

### Acknowledgment

We thank Dr. Welby G. Courtney for his valuable suggestions in editing the manuscript.

### Literature Cited

- (1) Engelmann, R. J. "The Hartford Raindrop Sampler and Selected

- Spectra"; AEC Res. and Dev. Rep. HW-73119, 1962.  
(2) Martin, A.; Barber, F. R. *Atmos. Environ.* **1974**, *8*, 325.  
(3) Cheng, L. *Ind. Eng. Chem. Process Des. Dev.* **1973**, *12*, 221.  
(4) Cheng, L. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 192.  
(5) Cheng, L. *Environ. Sci. Technol.* **1977**, *11*, 192.  
(6) Gunn, R.; Kinzer, G. D. *J. Meteorol.* **1949**, *6*, 243.

Received for review July 2, 1979. Accepted November 21, 1980.

## Preparative Isolation of Aquatic Humic Substances

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■ A useful procedure has been developed which utilizes adsorption chromatography followed by size-exclusion chromatography, hydrogen saturation by ion exchange, and lyophilization to obtain low-ash aqueous humic substances. The preparative concentration of aquatic humic substances is done by multiple reconcentration procedures even though initial concentrations of aqueous humus may be less than 25  $\mu\text{g/L}$ . The procedure yields concentration factors of 25 000 times for both humic and fulvic acid in water.

### Introduction

Aquatic humic substances are polar, straw-colored, organic acids that are derived from soil humus and terrestrial and aquatic plants. They generally comprise one-third to one-half of the dissolved organic carbon (DOC) in water. The role of humic substances in water chemistry is receiving increasing attention because humic substances are known to complex trace metals (1); they are a source of methyl groups for the production of chlorinated methanes in water treatment (2); and they are implicated in the complexation or solubilization of pesticides and hydrocarbons in the aqueous environment (1, 3). For researchers interested in the role of humic substances in water chemistry, it is often necessary to isolate preparative amounts of aqueous humus. Because the concentration of humic substances in water rarely exceeds 5 mg/L DOC, very large volumes of water (1000 L) must be processed in order to obtain gram quantities of humic substances. Although humic substances have been isolated from water by various methods including precipitation (4, 5), ultrafiltration (6), solvent extraction (7), and freeze-drying (8), there were no simple analytical techniques to remove and concentrate humic substances from large volumes of water until the recent development of macroporous resins for adsorption chromatography (9–13). Since the development of these resins, the theory of adsorption chromatography onto macroporous resins and the usefulness of these resins for removing trace organic solutes from water have been thoroughly examined (10, 14–25).

Methods of resin adsorption for isolation of aquatic humic substances are superior to the above-mentioned procedures (4–8), because they are quantitative by dissolved organic carbon analysis, they do not use organic solvents in preparation but isolate humus directly from water, they are simple and rapid for large volumes, and they separate the humic material from the inorganic substances in water. A disadvantage of these methods is the possible incorporation of organic matter from the adsorbent; therefore, careful resin cleanup is required.

This report presents the use of macroporous resins to obtain preparative quantities of low-ash, aquatic humic substances by adsorption chromatography, ion exchange, and lyophilization.

This method is novel, not in the use of macroporous resins but in the use of multiple cycles of adsorption and desorption to concentrate aquatic humus from water and to separate it from inorganic solutes and nonacidic organic components. With multiple recycling of eluates, preparative amounts of humic substances from groundwater are concentrated with original concentrations of aquatic humus of less than 50  $\mu\text{g/L}$  DOC.

### Experimental Procedures

**Resin Cleaning.** Amberlite XAD-8 resin (40–60 mesh which was obtained in cubic-foot quantities from Rohm and Haas) was extracted in a 4-L beaker with 0.1 N NaOH. Fines were decanted off after each daily rinsing of NaOH for 5 successive days. The DOC of the rinse dropped off exponentially from 1000 mg/L to 10 mg/L during this period. Next, the resin was Soxhlet-extracted sequentially for 24 h with methanol, diethyl ether, acetonitrile, and methanol and stored in methanol until used. Before column packing, methanol was rinsed from the resin with distilled water by using a slurry technique in a large beaker. The resin is packed as a methanol-water slurry and then rinsed with distilled water until free of methanol (less than 2 mg/L DOC), requiring ~50 bed volumes of water. The packed column is now rinsed 3 times, alternating from 0.1 N NaOH to 0.1 N HCl; this removes impurities which may otherwise be incorporated into the sample. It is paramount that this rinse precede sample application.

Glenco glass columns (3500 series) with 10-, 1-, and 0.25-L volumes were used for column chromatography, and samples were pumped with either a Cole-Palmer Masterflex pump or a Pharmacia peristaltic P-3 pump. Water was filtered through Millipore stainless-steel, 142-mm, plate filters fitted with Ag filters (Selas Flotronics).

**Procedure.** The procedure is outlined in Table I, and an example is included for clarity. The procedure begins with collection of the water sample in glass bottles with volumes of 4, 20, and 48 L, depending on the concentration of humic substances in the water and on the amount of aquatic humus required. The sample is then filtered through a silver-membrane filter (0.45 micrometer) to remove suspended matter (26). After filtration, the pH of the sample is lowered to 2.0 with concentrated HCl and pumped through a column of XAD-8 resin at 15 bed volumes per hour. The size of the XAD-8 column is chosen such that a solute with a  $k'$  (column-capacity factor) of 100 is 50% retained by the column. The  $k'$  is related to column size by the following equation:  $V_{EL} = 2V_O(1 + k')$ , where  $V_{EL}$  is the volume of sample that is applied to the column at 50% retention,  $V_O$  is the void volume of the column (60% of the bed volume), and  $k'$  is the column-capacity factor.

The hydrophobic acids (12) adsorbed onto XAD-8 are

**Table I. Isolation of Aquatic Humus by Adsorption Chromatography**

step	procedure	example
1	Silver filter water and lower pH to 2.0 with HCl.	Filter 150 L of river water (aquatic humus is ~4 mg/L) and add 120 mL of HCl.
2	Pass sample through column of XAD-8 resin.	Apply 150 L of water to a 1200-mL column (5 × 60 cm) of XAD-8.
3	Elute column with 0.1 N NaOH in reverse direction.	Elute column with 3 void volumes (1800 mL) of 0.1 N NaOH.
4	Acidify eluates and recycle through smaller XAD-8 column.	Acidify the eluate to pH 2 (1800 mL) and adsorb on a 60-mL column of XAD-8. Desorb with 108 mL of 0.1 N NaOH.
5	Chromatograph NaOH eluate on Enzacryl Gel with 0.1 N NaOH mobile phase.	Chromatograph 3 mL of eluate on 300-mL (2.5 × 60 cm) column of Enzacryl gel.
6	If low-molecular-weight acids are present, separate sample on this column, then reconcentrate on XAD-8 column.	Chromatograph remainder (105 mL) of eluate, 3 mL per run, if low-molecular-weight acids are present. Reconcentrate on 60-mL XAD-8 column.
7	Make humic/fulvic split at pH 1. Centrifuge and readsorb fulvic acid fraction on XAD-8. Rinse humic acid (HA) fraction with water until AgNO <sub>3</sub> test shows no Cl. Dissolve HA in 0.1 N NaOH and hydrogen saturate.	Add 2 mL of concentrated HCl to 108 mL of eluate, settle for 24 h, and centrifuge. Wash HA with water until free of Cl. Dissolve HA in 0.1 N NaOH and immediately hydrogen saturate (step 9). Dilute HA with water so that DOC is ~100 mg/L. This prevents precipitation of HA in ion-exchange resin.
8	Remove excess sodium chloride from fulvic acid (FA) in final XAD-8 reconcentration. 1. Apply FA at pH 2.0. 2. Rinse with 1 bed volume of water. 3. Reverse flow and elute column with 0.1 N NaOH.	Concentrate the 110 mL of FA eluate on a 20-mL column of XAD-8. Rinse with 20 mL of deionized water; reverse elute with 36 mL of 0.1 N NaOH.
9	Pass FA eluate through cation-exchange resin and hydrogen saturate. Pass HA in 0.1 N NaOH through cation-exchange resin and hydrogen saturate.	Pass the 36 mL of eluate through a 5-mL column of AG-MP-50 cation-exchange resin in hydrogen form. Rinse with 1 bed volume (5 mL) of deionized water.
10	Lyophilize sample to a low-ash aquatic humus.	Freeze-dry the 41 mL of sample in hydrogen form; 100% recovery of aquatic humus yields 600 mg.

eluted in reverse direction with 0.1 N NaOH at a flow rate of 5 bed volumes per hour. To enhance recoveries, the sample which elutes ahead of the NaOH eluate monitored by pH is saved and is recycled through the XAD-8 column with the sample from the next run. The total eluate (from all adsorption passes) is acidified and is recycled through the concentration process on a XAD-8 column.

Next, a 3-mL aliquot of the reconcentrate is passed through a 300-mL Enzacryl gel (Aldrich Chemical, Milwaukee, WI) column (27) to separate the humic substances from low-molecular-weight acids. If the low-molecular-weight acids constitute a significant part of the concentrate, the entire sample is fractionated. Because gel filtration dilutes the sample, each fraction is concentrated on XAD-8 at a pH of 2.0 and eluted with 0.1 N NaOH.

The reconcentrate from gel chromatography is adjusted to a DOC of 500 mg/L and a pH of 1.0 with concentrated HCl. After precipitating for 24 h, the sample is centrifuged. The material in solution is fulvic acid and the precipitate is humic acid. The fulvic acid is readsorbed onto XAD-8, and excess NaCl (from acidification during humic/fulvic split) is removed during this final reconcentration by rinsing the column with one bed volume of deionized water after all of the sample is adsorbed. The water will begin to elute the adsorbed organic acids (monitored by DOC and conductivity); at this time flow

is stopped and elution is reversed with 0.1 N NaOH as the eluent.

The humic acid precipitate is washed several times with deionized water and is centrifuged to remove excess NaCl and HCl. Next the humic acid is dissolved in a minimum amount of 0.1 N NaOH. Both the sodium humate and the sodium fulvate are passed through a strong cation exchange resin (AgMP-50) in the hydrogen-saturated form to convert the sodium salt of the acid to its free-acid form. Ca. 2.5 times more exchange resin in the hydrogen form is used than is required. The hydrogen-saturated acids are then freeze-dried to a low-ash form (28).

#### Results and Discussion

**Adsorption Chromatography.** The column distribution coefficients (*k*'s) of the majority of aquatic and soil humic

**Table II. Sample Volumes for Reconcentration vs. DOC of Sample**

Input DOC of sample, mg/L	no. of bed volumes of sample passed through column before breakthrough
5	50
25	30
50	25
100	15
200	10
500	5

**Table III. Recycling and Recovery Factors**

no. of recycles	humic concn (DOC)	recovery factor, %
Groundwater Sample, Superior, CO <sup>a</sup>		
0	20 µg/L	
1	1 mg/L	95
2	25 mg/L	90
3	500 mg/L	86
4	1500 mg/L	82
Surface Water (South Platte River), Denver, CO <sup>b</sup>		
0	1 mg/L	
1	150 mg/L	95
2	500 mg/L	90
Surface Water (Suwanee River), Fargo, GA <sup>c</sup>		
0	30 mg/L	
1	1000 mg/L	95

<sup>a</sup> Concentration factor is 25 000 times with a recovery of 80% or better.

<sup>b</sup> Concentration factor is 500 times with a recovery of 90% or better. <sup>c</sup> Concentration factor is 33 times with a recovery of 95% or better.

**Table IV. Test Compounds Separated from Fulvic Acid Solutions by Size-Exclusion Chromatography on Enzacryl Gel**

benzoic acid	cyclohexanecarboxylic acid
valeric acid	<i>p</i> -toluic acid
caproic acid	phenol
heptanoic acid	chlorophenol
octanoic acid	methylacrylic acid

substances at a pH of 2.0 are between 500 and 2000 (25); therefore, aquatic humus is quantitatively adsorbed when a  $k'$  of 100 is used. For most unpolluted, uncolored surface water, XAD-8 resin removes 30–50% of the DOC. The material which desorbs from the column in 0.1 N NaOH has been designated the hydrophobic-acid fraction (12, 13). In colored surface waters, adsorbed DOC that is recovered by XAD-8 resin will vary from 50% to 90% as hydrophobic acids.

The desorption is in reverse direction in order to increase the recovery of hydrophobic acids from the resin, and solutes with  $k'$ 's as large as 25 in the ionic state are efficiently removed. The hydrophobic acids (including humic substances) are desorbed because of ionization (13, 23, 24). This eluate of NaOH represents the first concentrate from the column. Depending on the initial concentration of humic substances in the water sample, this eluate will vary in concentration from 1 to 100 mg/L DOC. The initial two void volumes remove ~95% of the humic material, based on previous studies (25), and the next three void volumes remove another 2–5%. The hydrophobic acids have now been concentrated ~20 times overall, and the initial two void volumes are concentrated 50 times.

The resin-to-sample-volume ratios will change depending on the DOC of the input solution. Table II shows column sizes necessary to recover all of the hydrophobic acids as a function of DOC; it was derived empirically from reconcentrations of humic substances. Because the isotherm of the adsorption of hydrophobic acids on XAD-8 resin is L-shaped (15, 29), the capacity of the column drops off with increasing concentration. Therefore, much smaller volumes must be recycled for 100% recoveries. It is a good practice to collect the effluent during reconcentration and to monitor its DOC. If any significant breakthrough is occurring in the recycle process, it will be noted as an increasing DOC. In some groundwater samples, the recycling process has been repeated 4 times to achieve the concentration necessary for preparative separations. Table III shows recycling and recovery factors for several samples of groundwater and surface waters.

**Gel Chromatography.** Because there may be hydrophobic acids present in the eluate which are not humic substances, a 2-mL aliquot of the reconcentrate is passed through a 300-mL Enzacryl gel column to separate the humic substances from low-molecular-weight acids. The separation is based primarily on molecular size; however, organic acids with more than three charged sites per molecule may also separate by

charge exclusion (27). Because the mobile phase in gel chromatography is 0.1 N NaOH, the humic material is quantitatively removed from the column and adsorption by the gel has not been found, with recoveries of humic materials ~100% (27). At pH 13, the phenolic functional groups in the aquatic humus are ionic. This accomplishes two things. First, the phenolic functional group cannot hydrogen bond with the amide linkage of the resin, because the hydrogen atom is removed. And second, the humic molecule has increased solubility due to ionization of the functional group. Therefore, adsorption of the aquatic humus does not readily occur. This was confirmed with several different aquatic humic substances isolated from surface waters and groundwater. Finally, the Enzacryl gel is recommended, rather than a dextran gel (for example, Sephadex), because of its stability at pH 13 and good flow rates (1 bed volume per hour). The gel did not fractionate the humic substances; however, low-molecular-weight acids do separate (Table IV). Because the gel-filtration process is one of dilution, the humic substances are reconcentrated on the XAD-8 resin after gel filtration. The higher-molecular-weight substances (considered aquatic humus) elute first, at 110 mL, and if low-molecular-weight acids ( $M < 200$ ) are present, they will elute as a second peak at 150–200 mL.

Most concentrates of hydrophobic acids from natural waters do not need Enzacryl gel chromatography because low-molecular-weight acids are less than 5% of the concentrate of hydrophobic acids. When the concentration of humic substances in water is less than 0.5 mg C/L (as in groundwater), the possibility increases that low-molecular-weight acids are a greater proportion of the hydrophobic acids. If low-molecular-weight acids are present, the entire concentrate is fractionated on the Enzacryl gel column. If they are not present, which is commonly the case for surface waters, the sample is now ready for the humic/fulvic acid split.

**Humic/Fulvic Split, Cation Exchange, and Lypholization.** After reconcentration from gel chromatography the humic/fulvic split is made. The humic/fulvic split is defined (consistent with the nomenclature of soil chemistry) as humic substances which are soluble in base and acid (fulvic acid) or soluble in base and insoluble in acid (humic acid).

Because of the recycling process, excess NaCl, present in the acidified sample, would be converted to HCl in the cation-exchange resin. This excess HCl will not entirely lypholize, and it will create problems. A rinse with deionized water will elute the NaCl from the column containing the adsorbed aquatic humus, because the organic acids elute more slowly; they will not coelute with the NaCl. This process will rid the sample of excess NaCl, and the sodium humates and fulvates will exchange with hydrogen during ion exchange, leaving only the free acids in water which are freeze-dried to a low-ash form.

### Conclusions

The procedure outlined above, and shown in Table I, has been used to concentrate humic substances from various types of water samples, including river waters and groundwaters.

**Table V. Elemental Analyses of Humic Concentrates from Freshwaters**

sample	C	H	N	O	P	S	ash
Suwanee River fulvic acid (22 mg C/L)	54.65	3.71	0.47	39.28	0.20	0.50	0.95
Suwanee River humic acid (8 mg C/L)	57.24	3.94	1.08	39.13	0.20	0.63	0.56
Biscayne groundwater fulvic acid (6 mg C/L)	55.44	4.17	1.77	35.39	0.20	1.06	0.43
Biscayne groundwater humic acid (2.5 mg C/L)	58.28	3.39	5.84	30.14	0.22	1.43	0.10
Laramie-Fox Hills groundwater fulvic acid (0.050 mg C/L)	62.67	6.61	0.42	29.14	0.20	0.44	1.09
Laramie-Fox Hills groundwater humic acid (0.030 mg C/L)	62.05	4.92	3.21	23.45	0.46	0.96	5.12

The elemental analysis of humic substances isolated from the Suwannee River in southern Georgia, from the Biscayne groundwater near Miami, FL, and the Laramie-Fox Hills groundwater, Superior, CO, are shown in Table V. Typically, ash contents are less than 1% by this method (only exception is the humic acid from Laramie-Fox Hills groundwater). Therefore, it is possible to concentrate humic substances and purify them from the bulk of inorganic constituents in water, even when the DOC of the water is 0.7 mg C/L, and the humic concentration is 50  $\mu\text{g/L}$  DOC.

#### Literature Cited

- (1) Schnitzer, M.; Kahn, S. U. "Humic Substances in the Environment"; Marcel Dekker: New York, 1972.
- (2) Rook, J. J. *Environ. Sci. Technol.* **1977**, *11*, 478.
- (3) Van Vleet, E. S.; Quinn, J. G. *Environ. Sci. Technol.* **1977**, *11*, 1086.
- (4) Jeffrey, L. M.; Hood, D. W. *J. Mar. Res.* **1958**, *17*, 247.
- (5) Martin, F. D.; Pierce, R. H., Jr. *Environ. Lett.* **1971**, *1*, 49.
- (6) Gjessing, E. T. *Environ. Sci. Technol.* **1970**, *4*, 437.
- (7) Eberle, S. H.; Schweer, K. H. *Vom Wasser* **1974**, *41*, 27.
- (8) Malcolm, R. L. *Geol. Surv. Prof. Pap. (U.S.)* **1968**, *600-C*, 211.
- (9) Riley, J. P.; Taylor, D. *Anal. Chim. Acta* **1969**, *46*, 307.
- (10) Mantoura, R. F. C.; Riley, J. P. *Anal. Chim. Acta* **1975**, *76*, 97.
- (11) Weber, J. H.; Wilson, S. A. *Water Res.* **1975**, *9*, 1079.
- (12) Leenheer, J. A.; Huffman, E. W. D., Jr. *J. Res. U.S. Geol. Surv.* **1976**, *4*, 737.
- (13) Malcolm, R. L.; Thurman, E. M.; Aiken, G. R. *Trace Subst. Environ. Health* **1977**, *11*, 307.
- (14) Gustafson, R. L.; Albright, R. L.; Heisler, J.; Lirio, J. A.; Reid, O. T. *Ind. Eng. Chem. Prod. Res. Dev.* **1968**, *7*, 107.
- (15) Simpson, R. "The Separation of Organic Chemicals from Water"; Rohm and Haas: Philadelphia, PA, 1972.
- (16) Burnham, A. K.; Calder, G. V.; Fritz, J. S.; Junk, G. A.; Svec, H. J.; Willis, R. *Anal. Chem.* **1972**, *44*, 139.
- (17) Grieser, M. D.; Pietrzyk, D. J. *Anal. Chem.* **1973**, *45*, 1348.
- (18) Junk, G. A.; Richard, J. J.; Grieser, M. D.; Witiak, D.; Witiak, J. L.; Arguello, M. D.; Vick, R.; Svec, H. J.; Fritz, J. S.; Calder, G. V. *J. Chromatogr.* **1974**, *99*, 745.
- (19) Chu, C.; Pietrzyk, D. J. *Anal. Chem.* **1974**, *46*, 330.
- (20) Pietrzyk, D. J.; Chu, C. *Anal. Chem.* **1977**, *49*, 757.
- (21) Pietrzyk, D. J.; Chu, C. *Anal. Chem.* **1977**, *49*, 860.
- (22) Pietrzyk, D. J.; Kroeff, E. P.; Rotsch, T. D. *Anal. Chem.* **1978**, *50*, 497.
- (23) Thurman, E. M.; Aiken, G. R.; Malcolm, R. L. "Proceedings of the 4th Joint Conference on Sensing of Environmental Pollutants", 1977.
- (24) Thurman, E. M.; Malcolm, R. L.; Aiken, G. R. *Anal. Chem.* **1978**, *50*, 775.
- (25) Aiken, G. R.; Thurman, E. M.; Malcolm, R. L. *Anal. Chem.* **1979**, *51*, 1799.
- (26) Malcolm, R. L.; McKinley, P. W. "Methods for Analysis of Organic Substances in Water"; Goerlitz, D. F.; Brown, E., Eds.; U.S. Geological Survey Techniques of Water Resources Investigations Supplement I, 1972.
- (27) Thurman, E. M.; Malcolm, R. L. *Geol. Surv. Water-Supply Pap. (U.S.)* **1979**, No. 1817-G.
- (28) Malcolm, R. L. *J. Res. U.S. Geol. Surv.* **1976**, *4*, 37.
- (29) Gustafson, R. L.; Paleos, J. "Interactions Responsible for the Selective Adsorption of Organics on Organic Surfaces". In "Organic Compounds in Aquatic Environments"; Faust, S. J., Ed.; Marcel Dekker: New York, 1971.

Received for review July 2, 1980. Accepted December 12, 1980. The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

## Impact of Fossil Fuel Combustion on the Sediments of Lake Michigan

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■ The inputs of metals to a southern Lake Michigan sediment covary with the fluxes of charcoals whose morphologies and surface characteristics are indicative of different combustion processes—oil, coal, and wood burning. Sn, Cr, Ni, Pb, Cu, Co, Cd, Zn, and Fe showed increasing concentrations in sediments deposited between ca. 1930 and 1968, after which time they showed slight decreases in concentration. A similar profile was found for the total charcoal concentration. The maximum appears to be a consequence of the installation of improved control devices to remove fly-ash from the stack gases. During the time period following the maximum, there are reported lower levels of total suspended particulates in the terrestrial atmosphere adjacent to Lake Michigan. The increased metal and charcoal concentrations in recent sediments were accompanied by increased numbers of magnetic spherules of fly-ash.

#### Introduction

Natural and anthropogenic combustion processes mobilize a large variety of materials about the environment. Some of these materials may be toxic to living organisms or may degrade the environment; others may be innocuous. Since the nature of the combustion process often determines the types of materials released and since there is a very large number

of such processes, the fluxes of the combustion products to the environment can best be ascertained through field, as opposed to laboratory, studies. It was with this view in mind that we initiated an investigation of the combustion products in the sediments of Lake Michigan (1).

The deposits of Lake Michigan have received solid phases from a variety of combustion processes over the past century or two. Natural wood and brush burning were dominant before the 19th century. Forest clearance appears to have begun in the early 1800s on the basis of pollen studies and geochronological investigations (2, 3). Coal combustion becomes evident in the sedimentary record at the beginning of the 20th century through the characteristic morphologies and dimensions of the associated charcoal (1). Oil combustion charcoals were identified in strata deposited after 1928. In 1971, coal and oil burning contributed 6.4 and 1.4%, respectively, to the atmospheric particulates (4).

In our previous report, the morphologies and dimensions of the carbon particles indicated that in the period 1953–1978 ~76% had an origin in coal burning, 14% in oil burning, and 10% in wood burning. Before this work, several investigations emphasized the importance of coal burning (5, 6). The latter workers argued that 95% of the lead in the sediments of Lake Michigan could be accounted for by coal and gasoline combustion; over 95% of the lead dispersed was transported to the deposition site from land through the atmosphere.