ANALYTICAL METHOD FOR DISSOLVED-ORGANIC CARBON FRACTIONATION

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 79-4

Prepared in cooperation with

Huffman Laboratories, Inc.

ANALYTICAL METHOD FOR DISSOLVED-ORGANIC CARBON FRACTIONATION

By Jerry A. Leenheer and Edward W. D. Huffman, Jr.

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 79-4

Prepared in cooperation with

Huffman Laboratories Inc.

January 1979

UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, SECRETARY

GEOLOGICAL SURVEY

H. William Menard, Director

For additional information write to:

Jerry A. Leenheer
U.S. Geological Survey
Water Resources Division
Box 25046, Mail Stop 407
Denver Federal Center
Lakewood, Colorado 80225

CONTENTS

ILLUSTRATIONS

TABLE

ANALYTICAL METHOD FOR DISSOLVED-ORGANIC CARBON FRACTIONATION

By J. A. Leenheer and E. W. D. Huffman, Jr.[1/]

ABSTRACT

A standard procedure for analytical-scale dissolved organic carbon fractionation is presented, whereby dissolved organic carbon in water is first fractionated by a nonionic macroreticular resin into acid, base, and neutral hydrophobic organic solute fractions, and next fractionated by ion-exchange resins into acid, base, and neutral hydrophilic solute fractions. The hydrophobic solutes are defined as those sorbed on a nonionic, acrylic-ester macroreticular resin and are differentiated into acid, base, and nautral fractions by sorption/desorption controlled by pH adjustment. The hydrophilic bases are next sorbed on strong-acid ion-exchange resin, followed by sorption of hydrophilic acids on a strong-base ion-exchange resin. Hydrophilic neutrals are not sorbed and remain dissolved in the deionized water at the end of the fractionation procedure. The complete fractionation can be performed on a 200-milliliter filtered water sample, whose dissolved organic carbon content is 5-25 mg/L and whose specific conductance is less than 2,000 μmhos/cm at 25°C. The applications of dissolved organic carbon fractionation analysis range from field studies of changes of organic solute composition with synthetic fossil fuel production, to fundamental studies of the nature of sorption processes.

INTRODUCTION

Dissolved organic carbon (DOC) fractionation analysis is a recently developed analytical method for organic solutes in water, that serves as a compound classification. The classification is more specific than total organic solute concentration (DOC) and less specific than compound identification. The original report in which DOC fractionation methodology was presented (Leenheer and Huffman, 1976), gives the philosophy for, the research and development of, and the general preparative and analytical methods for DOC fractionation analysis. Since the publication of the original report, use of the analytical method by several researchers (about 250 analyses) has led to a standard procedure for the analytical-scale DOC fractionation analysis. The purpose of this report is to present a standard method for the analytical-scale DOC fractionation, and to provide some examples of its application.

The terms "hydrophobic and hydrophilic" are used in the definition of the six fractions of DOC fractionation analysis, and their meaning is defined by the method. The hydrophobic-hydrophilic organic solute separation is mainly dependent

[1/]Huffman Laboratories, Inc., Wheatridge, Colorado

on the distribution coefficient k', for organic-solute sorption on Amberlite XAD-8[2/], a nonionic, acrylic-ester macroreticular resin. The distribution coefficient, k', and its relation to the mass distribution coefficient, Dm, is shown as follows:

$$k' = \frac{\text{mass of solute sorbed on XAD-8}}{\text{mass of solute dissolved in water,}} \qquad (1)$$

$$Dm = k' \frac{\text{mL of water}}{\text{g of XAD 8}} \qquad (2)$$

The k' values where half the solute of that k' is either sorbed or desorbed from the XAD-8 resin are used to define the separations between the fractions. The experimental procedure of the analytical-scale DOC fractionation was designed so organic solutes that sorb from water at pH 7 and pH 2 on XAD-8 with a k' $\geq$ than 110 are termed hydrophobic, and organic solutes whose k' are <110 are termed hydrophilic. After the hydrophobic solutes at pH 7 are sorbed from the water sample, organic bases are desorbed from XAD-8 with 0.1 N HCl. Organic bases whose k' is $\leq$ 14 as cations in 0.1 N HCl are desorbed and are termed hydrophobic bases. After hydrophobic solutes at pH 2 are sorbed, organic acids are desorbed from XAD-8 by 0.1 N NaOH, and organic acid anions whose k' is $\leq$ 14 in 0.1 N NaOH are termed hydrophobic acids. The hydrophobic neutral fraction consists of acid, base, and neutral solutes whose k' >14 in the pH range of 1-13. Hydrophilic solutes that are not retained on XAD-8 are also separated into acid, base, and neutral fractions. The hydrophilic fraction retained on a strong-acid, ion-exchange resin is termed the hydrophilic base fraction. After removal of the hydrophilic bases, the sample is passed through a strong-base, ion-exchange resin and the organic solute fraction retained is called the hydrophilic acid fraction. Organic solutes not sorbed by any of the resin sorbents are called the hydrophilic neutral fraction.

A listing of k' values for various organic standard-compound sorption on XAD-8 is given in a report by Thurman, Malcolm, and Aiken (1978). Table 1 lists the types of compounds likely to be found in each fraction.

[2/] "The use of the brand name in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey."

Table 1.--Compound classes in organic solute fractions

Hydrophobic bases:	One and two-ring aromatic amines except pyridine.
Hydrophobic acids:	Aliphatic carboxylic acids of five to nine carbons, one and two-ring aromatic carboxylic acids, one and two-ring phenols, fulvic acid.
Hydrophobic neutrals:	Hydrocarbons; aliphatic alcohols, amides, esters, ketones, and aldehydes > five carbons; aliphatic carboxylic acids and aliphatic amines >nine carbons; aromatic carboxylic acids and aromatic amines of three rings and greater.
Hydrophilic bases:	Aliphatic amines $\leq$ nine carbons, amino acids, pyridine.
Hydrophilic acids:	Aliphatic acids of $\leq$ five carbons, polyfunctional acids.
Hydrophilic neutrals:	Aliphatic amides, alcohols, aldehydes, esters, and ketones $\leq$ five carbons; polyfunctional alcohols; carbohydrates.

DISSOLVED ORGANIC CARBON FRACTIONATION ANALYSIS

1. Range of application

Dissolved organic carbon fractionation analysis can be applied to water samples whose DOC concentrations range betwen 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 should 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 six-minute 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 1. A photograph of the pump and column assembly is shown in figure 2.

Dissolved organic carbon is first fractionated and classified into hydrophobic and hydrophilic organic solute classes based on the capability of the solute 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 classses are secondarily fractionated into acid, base, and neutral compound classes, thus giving a total of six characteristic DOC fractions.

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 upon 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 which 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 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.

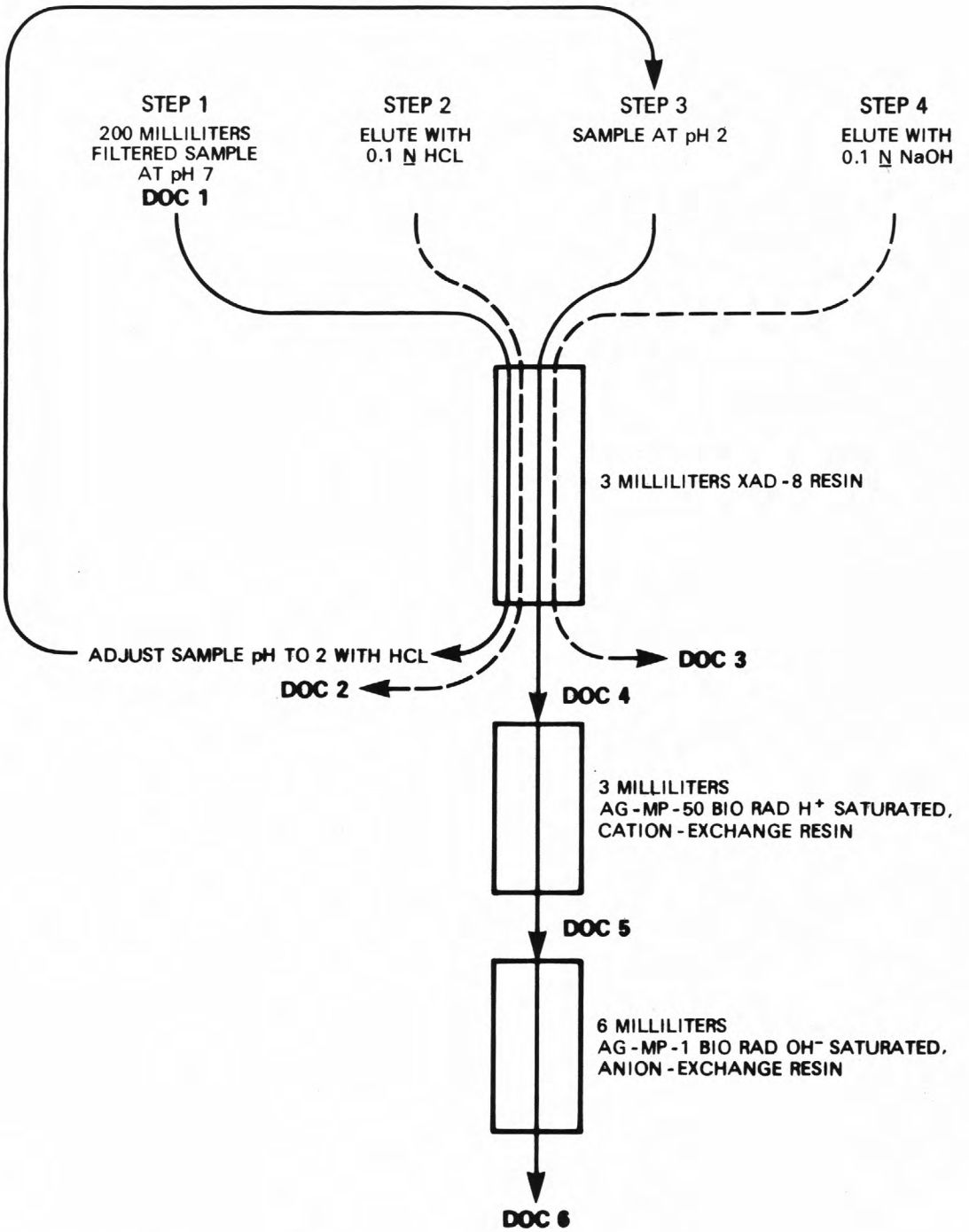

Figure 1.--Dissolved organic carbon fractionation analytical scheme.

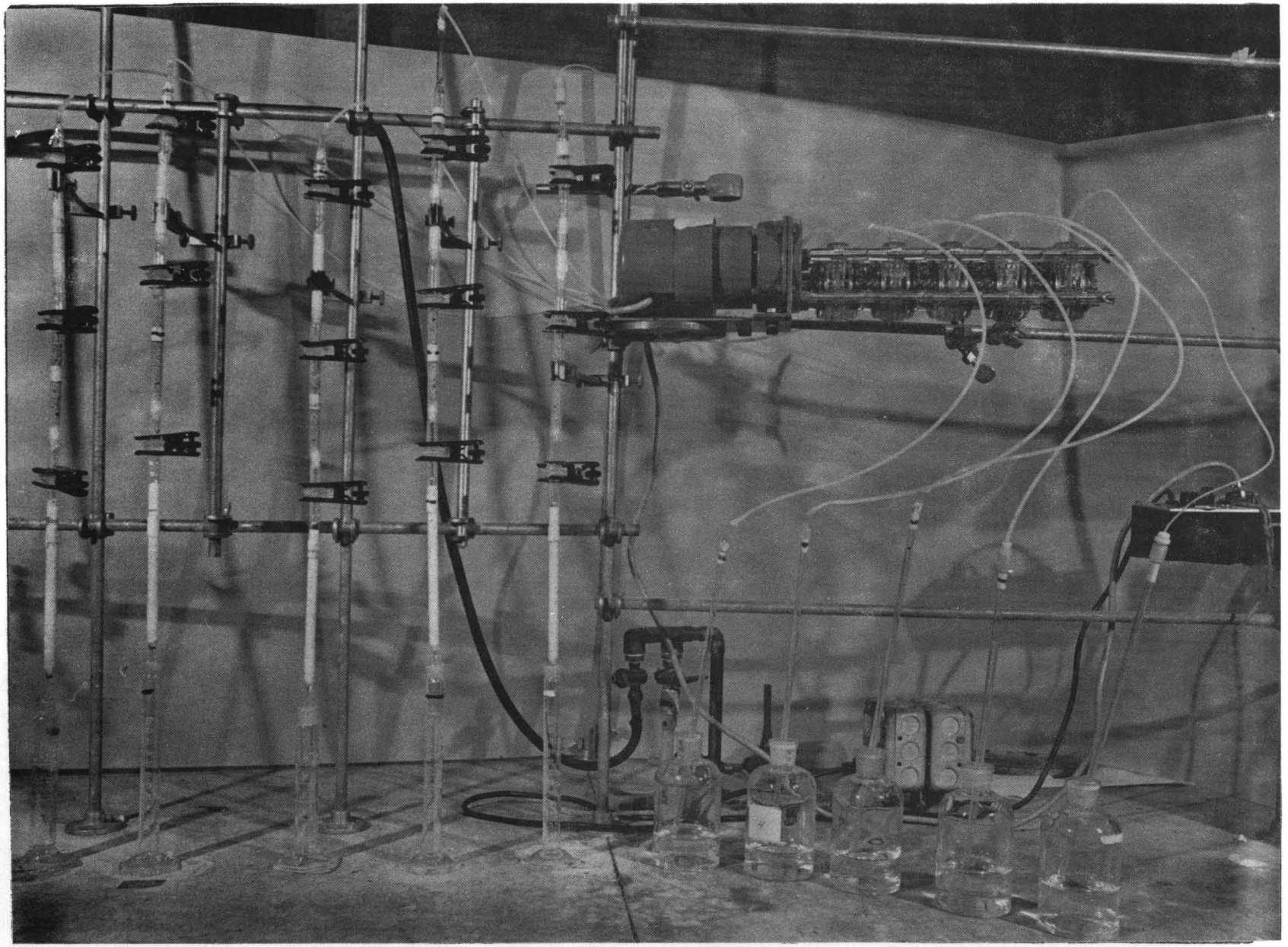

Figure 2.--Pump and column assembly for DOC fractionation analysis.

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 Oceanographic International, or equivalent.

4.2 Clamps: Size 18 pinch clamp with compression screw for ball and socket joints.

4.3 Columns: All columns are custom-prepared from 11 mm OD X 7 mm ID Pyrex glass tubing, and are connected with 18/7 ball-and-socket ground-glass joints.

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

4.3.2 Cation-exchange column: Column is 10 cm long between the base of the socket joint on 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: Column is 8 cm long between the four indentations placed at both 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 ball joints.

4.3.4 Tubing-column adaptors: Two socket-joint and two ball-joint fittings fused to 6 mm OD X 2 mm ID glass nipples are adaptors, which enable connection of the teflon tubing to the columns.

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: 1/8" OD X .085" ID (32 mm OD X 22 mm ID).

4.8 Silver membrane filter: 0.45 m porosity.

5. Reagents

5.1 Acetonitrile: Reagent grade.

5.2 Diethyl ether: Reagent grade.

5.3 Glass wool: Fine Fiber. Purify by Soxhlet extraction with methanol for 24 h.

5.4 Hydrochloric acid, 1.0 N and 0.1 N: Prepared by diluting 81.8 and 8.18 mL of 37.5 percent HCl to 1 liter, respectively, in carbon-free distilled water.

5.5 Methanol: Reagent grade.

5.6 Resin adsorbents: All three adsorbents must be extensively purified before use.

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

5.6.3 XAD-8 resin: Avaialable from Rohm and Haas, 20-50 mesh. Purify the XAD-8 resin by first slurrying with 0.1 N NaOH, 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, and 0.1 N: Prepared by dissolving 80 g, 40 g, and 4 g, respectively, of analytical reagent-grade sodium hydroxide in 1-liter 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 tap water in a glass still. Prepare bulk quantities of 50 liters or more per batch and store in clean glass containers. Water blank should be $\leq$ 0.2 mg/L DOC.

6. Procedure

6.1 Samples should be collected in organic-free glass containers. Two hundred millililiters should be filtered on site through a silver membrane filter of 0.45-micrometer porosity. Chilling to 4°C on ice is the recommended method of sample preservation.

6.2 Initial parameters: Before preparing the columns, take two 10-mL aliquots of sample for Oceanographic DOC analysis. This is DOC number 1 of figure 1. Also take a third 10-mL aliquot and determine pH and specific conductance on this aliquot. If the pH is less than 6.5, carefully adjust the pH to 7.0 by dropwise addition of 1.0 N NaOH to the sample. Once the DOC and specific conductance parameters are known, dilute or concentrate the sample as specified in the Range of Application section of this method.

6.3 Column packing and final resin purification: The final steps of the resin purification procedure occur 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 each column 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, and 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 with 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 6.3.1. Connect the packed column to the transfer tubing and pump, and pass 100 mL of reagent water, 100mL 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 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, and 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 one and two liters. This is the best point in the two-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 which may have been previously adsorbed from the reagent purification solvents.

6.6 Pump the water sample through just the XAD-8 column at 2 mL/min and precisely collect 160 mL of eluent in a 200-mL glass-stoppered graduate cylinder. Follow the sample with a 20-mL wash of reagent water so 180 mL total 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 with a glass stopper. This fraction is used to determine DOC number 2 in figure 1.

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

6.9 Clamp all three columns together in the following series: XAD-8 column first, cation-exchange column second, anion-exchange column third. Pump the 180 mL of acidified sample through the column series and take aliquots for DOC analysis 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 a 25-mL glass-stoppered graduate cylinder. This fraction is used to determine DOC number 6 in figure 1.

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 number 5 in figure 1.

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 graduate cylinder. This fraction is used to determine DOC number 4 in figure 1.

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 number 3 in figure 1.

6.10 Thoroughly shake and mix each of the collected fractions in the graduate cylinders before taking aliquots for DOC analysis. For samples with low DOC values, the oceanographic system of carbon analysis must be used. The Beckman 915 analyzer can be satisfactorily used if sample DOC is 15-25 mg/L.

6.11 Analyze each fraction for DOC using the methodology specified.

6.12 Run a complete DOC fractionation of a 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 1 and the procedural description for the definition of terms and sample fractions. All fraction parameter values should be given in mg/L DOC units calculated for the concentration in the original water sample prior to dilution or concentration. Following is the list of parameters and the computation formulae:

7.1 Total hydrophobic DOC (mg/L) = DOC number 1 - (1.125 X DOC number 4)

$$1.125 \text{ is a dilution coefficient} = \frac{\text{total volume}}{\text{sample volume}}$$

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

7.3 Hydrophobic base DOC (mg/L) = (DOC number 2 X 0.023)/.160

.023 is the fraction volume in liters

.160 is the sample volume in liters.

7.4 Hydrophobic acid DOC (mg/L) = (DOC number 3 X 0.023)/.160.

7.5 Hydrophobic neutral DOC (mg/L = Total hydrophobic DOC -

hydrophobic base DOC -

hydrophobic acid DOC

7.6 Hydrophilic base DOC (mg/L) = 1.125 X (DOC number 4 - DOC number 5).

7.7 Hydrophilic acid DOC (mg/L) = 1.125 X (DOC number 5 - DOC number 6).

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

The respective blank DOC values should be subtracted from the equivalent sample DOC fractions.

8. Report

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

9. Precision

Two factors influence precision: the variability of the reagent blank DOC which 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. Following is a list of the average deviations to be expected in the reagent blank for each fraction:

	Fraction	Average deviation (mg/L)
9.1	Total hydrophobic DOC	0.2
9.2	Total hydrophilic DOC	.2
9.3	Hydrophobic base DOC	.1
9.4	Hydrophobic acid DOC	.1
9.5	Hydrophobic neutral DOC	.4
9.6	Hydrophilic acid DOC	.5
9.7	Hydrophilic base DOC	.5
9.8	Hydrophilic neutral DOC	.3

EXAMPLE ANALYSIS

An example of the report format of a DOC fractionation analysis is provided below for a water sample collected from Hill Creek in Utah.

Hydrophobic solutes	Organic carbon (mg/L)	Percent of dissolved organic carbon
Total	3.6	49
Bases	0.1	1
Acids	2.2	30
Neutrals	1.3	18
Hydrophilic solutes		
Total	3.8	51
Bases	0.4	5
Acids	1.6	22
Neutrals	1.8	24

The DOC fractionation analysis shown above is representative for a surface water in the White River Basin region of Utah.

APPLICATIONS

Very few reports have been published citing DOC fractionation analysis data because of the newness of the methodology; therefore, most of the applications cited describe ongoing and unpublished research.

Field studies

The main application has been in the field, especially with the development of fossil-fuel energy resources in the western United States. Various environmental programs need data on organic solute compositions of water before, during, and after fossil-fuel-related energy development. Specific compound analysis of natural waters encountered before development involves identification of natural humic and fulvic acids, a very difficult analysis. After development, specific compound analysis involved gas-chromatographic, liquid-chromatographic, and mass-spectrometric analysis of thousands of pretrochemical contaminants, a very expensive and time-consuming analysis. DOC fractionation analysis is being used to determine and to monitor organic solutes changes where more specific information than DOC is needed without going to specific compound identification methods. After DOC fractionation has identified those organic solute fractions where major inputs or changes have occurred, specific compound analyses can be employed.

An example of a "before and after" organic-solute characterization using DOC fractionation analysis is given in a report by Stuber and Leenheer (1978) which describes the changes in organic solute compositions of a ground water as a result of in situ oil shale retorting. The Wyoming district of the U.S. Geological Survey is using DOC fractionation analyses in a similar manner to describe organic solute changes in ground water resulting from in situ coal gasification.

Many surface waters in the areas of Colorado and Utah where Green River oil shale occurs have been characterized using DOC fractionation analysis because of projected development of the oil shale resources. The Colorado District, U.S. Geological Survey has DOC fractionation data on most surface waters occurring in the Piceance Creek Basin, and the Utah District, U.S. Geological Survey, has similar data for surface waters in the White River Basin in Utah. The Area Oil Shale Office, Conservation Division, U.S. Geological Survey in Grand Junction, Colorado, has specified DOC fractionation analyses in the interim and production water-monitoring standards for development of the leased tracts C-a and C-b.

In field studies not related to fossil fuel development, the Bureau of Reclamation is using DOC fractionation analysis to characterize organic solutes in irrigation-return water before and after pretreatmnt for reverse-osmosis desalinization, at their experimental desalinization facility near Yuma, Arizona. Lastly, a study of the natural organic solutes which occur in the "black waters" of the Rio Negro River Basin in Brazil is being conducted by the primary author of this report. DOC fractionation analyses of these "black waters" are being used to compare and contrast the natural organic solute distributions in tropical waters versus organic solute distributions in surface waters formed in temperate climates.

A useful tool for detecting changes in organic-solute distributions as measured by DOC fractionation is to plot the data on a two-dimensional diagram as shown in figure 3. The shape of the polyhedron indicates the DOC distribution among the six fractions, and the area inside the polyhedron indicates the magnitude of the total DOC. The inspiration for this diagram came from the Stiff diagram (Stiff, 1951) used to plot distributions of major inorganic solutes. The data for figure 3 were taken from the example analysis for DOC fractionation given previously.

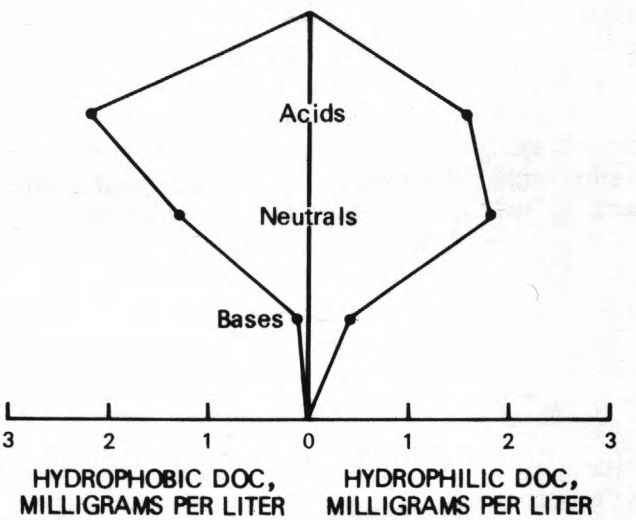

Figure 3.—Polyhedron representation of DOC fractionation data.

Research studies

Because DOC fractionation analysis is a fractionation based on sorption, the most logical research application is for studies on organic-solute sorption in aqueous systems. The report by Stuber and Leenheer (1978) describes how preparative-scale DOC fractionation methodology was used to study sorption of oil-shale retort-water organic solutes on processed oil shale. Analytical-scale DOC fractionation analysis is presently being used by the primary author of this report to study organic-solute sorption from oil-shale retort water onto soil sorbents.

Modifications of the preparative-scale DOC fractionation are being used by the junior author in conjunction with the Laramie Energy Technology Center, U.S. Department of Energy, and by Battelle Pacific Northwest Laboratories to generate organic solute fractions from oil shale retort waters for use in their toxicology testing programs. Analytical-scale DOC fractionations are used in these programs to assess and evaluate the preparative-scale fractionation.

Research into the nature of the hydrophobic solute fraction of DOC fractionation analysis has been reported by Thurman, Malcolm, and Aiken (1978). They developed a predictive capability for determining the sorptive-capacity factors of hydrophobic solutes on Amberlite XAD-8 based upon the solubility of organic solutes in water. A related report (Thurman, Aiken, and Malcolm, 1978) describes the use of Amberlite XAD resins to preconcentrate hydrophobic acids in water, and Amberlite XAD-8 appears to be the best sorbent for natural organic acids in water.

Future research

The greatest research need for DOC fractionation methodology is to better define the composition of the organic solutes in each of the six fractions. The procedure was developed using low molecular-weight organic compound mixtures dissolved in water containing simple inorganic salt matrixes. DOC fractionation analyses are being applied to natural waters containing high molecular-weight organic solutes; and to waste waters where solute-solute interactions at high solute concentrations, and complex salt matrixes alter the fractionation.

Lastly, DOC fractionation data could be used in mathematical models of organic solute transport of organic wastes in ground water. DOC fractionation analysis should present useful data on sorption coefficient parameters needed in mathematical models because it is an analysis based on sorption phenomena.

REFERENCES CITED

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

Stiff, H. A., Jr., 1951, The interpretation of chemical water analysis by means of patterns: J. Petrol. Technol., p. 15.

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

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

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

☆GPO 678-932