C_s = concentration of standard, in pg/μL,
V_1 = volume of standard injected, in μL, and
A_1 = integrated peak area of identified component in calibration standard.

7.2 Calculate the concentration of each identified component in the original water sample from the equation

$$\text{Concentration } (\mu g/L) = \frac{A_2 \times V_2}{V_3 \times W \times RF},$$

where

RF = response factor of identified calibration standard component, in area/pg,
A_2 = integrated peak area of identified sample component,
V_2 = final volume of sample extract, in mL,
V_3 = volume of sample extract injected, in μL, and
W = weight of sample in g, expressed in mL (1.000 mL = 1.000 g)

8. Report

8.1 Report concentrations of organochlorine compounds (except chlordane, perthane, toxaphene, PCB's, and PCN's) and organophosphorous insecticides as follows: less than 0.01 μg/L, as "less than 0.01 μg/L"; 0.01 to 0.10 μg/L, one significant figure; 0.10 μg/L and above, two significant figures.

8.2 Report concentrations of chlordane, perthane, PCB's, and PCN's as follows: less than 0.1 μg/L, as "less than 0.1 μg/L"; 0.1 μg/L and above, two significant figures.

8.3 Report concentrations of toxaphene as follows: less than 1.0 μg/L, as "less than 1.0 μg/L"; 1.0 μg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved insecticides and PCB's (Aroclors 1248 and 1254) in distilled water for seven replicates at each concentration are as follows:

Compound	*Concentration spiked (μg/L)*	*Mean concentration determined (μg/L)*	*Relative standard deviation (percent)*
Chlordane	0.13	0.09	13
	.25	.15	30
	.50	.39	13
Aroclor 1248	.20	.20	13
	.41	.28	23
	.82	.55	8.8
Aroclor 1254	.12	.07	28
	.24	.20	15
	.49	.24	4.1
Lindane	.014	.012	12
	.027	.035	11
	.054	.064	7.3
Heptachlor	.010	.007	15
	.020	.015	16
	.040	.042	4.3
Aldrin	.009	.008	17
	.017	.016	14
	.035	.042	5.0
Perthane	.12	.038	9.4
	.23	.17	16
	.47	.14	4.0
Endosulfan	.021	.015	8.9
	.042	.047	5.2
	.084	.077	6.7

Compound	Concentration spiked (µg/L)	Mean concetration determined (µg/L)	Relative standard deviation (percent)
p,p-DDE	.020	.025	19
	.040	.051	11
	.080	.15	3.3
p,p-DDD	.030	.020	13
	.060	.062	9.5
	.12	.13	6.2
p,p-DDT	.053	.033	19
	.11	.10	7.7
	.21	.23	7.0
Methoxychlor	.022	.016	8.5
	.044	.041	7.9
	.087	.079	5.0
Mirex	.020	.012	34
	.041	.028	21
	.082	.072	4.9
Diazinon	.23	.15	20
Malathion	.26	.13	32
Methyl parathion	.22	.16	9.2
Parathion	.15	.12	6.3
Methyl trithion	.15	.07	12
Ethion	.15	.12	7.4
Trithion	.25	.18	7.6

9.2 It is estimated that the percent relative standard deviation for total recoverable insecticides and PCB's will be greater than that reported for dissolved insecticides and PCB's.

Selected references

Goerlitz, D.F., and Brown, Eugene, 1972, Methods for analysis of organic substances in water: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A3, 40 p.

Goerlitz, D.F., and Law, L.M., 1971, Note on removal of sulfur interferences from sediment extracts for pesticide analysis: Bulletin of Environmental Contamination and Toxicology, v. 6, p. 9–10.

——— 1972, Chlorinated naphthalenes in pesticide analysis: Bulletin of Environmental Contamination and Toxicology, v. 7, p. 243–251.

——— 1974, Determination of chlorinated insecticides in suspended sediment and bottom material: Journal of the Association of Official Analytical Chemists, v. 57, p. 176–181.

Organochlorine and organophosphorous compounds, recoverable from bottom material (O–5104–83) and recoverable from suspended sediment (O–7104–83), gas chromatographic

Parameter	Codes: Recoverable from bottom material	Codes: Recoverable from suspended sediment
Aldrin	39333	39332
Chlordane	39351	39353
DDD	39363	39362
DDE	39368	39367
DDT	39373	39372
Diazinon	39571	39573
Dieldrin	39383	39382
Endosulfan	39389	82355
Endrin	39393	39392
Ethion	39399	82347
Polychlorinated biphenyls	39519	39518
Polychlorinated naphthalenes	39251	82361
Heptachlor	39413	39412
Heptachlor epoxide	39423	39422
Lindane	39343	39342
Malathion	39531	39533
Methoxychlor	39481	82351
Methyl parathion	39601	39603
Methyl trithion	39791	82345
Mirex	39758	39757
Parathion	39541	39543
Perthane	81886	82349
Toxaphene	39403	39402
Trithion	39787	82343

1. Application

This method is suitable for the determination of recoverable organochlorine insecticides, polychlorinated biphenyls (PCB's), polychlorinated naphthalenes (PCN's), and organophosphorous insecticdes in bottom material and suspended sediment containing at least 0.1 µg/kg of the analyte.

2. Summary of method

Organochlorine and organophosphorous insecticides, PCB's, and PCN's are extracted from suspended sediment and bottom material with acetone and hexane. The organophosphorous insecticides are determined by gas chromatography using flame-photometric detectors. The extracts are then purified using adsorption chromatography on an alumina column. If PCB's, PCN's, and toxaphenes are present, the extracts are further purified using a silica gel column. The organochlorine compounds are determined by gas chromatography using electron-capture detectors.

3. Interferences

Compounds having chemical and physical properties similar to the compound of interest may cause interference. Sulfur and organosulfur compounds will interfere, but these substances can be removed by treating the final extracts with mercury; however, the mercury treatment will also remove organophosphorous compounds.

4. Apparatus

4.1 *Alumina column*: To a 130-mm×10-mm id (inside diameter) glass tube having a coarse-porosity fritted disc, add 1 cm anhydrous sodium sulfate, 10 cm alumina, and 1 cm anhydrous sodium sulfate.

4.2 *Boiling chips*, granular, micro, Hengar H–1366C, or equivalent: Rinse with hexane, air dry, and heat at 300°C overnight.

4.3 *Centrifuge tube*, 30 mL, Pyrex, graduated.

4.4 *Concentrator*, Kuderna-Danish (K-D), 500-mL flask, 5.0-mL volumetric receiver, and one-ball Snyder column.

4.5 *Gas chromatograph*, Tracor model 550, or equivalent.

4.5.1 The following conditions are recommended for organochlorine compounds:

Columns, borosilicate glass, 1.8 m×2 mm id operated at 200°C: Column packing materials are (1) 3 percent SP 2100 on 100/120 mesh Supelcoport, or equivalent; and (2) 1.5 percent SP 2250 + 1.95 percent SP 2401 on 100/120 mesh Supelcoport, or equivalent.

Detectors, electron capture, operated at 345°C.

Injection port temperature, 220°C.

Carrier gas, nitrogen or 5 percent methane in argon, flow rate 30 mL/min.

4.5.2 The following conditions are recommended for organophosphorous pesticides:

Columns, borosilicate glass, 1.8 m×2 mm id operated at 175°C: Column packing materials are (1) 5 percent SP 2100 on 100/120 mesh Supelcoport, or equivalent; and (2) 2 percent SE–30 + 3 percent OV–210 on 100/120 mesh chromosorb HP, or equivalent.

Detectors, flame photometric, Melpar, or equivalent, operated at 210°C.

Injection port temperature, 210°C.

Carrier gas, helium or nitrogen, flow rate 30 mL/min.

4.6 *Glass filters*, 142 mm, 0.3 μm mean pore size, Gelman or equivalent: Prepare the filters by rinsing with acetone and hexane, evaporating the solvent, and heating overnight at 300°C.

4.7 *Glass wool*, fine, rinsed with hexane, air dried, and heated at 300°C overnight.

4.8 *Shaker*, wrist-action, Burrell or equivalent.

4.9 *Silica column*: To a 130-mm × 10-mm id glass tube having a coarse-porosity fritted disc, add 1 cm anhydrous sodium sulfate, 10 cm silica, and 1 cm anhydrous sodium sulfate.

5. Reagents

5.1 *Alumina adsorbent*, Woelm neutral aluminum oxide, or equivalent: Prepare deactivated adsorbent by adding 8 g deionized water to 92 g alumina and shake for at least 2 h on a wrist-action shaker. The alumina is tested for required deactivation by attempting to elute the compounds of interest from a test column according to the column fractionation scheme (table 3). If the test compounds do not elute with 20 mL hexane from the first alumina fraction, further deactivation is required.

5.2 *Mercury*, metallic, reagent grade.

5.3 *Pesticide mixed standards*, analytical reference grade, EPA analytical reference standards, or equivalent: Prepare individual stock solutions by weighing about 10 mg of each compound to at least three significant figures and quantitatively transfer each compound to a 25-mL volumetric flask. Dilute to volume with benzene and mix thoroughly. Aliquots are removed and diluted to volume with iso-octane to obtain final concentrations listed in table 4.

Table 3. Column fractionation scheme for alumina and silica columns for insecticides, PCB's, and PCN's in bottom material and suspended sediment

Alumina Column		
Fraction 1 (20 mL hexane eluate)	Fraction 2 (25 mL hexane eluate)	Fraction 3 (20 mL benzene eluate)
Aldrin	Dieldrin	
Chlordane	Endrin	Diazinon
p,p-DDD	Heptachlor epoxide	Ethion
p,p-DDE	Endosulfan	Parathion
p,p-DDT		Methyl parathion
Heptachlor		Malathion
Perthane		Trithion
Lindane		Methoxychlor
Mirex		
PCB's		
PCN's		
Toxaphene		

Silica Column	
Fraction 1 (25 mL hexane eluate)	Fraction 2 (30 mL benzene eluate)
Aldrin	Chlordane
Mirex	p,p–DDD
PCB's	p,p–DDE
PCN's	p,p–DDT
p,p–DDE	Perthane
	Heptachlor
	Lindane
	Toxaphene

5.4 *Silica adsorbent*, Woelm silica, 70–150 mesh, or equivalent: Prepare deactivated adsorbent by adding 0.2 g deionized water to 99.8 g silica and shake for at least 2 h on a wrist-action shaker. The silica is tested for required deactivation by attempting to reproduce the elution scheme in table 3. If the test compounds do not elute with 25 mL hexane from the first silica fraction, further deactivation is required.

5.5 *Sodium sulfate*, granular, anhydrous, heat overnight at 300°C and store in a covered beaker at 130°C.

5.6 *Solvents*, acetone, benzene, hexane, and iso-octane, distilled in glass, pesticide analysis quality, Burdick and Jackson, or equivalent.

5.7 *Water*, deionized, organic-free.

6. Procedure

All glassware must be washed in warm detergent solution, rinsed with organic-free water, and heated at 300°C overnight. Prior to use, all glassware is rinsed with the solvent. Do not use stopcock grease on any ground-glass joints. For bottom-material samples, begin at step 6.1. For suspended-sediment samples, first determine the weight of the water–suspended-sediment mixture, then filter the sample to isolate the suspended sediment. Use the filter and the retained sediment and begin at step 6.2.

Table 4. Concentrations of pesticides and PCB's in mixed standard solutions used for gas chromatograph calibration of bottom material

[Picograms per microliter]

Mixture number	Compound	High standard concentration	Low standard concentration
1	----Lindane	40	20
	Heptachlor	40	20
	Aldrin	40	20
	p,p-DDE	40	20
	p,p-DDD	40	20
	Mirex	40	20
	Methoxychlor	70	35
2	----Aldrin	40	20
	Heptachlor epoxide	40	20
	Dieldrin	40	20
	Endrin	40	20
3	----Chlordane	200	100
4	----Aldrin	40	20
	Endosulfan	40	20
	Perthane	40	20
	p,p-DDT	40	20
5	----Toxaphene	600	300
6	----o,p-DDE	40	20
	o,p-DDD	40	20
	o,p-DDT	40	20
7	----Aroclor 1016 (a PCB)	300	150
8	----Aroclor 1254 (a PCB)	400	200
9	----Aroclor 1260 (a PCB)	300	150
10	----Diazinon	100	50
	Malathion	130	65
	Ethion	100	50
11	----Methyl parathion	100	50
	Parathion	100	50
	Methyl trithion	200	100
	Trithion	200	100

6.1 Subsampling for determination of moisture:

6.1.1 Decant excess water from the bottom material. Use a spatula to thoroughly mix the moist solid. Weigh 10 g of solid into a tared weighing dish. Record the weight to three significant figures.

6.1.2 Place the tared dish containing the sample in an oven at 130°C overnight. Remove from oven, allow to cool, weigh, and record the weight to three significant figures.

6.2 Add either the filter from the suspended-sediment filtration or the calculated amount of bottom material (not more than 100 g) to a 500-mL Erlenmeyer flask with a ground-glass joint. Stir the sample and slowly add deionized water until the mixture has the consistency of paste or until water begins to separate from the solid.

6.3 Add 20 mL acetone to the Erlenmeyer flask containing the sample and stopper securely. Mix the contents of the flask for 20 min using the wrist-action shaker. Add 80 mL hexane and shake again for 10 min. Decant the extract into a 1-L separatory funnel containing approximately 600 mL deionized water.

6.4 Add another 20 mL acetone to the Erlenmeyer flask and mix for 20 min. Add 80 mL hexane, mix 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–hexane extract in the separatory funnel containing the deionized water.

6.5 Gently mix the contents of the separatory funnel for about 1 min, and allow the layers to separate. Discard the aqueous layer and collect the extract in a 500-mL Erlenmeyer flask. Add about 1 g anhydrous sodium sulfate to the flask, cover with foil, and allow to stand for at least 2 h or store in a refrigerator until the analysis can continue.

6.6 Quantitatively transfer the extract with hexane to a K-D flask fitted with a 5-mL volumetric receiver. Add a boiling chip, attach a one-ball Snyder column, and concentrate the extract to about 5

mL on a water bath at about 90°C. Remove the K-D apparatus from the water bath, allow to cool, dry the joints with a towel, and rinse the joints into the receiver with hexane. Disconnect the receiver and concentrate on an evaporative concentrator to 2–4 mL, rinsing down the sides of the receiver during concentration with small amounts of hexane. Adjust the volume of extract in the receiver to 5.0 mL with hexane.

6.7 Prepare an alumina column for adsorption chromatography cleanup, referring to table 3 for the fractionation scheme. Elute the column with 30 mL hexane to remove contaminants. Discard the eluate. Quantitatively transfer the extract obtained in step 6.6 to the top of the column and elute using 45 mL hexane (the column void volume is about 5 mL). Collect the first 20 mL (fraction 1) and the second 20 mL (fraction 2) in graduated centrifuge tubes. Change the elution solvent to benzene and collect 30 mL of eluate (fraction 3). Reduce the second and third fractions to 1.0 mL each on an evaporative concentrator and analyze by gas chromatography. Treat the first fraction as described in step 6.8.

6.8 Prepare a silica column. Elute the column with 30 mL hexane and discard the eluate. Reduce the volume of the first alumina fraction on an evaporative concentrator to about 0.5 mL and quantitatively transfer it to the top of the silica column. Add hexane to the top of the column and collect 25 mL of eluate (fraction 1) in a graduated centrifuge tube. As the last of the hexane enters the top sodium sulfate layer, add benzene to the top of the column and collect 30 mL of eluate (fraction 2) in a graduated centrifuge tube. Reduce the volume of each of these fractions to 1.0 mL on an evaporative concentrator and analyze each by gas chromatography. Sulfur can be removed from the first alumina or first silica fraction by adding several drops of mercury and shaking for at least 1 min. The addition of mercury is continued until no further reaction occurs, as evidenced by blackening of the mercury.

6.9 Prepare gas chromatograph calibration curves daily with the mixed standards listed in table 4. Operating conditions must be identical to those used for sample analysis. Calibrate both analytical columns. Record the volume of the standard injected and the retention time and integrated peak area of each component in the standard.

6.10 Inject an aliquot of sample extract into the gas chromatograph. Record the volume injected. Identify peaks by retention time. The identification must be made on both analytical columns. Record the retention time and integrated area of any identified peak. Dilute any extract containing an identifiable component above the highest standard (see table 4).

7. Calculations

7.1 Calculate the wet weight required for a dry weight equivalent of 50 g:

$$\text{Wet weight (in g)} = \frac{W_1}{W_2} \times 50 \text{ g},$$

where

wet weight = weight of sample used for extraction, in g,
W_1 = wet weight of sample, in g, and
W_2 = dry weight of sample, in g.

7.2 Calculate the response factor of each identified component in the calibration standard:

$$RF = \frac{A_1}{C_s \times V_1},$$

where

RF = response factor of identified component in calibration standard, in area/pg,
C_s = concentration of standard, in pg/μL,
V_1 = volume of standard injected, in μL, and
A_1 = integrated peak area of identified component in calibration standard.

7.3 Calculate the concentration of each identified component in the original bottom-material sample from the equation

$$\text{Concentration (μg/kg)} = \frac{A_2 \times V_2}{V_3 \times W \times RF},$$

where

RF = response factor of identified calibration standard component, in area/pg,
A_2 = integrated peak area of identified sample component,
V_2 = final volume of sample extract, in mL,
V_3 = volume of sample extract injected, in μL, and
W = dry weight equivalent of sample, in g.

7.4 Calculate the concentration of each identified component in the original suspended sediment from the following equation:

$$\text{Concentration (μg/L)} = \frac{A_2 \times V_2}{V_3 \times V_4 \times RF},$$