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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
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U.S. GEOLOGICAL SURVEY
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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."

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TWI 1-D2. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents, by W. W. Wood. 1976. 24 pages.
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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_o} 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.

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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.

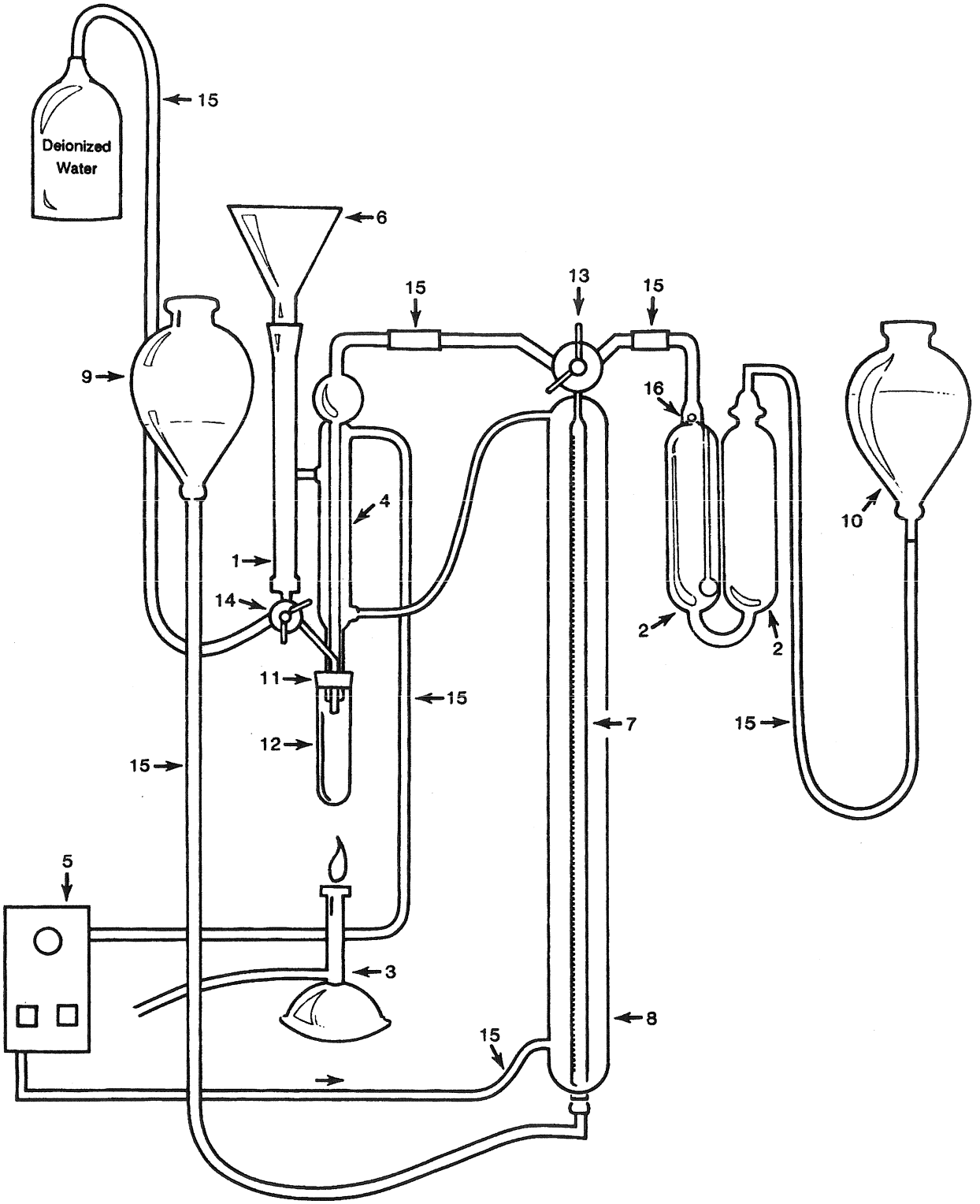

Figure 1.—Apparatus for the manometric determination of carbon dioxide.

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.

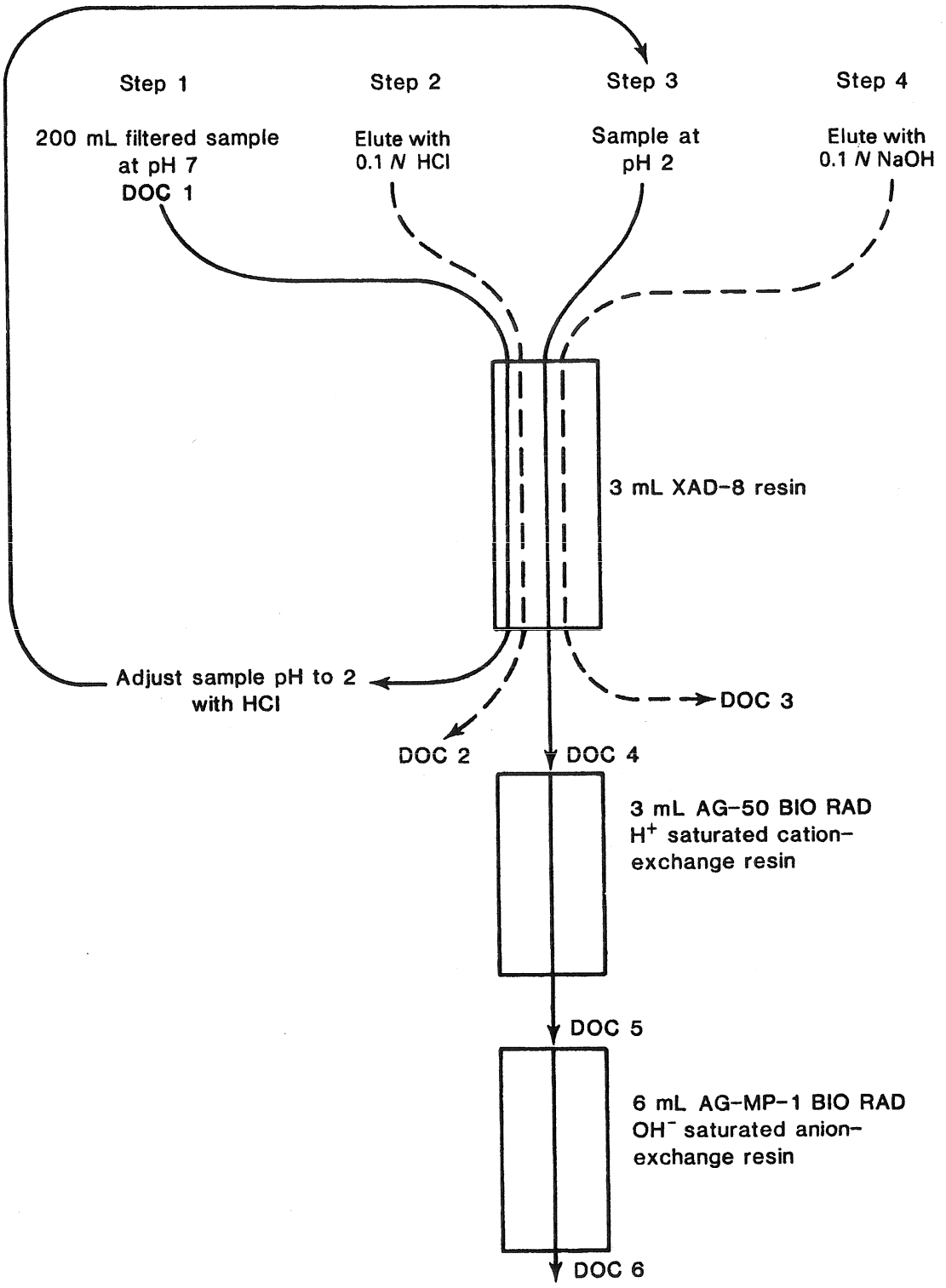

Figure 2. — Dissolved organic carbon fractionation analytical scheme.

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

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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

[Picograms 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 percent	Heptachlor 30 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.

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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:

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

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

V_4 = weight of sample in g expressed in mL (1.000 mL = 1.000g).

8. Report

8.1 Bottom material

8.1.1 Report concentrations of organochlorine compounds (except chlordane, perthane, toxaphene, PCB's, and PCN's) and organophosphorous insecticides in bottom material as follows: less than 0.1 µg/kg, as "less than 0.1 µg/kg" 0.1 to 1.0 µg/kg, one significant figure; 1.0 µg/kg and above, two significant figures.

8.1.2 Report concentrations of chlordane, perthane, PCB's, and PCN's in bottom materials as follows: less than 1.0 µg/kg, as "less than 1.0 µg/kg"; 1.0 µg/kg and above, two significant figures.

8.1.3 Report concentrations of toxaphene in bottom materials as follows: less than 10 µg/kg, as "less than 10 µg/kg"; 10 µg/kg and above, two significant figures.

8.2 Suspended sediment

8.2.1 Report concentrations of organochlorine compounds (except chlordane, perthane, toxaphene, PCB's, and PCN's) and organophosphorous insecticides in suspended sediment 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; 0.1 µg/L and above, two significant figures.

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

8.2.3 Report concentrations of toxaphene in suspended sediment 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

It is estimated that the percent relative standard deviation for recoverable insecticides and PCB's from bottom material and suspended sediment will be greater than that reported for dissolved insecticides and PCB's (method O–1104–83).

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 compounds, recoverable from fish tissue, gas chromatographic (O–9104–83)

Parameter	*Code*
Aldrin	None assigned.
Chlordane	
DDD	
DDE	
DDT	
Dieldrin	
Endosulfan	
Endrin	
Polychlorinated biphenyls	
Polychlorinated naphthalenes	
Heptachlor	
Heptachlor epoxide	
Lindane	
Methoxychlor	
Mirex	
Perthane	
Toxaphene	

1. Application

This method is suitable for the determination of organochlorine compounds in fish containing at least 0.1 µg/kg of the analyte.

2. Summary of method

A homogenized sample of whole fish or fish fillet is extracted with petroleum ether to isolate the fat. The organochlorine compounds are extracted from the fat with acetonitrile. The acetonitrile extract is diluted with water and extracted with petroleum ether to partition the organochlorine compounds.

The petroleum ether extract is concentrated and purified using adsorption chromatography. Organochlorine compounds are identified and quantified by gas chromatography using electron-capture detectors.

3. Interferences

Sulfur and organosulfur compounds will interfere, but these substances can be removed by treating the final extracts with mercury.

4. Apparatus

4.1 *Alumina column*: To a 130-mm×10-mm id 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 *Blender*, 3.8-L-capacity, Waring, three-speed with stainless steel container, cover, and blade assembly, or equivalent.

4.3 *Blender*, 1.2 L-capacity, Waring, with explosion-resistant motor base, borosilicate glass containers, vinyl/plastic cover, and stainless steel blade assembly, or equivalent.

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

4.5 *Concentrator, Kuderna-Danish (K-D)*, 500 mL, with 5-mL and 10-mL volumetric receivers and a one-ball Snyder column.

4.6 *Evaporative concentrator*, Organomation N-Evap, or equivalent.

4.7 *Fish tissue preparation equipment*, consisting of a nonporous ceramic or stainless steel cutting board, a heavy-duty stainless steel knife, and a stainless steel spatula having a 25-cm blade.

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

4.8.1 The following conditions are recommended:

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.

4.9 *Glass filter*, 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.

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

5. Reagents

5.1 *Acetonitrile, petroleum ether saturated*: Place 800 mL acetonitrile in a 1-L separatory funnel. Add sufficient petroleum ether (about 50 mL) so that after vigorously mixing, an excess of petroleum ether is visible above the acetonitrile. Draw off and retain the lower layer.

5.2 *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 according to the column fractionation scheme (table 5).

5.3 *Mercury*, metallic, reagent grade.

Table 5. Column fractionation scheme for alumina and silica columns for organochlorine insecticides, PCB's, and PCN's in fish

Alumina Column	
Fraction 1 20 mL hexane eluate	Fraction 2 20 mL hexane eluate
Aldrin	Dieldrin
Chlordane	Endrin
Heptachlor	Heptachlor epoxide
p,p–DDD	Endosulfan
p,p–DDE	
p,p–DDT	
Lindane	
Mirex	
Perthane	
PCB's	
PCN's	
Toxaphene	

Silica Column	
Fraction 1 (25 mL hexane eluate)	Fraction 2 (30 mL bezene 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 5.

5.5 *Sodium chloride*, granular, reagent grade: Heat at 300°C overnight before use.

5.6 *Sodium chloride solution*, saturated: Dissolve 360 g sodium chloride in 1,000 mL deionized water. Add additional sodium chloride in about 5 g increments, stirring well after each addition, until an excess of the salt is observed.

5.7 *Sodium hypochlorite solution*, (5 percent), Clorox bleach, or equivalent.

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

5.9 *Solvents*, acetonitrile, benzene, hexane, iso-octane, petroleum ether, distilled in glass, pesticide analysis quality, Burdick and Jackson, or equivalent.

5.10 *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 6.

Table 6. Concentrations of pesticides and PCB's in mixed standard solutions used for gas chromatograph calibration of fish tissue

[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

6. Procedure

All glassware must be washed in warm detergent solution, rinsed with organic-free water, and heated at 300°C overnight. Rinse all glassware, fish-preparation equipment, and blender containers with petroleum ether before use, and air dry. After use with fish samples, the glassware should be washed immediately in a warm solution of detergent and bleach to aid in the removal of residual oils and odor. Do not use stopcock grease on ground-glass joints.

6.1 Sample preparation:

6.1.1 Scrape the scales from whole fish samples and cut off tough fins. Discard scales and fins. Chop whole fish into small pieces. If sample is a fillet, slice into small pieces.

6.1.2 Add fish pieces to a stainless steel blender container, cover, and blend until a homogeneous sample is obtained. Weigh 50 g of blended sample and place in a tared, glass blender container. Record the weight of the sample in the glass blender container to three significant figures. (Use excess sample for a duplicate, or store it frozen if a rerun is needed.)

6.2 Extraction of fat from fish samples:

6.2.1 Add 100 g anhydrous sodium sulfate to the weighed fish in the glass blender container and blend until thoroughly mixed. Scrape the sides of the container with a spatula during mixing to ensure homogeneity.

6.2.2 Add 150 mL petroleum ether to the sample in the blender container, cover, and blend at high speed for 2 min using the explosion-resistant base. (Start blending at low speed to avoid splashing and gradually increase to high). CAUTION: Petroleum ether is extremely flammable. Provide additional air circulation around the blender base to prevent solvent fumes from contacting the motor housing.

6.2.3 Slowly decant the petroleum ether extract into a Buchner funnel fitted with filter paper. Slowly filter the extract into the filtration flask using a water aspirator. (Care must be taken to prevent solids from entering the filtrate.)

6.2.4 Scrape down the walls of the blender container and break up any caked material with a spatula. Add 100 mL petroleum ether, cover, and repeat the extraction (step 6.2.2), blending for 1 min. Scrape down the walls of the blender container and blend for another minute.

6.2.5 Slowly decant the petroleum ether extract into the Buchner funnel and filter.

6.2.6 Repeat steps 6.2.4 and 6.2.5. Quantitatively transfer the remaining fish residue from the blender to the Buchner funnel using the spatula and small amounts of petroleum ether to aid in the transfer. Continue aspirating until the residue appears dry.

6.2.7 Quantitatively transfer the filtrate to a 500-mL Erlenmeyer flask. Add 2 g anhydrous sodium sulfate, cover the flask, and allow to stand for at least 1 h.

6.2.8 Weigh a 10-mL receiver for the concentration step and record its weight to two significant figures. Quantitatively transfer the extract into a K-D flask fitted with the weighed receiver. Add a boiling chip, fit the K-D flask with a Snyder column, and concentrate the extract to about 5 mL on a water bath maintained at 90°C.

6.2.9 Remove the K-D apparatus from the water bath, disconnect the receiver, and place it on an evaporative concentrator to evaporate any remaining petroleum ether. The receiver contains the fat extract.

6.2.10 Weigh the receiver, record the weight, and calculate the weight of the extract. If the extracted fat weighs more than 3 g, take 3.0 g for the liquid–liquid partitioning (step 6.3) and use the formula in calculation 7.1 to determine the final sample weight. If the weight of the extracted fat is 3 g or less, the analysis is based on the weight of the original sample (step 6.1.1).

6.3 Liquid–liquid partitioning:

6.3.1 Quantitatively transfer the extract (3 g or less) to a 125-mL separatory funnel using small amounts of petroleum ether to bring the total volume to about 15 mL.

6.3.2 Add 30-mL petroleum-ether-saturated acetonitrile to the separatory funnel. Stopper and shake vigorously for at least 1 min, venting often. Allow the layers to separate.

6.3.3 Drain the acetonitrile layer (bottom) into a 1,000-mL saturated sodium chloride solution, and add 100 mL petroleum ether. Retain the fat extract in the 125-mL funnel.

6.3.4 Repeat steps 6.3.2 and 6.3.3 twice. Combine all acetonitrile extracts in the 1,000-mL separatory funnel.

6.3.5 Stopper the 1,000-mL separatory funnel and shake vigorously for 1 min, venting often. Allow the layers to separate and drain the aqueous layer into a 1-L glass bottle. Pour the petroleum ether extract from the funnel into a 250-mL Erlenmeyer flask.

6.3.6 Return the aqueous layer to the separatory funnel, add 100 mL petroleum ether to the bottle, swirl to rinse sides, and pour into separatory funnel.

6.3.7 Repeat the extraction (step 6.3.5). Allow the layers to separate, discard the aqueous layer, and add the extract to the Erlenmeyer flask containing the first extract (step 6.3.5). If the extract is highly colored, wash it twice by extracting it with 100-mL portions of deionized water. Discard the aqueous layers after each extraction and transfer the final extract to the 250-mL Erlenmeyer flask. Add 2 g sodium sulfate to the flask, cover, and allow the extract to stand over sodium sulfate for at least 1 h.

6.4 Concentration and cleanup:

6.4.1 Quantitatively transfer the extract with hexane to a K-D flask fitted with a 5-mL volumetric receiver. Add a boiling chip, attach a Snyder column, and concentrate the extract to about 5 mL on a 95°C water bath. Remove the K-D apparatus from the water bath, allow to cool, wipe the joints with a towel, disconnect the receiver, rinse the lower joint with hexane into the receiver, and concentrate the extract on an evaporative concentrator to 2–4 mL. Rinse down the sides of the receiver during concentration with small amounts of hexane. Adjust the volume of extract in the receiver to 5.00 mL with hexane.

6.4.2 Prepare an alumina column for the alumina fractionation, referring to table 5 for the fractionation scheme. Elute the column with 30 mL hexane to remove contaminants. Discard the eluate. Quantitatively transfer the extract from step 6.4.1 to the top of the column and elute using 45 mL hexane (the column holdup is about 5 mL). Collect the first 20 mL (fraction 1) and the second 20 mL (fraction 2) in graduated centrifuge tubes. Reduce the second alumina fraction to 1.0 mL on the evaporative concentrator and analyze by gas chromatography. Treat the first alumina fraction as described in step 6.4.3.

6.4.3 Prepare a silica column for the silica fractionation, referring to table 5. Elute the column with 30 mL hexane and discard the eluate. Reduce the volume of the first alumina fraction to about 0.5 mL on the evaporative concentrator 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 two fractions to 1.0 mL on the evaporative concentrator, and analyze each by gas chromatography.

Removal of sulfur from the first alumina and first silica fractions is accomplished 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.

6.5 Sample analysis:

6.5.1 Prepare gas chromatograph calibration curves daily with the mixed standards listed in table 6. 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.

6.5.2 Inject an aliquot of sample extract (from steps 6.4.2 and 6.4.3) 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.

7. Calculations

7.1 Determine the equivalent subsample weight from the following equation:

$$W = \frac{W_1 \times W_3}{W_2},$$

($W_1 = W_2$ when W_2 is equal to or less than 3 g)

where

W = equivalent subsample weight, in g,
W_1 = weight of fat taken for cleanup, in g,
W_2 = total weight of extracted fat, in g, and
W_3 = weight of original fish subsample, 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 (step 5.10),
V_1 = volume of standard injected, in μL (step 6.5.1), and
A_1 = integrated peak area of identified component in calibration standard (step 6.5.1).

7.3 Calculate the concentration of each identified component (see step 6.5.2) in the original fish 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 (step 7.2),
A_2 = integrated peak area of identified sample component (step 6.5.2),
V_2 = final volume of sample extract, in mL (step 6.4.3),
V_3 = volume of sample extract injected, in μL (step 6.5.2), and
W = equivalent subsample weight of fish, in g (calculation 7.1).

8. Report

8.1 Report concentrations of organochlorine compounds (except chlordane, perthane, and toxaphene) in fish samples as follows: less than 0.1 μg/kg, as "less than 0.1 μg/kg"; 0.1 to 1.0 μg/kg, one decimal; 1.0 μg/kg and above, two significant figures.

8.2 Report concentrations of chlordane, perthane, PCB's, and PCN's in fish samples as follows: less than 1.0 μg/kg, as "less than 1.0 μg/kg"; 1.0 μg/kg and above, two significant figures.

8.3 Report concentrations of toxaphene in fish samples as follows: less than 10 μg/kg, as "less than 10 μg/kg"; 10 μg/kg and above, two significant figures.

9. Precision

Precision data are not available.

Selected references

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. 1–10.

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Thompson, J.F., ed., 1974, Analysis of pesticide residues in human and environmental samples: Research Triangle Park, N.C., U.S. Environmental Protection Agency, Environmental Toxicology Division, Health Effects Research Laboratory, Sec. 5,A(1), p. 1–14.

(U.S.) Federal Water Pollution Control Administration, 1969, FWPCA method for chlorinated hydrocarbon pesticides in water and wastewater: Federal Water Pollution Control Administration, Cincinnati, Ohio, p. 29.

Chlorophenoxy acids, total recoverable (O–3105–83) and dissolved (O-1105-83), gas chromatographic

Parameter	Code: Total recoverable	Dissolved
2,4-D	39730	39732
2,4-DP	82183	82356
Silvex	39760	39762
2,4,5-T	39740	39742

1. Application

This method is suitable for the determination of chlorophenoxy acid herbicides, and their esters and salts, in water and water–suspended-sediment mixtures containing at least 0.01 µg/L of the analyte.

2. Summary of method

Chlorophenoxy acid herbicides and their esters are extracted with either diethyl or methyl t-butyl ether from an acidified water sample. The extracted herbicides are hydrolyzed to the free acids which are converted to their methyl esters with boron trifluoride-methanol and purified using adsorption chromatography. The methyl esters are determined by gas chromatography using electron capture detectors.

3. Interferences

Halogenated organic acids, and their salts and esters, may cause interference.

4. Apparatus

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

4.2 *Centrifuge tube*, 5 mL, Pyrex, graduated, with ground-glass stopper.

4.3 *Concentrator, Kuderna-Danish (K-D)*, 125-mL flask and 5.0-mL receiver, one-ball Snyder column, and modified micro-Snyder column, Kontes 569251, or equivalent.

4.4 *Florisil column*, a disposable glass pipet with glass-wool plug: Fill to a depth of 1.5 cm with florisil adsorbent, followed by 2 cm sodium sulfate.

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

4.5.1 The following conditions are recommended:

Columns, borosilicate glass, 1.8 m×2 mm id (inside diameter), operated at 180°C: Column packing materials are (1) 3 percent SP 2100 on 100/120 mesh Supelcoport; and (2) 3 percent SP 2250 on 100/120 mesh Supelcoport, or equivalent.

Detector, dual electron capture operated at 350°C.

Injection port temperature, 200°C.

Carrier gas, nitrogen, flow rate 20 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 *Sandbath*, Tecam, or equivalent.

5. Reagents

5.1 *Boron trifluoride-methanol esterification reagent*, 14 percent BF_3; (weight/volume; w/v) in methanol, Applied Science Labs, or equivalent.

5.2 *Florisil adsorbent*, commercially activated at 650°C, washed with hexane, allowed to air dry, and stored at 130°C in a glass-stoppered flask: Prior to use, the florisil is deactivated by adding 10 percent water by weight and shaking for at least 2 h

on a wrist-action shaker. The florisil is then tested for activity by attempting to elute the herbicides of interest with benzene from a test column. If the test compounds do not elute within 2.0 mL, further deactivation is required until the desired results are obtained.

5.3 *Potassium hydroxide solution*, 37 percent (w/v): Dissolve 78 g KOH reagent-grade pellets in 200 mL deionized water. Reflux for 8 h.

5.4 *Sodium sulfate, acidified*: Prepare a slurry of sodium sulfate with enough diethyl ether to cover the crystals, and acidify to pH 2 or less by adding a few milliliters of concentrated sulfuric acid. Determine the pH by transferring a small portion of the slurry to a beaker and removing the ether by evaporation. Add a few drops of deionized water to the crystals and measure the pH with pH paper. Allow to air dry overnight. Store in a covered Pyrex beaker or flask at 130°C.

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

5.6 *Sodium sulfate solution*, 5 percent (w/v): Dissolve 50 g neutral sodium sulfate in deionized water and dilute to 1 L.

5.7 *Solvents*, benzene, unpreserved diethyl ether or methyl t-butyl ether, and iso-octane, distilled in glass, pesticide analysis quality, Burdick and Jackson, or equivalent: Diethyl ether preserved with ethanol cannot be used in this procedure because it results in the formation of extraneous ethyl esters.

5.8 *Standards, methyl esters of chlorophenoxy acid herbicides*, EPA analytical reference grade or equivalent: Prepare a stock solution by weighing about 10 mg of compound to at least three significant figures and transfer to a 25-mL volumetric flask. Dilute to volume with benzene and mix thoroughly. Prepare a series of mixed-compound standards by volumetric dilution with iso-octane, as described in table 7.

5.9 *Sulfuric acid*, concentrated (sp. gr. 1.84), Mallinckrodt analytical reagent, A.C.S. grade, or equivalent.

5.10 *Sulfuric acid*, (1 + 3): Prepare by adding 1 part concentrated sulfuric acid to 3 parts deionized water. Store in a refrigerator at 4°C.

5.11 *Water*, deionized, organic-free.

Table 7. Concentration of herbicides in mixed standard solutions used for gas chromatograph calibration of water and water-suspended sediment

[Picograms per microliter]

Herbicide	High standard concentration	Low standard concentration
2,4-DP	100	50
2,4-D	100	50
2,4,5-T	40	20
Silvex	40	20

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 it will contact. Stopcock grease should not be used on ground-glass joints.

For the determination of dissolved components, filter the sample through a glass filter to remove the suspended material. Pour the filtrate into the original sample bottle and continue with the procedure.

6.1 Immediately upon receipt of a sample in the laboratory, it must be acidified to pH 2 or lower with concentrated sulfuric acid and stored at 4°C.

6.2 A blank must accompany each group of samples. For each sample, rinse a 1,000-mL separatory funnel and a 250-mL Erlenmeyer flask with ether.

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

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

6.5 Add 150 mL ether 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 the 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 ether extract into the Erlenmeyer flask. Extract the sample twice more, using 50 mL ether each time, and collect the extracts in the Erlenmeyer flask.

6.6 Add 15 mL distilled water, 2.0 mL 37 percent KOH, and a boiling chip to the extract. Fit the flask with a Snyder column and heat the assembly on a steam bath for a total of 90 min, during which time the ether will evaporate and the herbicide esters are hydrolyzed.

6.7 Remove the assembly from the water bath, allow to cool, and quantitatively transfer the water to a 125-mL separatory funnel. Extract the basic solution with 20 mL ether and discard the ether layer; repeat twice with 10 mL ether and discard the ether layers. The herbicide potassium salts remain in the aqueous phase. Add 2 mL sulfuric acid (1 + 3) to the contents of the funnel to bring the pH to 2 or below, and extract the aqueous phase with 20 mL ether; repeat twice with 10 mL ether to extract the herbicides in their acid forms. Collect the ether extracts in a 125-mL Erlenmeyer flask containing about 0.5 g acidified sodium sulfate. Cover the flask with foil and set aside for at least 1 h, or store in a refrigerator until analysis can continue.

6.8 Quantitatively transfer the ether extract into a K-D apparatus fitted with a 5-mL volumetric receiver. add 1 mL benzene and a boiling chip. Concentrate the extract to about 0.5 mL on a fluidized sandbath heated to 60–70°C. Under no circumstances should the extract be allowed to evaporate completely to dryness. Clear sand from the glass joint before opening. (Use a water bath at 80°C for methyl t-butyl ether extracts.) Rinse the bottom joint with benzene into the receiver.

6.9 After the benzene solution in the receiver has cooled, add 0.5 mL boron trifluoride-methanol reagent. The modified Snyder column is used as an air-cooled condenser, and the contents of the receiver are held at 50°C for 30 min in a sandbath. Cool the reaction mixture to room temperature and add sodium sulfate solution until the benzene-aqueous solution interface is observed in the restricted neck of the receiver. Stopper the receiver, shake vigorously for 1 min, and allow to stand for at least 1 h for phase separation. Loosen the stopper after shaking.

6.10 Transfer the benzene layer from the receiver to a florisil column. Elute with benzene until a total of 2.0 mL of benzene has been collected in a graduated centrifuge tube. Analyze the eluate by gas chromatography.

6.11 Prepare gas chromatograph calibration curves daily with the mixed standards listed in table 7. 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.

6.12 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.

7. Calculations

7.1 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, (step 5.8,
V_1 = volume of standard injected, in µL (step 6.11), and
A_1 = integrated peak area of an identified component in calibration standard (step 6.11).

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

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

where

RF = response factor of identified component in sample, in area/pg,
A_2 = integrated peak area of identified 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).

7.3 Calculate the free chlorophenoxy acid concentration:

$$\text{Concentration of acid (µg/L)} = C \times f,$$

where

C = concentration of methyl ester (calculation 7.2), and

$$f = \frac{\text{molecular weight of acid}}{\text{molecular weight of methyl ester}}.$$

8. Report

Report chlorophenoxy acid herbicide concentrations as follows: less than 0.01 µg/L, as "less than

0.01 µg/L"; 0.01 µg/L to 0.10 µg/L, one significant figure; 0.10 µg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved chlorophenoxy acids in deionized water for 35 replicates using diethyl ether is as follows:

Compound	Spiked concentration (µg/L)	Mean concentration determined (µg/L)	Relative standard deviation (percent)
2,4–D	0.10	0.075	10.0
Silvex	.048	.036	11.6
2,4,5–T	.058	.045	12.2

9.2 Precision for dissolved chlorophenoxy acids in deionized water for 35 replicates using methyl t-butyl ether is as follows:

Compound	Spiked concentration (µg/L)	Mean concentration determined (µg/L)	Relative standard deviation (percent)
2,4–D	0.10	0.083	10.1
Silvex	.048	.040	10.4
2,4,5–T	.056	.049	10.0

9.3 It is estimated that the percent relative standard deviation for total recoverable chlorophenoxy acids will be greater than that reported for dissolved chlorophenoxy acids.

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 Lamar, W.L., 1967, Determination of phenoxy acid herbicides in water by electron-capture and microcoulometric gas chromatography: U.S. Geological Survey Water-Supply Paper 1817–C, 21 p.

Chlorophenoxy acids, recoverable from bottom material (O–5105–83) and recoverable from suspended sediment (O–7105–83), gas chromatographic

Parameter	Code: Recoverable from bottom material	Code: Recoverable from suspended sediment
2,4-D	39731	39733
2,4-DP	34609	34608
Silvex	39761	39763
2,4,5-T	39741	39743

1. Application

This method is suitable for the determination of chlorophenoxy acid herbicides, and their esters and salts, in bottom material and in suspended sediment isolated from water containing at least 0.1 µg/kg and 0.01 µg/L of the analyte, respectively.

2. Summary of method

Chlorophenoxy acid herbicides and their esters are extracted with either diethyl or methyl t-butyl ether from an acidified slurry of bottom material or suspended sediment and water. The extracted herbicides are hydrolyzed to the free acids, which are converted to their methyl esters with boron trifluoride-methanol and purified using adsorption chromatography. The methyl esters are determined by gas chromatography using electron-capture detectors.

3. Interferences

Halogenated organic acids, and their salts and esters, may cause interference.

4. Apparatus

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

4.2 *Centrifuge tube*, 10-mL, Pyrex, graduated, with ground-glass stopper.

4.3 *Concentrator, Kuderna-Danish (K-D)*, 125-mL flask, 5.0-mL volumetric receiver, one-ball Snyder column, and modified micro-Snyder column, Kontes 569251 or equivalent.

4.4 *Florisil column*: To a 130 mm×10 mm id (inside diameter) glass tube having a coarse-porosity fritted disc, add 3 cm florisil and 1 cm anhydrous sodium sulfate.

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

4.5.1 The following conditions are recommended:

Columns, borosilicate glass, 1.8 m×2 mm id operated at 180°C: Column packing materials are (1) 3 percent SP 2100 on 100/120 mesh Supelcoport; and (2) 3 percent SP 2250 on 100/120 mesh Supelcoport, or equivalent.

Detector, dual electron capture operated at 350°C.

Injection port temperature, 200°C.

Carrier gas, nitrogen, flow rate 20 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 *Oven*, Precision model 18EGE, or equivalent, capable of maintaining 130°C.

4.9 *Sandbath*, Tecam, or equivalent.

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

5. Reagents

5.1 *Boron trifluoride-methanol esterification reagent*, 14 percent BF_3 (weight/volume; w/v) in methanol, Applied Science Labs, or equivalent.

5.2 *Florisil adsorbent*, commercially activated at 650°C, washed with hexane, allowed to air dry, and stored at 130°C in a glass-stoppered flask: Prior to use, the florisil is deactivated by adding 10 percent water by weight and shaking for at least 2 h on a wrist-action shaker. The florisil is then tested for activity by attempting to elute the herbicides of interest with benzene from a test column. If the test compounds do not elute within 10.0 mL, further deactivation is required.

5.3 *Hydrochloric acid*, concentrated (sp. gr. 1.19), analytical reagent, A.C.S. grade.

5.4 *Postassium hydroxide solution*, 37 percent (w/v): Dissolve 78 g KOH reagent-grade pellets in 200 mL deionized water. Reflux for 8 h.

5.5 *Sodium sulfate, acidified*: Prepare a slurry of sodium sulfate with enough diethyl ether to cover the crystals and acidify to pH 2 or less by adding a few mL of concentrated sulfuric acid. Determine the pH by transferring a small portion of the slurry to a beaker, removing the ether by evaporation, adding a few drops of deionized water to the crystals, and measuring the pH with pH paper. Allow to air dry overnight. Store in a covered Pyrex beaker or flask at 130°C.

5.6 *Sodium sulfate, granular, anhydrous*: Heat overnight at 300°C and store, covered at 130°C.

5.7 *Sodium sulfate solution*, 5 percent (w/v): Dissolve 50 g neutral sodium sulfate in deionized water and dilute to 1 L.

5.8 *Solvents*, acetone, benzene, unpreserved diethyl ether or methyl t-butyl ether, and iso-octane: Diethyl ether preserved with ethanol cannot be used in this procedure because it results in the formation of extraneous ethyl esters.

5.9 *Standards, methyl esters of chlorophenoxy acid herbicides*, EPA analytical reference grade, or equivalent: Prepare a stock solution by weighing about 10 mg of compound to at least three significant figures and transfer to a 25 mL volumetric flask. Dilute to volume with benzene and mix thoroughly. Prepare a series of mixed-compound standards by volumetric dilution with iso-octane as described in table 8.

Table 8. Concentration of herbicides in mixed standard solutions used for gas chromatograph calibration of bottom material

[Picograms per microliter]

Herbicide	High standard concentration	Low standard concentration
2,4-DP	100	50
2,4-D	100	50
2,4,5-T	40	20
Silvex	40	20

5.10 *Sulfuric acid*, concentrated (sp. gr. 1.84), Mallinckrodt analytical reagent, A.C.S. grade, or equivalent.

5.11 *Sulfuric acid*, (1 + 3): Prepare by adding one part concentrated sulfuric acid to three parts deionized water. Store in a refrigerator at 4°C.

5.12 *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 it will contact. Stopcock grease should not be used on ground-glass joints.

For bottom-material samples, begin at step 6.1.

For water–suspended-sediment mixtures, first determine the weight of the water, then filter the sample using a glass fiber filter to isolate the suspended sediment. Use the filter and the retained sediment to begin the procedure at step 6.2.

6.1 Moisture determination:

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 stopper. 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. Acidify the slurry to pH 2 or below by the dropwise addition of concentrated hydrochloric acid. Use pH paper to determine the pH. Periodically check the pH, adding more acid, if necessary, to maintain the pH at 2 or below.

6.3 Measure 20 mL acetone into the Erlenmeyer flask containing the acidified sample and stopper securely. Mix the contents of the flask for 20 min using the wrist-action shaker. Add 80 mL ether and shake again for 10 min. Decant the extract into a 1-L separatory funnel containing 400 mL of 5 percent sodium sulfate solution. Add 20 mL acetone to the Erlenmeyer flask and shake 20 min. Again, add 80 mL ether, shake 10 min, and decant the acetone-ether extract into the same separatory funnel. Repeat the process as in the second extraction one more time, and collect the acetone-ether extract in the separatory funnel containing the sodium sulfate solution.

6.4 Gently mix the contents of the separatory funnel for about 1 min. Allow the layers to separate. Discard the aqueous layer and collect the extract in a 500-mL Erlenmeyer flask.

6.5 Add 2 mL of 37 percent KOH and 30 mL distilled water to the extract in the 500-mL Erlenmeyer flask. Add a boiling chip and fit the flask with a one-ball Snyder column. Evaporate the ether on a water bath at 80°C in a hood, and continue the heating for a total of 90 min.

6.6 Remove the assembly from the water bath and allow it to cool. Remove the Snyder column. Quantitatively transfer the water to a 125-mL separatory funnel. Extract the basic solution once with 40 mL ether and discard the ether layer; repeat twice with 20 mL ether and discard the ether layers. The herbicides remain in the aqueous phase as their potassium salts. Add 5 mL (1 + 3) sulfuric acid to the contents of the funnel to lower the pH to 2 or below (measure with pH paper), and extract the aqueous phase with 40 mL ether; repeat twice with 20 mL ether. Collect the ether extracts in a 125-mL Erlenmeyer flask containing about 0.5 g acidified anhydrous sodium sulfate. Stopper the flask and set aside for at least 2 h or store in a refrigerator until analysis can continue.

6.7 Quantitatively transfer the ether extract into the K-D apparatus fitted with a 5-mL volumetric receiver. Add 1.0 mL benzene and a boiling chip. Concentrate the extract to about 0.5 mL on a fluidized sandbath heated to 60°–70°C. Under no circumstances allow the extract to evaporate completely to dryness. Clear sand from the glass joint before opening. Rinse the bottom joint with benzene into the receiver.

6.8 After the benzene solution in the receiver has cooled, add 0.5 mL boron trifluoride-methanol reagent. The modified Snyder column is used as an air-cooled condenser, and the contents of the receiver are held at 50°C for 30 min in a sandbath. Cool the reaction mixture to room temperature and add sodium sulfate solution until the benzene-aqueous solution interface is observed in the restricted neck of the receiver. Stopper the receiver, shake vigorously for 1 min, and allow to stand for at least 1 h for phase separation. Loosen the stopper after shaking.

6.9 Transfer the benzene layer from the receiver to a florisil column. Elute with benzene and collect 10.0 mL in a graduated receiver. Analyze the eluate by gas chromatography.

6.10 Prepare gas chromatograph calibration curves daily with the mixed standards shown in table 8. 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.

6.11 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.

7. Calculations

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

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

where

wet weight = amount of sample to be taken 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:

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

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
V_4 = weight of sample in g, expressed in mL (1.000 mL = 1.000 g).

7.5 Calculate the free phenoxy acid concentrations using the following equation:

$$\text{Concentration of acid (µg/L or µg/kg)} = C \times f,$$

where

C = concentration of methyl ester determined in calculation 7.3 or 7.4, and

$$f = \frac{\text{molecular weight of acid}}{\text{molecular weight of methyl ester}}.$$

8. Report

8.1 Report chlorophenoxy acid herbicide concentrations in bottom materials as follows: less than 0.10 µg/kg, as "less than 0.10 µg/kg"; 0.10 µg/kg and above, two significant figures.

8.2 Report chlorophenoxy acid herbicide concentrations in suspended materials as follows: less than 0.01 µg/L, as "less than 0.01 µg/L"; 0.01 to 0.10 µg/L, two decimals; 0.10 µg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for recoverable chlorophenoxy acids from bottom material and suspended sediment will be greater than that reported for dissolved chlorophenoxy acids (method O–1105).

Selected references

American Public Health Association, 1981, Standard methods for the examination of water and wastewater (15th ed.): Washington, American Public Health Association, Inc., 1,134 p.

American Society for Testing and Materials, 1983, Annual Book of ASTM Standards, Sect. 11, v. 11.01: Philadelphia, American Society for Testing and Materials, 752 p.

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 Lamar, W.L., 1967, Determination of phenoxy acid herbicides in water by electron-capture and microcoulometric gas chromatography: U.S. Geological Survey Water-Supply Paper 1817–C, 21 p.

Triazines, total recoverable, gas chromatographic (O–3106–83)

Parameter	*Code*
Ametryn	82184
Atrazine	39630
Cyanazine	81757
Prometon	39056
Prometryn	39057
Propazine	39024
Simazine	39055
Simetryn	39054
Alachlor	None assigned.
Trifluralin	None assigned.

1. Application

This method is suitable for the determination of triazine herbicides, alachlor, and trifluralin in water and water–suspended-sediment mixtures containing at least 0.1 µg/L of each constituent.

2. Summary of method

Triazine herbicides are extracted from water with methylene chloride following adjustment to pH 7 to 9. Optional adsorption chromatography on alumina is used for the elimination of most nonpesticide interferences. Identification is made by selective gas chromatographic separation through the use of two or more dissimilar column packing materials using a nitrogen specific detector.

3. Interferences

Solvents, reagents, glassware, and other sample-processing hardware may yield discrete artifacts or elevated baselines which may cause misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free of interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents in an all-glass system is required. Glassware should be cleaned by washing with hot detergent solution, rinsing with organic-free water, and heating overnight at 300°C.

4. Apparatus

4.1 *Alumina column:* To a 15-cm-long disposable Pasteur pipet, add a glass-wool plug, anhydrous sodium sulfate to a depth of 10 cm, 3 cm alumina, and 0.5 cm anhydrous sodium sulfate. Tap the column gently to promote settling to a uniform bed.

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

4.3 *Concentrator apparatus*, Kuderna-Danish (K-D), with a 500-mL flask, a 10.0-mL receiver, and a three-ball Snyder column.

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

4.5 *Gas chromatograph*, Hewlett-Packard model 5880A/Tracor model 560, or equivalent: Instrument must incorporate a glass-lined injection port and a glass column.

4.5.1 The following conditions are recommended:

Columns, borosilicate glass, 1.8 m×2 mm id (inside diameter) rendered inert by treatment with silanizing agent: Column packing materials are (1) 1 percent OV–101 on 100/120 mesh UltraBond 20 M or equivalent, operated at an oven temperature of 175°C; and (2) 100/120 mesh UltraBond PEGS, or equivalent, operated at an oven temperature of 200°C.

Detector, alkali flame ionization (N/P), operated at 300°C.

Injection port temperature, 200°C.

Carrier gas, helium, flow rate 35 mL/min.

Detector flows, hydrogen at 3.2 mL/min and air at 100 mL/min.

5. Reagents

5.1 *Alumina*, Woelm W 200, neutral, activity I: Prepare activity V (16 percent deactivation) by mixing 100 g activity I with 19 mL water. Mix on wrist-action shaker for 2 h and let stand overnight in a sealed container. Prepare fresh weekly.

5.2 *Borosilicate glass wool*, filtering grade, prewashed with hexane and heated overnight at 300°C.

5.3 *Potassium hydroxide*, 37 percent (weight/volume; w/v) aqueous solution prepared from reagent-grade KOH and reagent water.

5.4 *Sodium sulfate*, granular, anhydrous, heated overnight at 300°C and stored at 130°C.

5.5 *Solvents*, benzene, ethyl ether, hexane, and methylene chloride, pesticide residue quality, distilled in glass.

5.6 *Sulfuric acid*, 25 percent (volume/volume; v/v) prepared from high-purity concentrated H_2SO_4 (sp. gr. 1.84) and reagent water.

5.7 *Triazine standards*, EPA analytical reference grade or highest purity available: Dissolve 5 mg of standard in benzene in a 50-mL volumetric flask, dilute to volume, and mix. Dilute stock standard with hexane to working concentration shown in table 9.

6. Procedure

6.1 Rinse all glassware with methylene chloride before using. Do not use stopcock grease on ground-glass joints.

6.2 Weigh the sample and capped bottle to the nearest 0.1 g and record the weight.

Table 9. Concentration of triazines in mixed standard solutions used for gas chromatograph calibration

[Picograms per microliter]

Mixture number	Triazines	Low standard	Medium standard	High standard
1 -------	Atrazine	500	1000	5000
	Propazine	500	1000	5000
	Simazine	500	1000	5000
2 -------	Ametryn	500	1000	5000
	Prometon	500	1000	5000
	Prometryn	500	1000	5000
	Simetryn	500	1000	5000

6.3 Transfer the sample to a 2,000-mL separatory funnel using a stainless steel powder funnel.

6.4 Weigh the empty sample bottle with cap to the nearest 0.1 g and calculate the sample weight.

6.5 Dissolve 5 g sodium chloride in sample and adjust the pH to 7 to 9 using the potassium hydroxide solution or sulfuric acid solution as necessary.

6.6 Add 75 mL methylene chloride to sample bottle, swirl, and transfer to separatory funnel. Allow to drain, rinsing the walls of the bottle.

6.7 Insert the glass stopper and shake the funnel vigorously for 1 min. Vent the system several times during this initial shakeout.

6.8 Let stand undisturbed while layers clarify, and draw off the methylene chloride into a 250-mL glass-stoppered Erlenmeyer flask.

NOTE: Most water–suspended-sediment mixtures will require special treatment. If emulsions occur, add sufficient volume of hexane (50–75 mL) to float the extract. Shake the separatory funnel again to mix the solvents, and allow the layers to separate. Draw off the sample into the sample bottle. The remaining emulsion can be eliminated by vigorous shaking (CAUTION: Vent often). Decant the extract into a 250-mL glass-stoppered Erlenmeyer flask and return the sample to the separatory funnel. Proceed to step 6.9.

6.9 Repeat the extraction with two additional 50-mL portions of methylene chloride, collecting the organic layers in the flask.

6.10 Add 5 gm anhydrous sodium sulfate, stopper, and shake.

6.11 Quantitatively transfer the combined extracts to the K-D apparatus, add approximately 3 mL hexane as a keeper, add a boiling chip, and concentrate to 3–5 mL in a water bath maintained at 80°C.

6.12 Continue evaporation to approximately 0.5 mL in a warm water bath under nitrogen or helium stream using the N-Evap apparatus. Wash the walls of the tube with 5 mL hexane. Concentrate to 0.5 mL and wash the walls again with 5 mL hexane. Concentrate to 0.5 mL.

6.13 Bring the volume to 1 mL with hexane, and proceed to alumina column cleanup, if necessary.

6.13.1 Alumina column cleanup:

6.13.1.1 Quantitatively transfer the extract to the column using hexane. Elute the column with hexane until 6 mL has been eluted, and discard.

6.13.1.2 When the last of the hexane has just entered the sodium sulfate, elute the column with hexane-ethyl ether (2:1) until a 4-mL fraction has been collected.

6.13.1.3 Reduce the volume to 1.0 mL under a nitrogen or helium stream and proceed to gas chromatographic analysis.

6.14 Frequently use standard triazine mixtures to demonstrate the effectiveness of the alumina in characterizing the eluate composition and providing quantitative recovery.

6.15 Prepare gas chromatograph calibration curves daily with the mixed standards in table 9. 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 peak area of each component in the standard.

6.16 Chromatograph and identify the triazines by comparing retention time with standards (3-percent window for identification) using at least two of the dissimilar column packings described.

7. Calculations

7.1 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.

7.2 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

Report concentrations of total recoverable triazines, alachlor, and trifluralin as follows: less than 0.1 µg/L, as "less than 0.1 µg/L"; 0.1 to 1.0 µg/L, one decimal; 1.0 µg/L and above, two significant figures.

9. Precision

9.1 Recovery and precision (seven replicates) for total recoverable triazines in tapwater are as follows:

Compound	Amount spiked (µg)	Mean percent recovery	Standard deviation	Relative standard deviation (percent)
Prometon	0.5	85.5	10.9	12.8
	1.0	94.4	6.60	6.99
	5.0	87.0	5.92	6.81
Propazine	.5	82.3	11.6	14.1
	1.0	97.0	4.90	5.05
	5.0	91.7	5.74	6.26
Atrazine	.5	85.1	11.8	13.9
	1.0	97.3	4.35	4.47
	5.0	87.1	5.26	6.04
Prometryn	.5	87.3	9.98	11.4
	1.0	98.3	3.97	4.04
	5.0	81.5	4.50	5.53
Simazine	.5	81.0	12.0	14.8
	1.0	96.6	8.68	8.99
	5.0	61.8	9.41	15.2
Ametryn	.5	89.6	10.5	11.7
	1.0	97.2	4.52	4.65
	5.0	91.4	5.70	6.24
Simetryn	.5	87.7	1.01	11.5
	1.0	92.2	6.42	6.97
	5.0	88.3	7.38	8.36

9.2 Recovery and precision (10 replicates) for total recoverable triazines from a natural surface water are as follows:

Compound	Amount spiked (µg)	Mean percent recovery	Standard deviation	Relative standard deviation (percent)
Prometon	0.5	95.1	5.83	6.13
	1.0	96.9	2.08	2.15
	5.0	84.6	4.58	5.41
Propazine	.5	96.2	5.46	5.68
	1.0	100.9	2.06	2.05
	5.0	87.6	4.62	5.28
Atrazine	.5	96.0	7.34	7.65
	1.0	98.1	2.11	2.15
	5.0	85.5	5.14	6.01
Prometryn	.5	98.0	5.09	5.20
	1.0	77.9	1.67	2.15
	5.0	83.5	3.82	4.57
Simazine	.5	96.9	4.90	5.05
	1.0	98.8	4.91	4.97
	5.0	82.8	7.69	9.29
Ametryn	.5	101.1	8.82	8.73
	1.0	101.5	3.83	3.77
	5.0	87.8	4.03	4.58
Simetryn	.5	98.7	7.17	7.27
	1.0	94.7	2.08	2.19
	5.0	86.4	4.23	4.90

Carbamate pesticides, total recoverable, high-performance liquid chromatographic (O-3107-83)

Parameter	Code
Aldicarb	None assigned.
Carbaryl	39750
Carbofuran	None assigned.
3-Hydroxycarbofuran	None assigned.
Methomyl	39051
1-Naphthol	None assigned.
Propham	39052

1. Application

This method is suitable for the determination of carbamate pesticides in water or water-suspended-sediment samples containing at least 2 µg/L of the analyte.

2. Summary of method

The carbamates are extracted from water or water-suspended-sediment mixtures with methylene chloride. The extract is concentrated and analyzed by high-performance liquid chromatography (HPLC) using a C_{18} reverse phase column and a dual-channel variable-wavelength ultraviolet detector.

3. Interferences

Compounds that exhibit chemical and physical properties similar to the compounds of interest can interfere.

4. Apparatus

4.1 *Concentrator, Kuderna-Danish (K-D),* 500-mL capacity with a three-ball Snyder column and a 10-mL graduated receiver tube.

4.2 *Evaporative concentrator,* Organomation N-Evap, or equivalent.

4.3 *Filters*, 0.5 µm millipore FHUP, catalog no. 04700, or equivalent, and 0.45 µm millipore HAWP, catalog no. 04700, or equivalent.

4.4 *Liquid chromatograph*, Waters Associates ALC/GPC 204 liquid chromatograph equipped with a dual-channel variable-wavelength detector, a model 6000A solvent-delivery system, a model 660 solvent flow programmer, a model WISP 710A microprocessor, and a data module, or equivalent.

4.4.1 The following conditions are recommended:

Columns, Waters Associates Radial Compression Module with a Radial PAK reverse-phase cartridge (octadecylsilane permanently bonded to unmodified silica), 10 µm particle size, or equivalent.

Wavelengths, 254 and 280 nm.

Solvent, 45 percent water and 55 percent methanol at a flow rate of 1.0 mL/min isocratic.

4.5 *Solvent clarification kit*, Waters Associates 85113, or equivalent.

5. Reagents

5.1 *Carbamate and metabolite standards*, EPA analytical reference grade or highest purity available: Prepare by dissolving 5 mg of standard in acetonitrile in a 50-mL volumetric flask, dilute to volume, and mix. Dilute this stock solution with acetone to the working concentrations listed in table 10.

Table 10. Concentration of carbamates in mixed standard solutions used for liquid chromatograph calibration

[Nanograms per microliter]

Carbamate	Low standard	Medium standard	High standard
Propham	9	18	36
Methomyl	2	4	8
Carbaryl	2	4	8

5.2 *Phosphate buffer*, pH 7.5: Mix 50 mL of 0.1 *M* KH_2PO_4 with 41 mL of 0.1 *M* NaOH and dilute to 100 mL with deionized water.

5.3 *Potassium dihydrogen phosphate*, 0.1 *M*: Dissolve 13.6 g KH_2PO_4 in deionized water and dilute to 1 L.

5.4 *Sodium hydroxide*, 0.1 *M*: Dissolve 4 g NaOH pellets in deionized water and dilute to 1 L.

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

5.6 *Solvents*, HPLC quality, acetonitrile, methanol, tetrahydrofuran, and pesticide grade methylene chloride.

5.7 *Water*, organic-free.

6. Procedure

Glassware should be cleaned by washing with hot detergent solution, rinsing with deionized water, and heating overnight at 300°C. Just prior to use the glassware is rinsed with methylene chloride. Stopcock grease should not be used on the ground-glass joints.

6.1 Weigh the sample bottle plus the sample and record the weight. Pour the sample into a 1,000 mL-separatory funnel, add 10 mL phosphate buffer, and shake until well mixed. Weigh the empty sample bottle. Calculate the net sample weight and record the value obtained to three significant figures.

6.2 Add 75 mL methylene chloride to the sample bottle, swirl to rinse the sides of the bottle, and transfer the solvent to 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 separatory funnel vigorously for 1 min. Vent often. Allow the layer to separate and draw off the methylene chloride layer into a 250-mL Erlenmeyer flask that contains 1 g anhydrous sodium sulfate.

6.3 Repeat the extraction of the water sample two more times, using 50 mL methylene chloride each time. Combine all the organic extracts in the 250-mL Erlenmeyer flask containing the first extract.

6.4 Transfer the extract to a 500-mL K-D apparatus fitted with a three-ball Snyder column and a 10-mL receiver containing a micro boiling chip and 4 mL acetonitrile.

6.5 Place the apparatus on a hot-water bath (75–85°C) until the volume is reduced to about 4 mL. Remove from the heat and allow to cool. Wipe the joints with a towel. Rinse the bottom joint with acetonitrile into the receiver.

6.6 Further reduce the volume of solvent to about 1 mL on an evaporative concentrator with the water bath at 35°C. Rinse down the sides of the tube with 1 mL acetonitrile and concentrate to a final volume of 1.0 mL. Stopper until chromatographic analysis can begin.

6.7 Prepare the solvents for the mobile phase by filtering, using the solvent clarification kit and HAWP filters for water and FHUP filters for the organic solvents.

6.8 Prepare liquid chromatograph calibration curves daily by injecting the reference standards listed in table 10. Operating conditions need to be

identical to those used for sample analysis in step 6.9. Record the volume of the standard injected and the retention time and integrated peak area of each component in the standard.

6.9 Inject an aliquot of sample extract into the calibrated liquid chromatograph. Record the volume injected. Identify the peaks by retention time. Confirmation is obtained by measuring the peak area at the two different wavelenghths (254 and 280 nm) and comparing the ratio of the peak areas to that of the standard. Record the retention time and integrated area of any identified peak. Dilute any extract containing an identifiable component above the highest standard.

7. Calculations

7.1 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/ng,
C_s = concentration of standard component, in ng/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 orginial sample from the equation

$$\text{Concentration } (\mu g/L) = \frac{A_2 \times V_2}{RF \times V_3 \times W} \times 1{,}000,$$

where

RF = response factor of identified calibration standard, in area/ng,
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

Report concentrations of carbamates in water or water–suspended-sediment mixtures as follows: less than 2 μg/L, as "less than 2.0 μg/L"; 2.0 μg/L and above, two significant figures.

9. Precision

Single-operator precision was determined by spiking surface-water samples at four concentrations and four replicates performed on different days. Results are as follows:

Compound	Concentration spiked (μg/L)	Mean concentration recovered (μg/L)	Relative standard deviation (percent)
Methomyl	2.51	2.13	20
	5.02	3.80	11
	10.0	7.47	9.4
	20.1	15.5	7.3
Carbaryl	2.36	2.33	5.7
	4.72	4.58	4.8
	9.44	9.18	5.5
	18.9	18.6	3.4
Propham	7.05	5.68	13
	14.1	11.2	8.0
	28.2	22.2	7.7
	56.4	43.0	8.2

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.

Sparacine, C.M., and Hines, J.W., 1976, High-performance liquid chromatography of carbamate pesticides: Journal of Chromatography Science, v. 14, p. 549–555.

Oil and grease, extractable, extraction-gravimetric (O–3108–83)

Parameter	Code
Oil and grease, total (mg/L as oil and grease)	00556

1. Application

This method is suitable for the determination of oil and grease in water–suspended-sediment mixtures containing at least 1 mg/L of the analyte.

2. Summary of method

2.1 A sample is extracted twice with trichlorotrifluoroethane and the extract is evaporated at 20°C to leave a nonvolatile residue whose weight represents an estimate of the extractable organic matter in the sample.

2.2 The procedure approximates the determination of oils and grease in water, and is similar to Method 2778–70 described by the American Society for Testing and Materials (1982) and to Method 137, Oil and Grease, described by the American Public

Health Association and others (1981) in "Standard Methods for the Examination of Water and Wastewater."

3. Interferences

Organic solvents vary considerably in their ability to dissolve oil substances and other organic matter. Any method used to obtain an estimate of the amount of extractable organic matter must, of necessity, be highly empirical. Close attention to all operations of the analytical procedure is required to obtain reproducible results.

4. Apparatus

4.1 *Dish*, aluminum foil, 110 mm in diameter, 100-mL capacity.

4.2 *Funnel*, separatory, pear-shaped, 2-L capacity (Corning 6404, or equivalent).

5. Reagents

5.1 *Sodium sulfate*, anhydrous, granular.

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

5.3 *Sulfuric acid*, (1 + 1): Slowly and cautiously, with constant stirring and cooling, add 100 mL concentrated H_2SO_4 to 100 mL demineralized water.

5.4 *Trichlorotrifluoroethane solvent*, 1,1,2-Trichlorotrifluoroethane, b.p. 47.6°C, reagent grade.

6. Procedure

6.1 Collect approximately 900 mL of sample in a 1-L glass bottle.

6.2 Transfer the entire contents of the glass bottle to a 1,000-mL graduated cylinder. Record the volume. Prepare a 900-mL demineralized water blank and carry it through the sample-analysis procedure. Subtract the residual weight (blank) from the sample extract residual weight. If the weight of the blank exceeds 4.0 mg, a new bottle of solvent must be obtained to provide a blank of 4.0 mg or less.

6.3 Transfer the sample from the graduated cylinder to a 2-L separatory funnel, and add 5 mL sulfuric acid (1 + 1). Shake to mix thoroughly.

6.4 Rinse the glass bottle with 25 mL trichlorotrifluoroethane solvent and transfer the solvent to the graduated cylinder. Rinse the graduate and transfer the solvent to the separatory funnel. Shake vigorously for 2 min, stopping to vent the pressure as necessary.

6.5 Allow the layers to separate and then draw off the solvent and filter it through a small amount of anhydrous Na_2SO_4 placed on a small filter paper (Whatman No. 40, or equivalent) in a funnel. Collect the filtrate in a tared aluminum-foil dish.

6.6 Repeat steps 6.4 and 6.5, filtering the solvent through the same funnel and adding the filtrate to that already collected in the aluminum-foil dish.

6.7 Wash the filter paper with three 5-mL portions of solvent, collecting all washings in the aluminum-foil dish.

6.8 Evaporate the solvent collected in the aluminum-foil dish at room temperature (20°C) in a well-ventilated fume hood.

6.9 Rinse the inside of the aluminum-foil dish with demineralized water to remove traces of sulfuric acid. Dry the dish in a desiccator to remove water.

6.10 Weigh the residue in the dish after the water has evaporated.

7. Calculations

Determine the mg/L extractable organic matter in the samples as follows:

$$\text{Organic matter, extractable, mg/L} = \frac{R_x - R_b}{\text{mL sample}} \times 1{,}000,$$

where

R_x = weight of extracted residue, in mg, and

R_b = weight of solvent residue (blank), in mg.

8. Report

Report organic matter, extractable, water–suspended-sediment, concentrations as follows: less than 10 mg/L, nearest mg/L; 10 mg/L and above, two significant figures.

9. Precision

Precision data cannot be given for this determination because of the variable nature of the materials being extracted.

Selected references

American Public Health Association, 1981, Standard methods for the examination of water and wastewater (15th ed.): Washington D.C., American Public Health Association, Inc., p. 461.

American Society for Testing and Materials, 1982, Annual Book of ASTM Standards, Part 31, Water: Philadelphia, American Society for Testing and Materials, p. 627.

Oil and grease, extractable from bottom material, extraction-gravimetric (O-5108-83)

Parameter	*Code*
Oil and grease, recoverable from bottom material (mg/kg as oil and grease)	00557

1. Application

1.1 This method is suitable for the determination of oil and grease in air-dried bottom materials containing at least 1,000 mg/kg.

1.2 This method may be used for the determination of oil and grease in wet bottom materials if the appropriate moisture correction is applied.

2. Summary of method

A sample is extracted twice with trichlorotrifluoroethane and the extract is evaporated at 20°C to leave a nonvolatile residue whose weight represents an estimate of the extractable organic matter in the sample.

3. Interferences

Organic solvents vary considerably in their ability to dissolve oil substances and other organic matter. Any method used to obtain an estimate of the amount of extractable organic matter must, of necessity, be highly empirical. Close attention to all operations of the analytical procedure are required to obtain reproducible results.

4. Apparatus

4.1 *Dish*, aluminum foil, 110 mm in diameter, 100-mL capacity.

4.2 *Funnel*, separatory, pear-shaped, 2-L capacity (Corning 6404, or equivalent).

5. Reagents

5.1 *Sodium sulfate*, anhydrous, granular.

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

5.3 *Sulfuric acid*, (1 + 1): Slowly and cautiously, with constant stirring and cooling, add 100 mL concentrated H_2SO_4 to 100 mL demineralized water.

5.4 *Trichlorotrifluoroethane solvent*, 1,1,2-Trichlorotrifluoroethane, b.p. 47.6°C, reagent grade.

6. Procedure

6.1 Weigh, to the nearest mg, approximately 1 g of air-dried sample material. Alternatively, a wet sample may be weighed if a correction is made for moisture content.

6.2 Quantitatively transfer the weighed sample to a 2-L-capacity separatory funnel. Add approximately 900 mL demineralized water and shake to mix. Prepare a 900-mL demineralized water blank and carry it through the sample-analysis procedure. Subtract the residual weight (blank) from the sample extract residual weight. If the weight of the blank exceeds 4.0 mg, a new bottle of solvent must be obtained to provide a blank of 4.0 mg or less.

6.3 Add 5 mL sulfuric acid (1 + 1). Shake to mix thoroughly.

6.4 Add 25 mL trichlorotrifluoroethane and shake vigorously for 2 min, stopping to vent the pressure as necessary.

6.5 Allow the layers to separate and then draw off the solvent and filter it through a small amount of anhydrous Na_2SO_4 placed on a small filter paper (Whatman No. 40, or equivalent) in a funnel. Collect the filtrate in a tared aluminum-foil dish.

6.6 Repeat steps 6.4 and 6.5, filtering the solvent through the same funnel and adding the filtrate to that already collected in the aluminum-foil dish.

6.7 Wash the filter paper with three 5-mL portions of solvent, collecting all washings in the aluminum-foil dish.

6.8 Evaporate the solvent collected in the aluminum-foil dish at room temperature (20°C) in a well-ventilated fume hood.

6.9 Rinse the inside of the aluminum-foil dish with demineralized water to remove traces of sulfuric acid. Dry the dish in a desiccator to remove water.

6.10 Weigh the residue remaining in the dish after the water has evaporated.

7. Calculations

7.1 Determine the mg/kg extractable organic matter in the air-dried sample as follows:

$$\text{Organic matter, extractable, mg/kg} = \frac{R_x - R_b}{\text{sample weight in g}} \times 1{,}000,$$

where

R_x = weight of extracted residue, in mg, and

R_b = weight of solvent residue (blank), in mg.

NOTE: If wet bottom-material sample is used in preference to air-dried sample, a factor correcting for moisture content must be applied to above equation.

8. Report

8.1 Report organic matter, extractable, air-dried bottom material, concentrations as follows: less than 10,000 mg/kg, nearest 1,000 mg/kg; 10,000 mg/kg and above, two significant figures.

9. Precision

Precision data cannot be given for this determination because of the variable nature of the materials being extracted.

Fuel oils, light, total recoverable, gas chromatographic (O-3109-83)

Parameter	*Code*
Fuel oils, light, total recoverable (mg/L)	None assigned.

1. Application

This method is suitable for the determination of light fuel oils (C_{10}–C_{22}) in water or water–suspended-sediment mixtures at concentrations of 0.1 mg/L and above.

2. Summary of method

A water or water–suspended-sediment sample containing light fuel oils (diesel oils) is acidified and extracted with hexane. The extract is concentrated and analyzed by temperature-programmed gas chromatography using a flame-ionization detector. These oils possess a characteristic envelope which appears during the temperature-programmed run. This envelope, composed of the various hydrocarbon peaks, approximates the boiling range profile of the oil. The area of the envelope is reproducible and is the basis for quantitation. Characterization is based on comparison of the peaks in the residue chromatogram with those of a known oil sample.

3. Interferences

Any compound having chemical and physical properties similar to an analyte of interest may interfere.

4. Apparatus

4.1 *Boiling chip*, micro, granules, Hengar H-1366C, or equivalent.

4.2 *Concentrator apparatus*, Kuderna-Danish (K-D) type, with 10.0- and 4.0-mL receivers, 200- and 500-mL flasks, and a one-ball Snyder column.

4.3 *Evaporative concentrator*, Organomation N-Evap, or equivalent.

4.4 *Gas chromatograph*, Hewlett-Packard 5710, or equivalent.

4.4.1 The following conditions are recommended:

Columns, borosilicate glass, 1.8 m×2 mm id (inside diameter). Column packing is 5 percent OV–101 on 100/120 mesh Gas Chrom Q, or equivalent. A capillary column operated under appropriate conditions may also be used.

Temperature program, 3-min postinjection hold, 100°C to 230°C at 8°C/min, hold for 2 min, end of cycle.

Detector, flame-ionization operated at 250°C.

Injection port temperature, 210°C.

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

5. Reagents

5.1 *Fuel oil standard*: A sample of the oil being determined must be available from the manufacturer or other suitable source. The Environmental Protection Agency Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, has several standard oil references. Weigh about 10 mg of standard to at least three significant figures and quantitatively transfer it to a 25-mL volumetric flask. Dilute to volume with iso-octane. Prepare standards in iso-octane at concentrations of 100, 1,000, and 10,000 ng/μL.

5.2 *Sodium sulfate*, granular, anhydrous: The sodium sulfate should be heated at 300°C overnight and stored in a stoppered, glass container.

5.3 *Solvents*, acetone and hexane, pesticide residue quality, distilled in glass, Burdick and Jackson, or equivalent.

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

5.5 *Sulfuric acid*, 2 *N*: Add 53 mL concentrated H_2SO_4 slowly to 500 mL water. Cool and dilute to 1 L.

5.6 *Water*, reagent grade, organic-free.

6. Procedure

Glassware must be cleaned by washing with hot detergent solution, rinsing with deionized water, and heating overnight at 300°C. Just prior to use, the glassware is rinsed with methylene chloride. Do not use stopcock grease on ground-glass joints.

6.1 Refrigerate the sample until extraction. The extraction must be performed within 24 to 48 h after receipt to minimize oil degradation.

6.2 Weigh the bottle containing the sample and record the weight. Pour the sample into a 1-L

separatory funnel and weigh the empty sample bottle. Calculate the net sample weight and record the value obtained to three significant figures. Use 2 N sulfuric acid to adjust the pH to 1 to 2.

6.3 Add 20 mL hexane to the sample bottle, swirl, and pour into a separatory funnel. Allow bottle to drain.

6.4 Shake the funnel vigorously for 1 min, venting often to relieve pressure. Decant the solvent layer into a 500-mL Erlenmeyer flask.

6.5 Repeat steps 6.3 and 6.4 twice, for a total of three extractions.

6.6 Add about 5 g anhydrous sodium sulfate to the Erlenmeyer flask containing the extracts and allow to stand covered for at least 4 h.

6.7 Quantitatively transfer the extract to a K-D apparatus. Add a boiling chip, and concentrate on a water bath to about 5 mL. Remove the apparatus and dry the joints with a towel. Rinse the lower joint with hexane into the receiver.

6.8 Continue concentration on an evaporative concentrator until the volume is reduced to about 0.5 mL. Wash the walls of the receiver with small portions of hexane during concentration and dilute to 1.0 mL with hexane.

6.9 Prepare gas chromatograph calibration curves daily by injecting the series of reference standards. Operating conditions must be identical for samples and standards. Record the volume of the standard injected.

6.10 Inject an aliquot of sample extract into the gas chromatograph. Record the volume injected. Dilute any extract containing fuel oil in a concentration greater than the highest standard.

6.11 Determine the area under the envelope of the fuel oil standard. Choose the beginning and ending peaks so that a reproducible area will be measured when quantitating different standards and samples. Use the equations is section 7 to calculate the concentration of fuel oil in the sample.

7. Calculations

7.1 Calculate the response factor for the calibration standard:

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

where

RF = response factor of fuel oil in calibration standard, in area/ng,
C_s = concentration of standard, in ng/μL,
V_1 = volume of standard injected, in μL, and
A_1 = integrated peak area of calibration standard.

7.2 Calculate the concentration of fuel oil in the original water sample from the equation

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

where

RF = response factor of fuel oil in calibration standard, in area/ng,
A_2 = integrated peak area of sample,
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

Report concentrations of fuel oil in water or water–suspended-sediment mixtures as follows: less than 0.02 mg/L, as "less than 0.02 mg/L"; 0.02 to 0.1 mg/L, two decimals, 0.1 mg/L and above, two significant figures.

9. Precision

Single-operator precision data for No. 2 diesel fuel spiked into distilled and natural water samples are as follows:

Concentration of spiked fuel oil sample (mg/L)	Number of replicates		Mean concentration determined (mg/L)		Relative standard deviation (percent)	
	Distilled water	Natural water	Distilled water	Natural water	Distilled water	Natural water
0.085	5	5	0.064	0.058	28	22
.85	5	5	.68	.67	4.8	10
8.5	5	4	7.0	6.8	1.7	7.3

Phenols, total recoverable, colorimetric, 4-aminoantipyrine (O–3110–83)

Parameter	Code
Phenols, total recoverable (μg/L as phenol)	32730

1. Application

This method may be used to analyze water or water–suspended-sediment mixtures containing at least 1.0 μg/L of phenolic material.

2. Summary of method

Steam-distillable phenols react with 4-aminoantipyrine at pH 10.0 ± 0.2 in the presence of potassium ferricyanide to form a colored antipyrine

dye. This dye is extracted from aqueous solution with chloroform, and the absorbance is measured at 460 nm. This method is similar in principle to, but different in detail from ASTM Method D 1783–80 (American Society for Testing and Materials, 1982).

3. Interferences.

Phenol has been selected as the standard for reference. Substituted phenols may produce less color than phenol. The concentration of phenols determined by this method represents the minimum concentration of phenolic compounds present in the sample.

Certain bacteria, oxidizing and reducing substances, and highly alkaline waste waters may interfere with this method. Information for removal of major interferences may be found in ASTM Method D 1783–80.

4. Apparatus

4.1 *Distillation apparatus*, all glass, consisting of a 1-L Pyrex distilling apparatus and a water-cooled condenser (Corning 3360, or equivalent).

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

4.3 *Photometer*, spectrophotometer or filter photometer operating at 460 nm, and accommodating cells having light paths of 1.0 and 10 cm.

4.4 *Funnel*, Separatory, pear-shaped, 1,000 mL (Corning 6404, or equivalent).

5. Reagents

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

5.1 *Aminoantipyrine solution*, 2 g/100 mL: Dissolve 2.0 g of 4-aminoantipyrine in distilled water and dilute to 100 mL. This solution is not stable and must be prepared each day.

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

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

5.4 *Chloroform*, spectrophotometric grade.

5.5 *Copper sulfate solution*, 100 g/L: Dissolve 100 g of $CuSO_4 \cdot 5H_2O$ in water and dilute to 1 L.

5.6 *Phenol standard solution*, 1.00 mL = 1.00 mg phenol: Dissolve 1.00 g analytical reagent phenol in 1,000 mL freshly boiled and cooled distilled water. Solution is stable for 1 mo.

5.7 *Phosphoric acid solution*: Dilute 10 mL of 85 percent H_3PO_4 to 100 mL with phenol-free water.

5.8 *Potassium ferricyanide solution*, 8 g/100 mL: Dissolve 8.0 g of $K_3Fe(CN)_6$ in water, dilute to 100 mL, and filter. This solution is not stable and must be prepared each day.

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

6. Procedure

Samples should be protected from light and analyzed as soon as possible. The analyst is referred to "Standard Methods for the Examination of Water and Wastewater," 15th edition (American Public Health Association 1981) for the analysis of very alkaline or highly polluted water.

6.1 Measure a volume of sample containing less than 50 µg phenol (500 mL maximum) into a beaker. If less than 500 mL of sample is used, dilute sample with distilled water to 500 mL. Determine the pH and adjust to below 4.0, if necessary. (Add 5.0 mL copper sulfate solution if it was not added at sampling.) Transfer the solution to the distillation apparatus, add boiling stones, and distill. Collect 450 mL distillate and stop. Add 50 mL distilled water to the residue and proceed with distillation until 500 mL of distillate is collected.

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

6.3 Treat the sample, blank, and standards as follows: Add 1.0 mL ammonium chloride solution and 1.0 mL ammonium hydroxide, mix, and adjust the pH to 10.0 ± 0.2 with concentrated ammonium hydroxide. Add 3.00 mL aminoantipyrine solution and mix. Add 3.00 mL potassium ferricyanide solution and again mix. Allow the color to develop for 3 min. A clear to light-yellow solution should result.

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

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

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

7. Calculations

Calculate the phenolic content in the sample, in µg/L, as follows:

$$\text{Phenolic material (µg/L)} = \frac{\text{µg phenol in sample} \times 1{,}000}{\text{mL original sample}}.$$

8. Report

Report concentrations of phenolic material as follows: less than 1 µg/L, as "less than 1 µg/L"; 1 to 100 µg/L, nearest µg/L; 100 µg/L and above, two significant figures.

9. Precision

Single-operator precision (10 replicates) for phenol spiked into distilled water is as follows:

Phenol concentration (µg/L)	*Mean found (µg/L)*	*Relative standard deviation (percent)*
4.0	4.5	12
40	37	5.5

Selected references

American Public Health Association, 1981, Standard methods for the examination of water and wastewater (15th ed.): Washington D.C., American Public Health Association, Inc., 1,134 p.

American Society for Testing and Materials, 1982, Annual book of ASTM standards, Part 31, Water: Philadelphia, American Society for Testing and Materials, p. 789.

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.

Methylene blue active substances, total recoverable, colorimetric (O-3111-83)

Parameter	*Code*
Methylene blue active substances, total recoverable (mg/L as MBAS)	38260

1. Application

This method is applicable to the analysis of water or water–suspended-sediment mixtures containing at least 0.01 mg/L methylene blue active substances (MBAS) relative to linear alkyl sulfonate (LAS) standard.

2. Summary of method

Methylene blue reacts with anionic surfactants, both alkyl benzene sulfonates (ABS) and LAS, to form a blue-colored dye complex. The complex is extracted with chloroform, and the methylene blue active substances are determined spectrophotometrically. This method is similar in substance to the MBAS method in "Standard Methods for the Examination of Water and Wastewater," 15th edition (American Public Health Association, 1981).

3. Interferences

Phenols, proteins, and inorganic chloride, cyanate, nitrate, and thiocyanate will complex methylene blue and give a positive interference. With LAS concentrations from 0.0 to 0.1 mg/L, tests have shown no interference from the following individual constituents: 10 mg/L nitrite, 25 mg/L nitrate, 5 mg/L phenol, and 1 mg/L hydrogen sulfide. Organic amines cause low results.

4. Apparatus

4.1 *Spectrophotometer*, for use at 635 nm.

4.2 Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Chloroform*, spectrophotometric grade.

5.2 *Detergent*, primary stock standard, 1 mL = 1 mg LAS: Use reference LAS acid. An ampoule of LAS acid may be obtained from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH 45268. The ampoule has a shelf life of 2 yr when stored unopened in a cool, dark location. The LAS ampoule is labeled in percent active LAS (weight/volume). Weigh an amount of LAS acid equal to 1,000 g LAS on a 100 percent basis and dilute with demineralized water to 1,000 mL. To obtain the amount of active LAS, divide 1.000 g by the percent active stated on the ampoule label. For example, if the LAS solution is stated as 5.69 percent active, multiply 1.000 by 100 and divide by 5.69. The result, 17.575g, is the amount of LAS solution to be weighed out and diluted with demineralized water to 1,000 mL.

5.3 *Detergent working standard I*, 1.00 mL = 0.01 mg LAS: Dilute 10 mL of primary stock

standard to 1,000 mL with demineralized water. This has a shelf life of 1 mo when refrigerated.

5.4 *Detergent working standard II*, 1.00 mL = 0.001 mg LAS: Dilute 100 mL of working standard I to 1,000 mL with demineralized water. Prepare fresh daily.

5.5 *Methylene blue reagent*: Dissolve 0.35 g methylene blue in 0.01 *N* H_2SO_4 and dilute to 1 L with 0.01 *N* H_2SO_4.

5.6 *Phenolphthalein solution*: Dissolve 2.5 g phenolphthalein in 250 mL of 95 percent ethyl alcohol and add 250 mL deionized water. Then add 0.02 *N* NaOH dropwise until a faint pink color appears.

5.7 *Sodium hydroxide solution*, 0.5 *N*: Dissolve 10 g NaOH in deionized H_2O and dilute to 500 mL.

5.8 *Sulfuric acid solution*, 5 *N*: Cautiously, mix with cooling, 138 mL concentrated H_2SO_4 (sp. gr. 1.84) in 500 mL deionized water and dilute to 1,000 mL with deionized water.

5.9 *Sulfuric acid solution*, 0.1 *N*: Cautiously, mix 3 mL concentrated H_2SO_4 (sp. gr. 1.84) with deionized water and dilute to 1 L.

6. Procedure

All glassware must be rinsed with dilute HCl and deionized water immediately before use.

6.1 Pipet a volume of sample (100 mL maximum) containing less than 0.10 mg MBAS into a separatory funnel. Prepare a blank and standards in the same manner.

6.2 Add 2 drops of phenolphthalein solution to the samples and standards and adjust the pH to near neutral by the dropwise addition of 0.5 *N* NaOH or 0.1 *N* H_2SO_4. To the blank, standards, and samples add 1.0 mL of 5 *N* H_2SO_4, mix, and then add 5.0 mL methylene blue solution. Mix thoroughly.

6.3 Add 25.0 mL chloroform and shake the contents of the funnel for 30 s. Allow the layers to separate.

6.4 Drain off the lower chloroform layer into a 1.0-cm cell and measure the absorbance of the sample and standards against the blank at 635 nm.

7. Calculations

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

$$\text{mg/L MBAS (as LAS)} = \frac{W \times 1000}{S},$$

where

W = mg MBAS obtained from calibration curve minus mg blank MBAS, and

S = mL of sample.

8. Report

Report MBAS concentrations as follows: less than 0.01 mg/L, as "less than 0.01 mg/L"; 0.01 to 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Deviation of ±10 percent may be expected in the range of 1 to 5 mg/L, in surface water.

Selected references

American Public Health Association, 1981, Standard methods for the examination of water and wastewater (15th ed.): Washington, American Public Health Association, Inc., 1,134 p.

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.

TNT, RDX, and picric acid, total recoverable, high-performance liquid chromatographic (O–3112–83)

Parameter	*Code*
TNT	81360
RDX	81364
Picric acid	82340

1. Application

This method is suitable for the determination of 1,3,5-trinitro-1,3,5-triaza-cyclohexane (RDX), 2,4,6-trinitrophenol (picric acid), and 2,4,6-trinitrotoluene (TNT) in water or water–suspended-sediment mixtures containing at least 2 µg/L of analyte.

2. Summary of method

RDX, picric acid, and TNT are extracted from water or water–suspended-sediment mixtures with methylene chloride. The extract is concentrated and subjected to high-performance liquid chromatography (HPLC) analysis using a reverse-phase column and a dual-wavelength ultraviolet detector.

3. Interferences

Any compounds that exhibit chemical and physical properties similar to the compounds of interest can interfere.

4. Apparatus

4.1 *Concentrator apparatus*, Kuderna-Danish (K-D), with concentrator, 500-mL flask, one-ball and three-ball Snyder columns, and a 10-mL graduated receiver.

4.2 *Evaporative concentrator*, Organomation N-Evap, or equivalent.

4.3 *Filters*, 0.5 μm millipore FHUP, catalog no. 04700, or equivalent, and 0.45 μm millipore HAWP, catalog no. 04700, or equivalent.

4.4 *Liquid chromatograph*, Waters Associates ALC/GPC 204 liquid chromatograph equipped with a dual-channel, variable-wavelength detector, a model 6000A solvent-delivery system, a model 660 solvent-flow programmer, a model WISP 710A microprocessor, and a data module, or equivalent.

4.4.1 The following conditions are recommended:

Column, 300 mm×3.9 mm id (inside diameter) stainless steel packed with 10 μm particle size reverse-phase material: Waters Associates *u*–Bonapak C_{18} packing, or equivalent.

Wavelengths, 254 and 356 nm.

Solvent, 36 percent solution A (step 5.2.1) and 64 percent solution B (step 5.2.2) at a flow rate of 1.10 mL/min isocratic.

4.5 *Solvent clarification kit*, Waters Associates 85113, or equivalent.

4.6 *Shaker*, mechanical, wrist-action.

5. Reagents

5.1 *Hydrochloric acid*, concentrated (sp. gr. 1.19), reagent grade.

5.2 *Mobile phase solutions*: Prepare the ion pairing, tetrabutylammonium-phosphate solutions for the mobile phase using Waters Associates PIC Reagent A, or equivalent.

5.2.1 *Solution A*: Add one bottle of PIC reagent A to 1,000 mL organic-free water. Stir for 5 min and then filter through a 0.45-μm filter, type HAWP for aqueous solvents.

5.2.2 *Solution B*: Add one bottle of PIC reagent A to 1,000 mL acetonitrile. Stir for 5 min and then filter through a 0.45-μm filter, type FHUP for organic solvents.

5.3 *RDX, picric acid, and TNT standards*, analytical reference grade or highest purity available: These may be obtained from chemical specialty suppliers or from military sources. Weigh about 10 mg to three significant figures and dilute to 25 mL with acetonitrile. Prepare standards at 1, 5, and 10 ng/μL in acetonitrile.

5.4 *Sodium chloride*, anhydrous, granular: Prepare by heating at 300°C overnight.

5.5 *Solvents*, acetone, diethylether (unpreserved) methylene chloride, pesticide residue quality, distilled in glass, Burdick and Jackson, or equivalent: HPLC-grade acetonitrile.

5.6 *Water*, organic-free.

6. Procedure

6.1 Pour 500 mL water into a 1-L separatory funnel. Do not use stopcock grease on ground-glass joints.

6.2 Add 3 mL concentrated HCl and 85 g NaCl to the sample contained in the separatory funnel and shake until the salt is dissolved.

6.3 Add 75 mL methylene chloride to the separatory funnel. Stopper and shake for 1 min. Vent the pressure often. Allow the layers to separate and draw off the methylene chloride layer into a 250-mL Erlenmeyer flask.

6.4 Repeat the extraction twice using 50 mL methylene chloride each time. Combine the extracts in the 250-mL Erlenmeyer flask.

6.5 Quantitatively transfer the extract to a 500-mL K-D apparatus fitted with a three-ball Snyder column and a 20-mL receiver. Add a micro boiling chip and 4 mL acetonitrile.

6.6 Place the K-D apparatus on a hot-water bath (approximately 85°C). Reduce the volume of the extract to about 4 mL. Remove the K-D apparatus and allow it to cool. Wipe the joints with a towel. Rinse the lower joint with acetonitrile into the receiver.

6.7 Use the evaporative concentrator to reduce the volume of solvent to 0.8–0.9 mL by directing a stream of nitrogen onto the surface of the extract in the receiver in a water bath at 35°C.

6.8 Proceed to HPLC analysis.

6.9 The chromatographic system should be evaluated each day to determine retention volume and detector response for RDX, picric acid, and TNT. Prepare calibration curves daily by injecting 10 μL of a standard mixture at three concentrations (see step 5.3). Record the volume of the standard injected and the retention time and integrated peak area of each component in the standard. The operating conditions used for calibration must be identical to those used for sample analysis (step 6.10).

6.10 Add 0.1 mL PIC reagent A to the sample extract, mix, and make up to a volume of 1.0 mL; allow the extract to stand 10 min, and then inject 10 µL into the liquid chromatograph. Record the volume injected. Identify the peaks by retention time. Confirmation is made by measuring the peak area at two different wavelengths and comparing the ratio of the peak areas to the peak area ratio of the standard. Dilute any extract containing an identifiable component above the highest standards.

7. Calculations

7.1 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/ng,
C_s = concentration of standard component, in ng/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

$$\text{Concentration } (\mu g/L) = \frac{A_2 \times V_2 \times 1{,}000}{V_3 \times W \times RF},$$

where

RF = response factor of identified calibration standard component, in area/ng,
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

Report concentrations of TNT, RDX, and picric acid in water or water–suspended-sediment mixtures as follows: less than 2 µg/L, as "less than 2 µg/L"; 2.0 µg/L and above, two significant figures.

9. Precision

Single-operator precision for eight replicates, expressed in terms of percent relative standard deviation, is as follows:

Compound	Concentration spiked (µg/L)	Mean concentration recovered (µg/L)	Relative standard deviation (percent)
RDX	2.0	2.2	37
	4.0	3.9	20
	8.0	7.9	12
	16	16	11
Picric acid	2.0	2.2	10
	4.0	4.0	10
	8.0	7.6	4
	16	16	5
TNT	2.0	1.7	23
	4.0	3.0	17
	8.0	6.8	10
	16	14	11

Selected references

Goerlitz, D.F., and Law, L.M., 1975, Gas chromatographic method for the analysis of TNT and RDX explosives contaminating water and soil-core material: U.S. Geological Survey Open-File Report 75–182, 21 p.

——— 1979b, Direct analyses of RDX and TNT in water by high-performance liquid chromatograph: U.S. Geological Survey Open File Report 79–916, 11 p.

Goerlitz, D.F., 1979a, Analysis of picric acid in water by high-performance liquid chromatography: U.S. Geological Survey Open File Report 79–207, 7 p.

Polynuclear aromatic hydrocarbons (PNA), total recoverable, high-performance liquid chromatographic (O–3113–83)

Parameter	Code
Acenaphthene	34205
Anthracene	34220
Benzo(a)anthracene	34526
Benzo(g,h,i)perylene	34521
Benzo(a)pyrene	34247
Chrysene	34320
Dibenzo(a,h)anthracene	34556
Fluoranthene	34376
Fluorene	34381
Naphthalene	34696
Phenanthrene	34461
Pyrene	34469

1. Application

This method is suitable for the analysis of water and water–suspended-sediment mixtures for polynuclear aromatic hydrocarbons (PNA's) containing at least 1 µg/L of the analyte.

2. Summary of method

PNA's are extracted from water or water–suspended-sediment mixtures with methylene chloride. The extract is concentrated and subjected to high-performance liquid chromatographic

(HPLC) analysis using a 10-μm reverse-phase column and a dual-channel ultraviolet detector.

3. Interferences

Any compounds that exhibit chemical and (or) physical properties similar to the compounds of interest can interfere.

4. Apparatus

4.1 *Concentrator apparatus*, Kuderna-Danish (K-D), with a 500-mL flask, a three-ball Snyder column, and a 10-mL graduated receiver tube.

4.2 *Evaporative concentrator*, Organomation N-Evap, or equivalent.

4.3 *Filtering apparatus*, Millipore, or equivalent: The filtering apparatus consists of a 250-mL reservoir with a glass frit, and a 1,000-mL receiving reservoir with FH, Millipore no. FHUP 04700 and HA, Millipore no. HAWP 40700 0.45-μm filters for the corresponding organic and aqueous solvents, or equivalent.

4.4 *Liquid chromatograph*, Waters Associates ALC/GPC 204 liquid chromatograph equipped with a dual-channel, variable-wavelength detector, a model 6000A solvent-delivery system, model WISP 710A microprocessor with a model 730 data module and a model 720 system controller, or equivalent.

4.4.1 The following conditions are recommended:

Column, reverse-phase, micro-bondapak C_{18}–10 μm, Waters Associates, or equivalent.

Wavelengths, 254 and 313 nm.

Solvent, 40 to 80 percent acetonitrile/water, linear slope gradient at a flow rate of 1.0 mL/min.

5. Reagents

5.1 *PNA standards*, EPA analytical reference grade or highest purity available: Use methylene chloride as a solvent to prepare stock solutions in the approximate 100–300 ng/μL concentration range. Store in the dark at 4°C.

5.2 *PNA working-standard solution*: Prepare three standard mixtures of 12 PNA's at concentrations of 1, 5, and 10 ng/μL in acetonitrile, from step 5.1.

5.3 *Sodium sulfate*, granular, anhydrous: Heat overnight at 300°C and store at 130°C.

5.4 *Solvents*, HPLC-quality acetonitrile, and methylene chloride: Filter before use with the filtering apparatus described above (step 4.3).

5.5 *Water*, organic-free.

6. Procedure

Glassware must be cleaned by washing with a hot detergent solution, rinsing with deionized water, and heating overnight at 300°C. Just prior to use, the glassware is rinsed with solvent. Stopcock grease should not be used on ground-glass joints.

6.1 Weigh the bottle containing the sample and record the weight. Pour the sample into a 1-L separatory funnel. Weigh the empty sample bottle. Calculate the net sample weight and record the value obtained to three significant figures.

6.2 Add 50 mL methylene chloride to the sample bottle, swirl to rinse the sides of the bottle, and transfer the solvent to a 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 separatory funnel vigorously for 1 min. Vent often. Allow the layers to separate and draw off the methylene chloride layer into a 250-mL Erlenmeyer flask that contains 0.5 g anhydrous sodium sulfate.

6.3 Repeat the extraction of the water sample twice using 40 mL methylene chloride each time. Combine all organic extracts in the 250-mL Erlenmeyer flask.

6.4 Transfer the extract to a 500-mL K-D apparatus fitted with a three-ball Snyder column and a 10-mL receiver containing a micro boiling chip and 0.5 mL of acetonitrile.

6.5 Place the apparatus on a water bath at about 80°C and concentrate to about 5 mL. Remove from the heat and allow to cool. Dry the joints with a towel. Rinse the lower joint with acetonitrile into the receiver.

6.6 Further reduce the volume of solvent to about 1 mL on an evaporative concentrator. Rinse down the sides of the tube with 1 mL acetonitrile and concentrate to a final volume of 0.5 mL. Stopper until chromatographic analysis can begin.

6.7 Optimize the chromatographic conditions.

6.8 Prepare liquid chromatograph calibration curves daily by injecting the standards described in step 5.2. Operating conditions must be identical to those used for sample analysis (step 6.9). Record the volume of the standard injected and the retention time and integrated peak area of each component in the standard. The calibration should be performed at the beginning and end of a run, and after every fourth sample.

6.9 Inject an aliquot of sample extract into the liquid chromatograph. Record the volume inject-

ed. Identify the peaks by retention time. Confirmation is made by measuring the peak area at two different wavelengths and comparing the ratio of the peak areas to that of the standard. Record the retention time and integrated area of any identified peak. Dilute any extract containing an identifiable component above the highest standard. The 254-nm detector does not resolve some pairs of compounds. Determination at another wavelength, 313 nm, is necessary to distinguish between these pairs. For example, fluorene and acenaphthene each absorb at 254 nm and are not separated by the column. Acenaphthene, however, absorbs at 313 nm, whereas fluorene does not. The response ratio of acenaphthene calculated at 254 nm and 313 nm is 1:1; therefore, both peaks are analyzed. Chrysene and benzo(a)anthracene are not clearly distinguishable at 254 nm, but are at 313 nm. When these compounds are determined at both wavelengths, individual contributions to peak areas can be determined and concentrations calculated.

7. Calculations

7.1 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/ng,
C_s = concentration of standard component, in ng/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

$$\text{Concentration } (\mu g/L) = \frac{A_2 \times V_2 \times 1{,}000}{V_3 \times W \times RF},$$

where

RF = response factor of identified calibration standard component, in area/ng,
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 determined in g expressed in mL (1.000 mL = 1.000 g).

8. Report

Report concentrations of individual PNA's in water or water–suspended-sediment mixtures as follows: less than 1 μg/L, as "less than 1 μg/L"; 1 to 10 μg/L, one significant figure; 10 μg/L and greater, two significant figures.

9. Precision

Single-operator precision on seven replicates and recovery data determined by spiking water–suspended-sediment mixture samples with PNA's are as follows:

Compound	*Concentration spiked (μg/L)*	*Mean concentration recovered (μg/L)*	*Relative standard deviation (percent)*
Naphthalene	1.3	0.94	6.9
	2.6	1.41	20
	5.1	2.4	24
Fluorene	.64	.47	12
	1.3	.94	7.8
	2.6	1.6	14
Acenaphthene	2.8	2.01	8.5
	5.50	3.6	13
	11.	6.5	18
Phenanthrene	.21	.15	8.3
	.42	.36	6.3
	.84	.66	8.5
Anthracene	.052	.038	3.9
	.10	.076	5.1
	.21	.142	7.4
Pyrene	.32	.28	2.8
	.64	.58	3.4
	1.3	1.1	5.6
Fluoranthene	1.4	1.1	3.5
	2.8	2.5	5.5
	5.5	5.0	5.1
Benzo(a)anthracene	.43	.39	3.0
	.85	.80	3.4
	1.7	1.6	5.5
Benzo(a)pyrene	.15	.13	4.8
	.29	.29	7.5
	.58	.55	5.5
Dibenz(a,h)anthracene	.13	.12	6.9
	.26	.28	7.4
	.51	.50	5.0
Benzo(g,h,i)perylene	1.6	1.4	3.0
	3.2	3.2	5.8
	6.4	6.2	4.0
Chrysene	.64	.57	5.1
	1.3	1.3	5.2
	2.6	2.3	7.2

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Ethylene and propane, total recoverable, gas chromatographic, purge and trap (O–3114–83)

Parameter	*Code*
Ethylene	82357
Propane	82358

1. Application

This method is suitable for the determination of ethylene and propane in water or water–suspended-sediment mixtures containing at least 0.1 µg/L of the analyte. Concentrations higher than 100 µg/L may be determined by analyzing a smaller aliquot of the sample.

2. Summary of method

A sample is injected into a purge vessel and sparged with nitrogen. The effluent gas stream is dried and passed through an alumina trap at −95°C, where ethylene and propane are adsorbed by the alumina. The trap is heated to desorb gases, which are determined by gas chromatography using a flame ionization detector.

3. Interferences

Volatile compounds that have retention times similar to ethylene or propane on the analytical column can interfere.

4. Apparatus

4.1 *Adsorption tube*, Pyrex tubing, ¼ in od (outside diameter): Bend Pyrex tubing into a U-tube approximately 8 in long by 2 in wide. Charge the tube with 5 g activated alumina held in place with plugs of glass wool.

4.2 *Cold bath*, a Dewar flask large enough to accommodate the lower half of the adsorption tube: Maintain the bath at −75 to −100°C with either dry ice/acetone or a refrigerant probe such as the Neslab CC–100, or equivalent.

4.3 *Drying tubes*, Pyrex tubing, ½ in od by 8 in long: Fill the tubes with Drierite held in place with glass-wool plugs.

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

4.4.1 The following conditions are recommended:

Column, borosilicate glass, 1.8 m×2 mm id (inside diameter) operated at 90°C, packed with Porapak N, Q, or QS.

Detector, flame-ionization, operated at 250°C.

Injection port temperature, 110°C.

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

4.5 *Gas sampling valve*, six port, Valco V-6-HPa, or equivalent.

4.6 *Hot bath*, a heating mantle for a 1-L round-bottom flask filled with sand and powered by a variable-voltage transformer: The voltage is adjusted to maintain the sand at approximately 130°C.

4.7 *Purge vessel*: See figure 3.

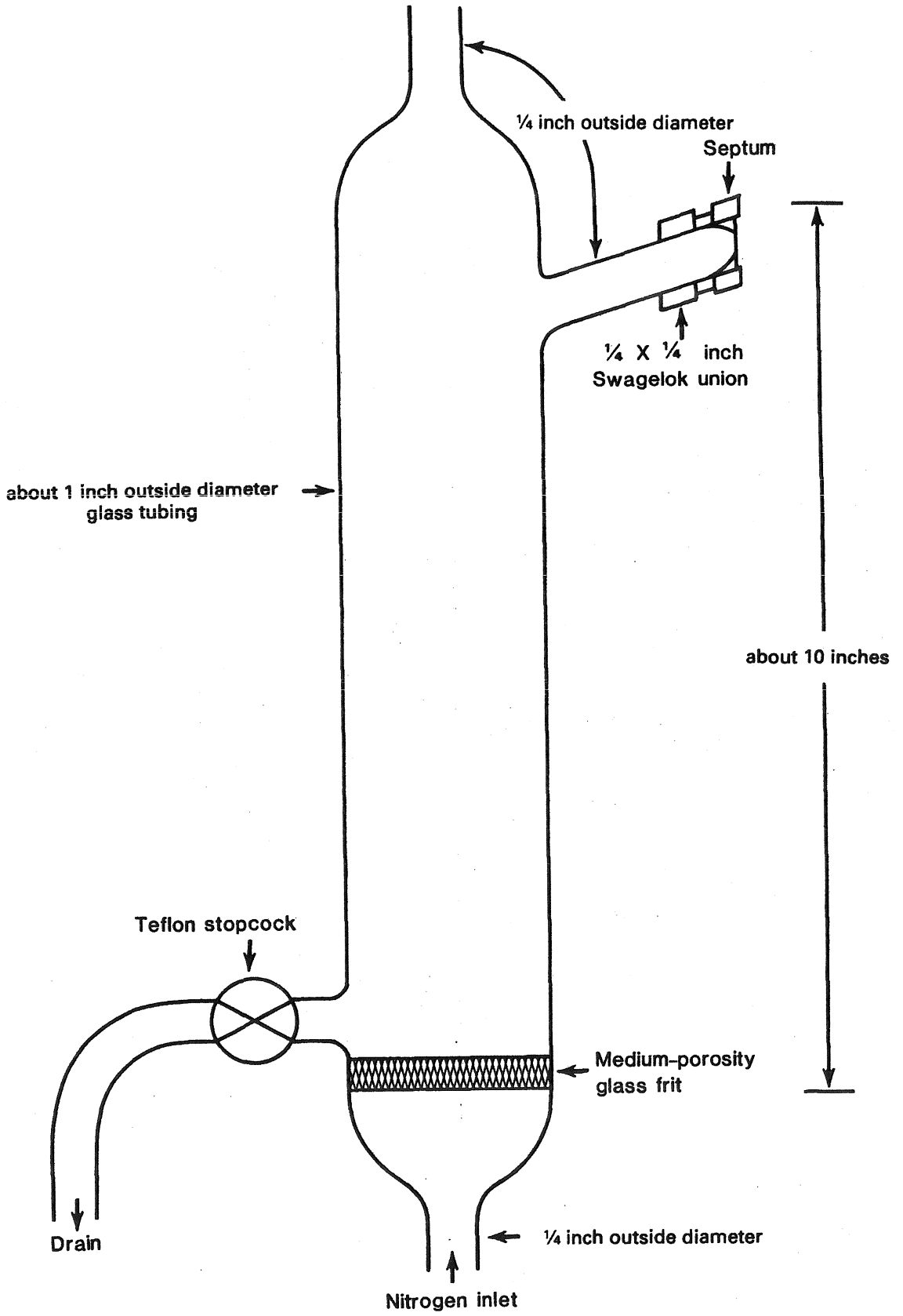
4.8 *Sample vial*, glass, 40 mL, screw cap, fitted with a Teflon-lined septum. Pierce 13075, or equivalent.

4.9 *Syringe needles*, 19 gauge, 3 in long.

4.10 *Syringes*, two syringes, 30 mL and 5 mL, glass, Luer-Lock, equipped with stopcocks, Becton-Dickinson 3152, or equivalent.

4.11 *Syringes, gas-tight*, syringes of 1.0-, 2.5-, 10-, and 50-mL capacities, Hamilton, or equivalent, used for delivery of calibration gas and equipped preferably with sideport needles.

4.12 *Teflon tubing*, ⅛ in od, used for the connecting lines.


¼ inch outside diameter
Septum
¼ X ¼ inch
Swagelok union
about 1 inch outside diameter
glass tubing
about 10 inches
Teflon stopcock
Medium-porosity
glass frit
Drain
¼ inch outside diameter
Nitrogen inlet

5. Reagents

5.1 *Alumina*, neutral aluminum oxide, activity grade I, Woelm, or equivalent.

5.2 *Calibration gas*, a certified gas mixture containing 10 ppm each of ethylene and propane in nitrogen: The regulator valve must be equipped with a stainless steel diaphragm. Equip the outlet from the regulator with an injection septum to facilitate withdrawal of aliquots of calibration gas with a gas-tight syringe.

5.3 *Drying agent*, indicating Drierite, 8-mesh: Anhydrous magnesium perchlorate (granular) is also suitable.

6. Procedure

Samples are to be collected in vials containing 1 mL formalin as a preservative and in a manner that precludes headspace formation. Samples need not be refrigerated since formalin prevents bacterial decomposition for at least 3 weeks, and probably longer. Rapid loss of ethylene and propane will occur if the preservative is omitted.

6.1 Adjust the flow of hydrogen and air to the flame-ionization detector to achieve a linear response from 1 to 100 ng of ethylene and propane.

6.2 Set the flow of nitrogen through the purging vessel at 30 to 35 mL/min. This is conveniently measured at the outlet port of the gas-sampling valve (see fig. 4).

6.3 Place the adsorption tube in the cold bath and set the gas-sampling valve as shown in figure 4.

6.4 Calibration procedure:

6.4.1 Inject an aliquot of calibration gas mixture into the purging vessel using a gas-tight syringe.

6.4.2 Start the timer and allow 12 min for complete adsorption of ethylene and propane by the alumina trap. NOTE: The minimum time required to completely strip the gases depends on the dead volume of the system (purging vessel, drying tube, adsorption tube, and connecting lines) and the flow through it.

6.4.3 Turn the gas sampling valve to the position that conducts the flow from the adsorption tube into the analytical column of the gas chromatograph. Immediately place the adsorption tube in the hot bath and begin digital peak integration. Record integrated peak areas.

6.4.4 Repeat steps 6.4.1 through 6.4.3 for as many other aliquots of calibration gas mixture as is necessary to cover the expected range of the samples.

6.5 Sample analysis:

6.5.1 Open a sample vial and fill a 30-mL glass syringe by closing the stopcock and pouring the sample gently into the barrel. Do not attempt to fill the syringe by suction.

6.5.2 Introduce 10 mL of sample into the purging vessel through the injection port.

6.5.3 Start the timer and allow the sample to be purged for 12 min (see NOTE above).

6.5.4 Turn the gas sampling valve to the position that conducts the flow from the adsorption tube into the analytical column of the gas chromatograph. Immediately place the adsorption tube in the hot bath and begin digital peak integration. Record integrated peak areas.

6.5.5 Drain the sample from the stripping chamber while gas chromatographic determination proceeds.

7. Calculations

7.1 Correction for calibration gas:

7.1.1 The calibration gas is 10 ppm by volume. This must be corrected to give the corresponding concentration by weight.

7.1.2 For 1 mL of 10 ppm calibration gas, the volume of ethylene and propane is 1.0×10^{-5} mL each.

7.1.3 Applying the ideal gas law at standard temperature and pressure (STP) where 1 mole of gas occupies 22.4 L,

$$N_2 = \frac{N_1 T_1 P_2 V_2}{T_2 P_1 V_1},$$

where

$N_1 = 1.0$ mole,
N_2 = number of moles ethylene or propane,
$T_1 = 273$°K (STP),
$P_1 = 760$ mm Hg (STP),
$V_1 = 22{,}400$ mL (volume of 1 mole gas at STP),
T_2 = actual temperature, in °K,
P_2 = actual atmosphere pressure, in mm Hg, and
$V_2 = 1.0\times10^{-5}$ mL (volume of ethylene or propane in 1.0 mL of calibration gas).

← Figure 3.—Purge vessel.

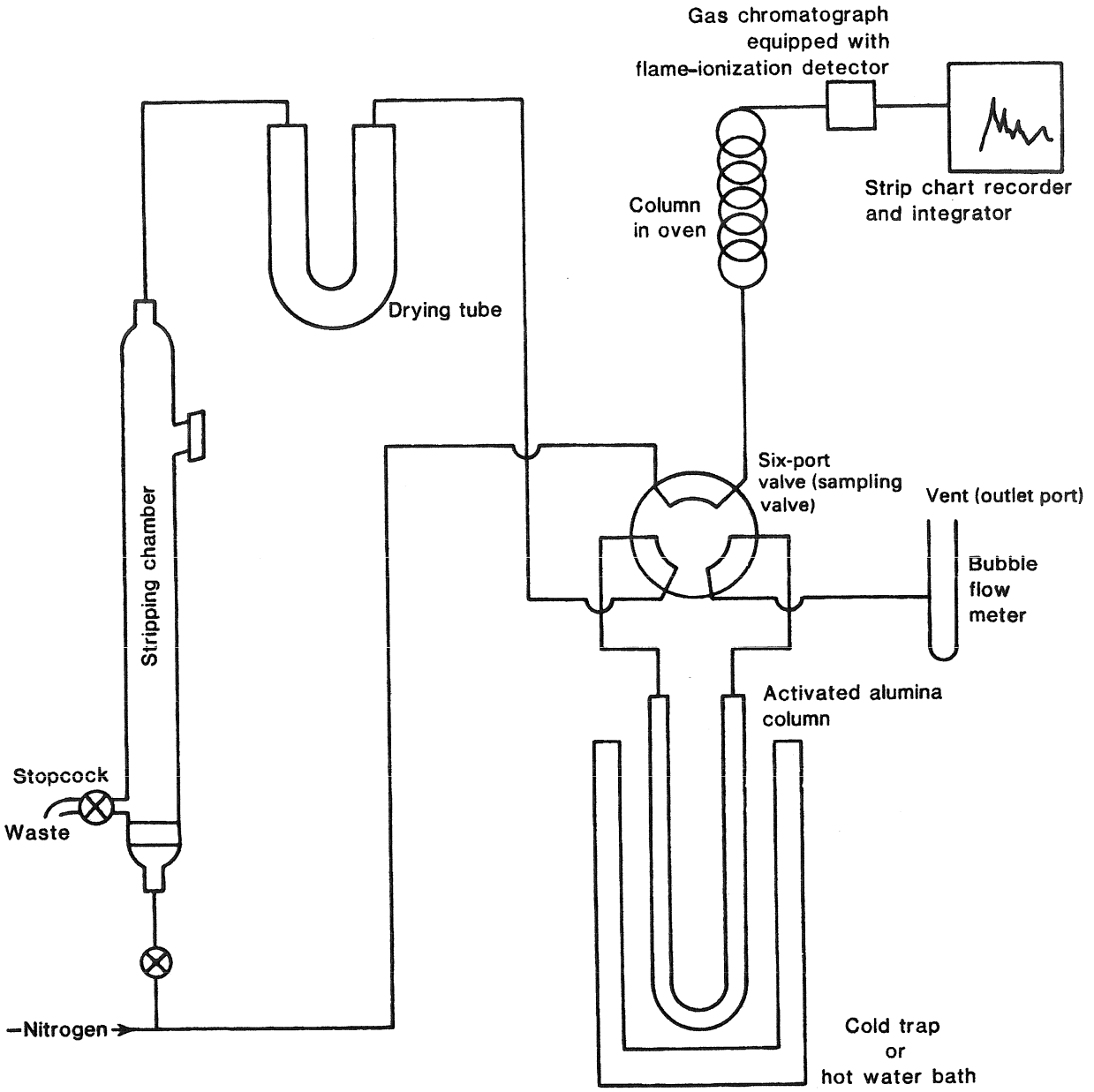


Figure 4.—Stripping and gas chromatographic system in the stripping mode.

7.2 For either ethylene or propane, calculate the concentration of ethylene or propane per mL of calibration gas from the following equation:

$$W_1 = \frac{N_1 \times MW \times 10^6}{V_3},$$

where

W_1 = concentration of ethylene or propane in calibration gas, in µg/mL,

V_3 = volume of calibration gas, in mL,

N_1 = number of moles of ethylene or propane, and

MW = molecular weight of ethylene or propane, in g/mole.

7.3 Calculate the response factor for the calibration curve from the following equation:

$$RF = \frac{A_1}{W_1 \times V_4},$$

where

RF = response factor of ethylene or propane, in area/µg,

A_1 = integrated peak area of standard,

V_4 = volume of calibration gas injected, in mL, and

W_1 = concentration of ethylene or propane calibration gas, in µg/mL.

7.4 The concentration of ethylene or propane in the sample is calculated from the following equation:

$$\text{Concentration (µg/L)} = \frac{A_2 \times 1{,}000}{RF \times V_5},$$

where

A_2 = integrated peak area of ethylene or propane,

RF = response factor of ethylene or propane, in area/µg, and

V_5 = volume of sample injected, in mL.

8. Report

Report concentration of ethylene and (or) propane as follows: concentrations less than 0.1 µg/L, as "less than 0.1 µg/L"; 0.1 to 1.0 µg/L, one decimal; 1.0 µg/L and above, two significant figures.

9. Precision

Solutions of ethylene and propane were prepared in deionized water and stored in sample vials (step 4.8) containing 1 mL formalin as preservative. Replicates were prepared to cover the concentration range of the method. All of the samples were analyzed within 3 weeks of preparation. Single-operator precision is as follows:

Concentration of ethylene (µg/L)	*Number of replicates*	*Standard deviation*	*Relative standard deviation (percent)*
0.072	7	0.002	2.8
.198	12	.006	3.0
1.69	11	.04	2.4
8.38	12	.10	1.2
16.0	12	.20	1.3
35.1	12	.6	1.7
82.4	11	2.1	2.5
132	11	3.0	2.3

Concentration of propane (µg/L)	*Number of replicates*	*Standard deviation*	*Relative standard deviation (percent)*
0.099	7	0.004	4.0
.257	12	.015	5.8
2.52	11	.05	2.0
12.9	12	.4	3.1
24.5	12	.4	1.6
53.5	12	.9	1.7
110	11	2.6	2.4
171	11	4.0	2.3

Selected reference

Shultz, D.J., Pankow, J.F., Tai, D.Y., Stephens, D.W., and Rathbun, R.E., 1976, Determination, storage, and preservation of low molecular weight hydrocarbon gases in aqueous solution: U.S. Geological Survey Journal of Research, v. 4, p. 247–251.

Purgeable organic compounds, total recoverable, gas chromatographic/ mass spectrometric, purge and trap (O–3115–83)

Parameter	*Code*
Chloromethane	34418
Bromomethane	34413
Vinyl chloride	39175
Chloroethane	34311
Methylene chloride	34423
1,1-Dichloroethene	34501
1,1-Dichloroethane	34496
Trans-1,2-Dichloroethene	34546
Chloroform	32106
1,2-Dichloroethane	32103
1,1,1-Trichloroethane	34506
Carbon tetrachloride	32102
Bromodichloromethane	32101
1,2-Dichloropropane	34541
Trans-1,3-Dichloropropene	34699
Trichloroethene	39180
Dibromochloromethane	32105
Benzene	34030
1,1,2-Trichloroethane	34511
Cis-1,3-Dichloropropene	34704
2-Chloroethylvinyl ether	34576
Bromoform	32104
1,1,2,2-Tetrachloroethane	34516
Tetrachloroethene	34475
Toluene	34010
Chlorobenzene	34301
Ethylbenzene	34371

1. Application

This method is suitable for the determination of purgeable organic compounds in water and water-suspended-sediment mixtures containing at least 3 µg/L of a reportable analyte.

2. Summary

A water sample is purged with helium. The purgeable organic compounds are carried with helium and trapped on a porous polymer trap. The trapped compounds are thermally desorbed into the gas chromatograph. These compounds are separated by gas chromatography (GC) and detected by mass spectrometry (MS).

3. Interferences

3.1 Any purgeable compound that elutes at a retention time similar to that of the analyte and produces an ion that is the same as the quantitation ion of the analyte is a potential interference. Common laboratory solvents such as methylene chloride, benzene, and chloroform may contaminate the sample and give erroneous results.

3.2 Special handling of samples, such as storage in a dessicator over activated charcoal, may be required to prevent contamination by common laboratory solvents.

4. Apparatus

4.1 *Gas chromatograph/mass spectrometer/data system*, Finnigan 3223, or equivalent.

4.1.1 *Gas chromatographic column*, borosilicate glass, 1.8 m×2 mm id (inside diameter) that has been deactivated and packed with 1 percent SP-1000 coated on 60/80 mesh Carbopack B, or equivalent.

4.1.2 *Gas chromatographic conditions*: GC conditions need to be optimized for each system. Use the purgeable standards (see step 5.3) to adjust conditions to obtain good peak separation in a reasonable amount of time. The following conditions should serve as a starting point for the optimization process:

Injector temperature	200°C
Carrier gas flow (He)	20 mL/min
Initial hold temperature	45°C
Initial hold time	4 min
Program rate	8°C/min
Final temperature	210°C
Final hold time	To end of data acquisition

4.1.3 *Mass spectrometer conditions*: Analyze the mass range 35–260 amu (atomic mass units) with a nominal electron energy setting of 70 eV at a scan rate sufficient to obtain a minimum of 5 scans per chromatographic peak.

4.2 *Purge and trap device*, Chemical Data Systems model 310, or equivalent: The trap is packed with the following adsorbents: 1 cm methyl silicone coated packing (3 percent SP-2100 on 80-mesh Supelcoport, or equivalent), followed by 15 cm Tenax, and ending with 8 cm silica gel (Davison grade 15), or equivalent. The silica gel may be replaced by 5 cm of Ambersorb resin (Rohm and Haas). New traps are conditioned by heating overnight at 240°C with helium flow (20 mL/min).

4.3 *Syringe*, gas-tight, 10 mL, equipped with a Teflon syringe valve and a 3-in×19-gauge needle.

5. Reagents

5.1 *BFB (4-Bromofluorobenzene) solution*: Fill a 50-mL volumetric flask to the mark with methanol and add a 1.0-μL capillary pipet filled with BFB to the volumetric flask. This solution contains 32 ng BFB per μL.

5.2 *Methanol*, pesticide analysis quality, Burdick and Jackson, or equivalent.

5.3 *Purgeable mixed standards*, EPA analytical reference grade or highest purity available: Purgeable standards may be purchased from various commercial sources or prepared from pure compounds. To prepare purgeable mixed standards, fill a 50-mL volumetric flask to the mark with methanol and, for each desired component, add a 1.0-μL capillary pipet filled with the authentic material to the volumetric flask. Mix thoroughly and store at 4°C. Calculate the concentration of each analyte from its density.

5.4 *Surrogates/internal standard solution*, bromochloromethane (EPA, or equivalent), 1-bromo-2-chloroethane (EPA, or equivalent), perdeuterobenzene (Pfaltz and Bauer, or equivalent), and fluorobenzene (the internal standard, Aldrich Chemical Co., or equivalent). Add a 1.0-μL capillary pipet filled with each component to a 50-mL volumetric flask filled to the mark with methanol. Mix thoroughly and store at 4°C. Add 5 μL to each sample, standard, and blank to monitor recovery and to provide an internal standard.

5.5 *Water*, organic-free.

6. Procedure

6.1 Condition the trap at 220°C for 10 min.

6.2 Mass spectrometer tuning:

6.2.1 Use perfluorotributylamine to tune the mass spectrometer in a manner that results in a satisfactory calibration of mass assignments as well as agreement with the criteria listed in step 6.2.2.

6.2.2 Set the MS to scan the mass range 35 to 260 amu. Set the GC column temperature to 220–230°C isothermal. Introduce 50 ng of BFB (1.6 μL of solution, step 5.1) by direct, on-column injection or by purging from 5 mL of reagent water. Obtain a background corrected mass spectrum of BFB and verify that all of the following criteria are met:

Mass	*Ion abundance criteria*
50	15 to 40 percent of mass 95
75	30 to 60 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5 to 9 percent of mass 95

Mass	*Ion abundance criteria*
173	<2 percent of mass 174
174	>50 percent of mass 95
175	5 to 9 percent of mass 174
176	>95 percent but <101 percent of mass 174
177	5 to 9 percent of mass 176

6.3 Blank analysis:

6.3.1 Remove the plunger from a 10-mL syringe and attach a closed syringe valve and needle. Open the sample vial and carefully pour the water into the barrel of the syringe until it overflows. Replace the syringe plunger, open the syringe valve, and vent any air present. Adjust the plunger to the 10.0-mL mark. Add 10 μL of the surrogate/internal standard solution through the valve, close the syringe valve, and mix.

6.3.2 Transfer 5.0 mL water into a clean purge tube. Close the syringe valve and retain the second 5.0-mL aliquot of water for future analysis, if needed. The second aliquot is preserved in this manner since the integrity of the original water sample is destroyed after it is opened.

6.3.3 Purge for 11 min.

6.3.4 Immediately begin the desorb cycle and data acquisition when purging is complete.

6.3.5 Begin the temperature program of the GC oven immediately upon completion of the desorb cycle.

6.3.6 Initiate the trap bakeout when data acquisition has ended.

6.3.7 Allow the trap to cool to room temperature and return the GC oven temperature to 45°C for the next analysis.

6.3.8 Analyze the mass spectral data for the three surrogates and the internal standard. Record the integrated area of the quantitation ion for each.

6.3.9 Examine the mass spectral data to verify that the analytical system is free from contamination.

6.4 Calibration:

6.4.1 Remove the plunger from a 10-mL syringe and attach a closed syringe valve and needle. Open the sample vial and carefully pour the organic-free water into the barrel of the syringe until it overflows. Replace the syringe plunger, open the syringe valve, and vent any air present. Adjust the plunger to the 10.0-mL mark. Add 10 μL of surrogate/internal standard solution. Also add 10 μL of purgeable standard solution. Close the syringe valve, and mix.

6.4.2 Transfer 5.0 mL water into a clean purge tube. Close the syringe valve and retain the second 5.0-mL aliquot of sample for future analysis, if needed. The second aliquot is preserved in this manner since the integrity of the original water sample is destroyed after it is opened.

6.4.3 Perform the analysis as described in steps 6.3.3 through 6.3.8.

6.4.4 Compare the recovery of the surrogates in the purgeable standard with that observed in the blank. Deviations of more than ±30 percent from theoretical are an indication of a problem (e.g., leakage in the purge and trap device) that needs to be corrected before proceeding further.

6.4.5 Process the data from the purgeable standard and record the integrated area of the quantitation ion of each component as well as its retention time.

6.4.6 Repeat steps 6.4.2 through 6.4.5 with as many other volumes of the purgeable standard solution as are necessary to define the working range of the analytical system.

6.5 Sample analysis:

6.5.1 Allow the water sample to come to room temperature.

6.5.2 Remove the plunger from a 10-mL syringe and attach a closed syringe valve and needle. Open the sample vial and carefully pour the sample into the barrel of the syringe until it overflows. Replace the syringe plunger, open the syringe valve, and vent any air present. Adjust the plunger to the 10.0-mL mark. Add 10 μL of the surrogate/internal standard solution. Close the syringe valve, and mix.

6.5.3 Transfer 5.0 mL of sample into a clean purge tube. Close the syringe valve and retain the second 5.0-mL aliquot of sample for future analysis, if needed. The second aliquot is preserved in this manner since the integrity of the original water sample is destroyed after it is opened.

6.5.4 Perform the analysis as described in steps 6.3.3 through 6.3.8.

6.5.5 Compare the recovery of the surrogates in the sample with that observed in the blank (step 6.3.8). If the recovery is not in the range of 70 to 130 percent, the sample should be reanalyzed.

6.5.6 Examine all of the mass spectral data from the sample. Identify analytes by a library search with a satisfactory match error. Positive identification is obtained when (1) the retention time is within 5 percent of the authentic material in the purgeable standard (step 6.4.5), and (2) three of the

characteristic ions of the analyte maximize within ± 1 scan of each other.

6.5.7 Integrate and record the area under the quantitation ion for each analyte identified in step 6.5.6. If the areas are greater than the calibration range of the analytical system, the sample needs to be reanalyzed using a smaller volume of sample. It may be necessary to add additional internal standard for smaller sample volumes.

6.5.8 If very high levels of analytes or contaminants are found in a sample, analyze a blank to demonstrate no carryover.

7. Calculations

7.1 External standard method:

7.1.1 Calculate a response factor for an analyte (step 6.4.5) according to the equation

$$RF = \frac{A}{C \times V},$$

where

RF = response factor of analyte, in area/ng,
C = concentration of analyte in purgeable standard, in ng/µL,
V = volume of purgeable standard analyzed, in µL, and
A = area of quantitation ion of analyte.

7.1.2 Calculate the concentration of the analyte in the original water sample from the equation

$$\text{Concentration (µg/L)} = \frac{A_s}{V_s \times RF},$$

where

A_s = area of quantitation ion of analyte in sample,
V_s = volume of original water sample analyzed, in mL, and
RF = response factor of analyte, in area/ng.

7.1.3 Calculate the percent recovery of each surrogate added to the water sample from the equation

$$\text{Recovery (percent)} = \frac{A_1}{A_2} \times 100,$$

where

A_1 = area of quantitation ion of surrogate in water sample, and
A_2 = area of quantitation ion of surrogate added to blank.

7.2 Internal standard method:

7.2.1 Calculate the response factor of an analyte (step 6.4.5) in the purgeable standard from the equation

$$RF = \frac{A_s}{C_s},$$

where

RF = response factor of analyte, in area/ng,
A_s = area of quantitation ion of analyte, and
C_s = amount of analyte in purgeable standard, in ng.

7.2.2 Calculate the response factor of the internal standard (step 6.4.5) in the purgeable standard from the equation

$$RFI = \frac{AI_1}{CI_1},$$

where

RFI = response factor of internal standard in purgeable standard, in area/ng,
AI_1 = area of quantitation ion of internal standard in purgeable standard, and
CI_1 = amount of internal standard in surrogate and internal standard solution, in ng.

7.2.3 Calculate a relative response factor from the equation

$$RRF = \frac{RF}{RFI},$$

where

RRF = relative response factor of analyte,
RF = response factor of analyte determined (step 7.2.1), and
RFI = response factor of analyte internal standard determined (step 7.2.2).

7.2.4 Calculate the concentration of an analyte in the original water sample from the equation

$$\text{Concentration (µg/L)} = \frac{A \times CI_2}{RRF \times AI_2 \times V},$$

where

A = area of quantitation ion of analyte in analyzed sample,
CI_2 = amount of internal standard in surrogate solution, in ng,
RRF = relative response factor determined (step 7.2.3),

AI_2 = area of quantitation ion of internal standard in analyzed sample (step 6.5.9), and

V = volume of original water sample analyzed, in mL.

7.2.5 Calculate the percent recovery of each surrogate added to the water sample from the equation

$$\text{Recovery (percent)} = \frac{A_1}{A_2} \times 100,$$

where

A_1 = area of quantitation ion of surrogate added to water sample, and

A_2 = area of quantitation ion of surrogate added to blank.

8. Report

Report concentrations of purgeable organic compounds in water or water–suspended-sediment mixtures as follows: less than 3 µg/L, as "less than 3 µg/L"; 3.0 µg/L and above, two significant figures.

9. Precision

Precision data are not available.

Selected references

Goerlitz, D.F., 1976, Determination of volatile organohalides in water and treated sewage effluents: U.S. Geological Survey Open-File Report 76–610, 14 p.

U.S. Environmental Protection Agency, 1979, Purgeables—Method 624: Federal Register, v. 44, no. 233, p. 69532.

Acid extractable compounds, total recoverable, gas chromatographic/ mass spectrometric (O–3117–83)

Parameter	*Code*
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601
2,4-Dimethylphenol	34606
4,6-Dinitro-2-methylphenol	34657
2,4-Dinitrophenol	34616
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39032
Phenol	34694
2,4,6-Trichlorophenol	34621
8-Methyldecanoic acid	76992
Undecanoic acid	77648

1. Application

This method is suitable for the determination of acid extractable compounds in water and water–suspended-sediment mixtures containing at least 3–5 µg/L of the analyte.

2. Summary

Acidic organic compounds are extracted from water and water–suspended-sediment mixtures with methylene chloride. The extract is concentrated and subjected to analysis by gas chromatography (GC) using a flame-ionization detector (FID) or a mass spectrometric (MS) detector.

3. Interferences

Compounds having chemical and physical properties similar to the compounds of interest may interfere.

4. Apparatus

4.1 *Boiling chip,* micro, carbon chips: Rinse with hexane, air dry, and heat at 300°C overnight. Treat with 5 percent aqueous sulfuric acid for 5 min. Rinse with deionized water until the washwater is neutral to pH paper. Heat at 130°C overnight.

4.2 *Concentrator, Kuderna-Danish (K-D),* 500-mL, all glass, with ground-glass joints, a 10.0-mL receiver, and a one-ball Snyder column.

4.3 *Evaporative concentrator,* Organomation N-Evap, or equivalent: Water bath must be maintained at 50°to 55°C.

4.4 *Gas chromatograph/mass spectrometer/data system,* Hewlett-Packard 5985B GC/MS (gas chromatograph/mass spectrometer), or equivalent: The gas chromatograph is used with one of the following options:

4.4.1 *Column,* fused silica capillary column, 25 m×0.20 mm id (inside diameter), SE–54 bonded column, 0.33-µm film thickness.

Detector, mass spectrometer.

Injection temperature, 260°C.

Carrier gas, 1 mL/min, helium.

Transfer line temperature, 285°C.

Mode, splitless injection.

Program rate, 45° to 300°C, 2.5-min initial hold, 6°C/min, 15-min final hold.

4.4.2 *Columns,* two fused silica capillary columns, 25 m×0.20 mm id, SE–54 bonded column, 0.33-µm film thickness.

Detectors, mass spectrometer and a flame-ionization detector, 285°C.

Injection temperature, 260°C.
Mode, splitless injection.
Carrier gas, 1 mL/min, helium.
Transfer line, 285°C.
Program rate, 45° to 300°C, 2.5-min initial hold, 6°C/min, 15-min final hold.

4.5 *pH paper,* hydrion, pH range 1 to 14.

5. Reagents

5.1 *Acidic organic compound standards,* EPA analytical reference grade or highest purity available: Weigh about 20 mg of the standard to three significant figures, quantitatively transfer it to a 100-mL volumetric flask, and dilute to volume with methylene chloride. Prepare dilutions in methylene chloride to obtain solutions containing 2, 10, and 20 ng/μL.

5.2 *DFTPP (Decafluorotriphenylphosphine) solution,* 50 ng/μL: Dilute 20 μL DFTPP (Supelco, or equivalent, 25 mg/mL solution) to 10 mL in a volumetric flask with methylene chloride.

5.3 *Internal standard,* perdeuterophenanthrene (phenanthrene-d_{10}), Kor Isotopes, Division of Kor, Inc., or equivalent; perdeuteronaphthalene (naphthalene-d_8), Aldrich Chemical Co., or equivalent; and perdeuterochrysene (chrysene-d_{12}), Kor Isotopes, Division of Kor, Inc., or equivalent: Weigh about 20 mg perdeuteronaphthalene, perdeuterophenanthrene, and perdeuterochrysene to three significant figures, quantitatively transfer to a 100-mL volumetric flask, and dilute to volume with methylene chloride.

5.4 *Sodium hydroxide,* pellets, reagent grade.

5.5 *Sodium hydroxide solution,* 37 percent (weight/volume; w/v): Dissolve 185 g sodium hydroxide pellets in 500 mL organic-free water and reflux 8 h. Cool and store at 4°C.

5.6 *Sodium sulfate,* anhydrous, granular, Mallinckrodt 8024, or equivalent: Heat at 300°C overnight, slurry with enough diethyl ether to cover the crystals, and acidify to pH 2 or less by adding a few millileters of concentrated sulfuric acid. Determine the pH by removing a portion of the slurry, evaporating the ether, adding water to the crystals, and testing the aqueous phase with pH paper. Evaporate the ether by allowing the slurry to stand in an open container under a fume hood. Store at 130°C in a glass-stoppered bottle.

5.7 *Solvents,* diethyl ether, unpreserved, distilled in glass, pesticide analysis quality, Burdick and Jackson, or equivalent; methylene chloride, isopropanol, glass distilled pesticide quality, Burdick and Jackson, or equivalent.

5.8 *Sulfuric acid, concentrated,* (sp. gr. 1.84), reagent grade, Mallinckrodt, or equivalent.

5.9 *Sulfuric acid,* (1 + 3): Prepare by adding one part concentrated sulfuric acid to three parts organic-free water. Store in a refrigerator at 4°C.

5.10 *Surrogate standards,* perdeuterophenol (phenol-d_6), Aldrich Chemical Co., or equivalent; dibromobenzene, FDA, or equivalent; 2,4,6-tribromophenol, FDA, or equivalent: Weigh 4 mg of each of the three compounds to three significant figures, quantitatively transfer to a 100-mL volumetric flask, and dilute to volume with isopropanol.

5.11 *Water,* organic-free.

6. Procedure

All glassware must be washed in warm detergent solution, rinsed with organic-free water, and heated at 300°C overnight. All glassware must be rinsed with (1 + 3) aqueous sulfuric acid, then rinsed with organic-free water until the washwater is neutral to pH paper, and then heated at 130°C overnight. Immediately before use, the glassware is rinsed with methylene chloride. Stopcock grease should not be used on ground-glass joints.

6.1 Immediately upon receipt of the sample in the laboratory, acidify to pH 2 or lower (as indicated by pH paper) with (1 + 3) sulfuric acid (approximately 3 mL), and store at 4°C. Extraction must begin within 48 h after receipt of the sample.

NOTE: Extraction may be carried out on the aqueous phase following extraction of the extractable base/neutral compounds (method O–3118).

6.2 A blank must accompany each set of samples. For each sample and blank, rinse a 2-L separatory funnel and a 500-mL Erlenmeyer flask with methylene chloride.

6.3 Weigh the capped sample bottle to three significant figures and record the weight for subsequent calculations.

6.4 Pour the sample into the separatory funnel and allow the sample bottle to drain completely.

6.5 Weigh the capped empty sample bottle to three significant figures and calculate and record the net sample weight.

6.6 Add 1.0 mL of the surrogate standard (5.10) to the sample in the separatory funnel.

6.7 Add 100 mL methylene chloride to the empty sample bottle and gently swirl to wash the

sides of the container with the solvent. The Teflon liner inside the cap is not rinsed because of the potential for contamination from solvent that has contacted the cap threads and the surface beneath the liner. Pour the contents of the bottle into the separatory funnel.

6.8 Stopper the separatory funnel and shake vigorously for at least 1 min, venting often to release the pressure. Allow the layers to separate.

6.9 Drain the organic layer into a 500-mL Erlenmeyer flask.

6.10 Add 50 mL methylene chloride to the separatory funnel. Stopper the separatory funnel and shake for at least 1 min, venting often to release the pressure. Allow the layers to separate.

6.11 Drain the organic layer into the Erlenmeyer flask.

6.12 Extract the sample one more time by repeating steps 6.9 and 6.10.

6.13 Add approximately 30 g sodium sulfate to the Erlenmeyer flask. Cover the Erlenmeyer flask with aluminum foil and set aside for no longer than 2 h. (Significant loss of analytes can occur from sample adsorption onto the sodium sulfate if the extract is allowed to remain in contact with the sodium sulfate for longer than 2 h.)

6.14 Quantitatively transfer the dried extract to a K-D apparatus, add a boiling chip, and attach a Snyder column.

6.15 Concentrate to about 5 mL by heating the apparatus on a 90°C water bath in a fume hood.

6.16 Allow the K-D flask to cool. Dry the apparatus with a towel, especially around the ground-glass joint.

6.17 Separate the Snyder column from the K-D flask and rinse the walls of the K-D flask with approximately 2 mL methylene chloride. Dry the joints with a towel. Separate the receiver from the K-D flask and rinse the ground-glass joint of the K-D flask into the receiver with methylene chloride.

6.18 Reduce the volume of the extract in the receiver to less than 0.9 mL on the evaporative concentrator. During the concentration procedure, rinse the receiver walls two or three times with small portions of methylene chloride.

6.19 Stopper the receiver with a ground-glass stopper and store the extract in a freezer until analysis can proceed.

NOTE: The extract obtained from the base/neutral extraction (method O–3118) and the extract from this acidic extraction can be combined for GC/MS analysis immediately before injection.

6.20 Immediately before analysis, add 0.05 mL of internal standard. Adjust the final volume of the sample extract in the receiver to 1.0 mL.

6.21 Mass spectrometer tuning:

6.21.1 Use perfluorotributylamine to tune the mass spectrometer in a manner that results in a satisfactory calibration of mass assignments as well as agreement with the criteria listed in step 6.21.2.

6.21.2 Set the MS to scan the mass range 40–450 amu (atomic mass units). Temperature program the GC from 45° to 275°C at 20°C per min with an initial hold of 1.5 min. Inject 50 ng (1 μL of solution, step 5.2). Obtain a background corrected mass spectrum of DFTPP and verify that all of the following criteria are met:

Mass	*Ion abundance criteria*
51	30–60 percent of mass 198
68	<2 percent of mass 69
70	<2 percent of mass 69
127	40–60 percent of mass 198
197	<1 percent of mass 198
198	Base peak, 100 percent relative abundance
199	5–9 percent of mass 198
275	10–30 percent of mass 198
365	>1 percent of mass 198
441	<mass 443
422	>40 percent of mass 198
443	17–23 percent of mass 442

6.22 Analyze the extract by injection of an aliquot into the GC/MS system optimized as follows:

6.22.1 For systems configured with option A, analyze the mass range 40 to 450 amu at a scan rate sufficient to obtain a minimum of 5 scans per chromatographic peak. Record the total ion current chromatogram and the mass spectrum of each peak.

6.22.2 For systems configured with option B, analyze the mass range 40 to 450 amu at a scan rate sufficient to obtain a minimum of 5 scans per chromatographic peak. Record the total ion current chromatogram and the mass spectrum of each peak as well as the data (retention time and integrated area of each peak) from the FID.

6.23 Process the data to determine the identity of the extractable acidic organic compounds in the following manner:

6.23.1 Identification of the target compound is accomplished by a computerized reverse search procedure employing a 25-scan retention time window.

6.23.2 Identification of the extractable acid compounds that are not target compounds is accomplished by a computerized library search versus the National Bureau of Standards library reference spectra on each peak. The best computer matches of mass spectra are reviewed manually.

6.24 Determine the largest characteristic ion and quantitate the area on this ion for any identified peak, including the internal standard peak and the surrogate standards peaks. Alternatively, if the system is configured with option B, the quantitation can be carried out on the FID trace rather than on the mass spectrum. The integrated area of an identified peak is recorded for subsequent calculations. The better chromatogram (FID or MS) is used for quantitation.

6.25 Confirm the surrogate compounds found in the sample by injecting an aliquot of the corresponding surrogate standards (step 5.10) into the gas chromatograph and analyze according to steps 6.22 through 6.24. Record the integrated area obtained.

6.26 Confirm any identified extractable acid compounds found in the sample by injecting an aliquot of the corresponding acidic organic compound standard (step 5.1) of about the same concentration into the gas chromatograph and analyze according to steps 6.22 through 6.24. If the concentration of the compound of interest exceeds the highest standard, dilute the extract and reanalyze it. Record the integrated area obtained. If an acid standard is not available, quantitate relative to the internal standard (see step 7.6).

7. Calculations

7.1 Calculations of response factors and relative response factors:

7.1.1 Compute the response factor of the surrogate standard (step 6.25) and each compound in the acid standard (step 6.26) using the following equation:

$$RF_i = \frac{A_{si}}{C_{si}},$$

where

RF_i = response factor of compound i in standard, in area/ng

C_{si} = amount of compound i injected, in ng/μL, and,

A_{si} = area of compound i peak.

7.1.2 Calculate the response factor of th internal standard using the following equation:

$$RFI = \frac{AI_1}{CI_1},$$

where

RFI = response factor of internal standard, in area/ng,

CI_1 = amount of internal standard in acid standard (step 5.1) injected, in ng, and

AI_1 = area of internal standard peak.

7.1.3 Calculate a relative response factor by the following equation:

$$RRF_i = \frac{RF_i}{RFI},$$

where

RRF_i = relative response factor,

RF_i = response factor of compound i, and

RFI = response factor of internal standard.

7.2 Calculations of recoveries of surrogates: Calculate the percent recovery of each surrogate standard recovered from the original water–suspended-sediment mixture using the following equation:

$$\text{Percent recovery} = \frac{A \times CI_2 \times V_3 \times 100}{RRF_i \times AI_2 \times C_s \times V_4},$$

where

A = area of identified surrogate peak in sample extract,

CI_2 = amount of internal standard injected, in ng,

RRF_i = relative response factor of surrogate i,

AI_2 = area of internal standard peak in sample extract,

C_s = concentration of standard, in ng/mL,

V_3 = final volume of extract, in mL, and

V_4 = volume of sample injected, in μL.

7.3 Calculations of concentrations of analytes: Calculate the concentration of each identified acid extractable compound in the original water or water–suspended-sediment mixture using the following equation:

$$\text{Concentration (μg/L)} = \frac{A \times CI_2 \times V_3 \times 1{,}000}{RRF \times AI_2 \times W \times V_4},$$

where

A = area of identified peak in sample,

CI_2 = amount of internal standard injected, in ng,

RRF = relative response factor,
AI_2 = area of internal standard peak in sample extract,
W = weight of sample extracted, expressed in mL (1.000g = 1.000 mL),
V_3 = final volume of extract, in mL, and
V_4 = volume of sample injected.

7.4 Calculations of concentrations of other compounds: The concentrations of all other identified extractable acid compounds in the original water sample, for which there are no standards, are calculated relative to the concentration of the internal standard and are semiquantitative for the purpose of a general organic scan. The response factor of the compound is assumed to be exactly equal to that of the internal standard. Calculate the concentration using the following equation:

$$\text{Concentration } (\mu g/L) = \frac{A \times V_3 \times 1{,}000}{RFI \times W \times V_4},$$

where
RFI = response factor of internal standard, in area/ng,
A = area of identified peak in sample,
W = weight of sample extracted, expressed in mL (1.000 g = 1.000 mL),
V_3 = final volume of extract, in mL, and
V_4 = volume of sample injected.

8. Report

8.1 Report concentrations of extractable acidic organic compounds (except 4-chloro-3-methyl phenol, 2,4,6-trichlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, and pentachlorophenol) in water and water–suspended-sediment mixtures as follows: less than 6.0 µg/L, as "less than 6.0 µg/L"; 6.0 µg/L and above, two significant figures.

8.2 Report concentrations of 4-chloro-3-methylphenol, 4-nitrophenol, 4, 6-dinitro-2-methylphenol, and pentachlorophenol as follows: less than 30 µg/L, as "less than 30 µg/L"; 30 µg/L and above, two significant figures.

8.3 Report concentrations of 2,4,6-trichlorophenol and 2,4-dinitrophenol as follows: less than 20 µg/L, as "less than 20 µg/L"; 20 µg/L and above, two significant figures.

9. Precision

9.1 Surrogate recoveries must be between 30 percent and 130 percent unless a matrix effect can be demonstrated. Water and water–suspended-sediment samples were spiked with surrogate standards and recoveries were determined by two operators in a single laboratory over an 8-mo period. Results are as follows:

Compound	Ion used for quantitation	Concentration range (ng/µL)	Number of samples analyzed	Average recovery (percent)	Relative standard deviation (percent)
Phenol-d_6	99	42–81	45	50	30
2,4-Dibromophenol	252	57–104	46	68	39
2,4,6-Tribromophenol	332	61–75	44	83	34

9.2 Deionized water samples were spiked with acid extractable compounds and recoveries were determined by two operators in a single laboratory over a 1-yr period. Results are as follows:

Compound	Ion used for quantitation	Concentration range (ng/µL)
4-Chloro-3-methyphenol	142	50–292
2-Chlorophenol	128	50-355
2,4-Dichlorophenol	162	50-316
2,4-Dimethylphenol	122	43-319
2,4-Dinitrophenol	184	58-436
2-Methyl-4,6-dinitrophenol	198	50-571
2-Nitrophenol	139	50-271
4-Nitrophenol	139	50-326
Pentachlorophenol	266	144-349
Phenol	94	50-331
2,4,6-Trichlorophenol	196	50-236

Compound	Number of samples analyzed	Average recovery (percent)	Relative standard deviation (percent)
4-Chloro-3-methyphenol	18	80	27
2-Chlorophenol	20	73	25
2,4-Dichlorophenol	18	84	21
2,4-Dimethylphenol	19	74	23
2,4-Dinitrophenol	15	67	26
2-Methyl-4,6-dinitrophenol	5	66	33
2-Nitrophenol	17	78	32
4-Nitrophenol	17	61	44
Pentachlorophenol	15	77	31
Phenol	19	53	44
2,4,6-Trichlorophenol	17	83	31

Selected references

Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L., 1981, Trace analysis for wastewaters: Environmental Science and Technology, v. 15, p. 1426–1435.

Realini, P.A., 1981, Determination of priority pollutant phenols in water by HPLC: Journal of Chromatography Science, v. 19, p. 124–129.

Sauter, A.D., Betowski, L.D., Smith, T.R., Strickler, V.A., Beimer, R.G., Colby, B.M., and Wilkison, J.E., 1981, Fused silica capillary column GC/MS for the analysis of priority pollutants: Journal of High Resolution Chromatography and Chemical Communication, v. 4, p. 366–384.

U.S. Environmental Protection Agency, 1979, Base/neutrals, acids, and pesticides—Method 625: Federal Register v. 44, no. 233, p. 69540.

Base/neutral extractable compounds, total recoverable, gas chromatographic/mass spectrometric (O-3118-83)

Parameter	*Code*
Acenaphthene	34205
Acenaphthylene	34200
Anthracene	34220
Benzidine	39120
Benzo(a)anthracene	34526
Benzo(b)fluoranthene	34230
Benzo(k)fluoranthene	34242
Benzo(g,h,i)perylene	34521
Benzo(a)pyrene	34247
4-Bromophenyl phenyl ether	34636
Butyl benzyl phthalate	34292
bis(2-Chloroethoxy)methane	34278
bis(2-Chlororethyl) ether	34273
bis(2-Chloroisopropyl) ether	34283
2-Chloronaphthalene	34581
4-Chlorophenyl phenyl ether	34641
Chrysene	34320
Dibenz(a,h)anthracene	34556
1,2-Dichlorobenzene	34536
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
3,3'-Dichlorobenzidine	34631
Diethyl phthalate	34336
Dimethyl phthalate	34341
Di-n-butyl phthalate	39110
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626
Di-n-octyl phthalate	34596
bis(2-Ethylhexyl) phthalate	39100
Fluoranthene	34376
Fluorene	34381
Hexachlorobenzene	39700
Hexachlorobutadiene	39702
Hexachlorocyclopentadiene	34386
Hexachloroethane	34396
Indeno(1,2,3-cd)pyrene	34403
Isophorone	34408
Naphthalene	34696
Nitrobenzene	34447
N-Nitrosodimethylamine	34438
N-Nitrosodiphenylamine	34433
N-Nitrosodi-n-propylamine	34428
Phenanthrene	34461
Pyrene	34469
2,3,7,8-Tetrachlorodibenzo-p-dioxin	34675
1,2,4-Trichlorobenzene	34551

1. Application

This method is suitable for the determination of methylene chloride extractable base/neutral compounds in water and water–suspended-sediment mixtures containing at least 5 µg/L of the analyte.

2. Summary of method

Organic base/neutral compounds are extracted from water and water-suspended-sediment mixtures with methylene chloride. The extract is concentrated and analyzed by gas chromatography (GC) using a flame-ionization detector (FID) or a mass spectrometric (MS) detector.

3. Interferences

Any compound having chemical and physical properties similar to an analyte of interest may interfere.

4. Apparatus

4.1 *Boiling chips,* micro, carbon chips: Rinse with hexane, air dry, and heat at 300°C overnight.

4.2 *Concentrator, Kuderna-Danish (K-D),* 500 mL, all glass, with ground-glass joints, a 10.0-mL receiver, and a one-ball Snyder column.

4.3 *Evaporative concentrator,* Organomation N-Evap, or equivalent: Water bath must be maintained at 50° to 55°C.

4.4 *Gas chromatograph/mass spectrometer/data system,* (GC/MS) Hewlett-Packard 5985 B GC/MS, or equivalent: The gas chromatograph is used with one of the following options:

4.4.1 *Columns,* fused silica capillary column, 25 m×0.20 mm id (inside diameter), SE-54 bonded column, 0.33-µm film thickness.

Detector, mass spectrometer (MS).
Injection temperature, 260°C.
Carrier gas, 1mL/min, helium.
Transfer line temperature, 285°C.
Mode, splitless injection.
Program rate, 45° to 300°C, 2.5-min initial hold, 6°C/min, 15-min final hold.

4.4.2 *Columns,* two fused silica capillary columns, 25 m×0.20 mm id, SE-54 bonded column, 0.33-µm film thickness.

Detectors, mass spectrometer, FID 285°C.
Injection temperature, 260°C.
Mode, splitless injection.
Carrier gas, 1 mL/min, helium.
Transfer line, 285°C.
Program rate, 45° to 300°C, 2.5-min initial hold, 6°C/min, 15-min final hold.

5. Reagents

5.1 *Base/neutral standards,* EPA analytical reference grade or highest purity available: Weigh 20 mg of the compound to three significant figures, quantitatively transfer to a 100-mL volumetric flask, and dilute to volume with methylene chloride. Prepare dilutions in methylene chloride to obtain solutions containing 2, 10, and 20 ng/µL.

5.2 *DFTPP (Decafluorotriphenylphosphine) solution,* 50 ng/μL: Dilute 20 μL DFTPP (Supelco, or equivalent, 25-mg/mL solution) to 10 mL in a volumetric flask with methylene chloride.

5.3 *Internal standards,* perdeuteronaphthalene (naphthalene-d_8), Aldrich Chemical Co., or equivalent; perdeuterophenanthrene (phenanthrene-d_{10}), Kor Isotopes, Division of Kor, Inc., or equivalent; and perdeuterochrysene (chrysene-d_{12}), Kor Isotopes, Division of Kor, Inc., or equivalent. Weigh about 20 mg of perdeuteronaphthalene, perdeuterophenanthrene, and perdeuterochrysene to three significant figures, quantitatively transfer to a 100-mL volumetric flask, and dilute to volume with methylene chloride.

5.4 *Sodium chloride,* reagent grade: Heat at 300°C overnight and store in a closed glass container.

5.5 *Sodium hydroxide,* 37 percent (weight/volume): Dissolve 185 g sodium hydroxide pellets in 500 mL organic-free water and reflux 8 hr. Cool and store at 4°C.

5.6 *Sodium sulfate,* granular, anhydrous, reagent grade: Heat at 300°C overnight and store in a glass-stoppered Erlenmeyer flask at 130°C.

5.7 *Solvents,* hexane, isopropanol, and methylene chloride, glass distilled, pesticide analysis quality, Burdick and Jackson, or equivalent.

5.8 *Surrogate standards,* 1-fluoronaphthalene, Aldrich Chemical Co., or equivalent; 2,2′-difluorobiphenyl, Pfaltz and Bauer Co., or equivalent; and p-dibromobenzene, FDA, or equivalent. Weigh 4 mg of each of the three compounds to three significant figures, quantitatively transfer to a 100-mL volumetric flask, and dilute to volume with isopropanol.

5.9 *Water,* organic-free.

6. Procedure

All glassware must be washed in a warm detergent solution, rinsed with organic-free water, and heated at 300°C overnight. Immediately before use, it must be rinsed with methylene chloride. Stopcock grease should not be used on ground-glass joints.

6.1 Immediately upon receipt of the sample, store at 4°C. Extraction must begin within 48 h following receipt of the sample.

6.2 A blank must accompany each group of samples. For each sample and blank, rinse a 2-L separatory funnel and a 500-mL Erlenmeyer flask with methylene chloride.

6.3 Weigh the capped sample bottle to three significant figures and record the weight for subsequent calculations.

6.4 Adjust the sample to pH 11, as indicated by pH paper, by the addition of sodium hydroxide solution.

6.5 Pour the sample into a separatory funnel containing 100 g sodium chloride. Allow the sample bottle to drain into the separatory funnel for several minutes. Stopper and shake until the salt is dissolved.

6.6 Weigh the empty, capped sample bottle to three significant figures, calculate and record the net sample weight.

6.7 Add 1 mL of the surrogate standard (step 5.8) to the sample in the separatory funnel.

6.8 Add 100 mL methylene chloride to the empty sample bottle and swirl to wash the sides of the container with the solvent. The Teflon liner is not rinsed because of the potential of contamination from solvent that has contacted the cap threads and the surface beneath the liner. Pour the contents of the bottle into the separatory funnel.

6.9 Stopper the separatory funnel and shake for at least 1 min, venting often to relieve pressure.

6.10 Drain the organic layer into a 500-mL Erlenmeyer flask containing approximately 30 g sodium sulfate.

6.11 Extract the sample two more times with 50 mL methylene chloride by repeating steps 6.8 through 6.10, collecting the two organic extracts in the Erlenmeyer flask containing the sodium sulfate.

NOTE: The aqueous phase may be retained and extracted for the acidic extractable organic compounds after adjusting the pH to 2 (method O–3117).

6.12 Cover the Erlenmeyer flask with aluminum foil and allow to stand at room temperature for approximately 4 h.

6.13 Quantitatively transfer the dried extract into a K-D apparatus, add a boiling chip, and attach a Snyder column.

6.14 Concentrate the extract to about 5 mL by heating the apparatus on a 80°C water bath in a fume hood.

6.15 Allow the K-D apparatus to cool. Dry the apparatus with a towel, especially around the ground-glass joint of the receiver.

6.16 Separate the Snyder column from the K-D flask and rinse the walls of the K-D flask with approximately 2 mL methylene chloride. Separate the receiver from the K-D flask and rinse the

ground-glass joint of the K-D flask into the receiver with methylene chloride.

6.17 Reduce the volume of the methylene chloride in the receiver to less than 0.9 mL on the evaporative concentrator. During the concentration, rinse the receiver walls two or three times with small portions of methylene chloride.

6.18 Stopper the receiver with a ground-glass stopper and store the extract at 4°C until analysis can proceed.

NOTE: The extract can be combined with the extract from the acidic extractable organic compounds (method O–3117) immediately before injection into the GC/MS.

6.19 Immediately before analysis, add 0.05 mL of internal standard. Adjust the final volume of the sample extract in the receiver to 1.0 mL.

6.20 Mass spectrometer tuning:

6.20.1 Use perfluorotributylamine to tune the mass spectrometer in a manner that results in satisfactory calibration of mass assignments as well as agreement with the criteria listed in step 6.20.2.

6.20.2 Set the MS to scan the mass range 40–450 amu (atomic mass units). Temperature program the GC from 45° to 275°C at 20°C/min with an initial hold of 1.5 min. Inject 50 ng (1 μL of solution, step 5.2). Obtain a background corrected mass spectrum of DFTPP and verify that all of the following criteria are met:

Mass	*Ion abundance criteria*
51	30–60 percent of mass 198
68	<2 percent of mass 69
70	<2 percent of mass 69
127	40–60 percent of mass 198
197	<1 percent of mass 198
198	Base peak, 100 percent relative abundance
199	5–9 percent of mass 198
275	10–30 percent of mass 198
365	>1 percent of mass 198
441	<mass 443
442	>40 percent of mass 198
443	17–23 percent of mass 442

6.21 Analyze the extract by injection of an aliquot into the GC/MS system optimized as follows:

6.21.1 For systems configured with option A, analyze the mass range 40 to 450 amu at a scan rate sufficient to obtain a minimum of 5 scans per chromatographic peak. Record the total ion current chromatogram and the mass spectrum of each peak.

6.21.2 For systems configured with option B, analyze the mass range 40 to 450 amu at a scan rate sufficient to obtain a minimum of 5 scans per chromatographic peak. Record the total ion current chromatogram and the mass spectrum of each peak as well as the retention time and integrated area of each peak from the FID.

6.22 Process the data to determine the identity of the extractable base/neutral compounds including the priority pollutants in the following manner:

6.22.1 Identification of the target compounds is accomplished by a computerized reverse search procedure employing a 25-scan retention time window.

6.22.2 Identification of the extractable base/neutral compounds that are not target compounds is accomplished by a computerized library search versus the National Bureau of Standards library reference spectra on each peak.

6.23 Determine the largest characteristic ion and quantitate the area on this ion for any identified peak, including the internal standard peak and the surrogate standards peaks. Alternatively, if the system is configured with option B, the quantitation can be carried out on the FID response rather than on the mass spectrometer response. The integrated area of an identified peak from the FID is recorded for subsequent calculations. The better chromatogram (FID or MS) is used for quantitation.

6.24 Confirm the surrogate compounds found in the sample by injecting an aliquot of the corresponding surrogate standards (step 5.8) into the gas chromatograph and analyze according to steps 6.21 through 6.23. Record the integrated area obtained.

6.25 Confirm any identified extractable base/neutral compounds found in the sample by injecting an aliquot of the corresponding base/neutral standard into the gas chromatograph and analyze according to steps 6.21 through 6.23. Record the integrated area obtained. If a base/neutral standard is not available, quantitate relative to the internal standard (see step 7.6).

7. Calculations

7.1 Calculations of response factors and relative response factors:

7.1.1 Calculate the response factor for each compound in the base/neutral standard or surrogate standard (step 6.23) using the following equation:

$$RF_i = \frac{A_{si}}{C_{si}},$$

where

RF_i = response factor of compound i in standard, in area/ng,

C_{si} = amount of compound i injected, in ng/μL, and

A_{si} = area of compound i peak in the standard.

7.1.2 Calculate the response factor of the internal standard using the following equation:

$$RFI = \frac{AI_1}{CI_1},$$

where

RFI = response factor of internal standard, in area/ng,

CI_1 = amount of internal standard in base/neutral standard, in ng injected, and

AI_1 = area of internal standard peak.

7.1.3 Calculate a relative response factor by the following equation:

$$RRF_i = \frac{RF_i}{RFI},$$

where

RRF_i = relative response factor, compound i,

RF_i = response factor of compound i, and

RFI = response factor of internal standard.

7.2 Calculations of recoveries of surrogates: Calculate the percent recovery of each surrogate standard recovered from the original Water- suspended-sediment mixture using the following equation:

$$\text{Percent recovery} = \frac{A \times CI_2 \times V_3 \times 100}{RRF_i \times AI_2 \times C_s \times V_4},$$

where

A = area of identified surrogate peak in sample extract,

CI_2 = amount of internal standard injected, in ng,

RRF_i = relative response factor of compound i,

AI_2 = area of internal standard peak in sample extract,

C_s = concentration of standard, in ng/μL,

V_3 = final volume of extract, in mL, and

V_4 = volume injected, in μL.

7.3 Calculation of concentrations of analytes: Calculate the concentration of each identified extractable base/neutral priority pollutant in the original water–suspended-sediment mixture using the following equation:

$$\text{Concentration (μg/L)} = \frac{A \times CI_2 \times V_3 \times 1{,}000}{RRF_i \times AI_2 \times W \times V_4},$$

where

A = area of identified peak in sample extract,

CI_2 = amount of internal standard injected, in ng,

RRF_i = relative response factor of compound i,

AI_2 = area of internal standard peak in sample extract,

W = weight of sample extracted, expressed in mL (1.000 g = 1.000 mL),

V_3 = final volume of extract, in mL, and

V_4 = volume injected, in μL.

7.4 Calculations of concentrations of other compounds: The concentrations of all other identified extractable base/neutral compounds in the original water sample for which there are no standards, are calculated relative to the concentration of the internal standard, and are semiquantitative for the purposes of a general organic scan. The response factor of the compound is assumed to be exactly equal to that of the internal standard. Calculate the concentration using the following equation:

$$\text{Concentration (μg/L)} = \frac{A \times V_3 \times 1{,}000}{RFI \times W \times V_4},$$

where

RFI = response factor of internal standard, in area/ng,

A = area of identified peak in sample,

W = weight of sample extracted, expressed in mL (1.000 g = 1.000 mL),

V_3 = final volume of extract, in mL, and

V_4 = volume injected, in μL.

8. Report

8.1 Report concentrations of extractable base/neutral organic compounds (except chrysene, benzo(a) anthracene, dioctyl phthalate, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo(a) pyrene, indeno(1,2,3-cd) pyrene, dibenz(a,h) anthracene, and benzo(g,h,i) perylene) in water and water–suspended-sediment mixtures as follows: less than 5.0 μg/L, as "less than 5.0 μg/L"; 5.0 μg/L and above, two significant figures.

8.2 Report concentrations of chrysene, benzo(a) anthracene, dioctyl phthalate, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo(a) pyrene, indeno(1,2,3-cd) pyrene, dibenz(a,h) anthracene, and benzo(g,h,i) perylene as follows: less than

10 µg/L, as "less than 10 µg/L"; 10µg/L and above, two significant figures.

9. Precision

9.1 Surrogate recoveries must be from 40 percent to 130 percent unless a matrix effect can be demonstrated. Water and water–suspended-sediment samples were spiked with surrogate standards and recoveries were determined by two operators in a single laboratory over an 8-mo period. Results are as follows:

Compound	*Ion used for quantitation*	*Concentration range (ng/µL)*	*Number of samples analyzed*	*Average recovery (percent)*	*Relative standard deviation (percent)*
1-Fluoronaphthalene	146	48–104	45	65	29
p-Dibromobenzene	236	51–107	46	67	26
2,2′-Difluorobiphenyl	190	43–79	46	68	20

9.2 Deionized water samples were spiked with base/neutral extractable compounds and recoveries were determined by two operators in a single laboratory over a 1-yr period. Results are as follows:

Compound	*Ion used for quantitation*	*Concentration range (ng/µL)*	*Number of samples analyzed*	*Average recovery (percent)*	*Relative standard deviation (percent)*
Acenaphthylene	152	190	2	105	---
Anthracene	178	100–177	5	66	45
Benzo(a)anthracene	228	69	5	79	23
Benzo(k)fluoranthene	252	50–71	2	98	---
Benzo(a)pyrene	252	50–100	5	115	22
bis(2-chloroethoxy)methane	93	50–100	3	64	---
4-Bromophenyl phenyl ether	248	100	5	43	6
4-Chlorophenyl phenyl ether	204	50	1	111	---
Chrysene	228	50–113	6	42	46
Dibenz(a,h)anthracene	278	69	1	71	---
Di-n-butyl phthalate	149	100	5	53	19
1,2-Dichlorobenzene	146	50–100	5	56	43
1,3-Dichlorobenzene	146	100–201	6	97	30
1,4-Dicholorobenzene	146	102	1	51	---
Diethyl phthalate	149	50–100	14	69	37
Dimethyl phthalate	163	199	1	19	---
2,4-Dinitrotoluene	165	50–106	6	63	19
Dimethyl phthalate	149	100	15	69	42
bis(2-ethylhexyl) phthalate	149	100	2	42	---
Fluorene	166	50–197	5	99	11
Fluoranthene	202	224	1	98	---
Hexachlorobenzene	284	50–76	3	91	---
Hexachlorobutadine	225	50–74	3	94	---
Indeno(1,2,3-cd)pyrene	276	50	1	104	---
Naphthalene	128	50–130	6	81	17
Nitrobenzene	77	219	1	50	---
N-Nitrosodimethylamine	74	50	1	68	---
N-Nitrosodiphenylamine	169	50	1	48	---
Phenanthrene	178	218	1	94	---
Pyrene	202	50–334	16	94	16
1,2,4-Trichlorobenzene	180	100	5	78	24

Selected references

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