economically feasible method of dechlorination.

Ward and DeGraeve (*6*) have shown that SO_2 was an effective way to eliminate the residual toxicity of chlorinated effluent. These investigators concluded that 17 freshwater fish and one macroinvertebrate were not affected after SO_2 dechlorination. Similar results have also been reported by other authors using various dechlorinating agents (*29–32*).

Chlorine will likely continue to be used for biofouling control and disinfecting purposes by power plants and sewage treatment plants, respectively. Therefore, all feasible means to reduce the toxicity of this biocide should be thoroughly investigated in order to minimize effects on aquatic organisms. In this preliminary study we have demonstrated that dechlorination with sulfur dioxide is an effective means to reduce the toxicity of chlorine to striped bass eggs and larvae in an estuarine system. Striped bass ichthyoplankton exposed to dechlorination for exposure periods of 4 h or less experienced minimal mortality. In contrast, concentrations of TRC greater than 0.13 mg/L were found to cause high mortality to larvae after 4 h of exposure; therefore, SO_2 dechlorination at exposure periods of 4 h or less could completely eliminate mortality.

We recommend future investigations on other estuarine organisms that may be subjected to SO_2 dechlorination associated with industrial effluent. Future studies should be conducted to evaluate the effects of short exposures of TRC–SO_2 followed by observation periods of several days in control conditions. This type of study would provide data on possible sublethal effects. The effects of interacting ΔT and dechlorination conditions should be evaluated in order to determine responses of aquatic organisms subjected to power-plant discharge conditions. Evaluation of possible acute and sublethal effects of halogenated organics resulting from dechlorination should also be evaluated.

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Comprehensive Approach to Preparative Isolation and Fractionation of Dissolved Organic Carbon from Natural Waters and Wastewaters

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Introduction

Two major limitations in the determination and testing of organic materials dissolved in various types of water are (1) the lack of practical isolation procedures that separate these organic materials from the water and inorganic salt matrix in which they are dissolved and (2) the lack of meaningful fractionation procedures to isolate similar groups of compounds for testing and analyses. Conventional solvent-extraction procedures used in organic analyses of drinking water have isolated on the average only ~10% of the dissolved organic solutes (*1*), and solvent extraction also generally is conceded to be ineffective in obtaining quantitative isolation of dissolved organic carbon (DOC) in natural waters and most

■ A series of resin adsorbents were used to isolate complex mixtures of organic solutes from water and inorganic salts and to fractionate these solutes into six compound classes. A multistep separation scheme, called preparative dissolved organic carbon fractionation, recovered 95% of the dissolved organic carbon from the resin adsorbents for an oil-shale retort wastewater and 115% for a river water. After further evaporative concentration and desalting procedures were used on the organic-solute fractions obtained from the resin adsorbents, 81% of the dissolved organic carbon was recovered from each sample. Organic-solute fractions of the river-water samples were characterized by infrared spectra that indicated a dissolved organic carbon fractionation into fulvic acid, hydrocarbon, protein, hydroxy acid, and polysaccharide compound classes. Preparative dissolved organic carbon fractionation can be used as a basis for quantitative and qualitative organic analysis of water, and it also can be used to generate organic-solute fractions for chemical and biological testing.

wastewaters. Adsorption techniques using various synthetic resins and granular activated carbon are much more efficient in removing organic solutes from water; however, low solute recoveries from the sorbent, especially from granular-activated carbon, have limited the use of adsorption techniques to analysis of only certain types of organic solutes (2). Evaporative techniques are limited to nonvolatile solutes, and there is no separation of organic solutes from inorganic salts. There is no single technique that can achieve quantitative isolation of all organic solutes from water, but the correct combination of various techniques into a comprehensive analytical procedure can result in the quantitative isolation of most organic solutes from water as predicted by Christman and Hrutfiord (3).

The first comprehensive isolation and fractionation procedure for determining organic solutes in various river waters was developed by Sirotkina et al. (4), who sequentially used (a) freeze concentration, (b) adsorption upon and desorption from ion-exchange celluloses, and (c) Sephadex-gel filtration. Total organic-solute losses did not exceed 10%; however, the utility of this procedure was more applicable to macromolecular polyelectrolytes found in natural waters rather than to low-molecular-weight organic contaminants found in many wastewaters.

An analytical procedure called DOC fractionation analysis developed by the author (5, 6) quantitatively classifies organic solutes into hydrophobic-base, -acid, and -neutral fractions and hydrophilic-base, -acid, and -neutral fractions, based upon their adsorption upon nonionic and ion-exchange resin adsorbents. Organic carbon quantitation of the analytical DOC fractionation procedure was based more on adsorption than desorption from the resin adsorbents; thus, use of the DOC fractionation procedure for preparative purposes was limited by various desorption problems (7). However, the basic approach and the initial results of the analytical DOC fractionation procedure were sufficiently promising to lead to the development of a preparative DOC fractionation scheme, where substitution of different adsorbents and modified procedures solved the limiting desorption problems. This report will detail the research and development of the preparative DOC fractionation procedure and will demonstrate its application to an oil-shale retort wastewater (designated Omega-9) and to a water sample collected from the South Platte River near Denver, CO.

The objectives for this comprehensive isolation and fractionation procedure are (1) recovery of greater than 90% of the DOC from the resin adsorbents, and recoveries of greater than 80% of the DOC after secondary concentration, and desalting procedures, (2) suitability for scaleup to large-volume samples so that milligram to gram-sized quantities of organic solutes in each fraction can be obtained, (3) an interpretable and reproducible fractionation, so that the constitution of each fraction can be reasonably predicted, (4) separation of organic solutes from inorganic salts of the sample, (5) low levels of contaminants introduced by reagents and resin adsorbents, and (6) applications to a variety of waters ranging from concentrated wastewaters to dilute natural waters.

Experimental Procedures

Water Samples. The acquisition, processing, and storage of the oil-shale retort wastewater sample is described in a report by Farrier et al. (8). The South Platte River was sampled March 10, 1980, at the Colorado Highway 224 bridge, located 1 mi downstream from the outfall of the Denver metropolitan sewage treatment plant. The retort-water sample was pressure filtered through cartridge-type glass-fiber filters with a nominal 0.4-μm exclusion. The river-water sample was pressure filtered through a 0.45-μm pore-size silver-membrane filter, as described by Malcolm and Leenheer (9). All water samples to be processed through the preparative DOC fractionation procedures should be filtered as suspended solids will foul the resin adsorbents.

Analytical Procedure. The flow chart of the preparative scheme of DOC fractionation is given in Figure 1. All columns should be constructed of glass with Teflon end caps and fittings. Connecting tubing should be either glass or Teflon, and peristaltic pumps equipped with silicone–rubber pump tubing with flow rates from 1 to 50 mL/min are suitable for pumping water samples through the columns. Organic solvents should not be pumped with peristaltic pumps because of pump-tubing degradation; they can be pumped with the FMI Lab

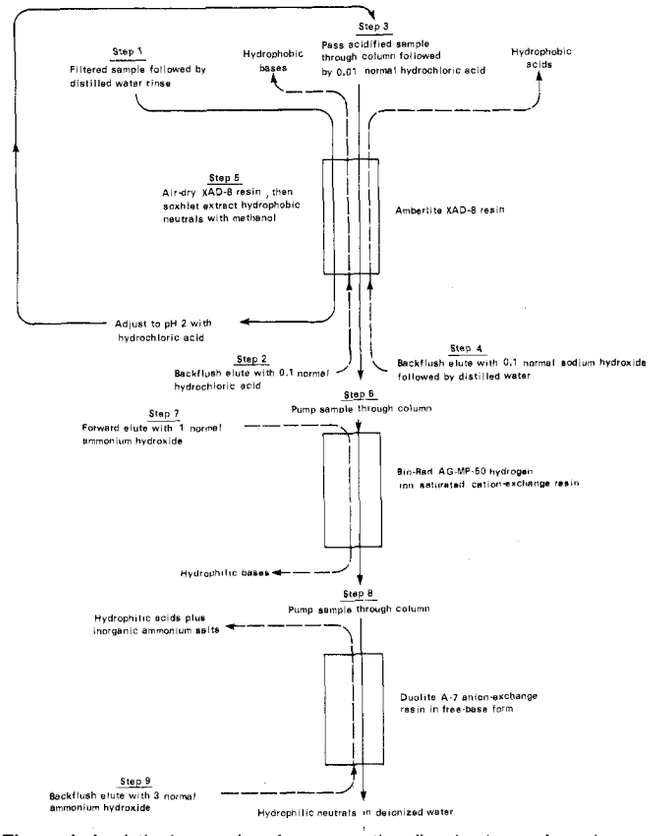

Figure 1. Analytical procedure for preparative dissolved organic carbon fractionation.

Pump Model RPSY which has no plastic materials to degrade.

Resin Cleanup Procedures. Amberlite XAD-8 Resin. This resin is available from Rohm and Haas as an industrial-grade preparation in 20–40-mesh beads. It is a macroporous methylmethacrylate copolymer with an average surface area of 450 m^2/g and an average pore diameter of 250 Å.

Prepare the XAD-8 resin by sieving out the large beads with a 500-μm sieve, slurring with 0.1 N NaOH, decanting off the fines, and storing the remainder in 0.1 N NaOH for 24 h. Remove organic resin contaminants by sequential 24-h Soxhlet extractions with acetone and hexane. Slurry the resin in methanol and pack the column to be used. Pump methanol through the column until the effluent is free of hexane and then pump distilled water until the DOC of the effluent is 1 mg/L or less. The XAD-8 resin column should be rinsed with 0.1 N NaOH, 0.1 N HCl, and distilled water just before application of the sample. Cleaned XAD-8 resin should be stored in methanol.

Bio-Rad AG-MP-50 Cation-Exchange Resin. AG-MP-50 is a strong acid, sulfonated, polystyrene macroporous resin. Purify by Soxhlet extraction of hydrogen-form resin (20–50-mesh beads) with methanol for 24 h. Slurry resin with distilled water and pack the column to be used. Pump 3 N NH_4OH through the column until breakthrough of ammonia is observed. Hydrogen-saturate the resin by pumping four bed volumes of 2 N HCl through the resin and rinse with distilled water until the specific conductance of the effluent is less than 10 μmho. This resin should be stored in methanol.

Duolite A-7 Anion-Exchange Resin. Duolite A-7 is a weak base, macroporous, phenol–formaldehyde condensation product, which is available from Diamond Shamrock as an industrial-grade preparation in the form of flakes up to 1 mm in diameter. Prepare the A-7 resin by sieving out the large flakes with a 1.4-mm sieve. Remove the fines by slurrying in distilled water and decanting. Soxhlet extract the resin with acetone for 24 h. Slurry with distilled water and pack in the column to be used. Pump 1 N HCl through the column until the DOC of the effluent is 1 mg/L or less. The resin initially has a high DOC bleed with 1.0 N HCl, and the resin bed expands ~30% during conversion from the free-base form to the hydrochloride form. Therefore, when the column is packed with free-base-form resin, enough column head space should remain to allow resin expansion. Following the HCl rinse, pump 3 N NH_4OH through the column until the resin is in the free-base form. The free-base-form resin has a yellow color, and the hydrochloride form has an off-white color. Finally, pump distilled water through the column until the specific conductance of the effluent is less than 10 μmho. The resin can be stored in water and can be reused after repeating the 3 N NH_4OH and distilled-water rinses.

Determination of Resin Adsorbent Quantities. Amberlite XAD-8 Resin. Adsorption or elution of organic solutes on XAD-8 resin determines the hydrophobic–hydrophilic separation of the DOC fractionation. This arbitrary hydrophobic–hydrophilic designation is controlled by the polarity of the solute and by the ratio of the resin quantity to the volume of water passed through the resin bed. As most organic solutes (including hydrophilic solutes) show some affinity for XAD-8, the hydrophobic–hydrophilic break is not clear-cut but is an operationally defined separation in which the crossover of hydrophilic solutes into the hydrophobic fraction can be mathematically defined. For the DOC fractionation, hydrophobic solutes are defined as those solutes that are greater than 50% retained on XAD-8 at a given ratio of resin to water passed through the column, and hydrophilic solutes are defined as those solutes that are greater than 50% eluted at the same ratio of resin to water eluent.

This hydrophobic–hydrophilic designation in frontal adsorption chromatography is illustrated in Figure 2 by the breakthrough curve of a hypothetical organic solute in the XAD-8 column effluent. Examination of the breakthrough curve of Figure 2 shows that the integrated area of solute adsorption equals the integrated area of solute elution at $2V_E$. To design a DOC fractionation, it is useful to refer to the column distribution coefficient, $k'_{0.5r}$, of a hypothetical solute which is 50% retained and 50% eluted at the hydrophobic–hydrophilic break. This $k'_{0.5r}$, called the hydrophobic–hydrophilic break $k'_{0.5r}$, is determined by the following calculations.

The breakthrough (elution) volume V_E of a solute from an XAD-8 resin column can be described by the following equation:

$$V_E = V_0(1 + k') \quad (1)$$

V_0 = void volume

k' = (mass of solute sorbed on XAD-8)/(mass of solute dissolved in water) (2)

Because the breakthrough volume V_E, where effluent concentration is 50% of influent concentration, does not correspond to the effluent volume of 50% retention and 50% retention, $V_{0.5r}$ is defined as

$$V_{0.5r} = 2V_E \quad (3)$$

To define the hydrophobic–hydrophilic break $k'_{0.5r}$ for $V_{0.5r}$, substitute eq 3 into eq 1 to give

$$V_{0.5r} = 2V_0(1 + k'_{0.5r}) \quad (4)$$

For example, if a 1-L water sample is processed through a DOC fractionation whose hydrophobic–hydrophilic break is at $k'_{0.5r} = 50$, the following calculations are made to determine the quantity of XAD-8 resin required: $V_{0.5r} = 1000$ mL; $k'_{0.5r} = 50$. Solving eq 4 for V_0 gives $V_0 = 9.8$ mL. As the void volume of XAD-8 resin is ~65% of its bulk column volume, a 9.8 ml/0.65 = 15 mL column of XAD-8 resin is required.

Bio-Rad AG-MP-50 Cation-Exchange Resin. The amount of cation-exchange resin required is determined by the exchange capacity of the resin, the milliequivalents of cations in the sample, and the competition of hydrogen ion at pH 2 with the various cations of the sample for exchange sites on the resin. The exchange capacity of AG-MP-50 cation-exchange resin is a constant, 4.9 mequiv/g. The milliequivalents of cations in the sample can be estimated by the following equation (*10*):

$$\text{mequiv of salt/L} = 12.5L \quad (5)$$

where L = specific conductance, in mmho/cm at 25 °C. The factor 12.5 is an average value for a mixture of salts normally found in water between pH 5 and 9. The factor for single-salt solutions can vary between 8 and 20. The amount of AG-

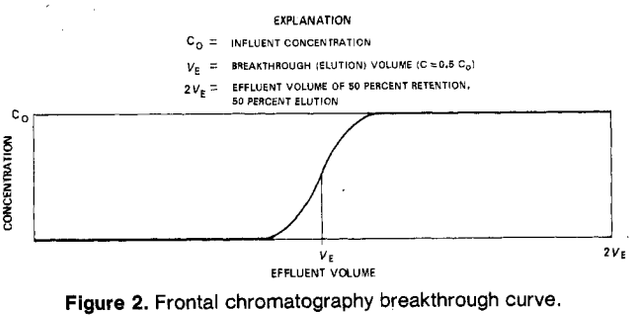

Figure 2. Frontal chromatography breakthrough curve.

MP-50 resin needed for hydrogen-saturation of a water sample assuming quantitative exchange is calculated by eq 6

$$g = V \text{ (mequiv of salt/L)/exchange capacity} \quad (6)$$

where g = weight of resin in grams and V = sample volume in liters.

For ion-exchange columns, elution of a sorbed cation by a specific ion in the mobile phase can be calculated by the following equation (*11*, p 222):

$$V_E = Dg + V_0 \quad (7)$$

where V_E = breakthrough (elution) volume in milliliters, D = weight distribution coefficient, g = weight of resin in grams, and V_0 = void volume.

For the hydrogen-saturated AG-MP-50 cation-exchange resin, hydrogen ion in the acidified sample (pH 2, 10 mequiv/L H^+) is the eluent cation. The most weakly bound cation on AG-MP-50 (excepting hydrogen and lithium) which is present in most water samples is sodium; therefore, sodium breaks through first, if insufficient resin is contained in the column. The weight distribution coefficient D^{Na} for hydrogen-saturated AG-MP-50 is calculated by the following equation (*11*, p 212):

$$D^{Na} = ([H]_r/[H])K_H{}^{Na} = 686 \quad (8)$$

where $[H]_r = 4.9$ mequiv, $[H] = 0.01$, and the $K_H{}^{Na}$ exchange constant was estimated as 1.4 for AG-MP-50 (*11*, p 202).

For water samples containing relatively moderate to large salt concentrations, an ion-exchange front moves faster through the column than sodium ion eluted with 0.01 N hydrogen ion, and eq 6 should be used to calculate resin quantity. However, for samples containing relatively small salt concentrations, the sample volume (V of eq 6) may exceed the sodium ion elution volume (V_E of eq 7), and eq 7 should be used to calculate resin quantity, with the sample volume being substituted for V_E. The point at which V of eq 6 equals V_E of eq 7 is for a sample whose specific conductance equals 572 μmho. Finally, the resin quantity estimates obtained by eq 6 or 7 should be doubled to cover uncertainties in the previous estimates and various physical processes, which cause dispersion of the adsorbed cations in the resin column.

Duolite A-7 Anion-Exchange Resin. The amount of Duolite A-7 required does not depend on its maximum or total ion-exchange capacity, but rather it depends on the milliequivalents of acid adsorbed as a function of pH. The sorption of HCl on Duolite A-7 as a function of pH was determined by Kim et al. (*12*), and it linearly varies from 9.5 mequiv/g at pH 1, 7 mequiv/g at pH 2, 4.5 mequiv/g at pH 3, to 2 mequiv/g at pH 4. After determining the pH of the column influent, one can determine the stoichiometric quantity of resin required by eq 6 after substituting acid sorption for exchange capacity. Because of the moderately slow kinetics of acid sorption on the free-base-form resin, the stoichiometric resin quantity should be doubled, and the flow rate should not exceed 15 bed volumes/h.

Monitoring the Dissolved Organic Carbon Fractionation. The most important parameter for monitoring the fractionation is DOC. The organic carbon analyzer should be able to determine DOC in water in 5 min or less with a precision of ±0.5 mg/L DOC. A Beckman Model 915-A carbon analyzer was used for the work in this report, and its precision was ±0.5 mg/L DOC. The capability to determine DOC in methanol is also desirable but not essential; it is determined by a modified Dohrmann DC-50/52 carbon analyzer (as described by Casterline and Leenheer (*13*)). Other instruments required for monitoring the DOC fractionation are a fraction collector (5–20-mL capacity), a specific conductance meter (0.1 μmho to 500 mmho range) with a flow-through cell, and a pH meter.

Generation of Each Dissolved Organic Carbon Fraction. Hydrophobic-Base Fraction. The filtered sample is pumped through the XAD-8 column at a flow rate not to exceed 30 bed volumes/h. Following the sample, 2.5 bed volumes of distilled-water rinse are pumped into the XAD-8 column. The influent and effluent tubings are then reversed, and the hydrophobic bases are backflush eluted with 0.25 bed volume of 0.1 N HCl, followed by 1.5 bed volumes of 0.01 N HCl. The resin bed must be slightly compressed by glass-wool packing at the top of the column to avoid redistribution of the resin beads during backflush elution. About the first 0.60 bed volume of effluent obtained during backflush elution is distilled water rinse. DOC, pH, and specific conductance must be carefully monitored to detect initial desorption of the hydrophobic-base fraction. The distilled-water effluent obtained before desorption of the hydrophobic-base fraction is recombined with the sample effluent.

The hydrophobic-base desorption curve is determined by periodic determinations of DOC of the column effluent, and, after 1.25 bed volumes are collected after HCl breakthrough, desorption of the hydrophobic-base fraction is virtually complete. DOC determinations are made on the sample before and after passage through the XAD-8 column and also are made on the total hydrophobic-base fraction. The volume of the hydrophobic-base fraction can be further reduced 10–15-fold by vacuum-rotary evaporation at 40 °C. This fraction should be stored in acid solution, as neutralization of the sample may cause losses through volatilization and the formation of an immiscible oil. The HCl concentration of the base concentrate after evaporation ranges from 0.3 to 0.5 N.

Hydrophobic-Acid Fraction. The sample effluent from the XAD-8 column is acidified to pH 2 with HCl and recycled through the XAD-8 column at 30 bed volumes/h or less. The nonsorbed portion of the sample is displaced from the resin by 1 bed volume of 0.01 N HCl rinse. Hydrophobic acids are desorbed by backflush elution with 0.25 bed volume of 0.1 N NaOH, followed by 1.5 bed volumes of distilled water. The hydrophobic-acid desorption curve is determined as before, and the void volume of 0.01 N HCl rinse collected before hydrophobic-acid desorption is recombined with the sample. Determinations of DOC are made on the sample effluent and the hydrophobic-acid fraction.

Volume of the hydrophobic-acid fraction can be further reduced 10–15-fold by vacuum-rotary evaporation at 40 °C. This fraction should be titrated to pH 8 with HCl before evaporation to avoid solute alteration by oxidation or hydrolysis. Salt concentration of the concentrate after evaporation ranges from 0.3 to 0.4 N.

Hydrophobic-Neutral Fraction. Pump the XAD-8 column dry after the elution of the hydrophobic-acid fraction. Unpack the column and spread the XAD-8 beads upon sheets of aluminum foil, where they are allowed to dry at room temperature for 15 h. The dried beads are packed in a Soxhlet extractor and Soxhlet-extracted with anhydrous methanol until 5 bed volumes of methanol has passed through the XAD-8 resin. The volume of methanol in the boiling flask should only be 10–20% of the resin bed, so subsequent evaporative concentration of this fraction is unnecessary. This Soxhlet-extraction procedure for the hydrophobic-neutral fraction was developed and tested by Huffman (*14*).

The DOC in the methanol concentrate can be determined by (1) using the Dohrmann DC-50/52 analyzer, by a procedure developed by Casterline and Leenheer (*13*), or (2) evaporating an aliquot of the methanol concentrate under a stream of dry air at 40 °C, weighing the residue, and determining the organic carbon in the residue (*14*). Volatile hydrophobic neutral compounds are lost in the second procedure.

Hydrophilic-Base Fraction. The sample, which now contains only hydrophilic solutes, is pumped through the

column containing the hydrogen-saturated AG-MP-50 cation-exchange resin, at a flow rate no greater than 30 bed volumes/h. Hydrophilic bases are desorbed by forward elution with 1.0 N NH_4OH. Specific conductance, DOC, and pH are all used to determine the hydrophilic-base elution peak. The deionized-water effluent (due to removal of NH_4OH by the column), which precedes the DOC elution peak, was not discarded but was combined with the sample effluent. The hydrophilic bases elute in ~0.6 bed volume, but the volume of the elution peak may vary, depending on the composition of the hydrophilic-base fraction.

The hydrophilic-base fraction is virtually salt free, because the NH_4OH eluent does not displace other metallic cations from the exchange resin in the volume in which the hydrophilic bases elute. Excess ammonium can be removed by vacuum-rotary evaporation, but volatile amines are also lost during this procedure.

Hydrophilic-Acid Fraction. The sample, now containing only hydrophilic acids and neutral compounds, is pumped through the column containing the Duolite A-7 anion-exchange resin at a flow rate not exceeding 15 bed volumes/h. The specific conductance of the sample effluent should not exceed 10 μmho. If the specific conductance exceeds this value, the sample should be recycled through the AG-MP-50 and Duolite A-7 columns. The sample is displaced from the column with 1.0 bed volume of distilled-water rinse. Hydrophilic organic acids and all inorganic anions are backflush eluted from the column with 3 N NH_4OH, and specific conductance, DOC, and pH are used to determine the elution curve. Hydrophilic acids desorb in ~2 bed volumes.

At this point, the hydrophilic-acid fraction contains all of the inorganic as well as organic anions as ammonium salts. The procedure used for desalting is shown in Figure 3. The hydrophilic-acid fractions are concentrated by vacuum-rotary evaporation until ammonium chloride crystals form (~5 N NH_4Cl). The concentrate is acidified to pH 1 with HCl, and 0.1 bed volume of concentrate is applied to the top of the XAD-8 column. The concentrate is pumped through the column at 5 bed volumes/h with 0.1 N HCl, followed by distilled water as the eluent. Forward elution is continued, until 95% of the salt peak (detected by the specific conductance meter) has eluted from the column. Hydrophilic organic acids, which are separated from the inorganic salts by adsorption on the column, are then backflush-eluted with 0.1 N NaOH followed by distilled water.

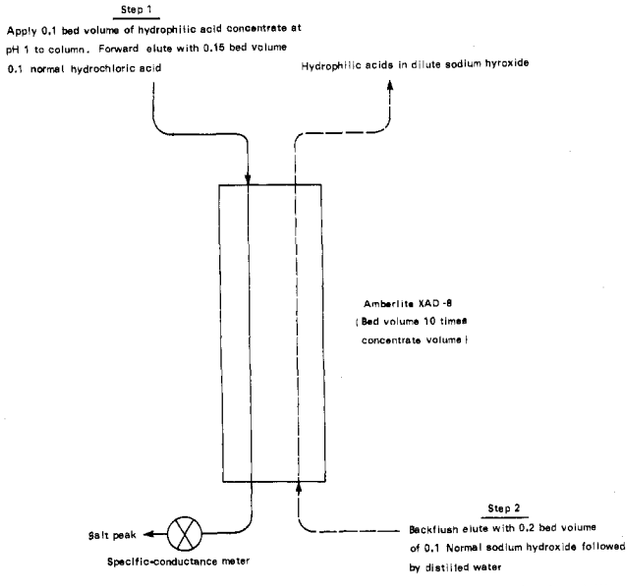

Figure 3. Chromatographic desalting procedure for hydrophilic acids.

This desalting procedure can be repeated in progressively smaller XAD-8 columns to decrease the salt concentration of the hydrophilic-acid concentrate as the mobile phases of the procedure add small amounts of HCl and NaOH to the concentrate solution. The point at which 95% of the salt peak elutes from the column corresponds to 50% retention of a solute whose $k'_{0.5r} = 0.12$. Therefore, organic solutes with a $k'_{0.5r}$ less than 0.12 cannot be desalted by this procedure.

Hydrophilic-Neutral Fraction. Hydrophilic neutral organic solutes contained in the deionized-water sample should be concentrated by freeze concentration, as described by Shapiro (*15*). As there are no salts remaining to form precipitates, and the remaining organic solutes are very soluble, 10–100-fold concentration factors are easily attainable without significant losses of volatile constituents. The Shapiro-type freeze concentrator sold by Virtis (Model 3-100) was used for the work described in this report.

Results and Discussion

An estimate of the relative quantities of organic and inorganic solutes of the two samples is given in Table I.

Preparative Dissolved Organic Carbon Fractionation of Omega-9 Retort Water. Ten liters of Omega-9 retort water were fractionated to obtain gram-sized quantities of organic solutes in each fraction to be used for biological testing. The major inorganic constituents of Omega-9 retort water are ammonium (3470 mg/L), sodium (4333 mg/L), bicarbonate (15 940 mg/L), thiosulfate (2740 mg/L), sulfate (1990 mg/L), and chloride (824 mg/L) (*16*). Previous attempts to scale up and modify the analytical DOC fractionation for preparative purposes using retort-water samples met with limited success, because of the formation of sulfur precipitates, due to the decomposition of thiosulfate in acid, outgassing of carbon dioxide when bicarbonate decomposed in the cation-exchange resin, and, most seriously, low recoveries of sorbed hydrophilic solutes from the cation- and anion-exchange resins (*6*, *17*).

Abrams and Breslin (*18*) reported that much greater recoveries of humic and fulvic acids sorbed from water were obtained by NaOH desorption from weak-base anion-exchange resins than from strong-base anion-exchange resins. Tests of various weak-base resins (*19*) indicated that the Duolite A-7 weak-base anion-exchange resin with the phenolformaldehyde matrix gave the greatest recoveries. This resin also had desirable characteristics of low DOC bleed after cleanup, high sorptive capacity factors, macroporous structure, and rapid adsorption and desorption kinetics and was inexpensive.

The sulfur-precipitation problem was solved by allowing the sulfur-formation reaction to go to completion during a 2-week period, after sample acidification in step 3 (Figure 1), allowing precipitated sulfur to settle out of the sample, and decanting. Minimal amounts of DOC adsorbed upon or coprecipitated with the elemental sulfur were lost by discarding the sulfur. Bicarbonate also was quantitatively decomposed outside the columns by sample acidification and, thereby, did not present any additional problems.

The remaining problem was low recoveries of hydrophilic bases from the cation-exchange resins (AG-MP-50). As the Duolite A-7 resin performs best when used in the free-base

Table I. Specific Conductance, pH, and Dissolved Organic Carbon of Water Samples

sample	specific conductance, μmho	pH	DOC, mg/L
Omega-9 oil-shale retort water	18600	8.6	977
South Platte River	445	7.9	7.5

form for the sorption of acids, the strong-acid cation-exchange resin (AG-MP-50) is required to hydrogen saturate the water sample. Most of the basic solutes in retort water are aromatic amines (*20*), which fractionate into both the hydrophobic-base fraction (di- and trimethylpyridines, quinolines) and the hydrophilic-base fraction (pyridine, aniline, picolines) in the analytical DOC fractionation. The most hydrophilic aromatic amine is pyridine, whose k' on XAD-8 is 15. Therefore, to maximize the total recovery of basic solutes, we lowered the hydrophobic–hydrophilic break of the DOC fractionation to $k'_{0.5r} = 4$, so that all of the aromatic amines including pyridine would be recovered in the hydrophobic-base fraction after sorption on XAD-8. A 4000-mL column of XAD-8 resin was required to process the 10 L of Omega-9 plus 10 L of rinse to obtain the hydrophobic–hydrophilic break at $k'_{0.5r} = 4$.

The column recoveries and overall recoveries of organic solutes are given in Table II, and the DOC fractionations, both preparative and analytical, are given in Table III. The recovery data in Table II show that the total column recovery (94.7%) is excellent, and the overall recovery (81%) is good. The only poor column recovery was in the hydrophilic-base fraction, but, as it constitutes only 4% of the retort-water DOC, overall DOC loss at this point was only 2%.

Regarding losses during secondary concentration and evaporation procedures, losses in the hydrophobic-base and -acid fractions occurred during rotary-vacuum evaporation. Most of these losses were due to entrainment in liquid droplets (boiling spatter) rather than true volatility losses. Most of the DOC loss of the hydrophilic-acid fraction occurred during the XAD-8 column desalting procedure. The salt-elution and DOC-elution curves are shown in Figure 4. Ca. 18% of the hydrophilic acids was lost with the inorganic salts, during the initial desalting stage. The "long tail" of the DOC-elution curve of Figure 4 accounts for and enables the 82% recovery upon the subsequent backflush desorption of the column. Additional small losses were incurred during rotary-vacuum evaporation and secondary stages of desalting.

Freeze concentration accounted for all of the loss of the hydrophilic-neutral fraction. Eighty percent of the total DOC loss occurred in the final volume reduction from 1.0 L to 240 mL. A smaller freeze concentrator for the final volume reduction might reduce this loss. Solute losses during freezing are considered to occur by entrapment in the ice; thus, they are largely nonselective losses.

It is obvious, upon examination of the preparative and analytical DOC fractionations given in Table III, that decreasing of the hydrophobic–hydrophilic break from $k'_{0.5r} = 45$ for the analytical fractionation to $k'_{0.5r} = 3.8$ for the preparative fractionation caused a large shift in DOC to the hydrophobic portion of the fractionations. For wastewaters with relatively large organic-solute concentrations, where large concentration factors are not required, shifting the DOC fractionation to the hydrophobic portion is desirable because of the greater recoveries generally obtained with the hydrophobic fractions. The relative proportions of total acids, bases, and neutrals are still similar for both the preparative and analytical DOC fractionations, which indicate a relatively distinct fractionation based on acid, base, and neutral characteristics of the organic solute.

Preparative Dissolved Organic Carbon Factionation of South Platte River Sample. Five liters of the South Platte River sample was processed through the preparative DOC fractionation procedure, with the hydrophobic–hydrophilic break being set at $k'_{0.5r} = 43$. After filtration through the silver-membrane filter, the sample retained a slight oil film on the water surface and slight cloudiness in the filtrate, which indicated the presence of colloidal material with particle diameters less than 0.45 μm.

Column recoveries and overall recoveries of organic solutes are given in Table IV, and the DOC fractionations, based on both adsorption and desorption, are given in Table V. Column recoveries exceed 100%, most likely because DOC concentrations determined in the sample were low. Large recoveries due to resin bleed are unlikely because DOC bleeds in acid and base eluent blanks of the clean resin columns were 1.0 mg/L or less. Low sample DOC concentrations resulted from the acidification and sparging procedure used to remove inorganic carbon. When samples were acidified, the colloid suspension, which fractionated into the hydrophilic-base and -acid classes, precipitated, and less soluble compounds (hydrophobic neutrals) probably coprecipitated. Precipitates were not representatively subsampled by the syringe-injection technique used in carbon analysis. Losses of volatile hydropho-

Table III. Preparative and Analytical Dissolved Organic Carbon of Omega-9 Retort Water

fraction	dissolved organic carbon, % preparative fractionation	analytical fractionation
total hydrophobic solutes	76 ($k'_{0.5r} = 3.8$)	49 ($k'_{0.5r} = 45$)
total hydrophilic solutes	24	51
hydrophobic bases	21	13
hydrophobic acids	30	19
hydrophobic neutrals	25	17
hydrophilic bases	4	12
hydrophilic acids	14	29
hydrophilic neutrals	6	10
total bases	25	25
total acids	44	48
total neutrals	31	27
DOC (mg/L)	977	977

Table II. Organic Solute Recoveries for Preparative Dissolved Organic Carbon Fractionation of Omega-9 Retort Water

fraction	column recoveries carbon adsorbed, mg	carbon desorbed, mg	recovery, %	overall recoveries after secondary concentration and desalting procedures carbon, mg	overall recovery, %
hydrophobic bases	2080	2080	100	1740	84
hydrophobic acids	2857	2857	100	2542	89
hydrophobic neutrals	2440	2147	88	2147	88
hydrophilic bases	357	189	56	178	50
hydrophilic acids	1367	1312	96	862	63
hydrophilic neutrals	595 (in column effluent)	595 (in column effluent)		348	58
totals	9696	9180	94.7	7817	81

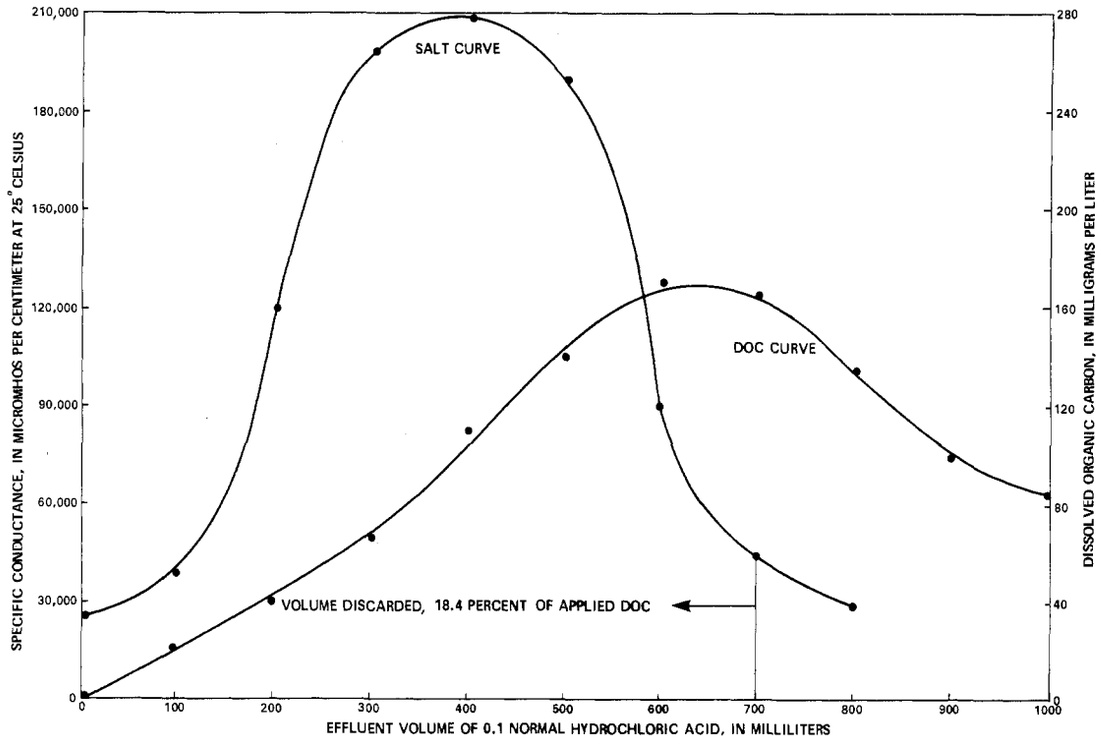

Figure 4. Salt and dissolved organic carbon elution curves obtained during chromatographic desalting of hydrophilic-acid fraction from Omega-9 retort water using an XAD-8 resin column.

Table IV. Organic Solute Recoveries for Preparative DOC Fractionation of South Platte River Sample

fraction	column recoveries			overall recoveries after secondary concentration and desalting procedures	
	carbon adsorbed, mg	carbon desorbed, mg	recovery, %	carbon, mg	overall recovery, %
hydrophobic bases	0.45	0.45	100	0.36	80
hydrophobic acids	6.76	6.76	100	6.58	97
hydrophobic neutrals	11.85	15.43	130	15.43	130
hydrophilic bases	9.54	9.75	102	5.70	58
hydrophilic acids	6.79	8.55	126	5.05	59
hydrophilic neutrals	2.11 (in column effluent)	2.11 (in column effluent)		1.91	91
totals	37.5	43.05	115	35.03	81 (of desorbed C)

bic-neutral compounds also occurred during the 6-min sparge with nitrogen gas.

All of the remaining solute losses occurred during secondary concentration and desalting procedures. Vacuum-rotary evaporation of the hydrophilic-base fraction caused a 42% loss of volatile compounds, and desalting of the hydrophilic acids resulted in 28% of the DOC, which eluted and was lost with the salt peak. Remaining losses of the hydrophilic-acid fraction occurred with vacuum-rotary evaporation.

The DOC fractionation (Table V) was very similar to the DOC fractionation of a sample obtained at the same site by Thurman and Malcolm (*21*), although the sample fractionated by Thurman and Malcolm contained more than twice the DOC. The fraction percentages changed slightly when the calculation was based on desorption rather than adsorption. The sample DOC increased from 7.5 to 8.6 mg/L when summation of the desorbed carbon was used to determine DOC. Because of the losses of carbon incurred with sample DOC determinations, the DOC value of 8.6 mg/L is probably the better value, and the DOC fractionation based on desorption is the more accurate. Another reason for the greater accuracy of the DOC fractionation based on desorption is the 10–100-fold concentration factor for DOC in each fraction, which decreased the errors incurred in the DOC determinations.

The final concentrate of each DOC fraction was freeze-dried, and an infrared spectrum was made on each fraction, to obtain a qualitative description of DOC in the South Platte River and to illustrate the completeness of the DOC fractionation. The various infrared spectra are given in Figure 5.

Acid and base fractions were neutralized to pH 7 and incorporated as salts into potassium bromide micropellets for infrared spectra determination. Insufficient material was isolated in the hydrophobic-base fraction to determine a valid infrared spectrum of this fraction. The hydrophobic-neutral fraction was run as a cast film on a silver chloride window, after evaporation of the methanol solvent.

The most prominent features of the hydrophobic fractions (spectra A and B, Figure 5) are the aliphatic hydrocarbon absorption bands at 2930, 2860, and 1455 cm^{-1}. The hydrophilic fractions (spectra C–E) are characterized by strong O–H stretching absorption bands from 2800 to 3600 cm^{-1} and by C–O stretching bands from 1050 to 1250 cm^{-1}. Acid fractions (spectra A and C) show strong carboxylate salt absorption bands near 1600 and 1400 cm^{-1}. The hydrophilic-base fraction (spectrum D) does not show any clearly defined basic amino groups, because of the interference of hydroxyl groups which absorb in the same region; however, the broad absorption band

from 1600 to 1700 cm^{-1} indicates the amide I and II bands, which are indicative of the proteinaceous materials likely to be found in this fraction.

Although each fraction has several distinguishing features in the infrared spectra, which indicate a relatively distinct and meaningful DOC fractionation, the multiplicity and the broadness of the infrared absorption bands indicate that each fraction contains a mixture of polyfunctional compounds. The hydrophobic-acid fraction gives infrared spectra very similar to those of a soil fulvic acid (*22*). The hydrophobic-neutral fraction appears to be a mixture of hydrocarbons and carbonyl compounds. As mentioned earlier, hydrophilic bases are most likely amphoteric proteinaceous constituents of DOC. The strong hydroxyl and carboxyl character of the infrared spectra of the hydrophilic-acid fraction indicates a mixture of various hydroxy acids. Finally, the infrared spectra of the hydrophilic-neutral fraction are similar to polysaccharide spectra (*23*).

Table V. Preparative DOC Fractionation of South Platte River Sample

fraction	based on adsorption % DOC	based on desorption, % DOC
total hydrophobic solutes	51	52
total hydrophilic solutes	49	48
hydrophobic bases	1.2	1.0
hydrophobic acids	18.0	15.7
hydrophobic neutrals	31.6	35.8
hydrophilic bases	25.4	22.6
hydrophilic acids	18.1	19.9
hydrophilic neutrals	5.6	4.9
total bases	26.6	23.6
total acids	36.1	35.6
total neutrals	37.2	40.7
dissolved organic carbon (mg/L)	7.5	8.6

Development Status of Dissolved Organic Carbon Fractionation. The analytical DOC fractionation, developed in 1976 (*5*), has been tested by various organic solute standards in distilled water and inorganic salt matrixes (*5*, *24*). Precision data obtained by using standards, samples, and distilled-water reagent blanks indicate that average deviations of 0.1–0.5 mg/L for each DOC fraction can be expected for the analytical method (*6*).

Precision and accuracy data for the preparative DOC fractionation presented in this report were not generated because of the large-scale effort required, but data for the analytical DOC fractionation as it pertains to XAD-8 and AG-MP-50 resins should be transferable, the only difference being the scale of fractionation. A distilled-water blank was run as part of the resin cleanup procedure for the preparative DOC fractionation; resin bleeds and reagent blanks did not exceed 1.0 mg/L DOC. The Duolite A-7 resin used for the preparative fractionation has only been tested with acetate and thiocyanate (*19*).

Primary needs for continued development of DOC fractionation, both analytical and preparative methods, are to calibrate the fractionation procedures with a wide variety of organic solute standards and test their applicability to a wide variety of waters. The variability of resin absorbents as supplied by the manufacturers also needs to be better assessed.

Possible Modifications of Preparative Dissolved Organic Carbon Fractionation. Analytical-Procedure Modifications. Three possible modifications of the analytical procedure for preparative DOC fractionation are shown in Figure 6. All three modifications use the cation-exchange resin as the means of acidifying the sample instead of adding HCl. The advantage of this modification is that no inorganic anions are added to the sample which must later be removed from the hydrophilic acids. Disadvantages are (1) the pH of the sample is not decreased to pH 2 or less if strong acid anion (chloride, sulfate) concentration in the sample is less than 10 mequiv/L, and, as a result, hydrophobic acids are not effectively sorbed by XAD-8 resin in the next column, (2) decomposition of carbonate and bicarbonate causes outgassing of carbon

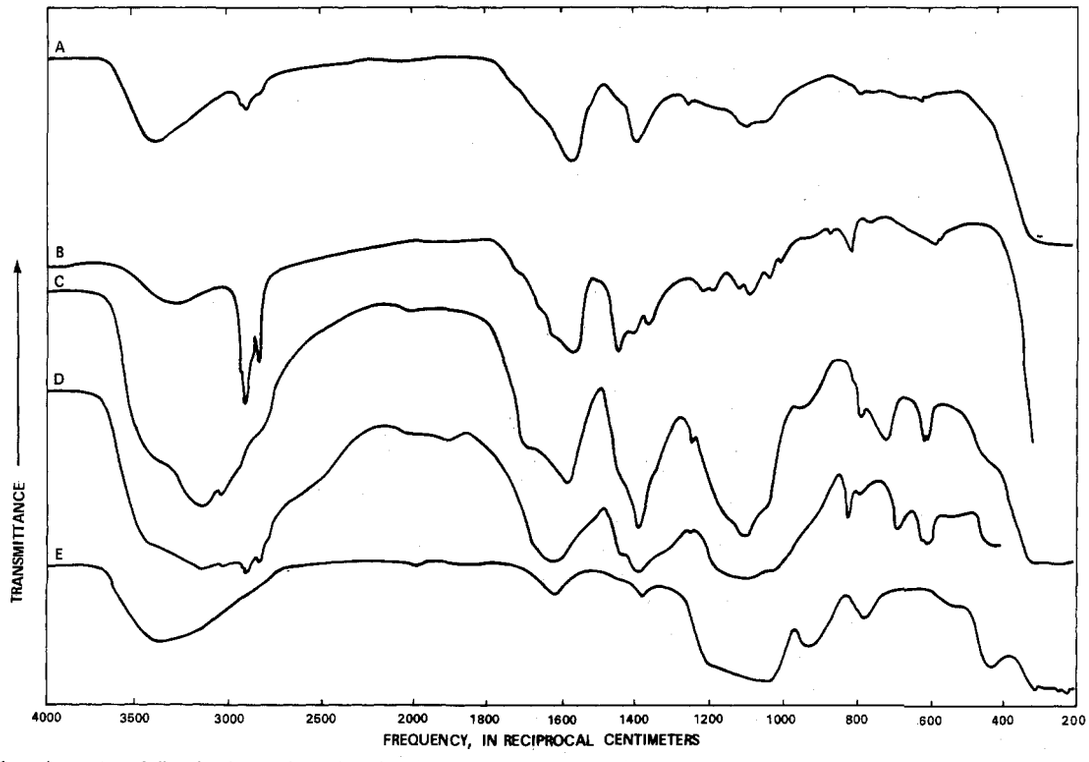

Figure 5. Infrared spectra of dissolved organic carbon fractions obtained from the South Platte River sample: (A) hydrophobic acids; (B) hydrophobic neutrals; (C) hydrophilic bases; (D) hydrophilic acids; (E) hydrophilic neutrals.

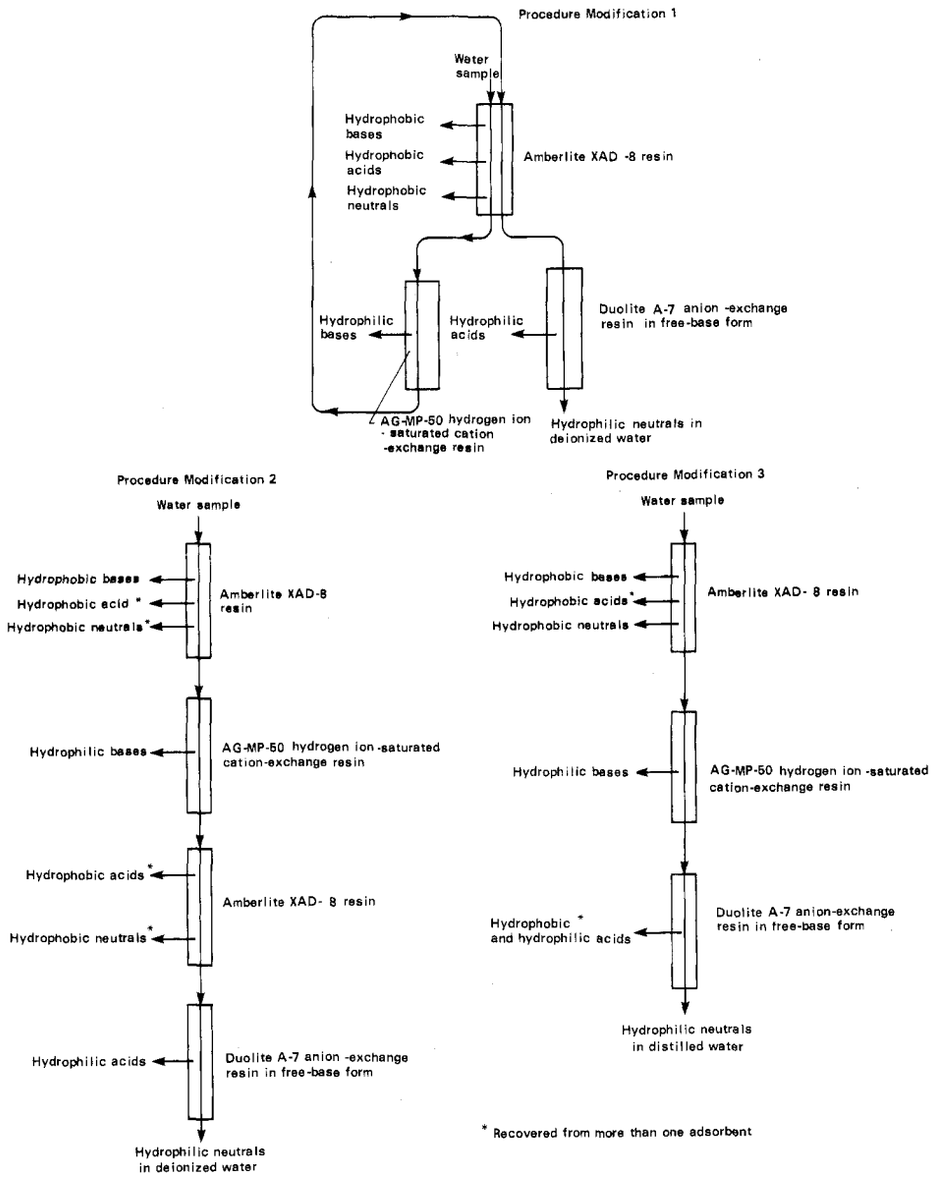

Figure 6. Analytical-procedure modifications for preparative dissolved organic carbon fractionation.

dioxide in the cation-exchange column, and (3) formation of precipitates (such as elemental sulfur with oil-shale retort water) causes fouling of the cation-exchange resin.

Analytical-procedure modification 1 has been used with an Omega-9 retort-water preparative DOC fractionation (*19*), and it can be applied to most water samples if the previously discussed limitations do not prohibit its use. Analytical-procedure modification 2 eliminates the sample recycle step through the XAD-8 column after acidification by inserting an extra XAD-8 column in the procedure. The advantage of this procedure is that the sample can be simultaneously pumped through all of the columns in series without pausing for the sample recycle step. The disadvantage is that the extra XAD-8 column splits the hydrophobic-acid and -neutral fractions between two separate columns. Analytical-procedure modification 3 also avoids the sample recycle step without the addition of an extra XAD-8 column. In this procedure, the hydrophilic acids and most of the hydrophobic acids are recovered together from the Duolite A-7 resin. The advantage of this procedure is its simplicity. Potential disadvantages include the loss of clearly defined DOC fractions, the need for a secondary separation of hydrophobic and hydrophilic acids, and the possible small recoveries of hydrophobic acids from the Duolite A-7 anion-exchange resin.

Solute Desorption Modifications. Many water samples do not contain significant concentrations of hydrophobic bases. On these samples, the water can be initially acidified to pH 2 and passed through the procedure illustrated in Figure 1 without generating a hydrophobic-base fraction and without sample recycle through the XAD-8 resin column. On certain natural waters and wastewaters, it is useful to separate weak phenolic acids from strong carboxylic acids. Thurman (*25*) found that a two-step desorption procedure using first $NaHCO_3$ (pH 8) buffer elution to desorb carboxylic acids, followed by NaOH (pH 13) elution to desorb phenolic acids, separated these two classes of acids for both the hydrophobic acids adsorbed on XAD-8 resin and the hydrophilic acids adsorbed on Duolite A-7 resin. For coal-coking and coal-gasification wastewaters, which contain significant concentrations of both hydrophobic bases and weak hydrophobic acids, a cleaner hydrophobic-base fraction (free from phenols) is obtained, if the distilled-water rinse in Figure 1, step 1, is replaced with a 0.1 N NaOH rinse, to elute the adsorbed phenols from the column before elution of the hydrophobic bases (20).

Hydrophilic-Acid Desalting Modifications. If k' values for hydrophilic-acid adsorption upon XAD-8 resin do not decrease significantly when the pH of the mobile phase is in-

creased from pH 1 to pH 2, use of 0.01 N HCl (pH 2) as the mobile phase during the adsorption step of the desalting procedure (Figure 2) will decrease by 10-fold the amount of chloride in the final concentrate. A more hydrophobic adsorbent, such as Amberlite XAD-2, or a pellicular absorbent (octadecyl silica) with more theoretical plates to give better column performance may significantly improve the chromatographic desalting procedure.

If the inorganic anion to be removed from the hydrophilic acids is chloride, it can be removed by precipitation upon a silver-saturated, strong-acid cation-exchange resin. Hydrophilic acids which elute with the salt peak in the chromatographic desalting procedure can possibly be desalted by ultrafiltration or gel-permeation filtration.

Conclusions

The high recoveries of DOC from two water samples with widely divergent natures by using the preparative DOC fractionation presented in this report indicate that complex mixtures of organic solutes in water can be quantitatively isolated from water and inorganic salts and can be distinctly fractionated into more homogeneous groups. Preparative DOC fractionation and its modifications can be used as a basis for quantitative and qualitative organic analysis of water and can also be used to generate organic-solute fractions for chemical and biological testing.

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Mechanism of Atmospheric Photooxidation of Organic Compounds. Reactions of Alkoxy Radicals in Oxidation of *n*-Butane and Simple Ketones

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Introduction

Alkoxy radicals play an important role in the breakdown of hydrocarbons and other organic compounds in atmospheric photooxidation. They are produced primarily by the fast O-atom transfer reaction of peroxy radicals, RO_2, and NO, in which NO_2 and RO· are formed. Three modes of reaction have been identified for alkoxy radicals formed under atmospheric conditions (*1–3*). The first mode, reaction with O_2 to give a carbonyl compound and HO_2, is potentially important for primary and secondary alkoxy radicals (1-RO and 2-RO) but not for tertiary radicals (3-RO) since they contain no labile α-H atom. Decomposition to give a carbonyl compound and a radical fragment is most rapid for 3-RO and decreases with decreasing substitution on the α-C atom. The third pathway is isomerization in which internal H-atom abstraction by the O radical center occurs; steric requirements restrict this process to alkoxy radicals which have H atoms on the C atom in position 4 or 5 relative to the C–O group and is therefore only important in the oxidation of hydrocarbon species having a carbon chain length ≥ 4.

Although a considerable amount of qualitative information on alkoxy radical behavior has been obtained, there are rather few experimental data for the rate constants of the various reaction pathways, even for the RO· radicals derived from simple alkanes (*4*). Little or no direct information concerning the substituted alkoxy radicals which contain different functional groups, such as are formed during the breakdown of olefins, carbonyl compounds, etc., is available. For the

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