A Filtration and Column-Adsorption System for Onsite Concentration and Fractionation of Organic Substances from Large Volumes of Water

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UNITED STATES DEPARTMENT OF THE INTERIOR

WILLIAM P. CLARK, Secretary

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

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FACTORS FOR CONVERTING INCH-POUND UNITS TO INTERNATIONAL SYSTEM OF UNITS (SI)

The International System (SI) is a consistent system of metric units adopted by the Eleventh General Conference of Weights and Measures in 1960. Selected factors for converting inch-pound units used in this report to SI units given below.

INCH–POUND UNITS	Multiply BY	TO OBTAIN SI UNITS
Length		
micrometer (μm)	0.00003937	inch (in.)
centimeter (cm)	.3937	inch (in.)
meter(m)	3.281	foot (ft)
kilometer (km)	.6214	mile (mi)
Volume		
milliliter (mL)	.03382	ounce, fluid (oz)
liter (L)	.2642	gallon (gal)
Flow		
liters per minute (L/min)	.2642	gallons per minute (gal/min)
Mass		
gram (g)	.03527	ounce, avoirdupois (oz)
Temperature		
degree Celsius (°C)	$F=9/5°C+32$	degree Fahrenheit (°F)
Specific conductance		
microsiemens per centimeter at 25°Celsius (μS/cm at 25°C)	1.000	micromho per centimeter at 25°Celsius (μmho/cm at 25°C)
Pressure		
bars (b)	14.5038	pounds per square inch (lb/in.^{2})

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By J. A. Leenheer *and* T. I. Noyes

ABSTRACT

A portable filtration and column-adsorption system which can concentrate suspended sediment and dissolved-aqueous organic substances onsite was developed. Organic solutes also are fractionated into hydrophobic- and hydrophilic-acid, base, and neutral fractions. Subsequent isolation of organic solutes from fraction concentrates and extraction of organic constituents in suspended sediment entrained on filter tubes is performed by a variety of procedures in the laboratory. Three surface-water samples and one ground-water sample ranging in volume from 300 to 1,100 liters were processed through the filtration and column-adsorption system, yielding from about 0.8 to 3.0 grams of recovered organic carbon per sample.

INTRODUCTION

Organic constituents of natural surface and ground waters usually comprise only 1 to 10 percent of the dissolved and suspended solids in these waters. Therefore, any research of organic constituents in water requiring significant quantities of material (100 mg (milligrams) to 10 g (grams)) also requires processing hundreds to thousands of liters of water to obtain sufficient study material. Water-processing procedures may involve sediment removal, solute concentration, solute fractionation, organic- and inorganic-constituent separation, and drying. The most important water-processing procedure is the concentration process; the other procedures are more manageable when the water volume has been decreased.

Previous organic-constituent-isolation procedures from water have used solvent extraction (Wu and Suffet, 1977), adsorption chromatography (Thurman and Malcolm, 1981), evaporation (Katz and others, 1972), freeze drying (Malcolm, 1968), freeze concentration (Shapiro, 1961), and reverse osmosis (Deinzer and others, 1975). However, most of these procedures have one or more of the following limitations: (1) Lack of capability to process a sufficient volume of water; (2) no discrimination between organic and inorganic constituents; and (3) noncomprehensiveness for all organic constituents.

Recently a comprehensive approach to the isolation of dissolved organic constituents from water was devised, based upon adsorption chromatography (Leenheer, 1981). This report will detail how this comprehensive approach, called preparative dissolved-organic-carbon fractionation, was scaled to process large volumes of water at the sampling site with added filtration devices to remove and recover suspended-sediment constituents.

CONSTRUCTION OF FILTRATION AND COLUMN-ADSORPTION SYSTEM

The filtration and column-adsorption system is housed in a mobile laboratory for onsite operation. A flow diagram of water delivery to and from the mobile laboratory is shown in figure 1A, and water flow through the filtration and column-adsorption system is shown in figure 1B. The various organic-solute fractions obtained from the adsorption columns are shown in the flow chart of figure 2.

A water-submersible centrifugal pump (Little Giant Model 3E–12NDVR*) was used to deliver untreated water to the overflow reservoir inside the laboratory. This pump could deliver about 5 L/min (liters per mitute) at a 6-m (meter) head of water. If more than a 6-m head of water is required at a sampling site, a more powerful pump would be necessary; a pumping rate of 5 L/min is the minimum requirement. The pump was equipped with a polypropylene screen to remove course particulate material, and the water-delivery tubing to the laboratory consisted of 1.77-cm (centimeter) O.D. × 1.33-cm I.D. Teflon tubing.

The overflow reservoir was built from a 49-L (liter) plastic carboy, with a 2.65-cm I.D. overflow port placed about half-height on the side of the carboy. Tygon tubing (2.65-cm I.D.) was used to transport excess water from the reservoir back to the body of water being sampled.

After water had passed through the filtration and column-adsorption system, it was delivered via 0.95-cm I.D. Tygon tubing to a 46-L glass collection jug, where the volume of water processed was measured. The jug was marked at 5-L intervals for volume measurement.
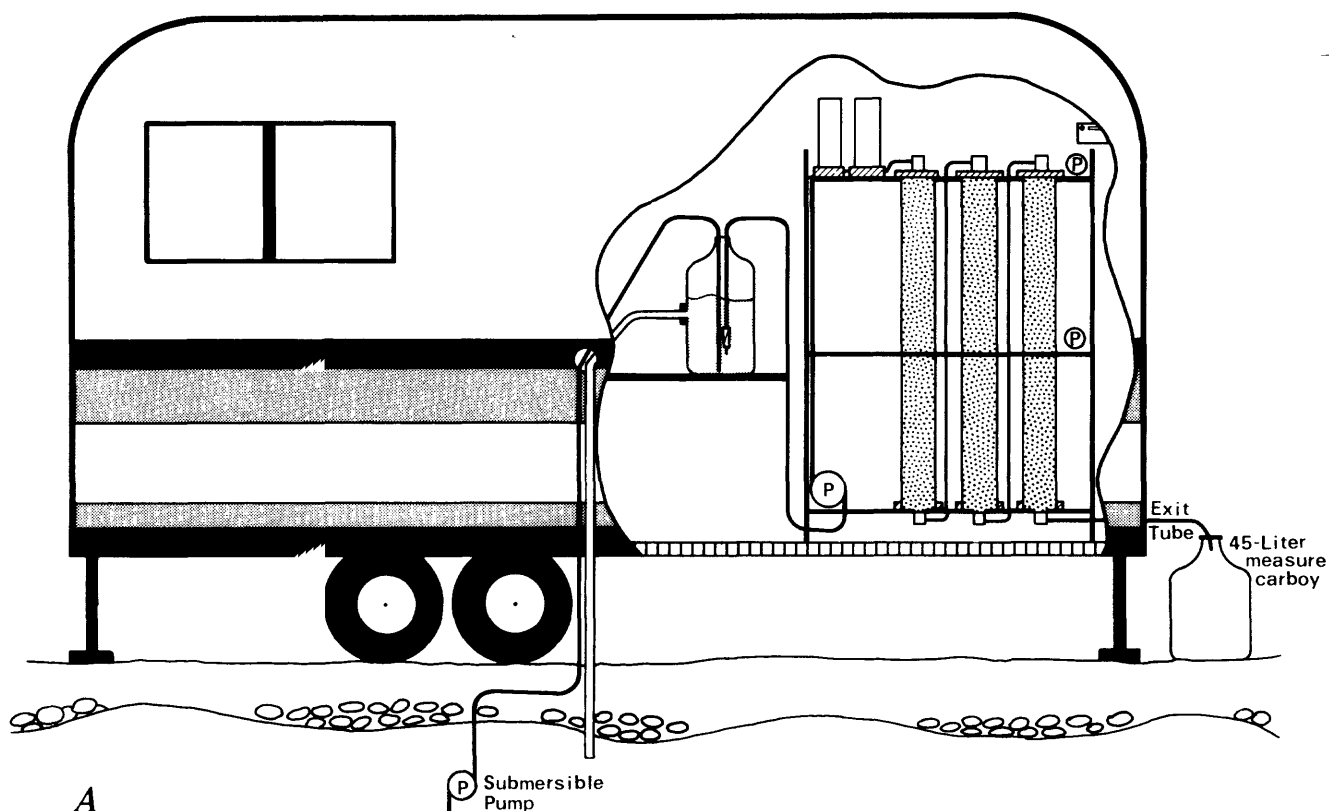
Figure 1. Flow of water A, through mobile laboratory and B, through filtration and column-adsorption system.

Three pumps were used on the filtration and column-adsorption system. A variable-flow, positive-displacement pump (Flotec Model R2S1–1104V) was used to pump water from the overflow reservoir through the filtration and column-adsorption system. This pump delivered about 2.75 bars of water pressure to the system, which resulted in a flow rate of about 3 L/min when the filters were not plugged with sediment. A peristaltic pump (Cole-Parmer Masterflex) was used to pump the reagents used to desorb each column. Teflon-lined, peristaltic-pump tubing (0.80-cm I.D.) was used at a flow rate of about 1 L/min. Finally, a small rotating-and-reciprocating piston pump (FMI Lab Pump Model RPSY) was used to infuse 10 N NaOH (sodium hydroxide) into a recirculating titration system for the anion-exchange and resin-desorption procedure.

The tubing used to connect the positive-displacement pump to the filters, valves, and columns was 1.90-cm O.D.×1.58-cm I.D. Teflon. The smaller-sized Teflon tubing (1.77-cm O.D.×1.33-cm I.D.) was used in conjunction with the peristaltic pump used in the column-desorption procedure. Lastly, 0.31-cm O.D.×0.16-cm I.D. Teflon tubing was used to infuse 10 N NaOH into the anion-exchange column.

The filtration system consisted of two stainless-steel, cartridge-filter units (Balston 20/35–800), connected in series between the pump and columns (fig. 1B). Each unit contained a glass-fiber filter tube 5.08-cm I.D.×22.86-cm long, with the glass fibers held together with an inorganic binder. The first filter unit after the pump contains a filter tube (Type DH) rated to retain 98 percent of particles 25 µm (micrometers) in diameter and the second filter unit contains a filter tube (Type AAH) rated to retain 98 percent of particles 0.3 µm in diameter.

The three glass columns containing the resin adsorbents were 10-cm I.D.×120-cm long, with Teflon end plates (Bethesda Research Labs No. 1307 TR). The column containing the XAD–8 resin had nylon mesh containing bottom-end plates at both ends of the column, to allow upward reverse elution without loss of resin beads into the column tubing. Bed volume of each column was 9,420 mL (milliliters).

Three-way, 1.27-cm I.D., PVC ball valves (Chemtrol Model B) were placed at the top and bottom of each column (fig. 1B) to interface the column-adsorption pumping system with the column-desorption pumping system. Four two-way, 1.27-cm I.D., union-ball valves (GSR–NSF–PWSE) were placed at the points indicated in figure 1B to bleed air from the tubing and columns as the adsorption- and desorption-pumping system was turned on. A 1.27-cm I.D. PVC foot valve with screen (GF type 050) was placed on the end on the inlet tubing from the

Stainless-steel filters

25 micrometers   0.3 micrometer

Specific-conductance meter and cell

Desorption pump (to inlets)

Desorption inlets

Air bleed   Air bleed   Air bleed

Overflow reservoir

Overflow to source

Foot valve

XAD-8   MSC-1-H   A-7

Sodium hydroxide infusion pump

Drain

10 $\underline{N}$ Sodium hydroxide

Adsorption pump

Air bleed

Desorption outlets

Desorption-pump intake

Exit tubing

B

EXPLANATION

ADSORPTION TUBING

DESORPTION TUBING

AIR BLEED TUBING

1-WAY VALVE

2-WAY VALVE

3-WAY VALVE

overflow reservoir to maintain the water pressure on the positive-displacement pump during filter-tube changes. A three-port Teflon valve with 0.32-cm O.D. Teflon tubing connectors (Bethesda 1320 YE) was connected to the air-bleed port on the top end plate of the column containing the Duolite A–7 resin, to allow both air bleed and regulation of the 10 N NaOH infusion into the column.

All connections to the Teflon tubing, pumps, columns, and filters were made with No. 316 stainless-steel pipe or Swagelok fittings, with the exception of the col-
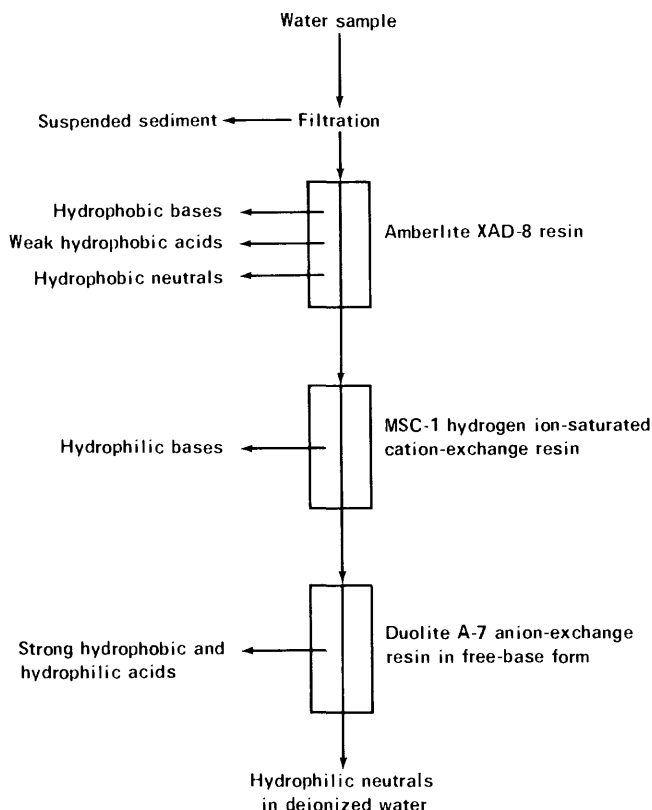
Water sample
↓
Suspended sediment ←——— Filtration
↓

Hydrophobic bases ←——
Weak hydrophobic acids ←——   Amberlite XAD-8 resin
Hydrophobic neutrals ←——

↓

Hydrophilic bases ←——   MSC-1 hydrogen ion-saturated
cation-exchange resin

↓

Strong hydrophobic and ←——   Duolite A-7 anion-exchange
hydrophilic acids   resin in free-base form

↓

Hydrophilic neutrals
in deionized water

Figure 2. Organic-solute fractions desorbed from column-adsorption system.

umn-desorption exit ports, where a Teflon tube-fitting union (Galtek SU8N, PSI–125) was used for quick disconnects of a section of 0.95-cm I.D. Teflon tubing used to deliver the desorbed sample to the collection bottles. Stainless-steel nipples were used to connect the peristaltic tubing to the desorption tubing leading to each of the three columns.

The required instrumentation was a specific-conductance meter, a pH meter, a magnetic stirrer, and a scale. The specific-conductance meter (capable of reading to 0.1 μS/cm (microsiemens per centimeter) at 25° Celsius) is used to monitor the water leaving the filtration and column-adsorption system. A small fraction of the flow is diverted by a pinch clamp on the Tygon tubing through a T connector to the specific-conductance flow cell. The pH meter and magnetic stirrer are used to monitor pH during the water-recycle desorption process of the column containing the Duolite A–7 resin. The scale (measuring to the nearest 0.1 g) is used to weigh the pellet reagent NaOH and concentrated H_2SO_4 (sulfuric acid) for preparation of reagent solutions.

The filtration and column-adsorption apparatus was mounted in a custom-made 1.90-cm thick plywood cabinet. Cabinet dimensions were 156-cm high, 71-cm wide, and 53-cm deep. The cabinet was left open in front for access and the three columns were vertically mounted

in a triangular arrangement with the XAD–8- and Duolite A–7-resin columns in front and the MSC–1–H-resin column in back. The cabinet is held together and the columns held in place by three shelves mounted at 25, 84, and 146 cm from the base. The two cartridge filters are mounted on the left side (facing the cabinet) of the top shelf with steel-plate reinforcement on top and bottom of the plywood under the filter units. The three steel-nipple inlets to the desorption tubing network are mounted through the right front side of the top shelf and are surrounded by a 25-cm high plexiglass shield to protect the operator from caustic desorption reagents, should the peristaltic-pump tubing become disconnected from the nipples. The peristaltic pump used for desorption is mounted on the back right side of the top shelf; the 10 N NaOH infusion pump is mounted on the front right side of the middle shelf; and the positive-displacement pump used to pump the water sample through the system is mounted on the front left side of the bottom shelf. A multiple-switched outlet strip was mounted on the outside of the left side of the cabinet to supply power to the various pumps and instrumentation. The cabinet was painted with an epoxy-based paint resistant to water and chemical reagents. Power was generated onsite by a 3.5-kW (kilowatt) AC generator.

Reagents required are 10 N, 1.0 N, and 0.1 N NaOH, concentrated H_2SO_4 and 2.0 N H_2SO_4 if the MSC–1 cation-exchange resin is regenerated onsite. Reagent-grade acid and base are used, and either reagent-grade water produced in the laboratory or the deionized water produced onsite by the column-adsorption system can be used as reagent water. Preparation and cleanup of the resin adsorbents are described in detail in a previous report (Leenheer, 1981) except 1 N NaOH needs to be substituted for 3 N NH$_4$OH (ammonium hydroxide) used previously. The MSC–1–H cation-exchange resin was substituted for the Bio-Rad AG–MP–50 resin used previously (Leenheer, 1981), because of its less expensive cost and similar properties.

OPERATION OF FILTRATION AND COLUMN-ADSORPTION SYSTEM

As the cleaned resins sit in water for long periods of time between various sample runs, significant quantities of organic bleed products accumulate and have to be rinsed from the columns immediately prior to the sample run. Each column needs to be individually rinsed with deionized water until the specific conductance of the effluent is less than 10 μS/cm. The three columns need not be rinsed in series, as the Duolite A–7 resin collects the resin bleed from the XAD–8 and MSC–1 resins. Resin-bleed contributions decrease during successive uses of the filtration and column-adsorption system.

Upon arrival of the mobile laboratory at the sam-

pling site, the submersible centrifugal pump is placed where a representative water sample can be obtained. The various delivery and exit tubing and electrical lines of the filtration and column-adsorption system are assembled, and the overflow reservoir is filled to the overflow point by turning on the submersible centrifugal pump. After assembling the filters and priming the positive-displacement pump, the inlet tubing with the foot valve is placed in the overflow-reservoir, and the positive-displacement pump is turned on at the switched outlet strip. Initially, the water flow is diverted through the bleed valve at the top of the XAD–8-resin column to allow air displacement from the filters and tubing. At this point, all the three-way valves are open to allow water flow through the columns, except the three-way valve at the top of the Duolite A–7-resin column, which is closed. After air is displaced, water flow through the system is begun by simultaneously closing the bleed valve and opening this three-way valve. The pump is run at full speed and the volume of water processed is determined by collection in the calibrated glass jug. Specific conductance of the processed water should stabilize between 0.5 and 3.0 μS/cm.

Initial water flow through the system should be between 2 and 3 L/min. When the flow slows to 0.5 L/min or less, the filters need to be changed. First, the pump speed is decreased to lessen the back pressure on the filter tubes when the pump is turned off; if this is not done, the filter tubes may split. Then, the pump is switched off and the three-way valve on top of the XAD–8-resin column is turned off. The filters are drained by removing the plugs from the drain ports, and the plugged filter tubes are removed, wrapped in aluminum foil, and stored for later processing of the suspended sediment. The system is started as before, and the filtration cycles are repeated until the specific conductance of the column effluent increases to 10–15 μS/cm, which denotes salt breakthrough from the ion-exchange columns.

After the adsorption run has been completed, the columns are individually desorbed to recover the organic solute. Weak hydrophobic acids (including phenols) are desorbed from the XAD–8-resin column by passing 2.5 L of 0.1 N NaOH, followed by 15 L of reagent water rinse in an upflow direction through the column. The peristaltic pump and desorption-tubing system is used for all column desorptions. The 17.5 L of eluate is neutralized to pH 7 with concentrated H_2SO_4 immediately after collection to prevent alkaline oxidation and hydrolysis reactions. A hydrophobic-base fraction also can be generated from the XAD–8-resin column by substituting 0.1 N HCl (hydrochloric acid) for the desorption reagent and 0.01 N HCl for the rinse. The hydrophobic-neutral fraction can be recovered by drying the XAD–8 beads after desorption of the previous two fractions, and after Soxhlet extraction with CH_3OH (methanol) as described in our previous report (Leenheer, 1981).
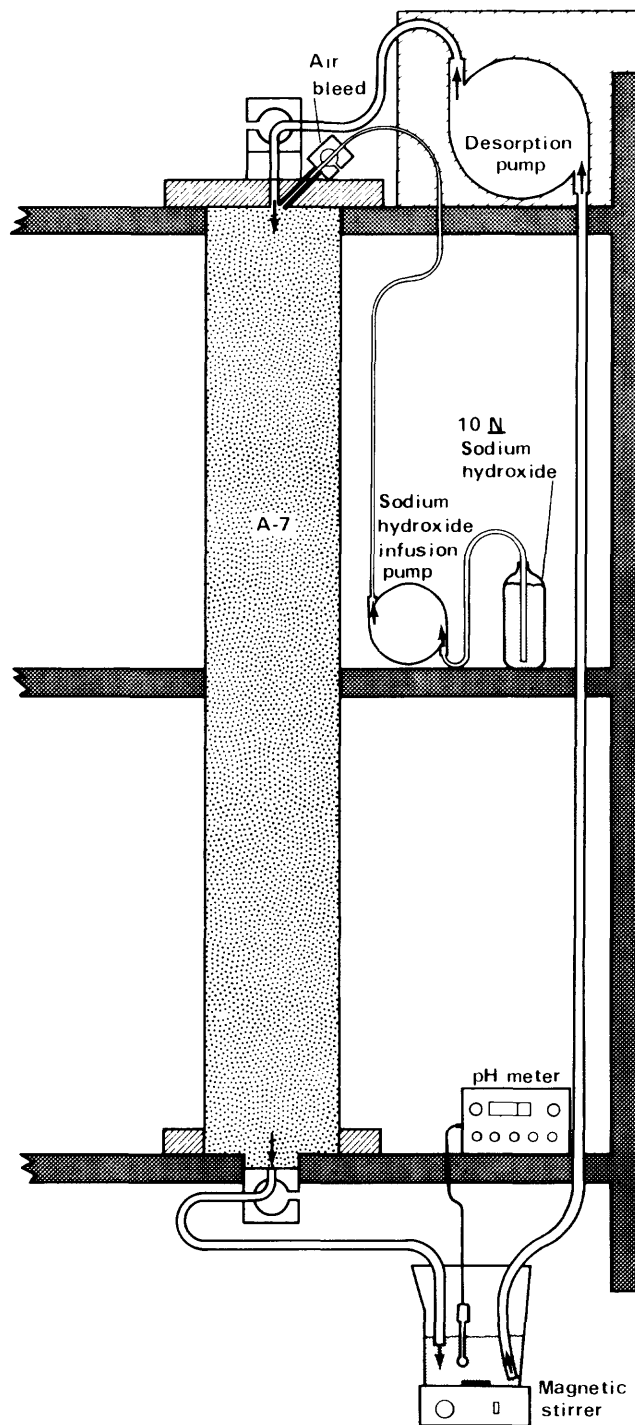
Figure 3. Recirculating titration system of column containing Duolite A–7 resin.

Hydrophilic bases are desorbed by passing 1.0 N NaOH in a downflow direction through the cation-exchange resin. At the point of base break-through, as detected by pH increases, fraction collection and reagent-water rinse are begun. A total of 15 L is collected, and this fraction also is neutralized to pH 7 with concentrated H_2SO_4.

EXPLANATION:

Chloride anion (Cl⁻)

Ethanol (CH₃OH)

Hydrochloric acid (HCl)

Hydrofluoric acid (HF)

Methanol (CH₃OH)

Silicic acid Si(OH)₄

Silicon tetrafluoride (SiF₄)

Silver chloride (AgCl)

Silver nitrate (AgNO₃)

Sodium (Na)

Sodium hydroxide (NaOH)

Sodium sulfate decahydrate (Na₂SO₄ × 10 H₂O)

Trifluoroacetic acid (CF₃COOH)

Water (H₂O)

Lastly, the Duolite A–7-resin column is desorbed by infusing 10 N NaOH into recycled column water, as diagrammed in figure 3. The pH of the recycled water is allowed to increase to pH 11.5, at which point infusion of 10 N NaOH is stopped; the recycle loop is broken; and desorbed strong hydrophobic acids and hydrophilic acids are eluted from the column in a downward direction, with 15 L of water. This fraction also is neutralized to pH 7 with concentrated H₂SO₄.

For most applications, one adsorption and desorption cycle generates sufficient material, so that multiple cycles are not necessary. However, the columns can be regenerated onsite and multiple runs performed. The XAD–8 and Duolite A–7 resins virtually are regenerated after the onsite desorptions, and they only have to be rinsed with water until their effluent specific conductances are 10 μS/cm or less. The MSC–1–H cation-exchange resin has to be hydrogen-saturated by passing 40 L of 2 N H₂SO₄ through the column, using the peristaltic pump, followed by distilled water, until the specific conductance of the effluent is 10 μS/cm or less.
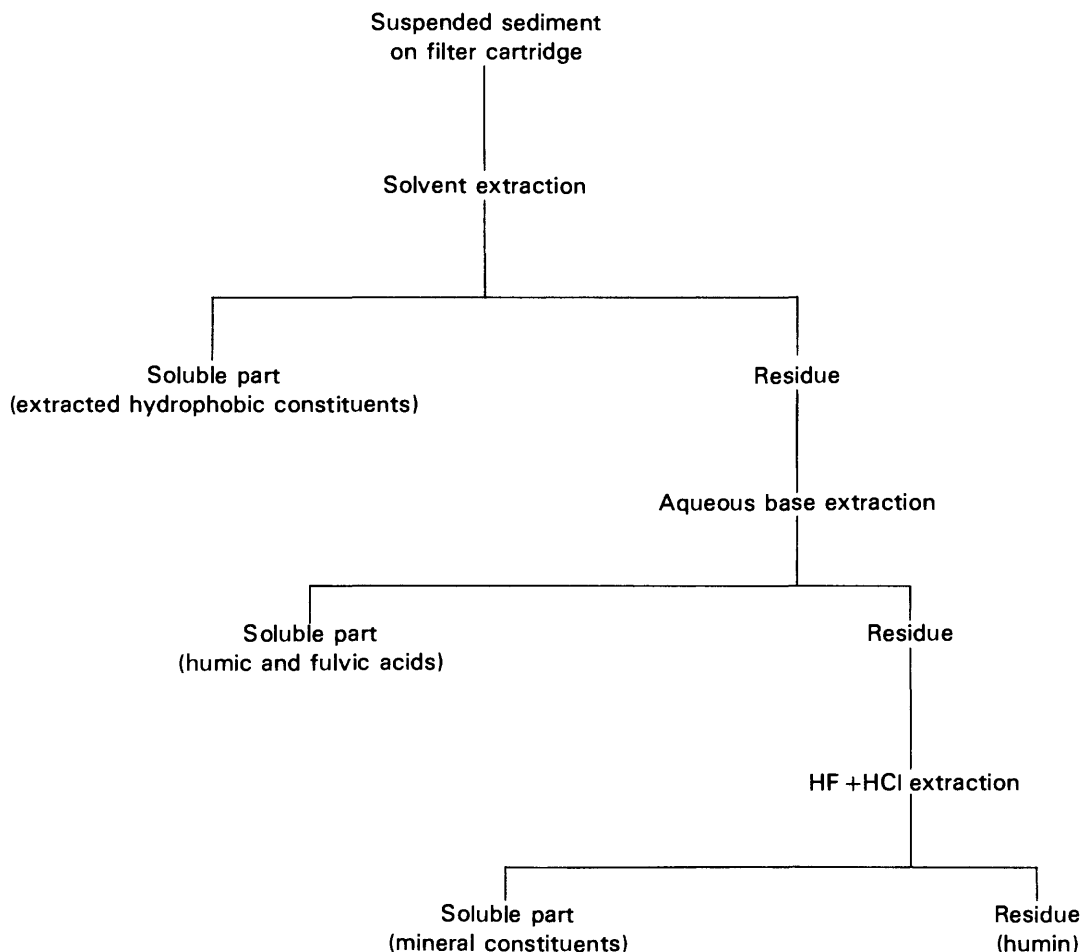
Figure 4. Flow charts of laboratory desalting and fractionation procedures applied to onsite concentrates.

Weak hydrophobic acids (W-HPO-A)
concentrate

Adsorb on XAD-8 resin, pH 7

Adsorbate (W-HPO-A)   Eluate (salts)

Reverse elute with 0.1 N NaOH, then H_2O

Adjust pH to 7

Solvent extraction

Solvent phase   Water phase
(volatile W-HPO-A)   (non-volatile W-HPO-A)

Adjust pH to 2

Adsorb on XAD-8 resin, rinse
with 0.01 N CF_3COOH

Adsorbate   Eluate (salts)

Reverse elute with CH_3OH

Vacuum-rotary evaporation

Distillate   Concentrate
CH_3OH, H_2O, and CF_3COOH

Freeze-dry

Non-volatile W-HPO-A

Figure 4. Continued

CONCENTRATE EXTRACTION AND DESALTING PROCEDURES

The concentrate fractions obtained from the filtration and column-adsorption system still contain a mixture of organic and inorganic constituents in water; they need to be further processed in the laboratory to isolate low-ash organic fractions suitable for study. Flow charts of these final processng procedures are presented in figure 4.

Suspended sediment retained on the glass-fiber filter tubes needs to first be Soxhlet-extracted with an organic-solvent pair, such as hexane-acetone or benzene-methanol, to isolate adsorbed hydrophobic constituents. Next, humic and fulvic acids can be extracted and isolated by classical base extraction methods (Stevenson, 1982), and the non-extractable humin fraction can be isolated by HF-HCl (hydrofluoric-hydrochloric acid) digestion of the glass fiber and mineral matrix (Leenheer and Moe, 1969).

```
                         Hydrophobic base (HPO-B)
                              concentrate
                                  |
                         Adsorb on XAD-8 resin, pH 10
                                  |
          _____
          |                                                         |
   Adsorbate (HPO-B)                                         Eluate (salts)
          |
 Reverse elute with 0.1 N HCl, then 0.01 N HCl
          |
   Adjust pH to 10
          |
   Solvent extraction
          |
   _____
   |                                                 |
 Solvent phase                                   Water phase
 (volatile (HPO-B)                           (non-volatile (HPO-B)
                                                     |
                                              Adjust pH to 10
                                                     |
                                        Adsorb on XAD-8 resin, rinse with H2O
                                                     |
                     _____
                     |                                                    |
                 Adsorbate                                         Eluate (salts)
                     |
          Reverse elute with CH3OH
                     |
          Vacuum-rotary evaporation
                     |
          _____
          |                                        |
 Distillate (CH3OH + H2O)                      Concentrate
                                                    |
                                              Freeze-dry
                                                    |
                                          Non-volatile HPO-B
```
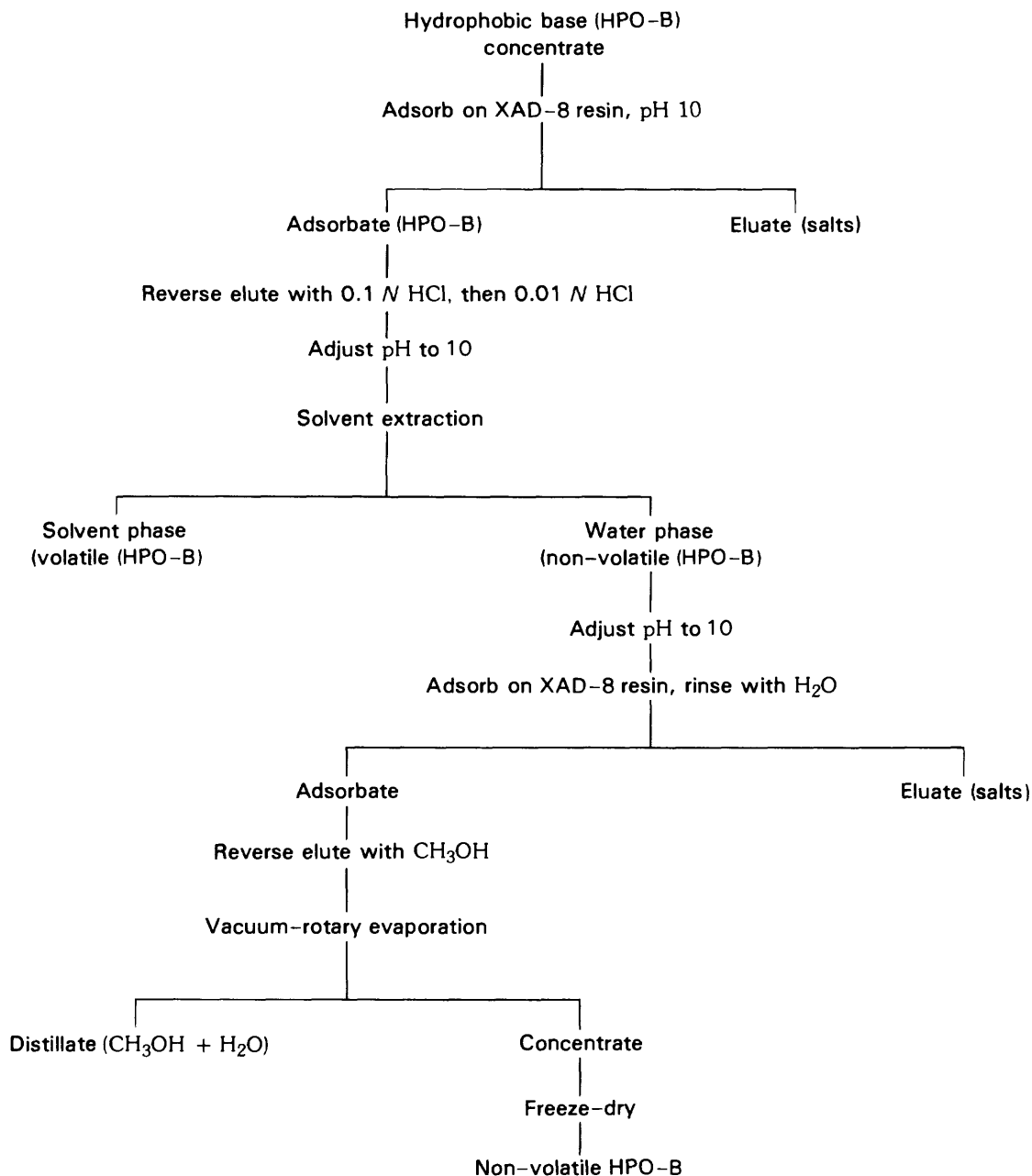
Figure 4. Continued

The hydrophobic-base fraction needs to be reconcentrated at pH 10 and the weak hydrophobic-acid fraction needs to be reconcentrated at pH 7, on a 160-mL XAD–8-resin column and backflush desorbed with 40 mL of 0.1 N HCl (the hydrophobic-base fraction) and 0.1 N NaOH (the weak hydrophobic-acid fraction) followed by 240 mL of 0.01 N HCl (the hydrophobic-base fractions) and 240 mL of distilled water (the weak hydrophobic-acid fraction). At this point, volatile-extractable hydrophobic bases (aromatic amines) and weak hydrophobic acids (phenols) need to be solvent-extracted from the 280-mL concentrates (adjusted to pH 10 for the aromatic amines, and pH 7 for the phenols) with three successive 100-mL extractions with methylene chloride or diethyl ether. These solvent concentrates then can be further decreased in volume by Kuderna-Danish evaporation. The nonvolatile, nonextractable parts need to be decreased in volume to about 50 mL by vacuum-rotary evaporation. The nonvolatile weak hydrophobic acids need to be acidified to pH 2 with H_2SO_4, reapplied to the XAD–8-resin column, and rinsed with 150 mL of 0.01 N CF_3COOH (trifluoroacetic acid). Next, they are backflush-desorbed with 150 mL of CH_3OH; most of the CH_3OH and CF_3COOH is removed by vacuum-rotary evaporation to 50 mL. This concentrate

Hydrophobic neutrals (HPO-N)
(adsorbed on XAD-8 resin)

|
|
Air-dry XAD-8 resin
|
|
Soxhlet extract
with CH₃OH
|
|

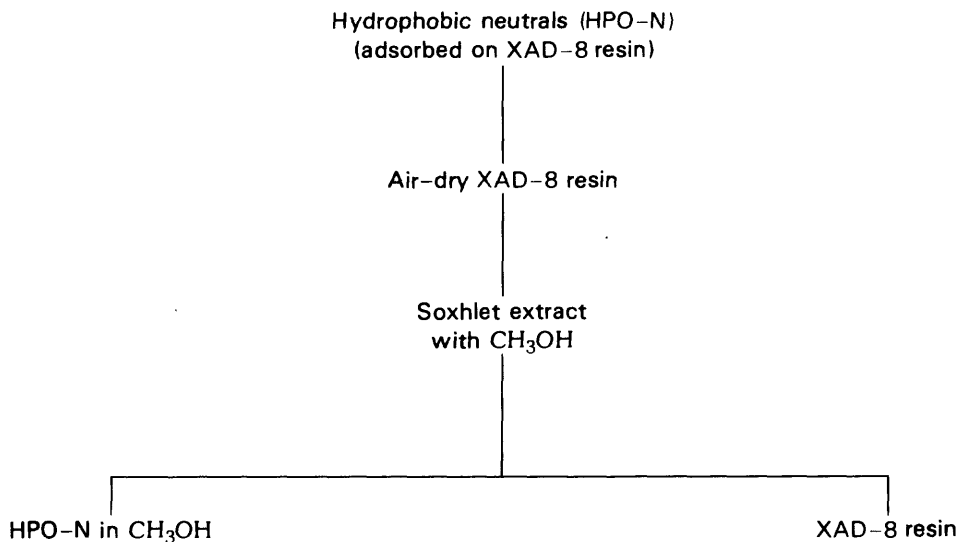HPO-N in CH₃OH   XAD-8 resin

Figure 4. Continued

is diluted to 100 mL with distilled water; nonvolatile, weak hydrophobic acids are isolated by freeze-drying. A filter needs to be placed in the vacuum port of the freeze-dry flask to prevent loss of the fluffy freeze-dried material. Nonvolatile weak hydrophobic bases are isolated similarly, except they are reconcentrated at pH 10, and a distilled-water rinse is used.

The hydrophilic-base fraction recovered from the MSC-1 resin and the strong hydrophobic and hydrophilic acids recovered from the Duolite A-7 resin are decreased in volume by vacuum-rotary evaporation at 40°C (Celsius), until $Na_2SO_4 \cdot 10 \ H_2O$ (sodium sulfate decahydrate) salts begin to precipitate. These fractions are diluted with 40°C water to dissolve the $Na_2SO_4 \cdot 10 \ H_2O$; centrifuged to remove humic-acid precipitate; and chilled to 4°C overnight, after placing a seed crystal of $Na_2SO_4 \cdot 10 \ H_2O$ in the solution. Long transparent crystals of $Na_2SO_4 \cdot 10 \ H_2O$ grow in solution and remove significant quantities of sodium, sulfate, and water. After recrystallization the supernatant solution is separated from the crystals by pouring the suspension through a funnel with a glass-wool plug and washing the crystals with a minimum volume of reagent water chilled to 4°C. The recrystallization step with the hydrophilic-base fraction is repeated a second time to decrease the volume to 50 to 100 mL.

The hydrophilic-base fraction is isolated from water by acidifying this fraction to pH 2 with H_2SO_4 and applying the concentrate to a XAD-8-resin column, whose bed volume is 10 times the concentrate volume. Salts are rinsed through the column with a pH 2 CF_3COOH rinse, and the salt-elution curve is monitored by a specific-conductance meter, as described previously (Leenheer, 1981). After passage of the salt peak, the CF_3COOH rinse is stopped, and adsorbed hydrophilic bases are desorbed by reverse elution of the column with CH_3OH. Most of the

CH_3OH and CF_3COOH is removed by vacuum-rotary evaporation. When an organic precipitate or film begins to form in the concentrate, the concentrate is diluted threefold with distilled water, and the water is removed by freeze drying.

After the first recrystallization step, the strong hydrophobic- and hydrophilic-acid fraction is acidified to pH 2 with H_2SO_4, and precipitated humic acids are removed by centrifugation. Volatile acids are removed by vacuum-rotary evaporation of this fraction to a volume where salts begin to precipitate, and the condensate is neutralized to pH 7 with NaOH. Volatile-acid salts are isolated from water by freeze-drying the neutralized condensate.

Nonvolatile hydrophobic and hydrophilic acids next are applied to two 160-mL columns of XAD-8 resin connected in series, followed by 300-mL of a pH 2 CF_3COOH rinse. Organic acids that elute through the column with the salts and CF_3COOH rinse are called hydrophilic acids; organic acids that adsorb are called nonvolatile hydrophobic acids. Nonvolatile hydrophobic acids from the XAD-8-resin columns are eluted in a reverse direction, by passing 100 mL of 0.1 N NaOH, followed by 200 mL of distilled water, through the columns; the NaOH is immediately removed, and the acids are hydrogen-saturated by placing a 40-mL column of hydrogen-saturated MSC-1 resin in series, after the XAD-8-resin columns, during the desorption process. Trifluoroacetic acid is removed by vacuum-rotary evaporation of the 300-mL fraction volume to 50 mL. Nonvolatile hydrophobic acids are isolated from water by diluting the 50 mL to 150 mL with distilled water and freeze-drying this fraction.

The hydrophilic-acid fraction still contains appreciable quantities of sodium chloride and sulfate salts. Chloride is removed by adding silver-saturated MSC-1 ca-
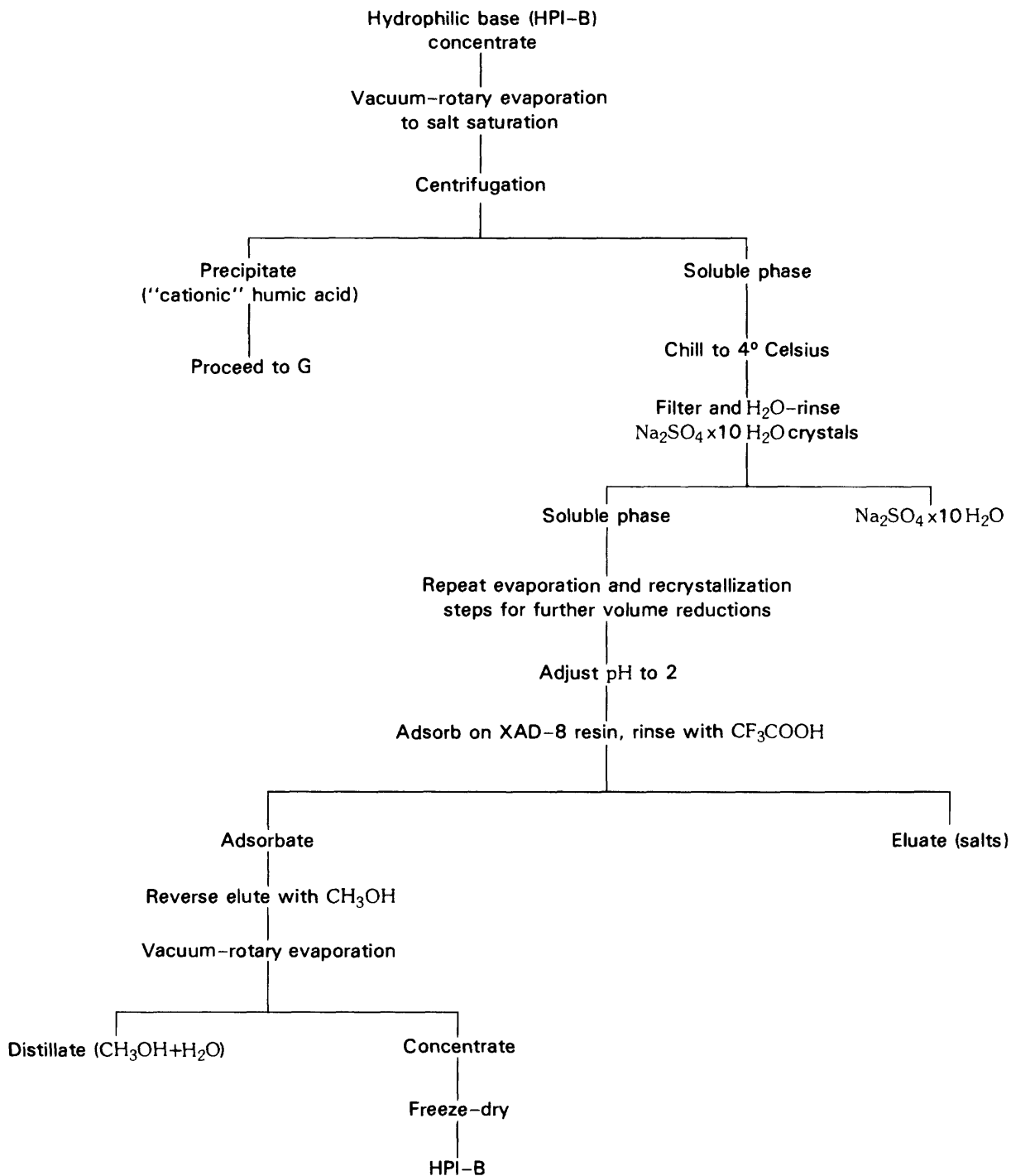
Hydrophilic base (HPI-B)
concentrate

|

Vacuum-rotary evaporation
to salt saturation

|

Centrifugation

Precipitate
("cationic" humic acid)

Proceed to G

Soluble phase

|

Chill to 4° Celsius

|

Filter and H_2O-rinse
$Na_2SO_4 \times 10\ H_2O$ crystals

Soluble phase $Na_2SO_4 \times 10\ H_2O$

|

Repeat evaporation and recrystallization
steps for further volume reductions

|

Adjust pH to 2

|

Adsorb on XAD-8 resin, rinse with CF_3COOH

Adsorbate   Eluate (salts)

|

Reverse elute with CH_3OH

|

Vacuum-rotary evaporation

Distillate (CH_3OH+H_2O)   Concentrate

|

Freeze-dry

|

HPI-B

Figure 4. Continued

tion-exchange resin to the stirred hydrophilic-acid frac-
tion, until a negative silver nitrate test for chloride is ob-
tained on an aliquot of the supernatent solution. Silver
chloride precipitate and resin are removed by centrifuga-
tion; the precipitate and resin are washed with reagent
water; and the washings are combined with the original
supernatent liquid. Sulfate is removed by passing the sam-
ple through a hydrogenaturated MSC column, adjusting
to pH 2 with NaOH, adding three volumes of CH_3CH_2OH
(ethanol), and chilling to 4°C overnight. Precipitated sodi-
um sulfate decahydrate is removed by centrifugation.
Ethanol is removed next by vacuum-rotary evaporation of
this fraction to about 10 mL. This fraction is hydrogen-
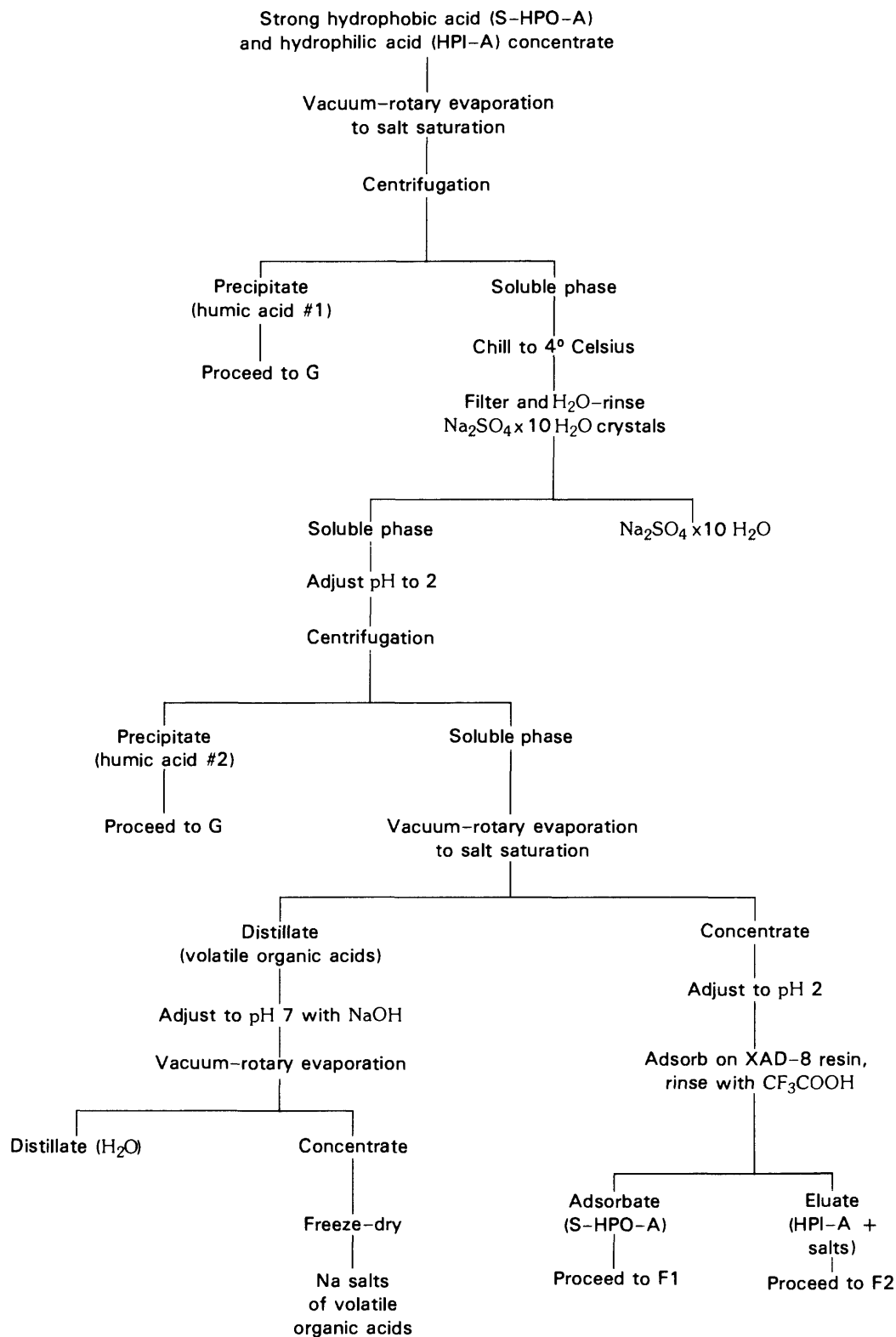saturated by passing the concentrate plus 80 mL of water

Strong hydrophobic acid (S-HPO-A)
and hydrophilic acid (HPI-A) concentrate

Vacuum-rotary evaporation
to salt saturation

Centrifugation

Precipitate
(humic acid #1)

Proceed to G

Soluble phase

Chill to 4° Celsius

Filter and H_2O-rinse
$Na_2SO_4 \times 10\, H_2O$ crystals

Soluble phase

Adjust pH to 2

Centrifugation

Precipitate
(humic acid #2)

Proceed to G

$Na_2SO_4 \times 10\, H_2O$

Soluble phase

Vacuum-rotary evaporation
to salt saturation

Distillate
(volatile organic acids)

Adjust to pH 7 with NaOH

Vacuum-rotary evaporation

Distillate (H_2O)

Concentrate

Freeze-dry

Na salts
of volatile
organic acids

Concentrate

Adjust to pH 2

Adsorb on XAD-8 resin,
rinse with CF_3COOH

Adsorbate
(S-HPO-A)

Proceed to F1

Eluate
(HPI-A +
salts)

Proceed to F2

Figure 4. Continued

rinse through a 40-mL column of hydrogen saturated MSC-1 resin. Water and CF_3COOH are removed by vacuum-rotary evaporation of the concentrate to a moist residue. The residue is resolubilized in water, titrated to pH 7 with NaOH, and the sodium salts of nonvolatile hydrophilic acids are isolated from water by freeze-drying.
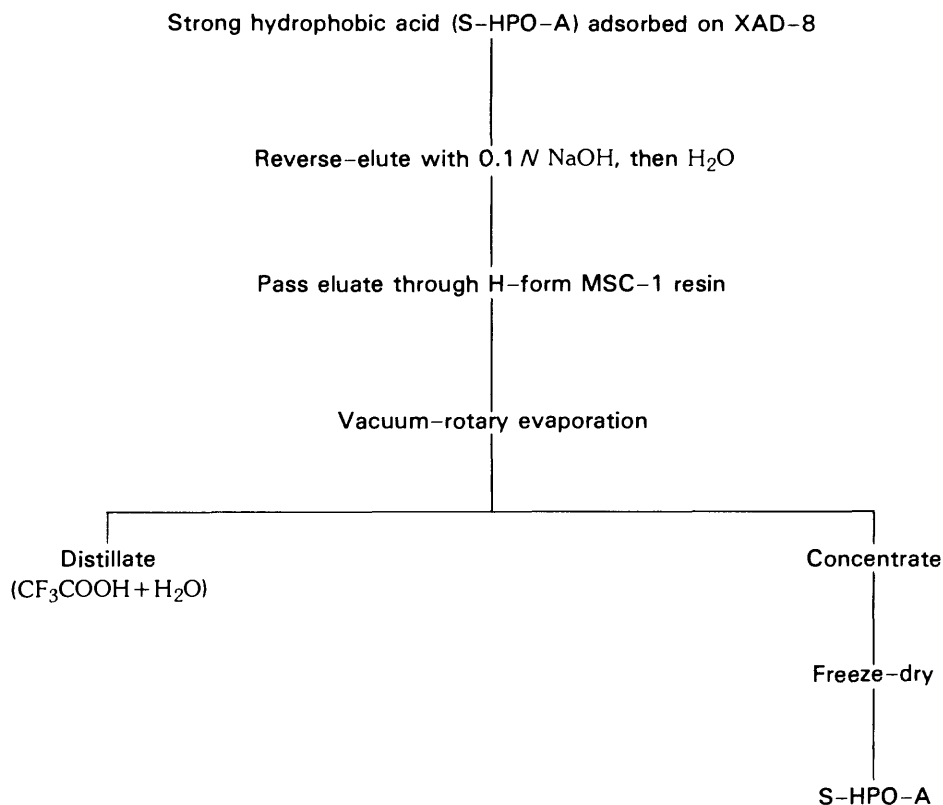
Strong hydrophobic acid (S-HPO-A) adsorbed on XAD-8

Reverse-elute with 0.1 N NaOH, then H_2O

Pass eluate through H-form MSC-1 resin

Vacuum-rotary evaporation

Distillate
($CF_3COOH + H_2O$)

Concentrate

Freeze-dry

S-HPO-A

Figure 4. Continued

Humic acid obtained from the evaporative concentration and acidification processing steps of the various fractions commonly contains a significant colloidal-clay content. This clay can be removed by treatment with aqueous HF-HCl (Leenheer, and Moe, 1969); however, generally, a major part of aquatic humic acid is converted to aquatic fulvic acid, when clay is removed. This converted fulvic acid can be recovered from the HF-HCl solution by using the hydrophobic-acid isolation procedure discussed previously, except all plastic columns, tubing, and peristaltic pumps need to be used to avoid HF attack on glass components.

Finally the hydrophilic-neutral fraction can be recovered from the deionized water, which has passed through the filtration and column-adsorption system. If only nonvolatile, hydrophilic-neutral components are desired, volume of this fraction can be decreased by vacuum-rotary evaporation. If volatile and nonvolatile components are desired, freeze concentration needs to be used to decrease the volume. Samples for analyses of volatile hydrophilic neutral components need to be directly analyzed without drying, preferably by direct aqueous injection-gas chromatography of the freeze-concentrated fraction. Nonvolatile hydrophilic neutral components can be isolated by freeze-drying the fraction concentrate, but they will be found in a matrix of silicic acid, which also passes through the resin-adsorbent columns. Silicic acid

is removed by suspending the freeze-dried fraction in 50 mL of water and adding concentrated HF until the silica dissolves. Silica then is removed by volatilization through vacuum distillation or freeze-drying.

DISCUSSION OF PROCEDURE MODIFICATIONS

A number of significant modifications were made to the original methods (Leenheer, 1981) to improve the fractionation and isolation of organic substances in water using the filtration and column-adsorption system. After the discovery that sodium sulfate could be removed easily by recrystallization and final precipitation with CH_3CH_2OH (Robinson, 1980), H_2SO_4 was substituted for HCl at all procedural steps where acidification with a nonvolatile acid was required. Sulfuric acid also is more convenient for use in an onsite laboratory, because of its concentrated nature and lack of corrosive fumes, compared to HCl.

Ammonium hydroxide was deleted as a reagent and NaOH was substituted, because of concern of oxidative coupling of ammonia into polyphenolic structural units in aquatic humic substances. Much of the added sodium later is removed by sodium sulfate recrystallization or XAD-8-resin-column-desalting processes. Even most very hydro-
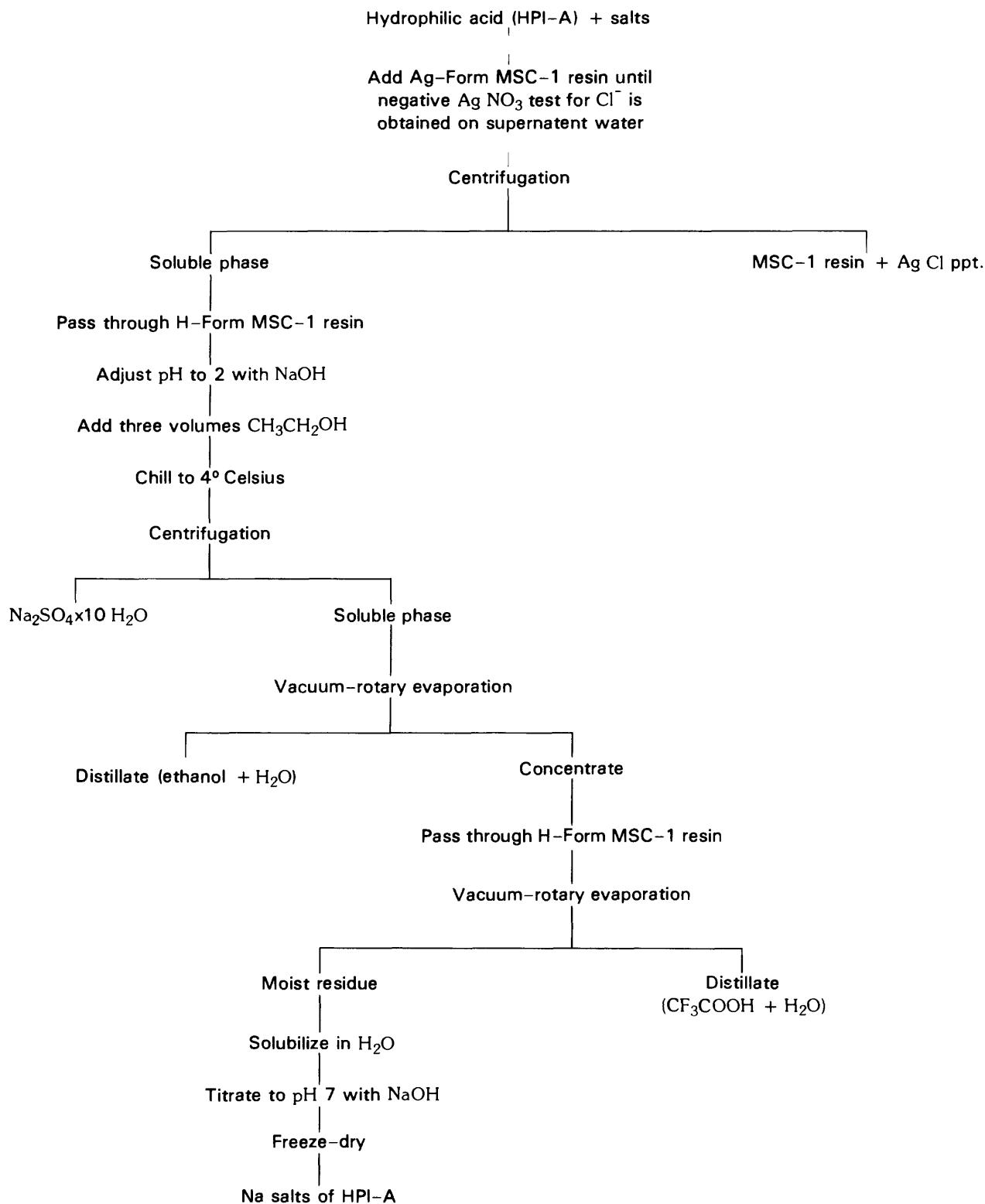
Hydrophilic acid (HPI-A) + salts

Add Ag-Form MSC-1 resin until negative Ag NO_3 test for Cl^- is obtained on supernatent water

Centrifugation

Soluble phase   MSC-1 resin + Ag Cl ppt.

Pass through H-Form MSC-1 resin

Adjust pH to 2 with NaOH

Add three volumes CH_3CH_2OH

Chill to 4° Celsius

Centrifugation

$Na_2SO_4 \times 10\ H_2O$ Soluble phase

Vacuum-rotary evaporation

Distillate (ethanol + H_2O)   Concentrate

Pass through H-Form MSC-1 resin

Vacuum-rotary evaporation

Moist residue   Distillate ($CF_3COOH + H_2O$)

Solubilize in H_2O

Titrate to pH 7 with NaOH

Freeze-dry

Na salts of HPI-A

Figure 4. Continued

philic amino acids can be separated from inorganic salts by adsorption, when the column-capacity factor of one-half retention ($k'_{0.5r}$) is limited to $k'_{0.5r} \leq 2.0$ during col-umn-desalting procedures (Leenheer, 1981; Kroeff and Pietrzyk, 1978).
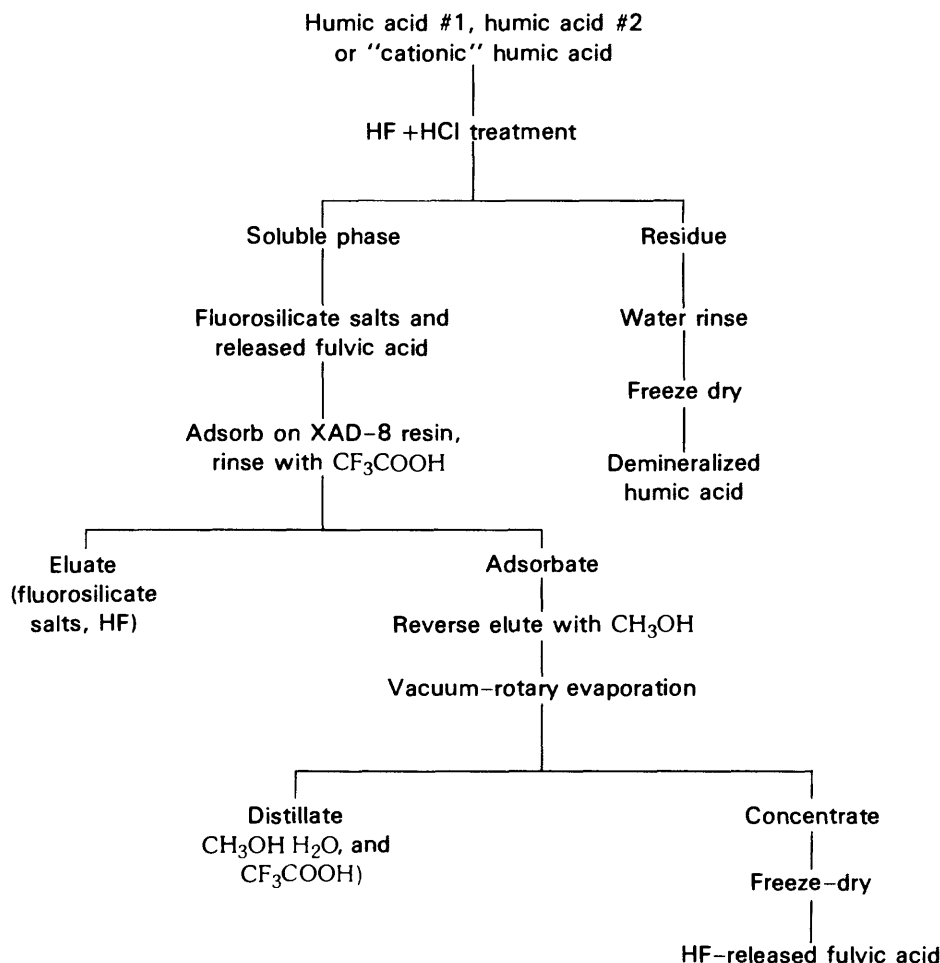
The Duolite A-7-resin column, recycle-desorption

Humic acid #1, humic acid #2
or "cationic" humic acid

HF +HCl treatment

Soluble phase Residue

Fluorosilicate salts and Water rinse
released fulvic acid

Freeze dry

Adsorb on XAD-8 resin,
rinse with CF₃COOH Demineralized
humic acid

Eluate Adsorbate
(fluorosilicate
salts, HF) Reverse elute with CH₃OH

Vacuum-rotary evaporation

Distillate Concentrate
CH₃OH H₂O, and
CF₃COOH) Freeze-dry

HF-released fulvic acid

Figure 4. Continued

loop with NaOH infusion (fig. 3) was a significant improvement, because it enabled stoichiometric desorption of the Duolite A–7 resin without large excess quantities of base accompanied by alkaline pH, which might oxidize and hydrolyze organic-acid constituents. This efficient desorption procedure also favored omission of the acidification and recycle step of the water sample through the XAD–8-resin column originally used to separate hydrophobic and hydrophilic acids (Leenheer, 1981), because these acid fractions could be separated easily during column-desalting procedures on the desorbed concentrate from the Duolite A–7-resin column.

The use of volatile, column-desorption reagents, such as CF₃COOH and CH₃OH, allowed final isolation of nonvolatile organic constituents free of reagents. After removal of most of these reagents by vacuum-rotary evaporation, it was necessary to dilute the concentrates 3- to 10-fold with water before freeze-drying, to avoid a large depression of the freezing point of ice by final concentrations of these volatile reagents.

Finally, all the organic fractions obtained from the Duolite A–9 resin had to be passed through the MSC–1–H cation-exchange resin at some point in the processing procedure, to purify these fractions of the Duolite A–7-resin bleed that was mostly cationic in nature. Formic acid and formaldehyde also bled from the Duolite A–7 resin, but these were lost during the evaporation process and contaminated only the volatile fractions.

APPLICATIONS AND RESULTS

The filtration and column-adsorption system has been used on four water samples: (1) The White River was sampled 32 kilometers east of Rangely, Colorado in September 1981, during low-flow conditions, and (2) in June 1982, during high-flow conditions; (3) ground water associated with oil-shale deposits in Colorado was sampled from well D–8 at the Rio Blanco Oil Shale Corporation's in situ retorting operation in October 1981; and (4) the Platte River was sampled by R. L. Wershaw of the U.S. Geological Survey at the Waterton, Colorado, water-treatment plant in December 1981. The quantity and
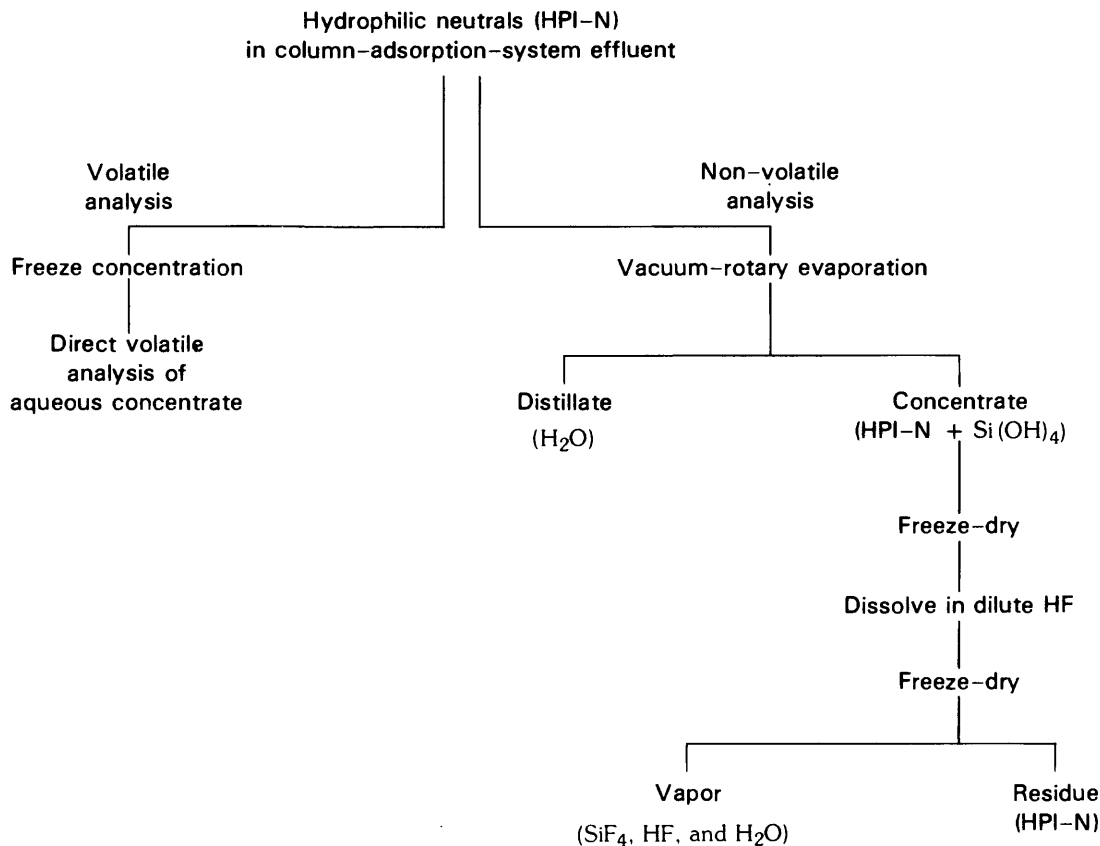
Hydrophilic neutrals (HPI–N)
in column–adsorption–system effluent

Volatile
analysis

Non-volatile
analysis

Freeze concentration

Vacuum–rotary evaporation

Direct volatile
analysis of
aqueous concentrate

Distillate
(H_2O)

Concentrate
(HPI–N + Si$(OH)_4$)

Freeze–dry

Dissolve in dilute HF

Freeze–dry

Vapor
(SiF_4, HF, and H_2O)

Residue
(HPI–N)

Figure 4. Continued

percentage of dissolved organic carbon recovered for these four sampling trips are summarized in table 1.

Organic-carbon recoveries are underestimated in table 1, because hydrophobic- and hydrophilic-neutral fractions were not quantitatively recovered and the carbon determined for these samples. These two fractions comprise about 25 ± 10 percent of the carbon in analytical-scale dissolved organic-carbon fractionations (Leenheer and Huffman, 1979) performed on these water samples. The dissolved organic-carbon content remained constant only in the ground-water sample during the sampling period; variations in dissolved organic-carbon content with time is the most probable reason for small recoveries (White River, September 1981) or large recoveries (White River, June 1982), as only one sample for dissolved organic-carbon determination was collected during the 2- to 4-day sampling periods.

The ion-exchange columns were used to their capacity only on the White River, September 1981 sampling trip. The following factors limited the volume of water processed on the other sampling trips. A significant sediment load in the White River during spring runoff in June 1982 limited the volume of water filtered per filter pair to 20-50 L, and the sediment caused erosion of the epoxy-fiberglass composite impeller in the positive-displacement

pump, which resulted in a gradual loss of system pressure. The Platte River sample was limited by freezing of the water in the system tubing outside of the mobile laboratory during a snowstorm, and the well D–8 ground-water sample was limited by the large hydrogen sulfide content of this sample. Hydrogen sulfide was removed prior to sample processing by precipitation with zinc sulfate, and the significant load of zinc sulfide limited the volume by plugging the available filter tubes. A major proportion of the anion content in all four samples consisted of carbonate and bicarbonate, which caused carbon dioxide outgassing in the MSC–1 and Duolite A–7-resin columns, when the column pressure decreased during plugging of the filters with sediments. Carbonic acid also is the most weakly adsorbed constituent on Duolite A–7 resin of all major anions in water, and it caused the specific-conductance breakthrough in the White River sample collected in September 1981. In all instances, however, sufficient water volume was processed to obtain enough isolated organic material for the particular study being performed.

In water relatively free from sediment, about 1,000 L of water can be processed during an 8-hour day. Another 8-hour day is needed to desorb the system and a third 8-hour day is needed to regenerate the system on-site for another adsorption cycle.

Table 1. Organicarbon recoveries using filtration and column-adsorption system
[mg/L, milligrams per liter; L, liter; mg C, milligrams carbon]

Sample	Dissolved organic carbon (mg/L)	Water volume (L)	Hydrophobic bases (mg C)	Weak hydrophobic acid (mg C)	Hydrophilic bases (mg C)	Strong hyrophobic and hydrophilic acids (mg)	Organic carbon recovery (percent)
Column desorption blank	---	-----	9.9	23.8	3.9	30.1	---
White River; Rangely, Colo.; Sept. 1981	2.3	1,091	[1]1.5	[1]51	[1]46	[1]1,498	64
Well D–8; oil-shale deposits in Colorado; Oct. 1981	2.9	304	[1]12.9	[1]12	[1]19	[1]742	89
Platte River; Waterton, Colo.; Dec. 1981	1.4	1,136	----	-----	[1]41	[1]1,085	71
White River; Rangely, Colo.; June 1982	2.7	725	----	[1]188	[1]258	[1]2,563	154

[1] Values after subtracting column-desorption blank.

CONCLUSIONS

The major conclusion of this study is that a practical system for comprehensive isolation of most types of organic substances found in water has been built and tested. This filtration and column-adsorption system should have many potential applications, including fractional toxicity and mutagenicity testing, water-treatment process testing, and determination of undiscovered organic substances and compounds in water.

REFERENCES CITED

Deinzer, M., Meltin, R., and Mitchell, D., 1975, Trace organic contaminants in drinking water; their concentration by reverse osmosis: Water Resources Research, v. 9, p. 799–805.

Katz, S., Pitt, W. W., Scott, C. D., and Rosen, A. A., 1972, The determination of stable organic compounds in waste effluents at microgram per liter levels by automatic high-resolution ion exchange chromatography: Water Resources Research, v. 6, p. 1029–1037.

Kroeff, E. P., and Pietrzyk, D. J., 1978, Investigation of the retention and separation of amino acids, peptides, and derivatives on porous copolymers by high performance liquid chromatography: Analytical Chemistry, v. 50, p. 502–511.

Leenheer, J. A., 1981, Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and waste waters: Environmental Science and Technology, v. 15, p. 578–587.

Leenheer, J. A., and Huffman, E. W. D., Jr., 1979, Analytical method for dissolved organic carbon fractionation: U.S. Geological Survey Water-Resources Investigations 79–4, 16 p.

Leenheer, J. A., and Moe, P. G., 1969, Separation and functional group analysis of soil organic matter: Soil Science Society of America Proceedings, v. 33, p. 267–269.

Malcolm, R. L., 1968, Freeze-drying of organic matter, clays, and other earth materials: U.S. Geological Survey Professional Paper 600–C, p. C200–C216.

Robinson, T., 1980, The organic constituents of higher plants (4th ed.): North Amherst, Mass., Cordus Press, p. 46–47.

Shapiro, J., 1961, Freezing-out, a safe technique for concentration of dilute solutions: Science, v. 133, p. 2063–2064.

Stevenson, F. J., 1982, Humus chemistry: New York, Wiley-Interscience, p. 26–54.

Thurman, E. M., and Malcolm, R. L., 1981, Preparative isolation of aquatic humic substances: Environmental Science and Technology, v. 15, p. 463–466.

Wu, C., and Suffet, I. H., 1977, Design and optimization of a Teflon helix continuous liquid-liquid extraction apparatus and its application for the analysis of organophosphate pesticides in water: Analytical Chemistry, v. 49, p. 231–237.