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Isolation of Organic Materials from *in Situ* Oil Shale Retort Water Using Macroreticular Resins, Ion Exchange Resins, and Activated Carbons

ABSTRACT: Organic materials in an oil shale retort water produced *in situ* were fractionated using macroreticular resins, ion exchange resins, and activated carbon. Approximately 50 percent of the material was adsorbed on the macroreticular resin. Of the materials adsorbed on the macroreticular resin, 26 percent were basic, 36 percent were acidic, and 38 percent were of neutral character. Of materials passing through the resin, 21 percent were adsorbed on a cation exchange resin (basic), 58 percent were adsorbed on anion exchange resins (acidic), and 20 percent were not adsorbed (neutral). Activated carbon adsorbed quantities of material similar to those adsorbed by the ion exchangers if the sample was acidified before adsorption. Based on these fractionation experiments, a procedure to perform a preparative scale fractionation of an oil shale retort water produced *in situ* into representative organic compound classes has been developed. The four primary fractions isolated include hydrophobic bases, hydrophobic neutrals, carbon adsorbables, and nonadsorbables.

KEY WORDS: organic carbon, dissolved organic fractionation, oil shale retort water

As the petroleum reserves of the United States decrease in abundance, development of alternative fuels such as shale oil is essential. *In situ* oil shale processing is an attractive technology. A major consequence of *in situ* processing technologies developed to date is the production of copious quantities of by-product water. The possibility of obtaining as much as one barrel of retort water for every barrel of product oil poses serious environmental and technological problems [1].[2]

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

A large quantity (47 128 litres) of an oil shale retort water produced *in situ* has been collected and preserved [2,3]. The composition of the retort water produced *in situ* used in this study represents an approximate average of changing compositions observed during the course of the experimental burn [1]. This sample has been collected to allow for use by a number of investigators and thus provide an opportunity for an interdisciplinary evaluation of a single sample type. The experiments reported in this study are exclusively concerned with this reserve of retort water.

As a result of the diversity and complexity of the dissolved organic constituents, specific methods for individual compound analysis and techniques such as gas chromatography–mass spectroscopy have limited application to the overall characterization of the organic materials in oil shale retort waters. There exists a need for general characterization methods that will provide insight into the overall organic composition of such waters. One method that shows promise in this direction is the recently reported high-performance liquid chromatographic technique for fingerprinting or profiling dissolved organics [4]. Rubin et al [5] have developed a liquid–liquid extraction procedure for the fractionation of organic compounds in coal gasification and oil shale retorting by-product waters. Leenheer and Huffman [6] have recently developed a physical separation scheme utilizing macroreticular and ion exchange resins to reproducibly separate organic compounds into groups that are quantitated on the basis of their relative contribution to the total dissolved organic carbon (DOC) in the water sample. This scheme, referred to as the DOC fractionation scheme, is generally superior to fractionation schemes involving liquid–liquid partitioning and carbon adsorption.

Whereas, the DOC fractionation provides an analytical means of characterizing the nature of organic materials in retort water, a preparative fractionation scheme provides a means of determining the effects of related types of compounds in various systems. Preparative fractionation will allow studies to delineate biologically active materials, studies of the fates of various types of materials in the environment, and more detailed chemical and physical characterization.

A preparative fractionation procedure designed to obtain fractions from oil shale retort water for subsequent biological and environmental studies should have the following characteristics:

1. The quantity and quality of material recovered in each fraction must be reproducible between each batch of material fractionated.

2. Recoveries of materials in each fraction should be maximized and any incomplete recoveries documented.

3. The fractions should represent a cohesive group of materials suitable for additional subfractionation with minimal overlaps between fractions.

4. A limited number of fractions should be produced at each level of fractionation. This provides great cost savings in certain expensive biological experiments.

5. The procedure should be adaptable to producing at least several gram quantities of products in major fractions.

6. The products should contain minimal artifacts or adulteration due to the fractionation procedure.

Workers at Oak Ridge National Laboratory [5,7] have developed a fractionation procedure based on liquid–liquid extraction and subsequent column chromatography for both oil and water products. They have found their solvent extraction procedure to produce fractions suitable for biological characterization. However, solvent extraction is not an efficient method for removing polar organic compounds from aqueous solutions [6].

The objectives of the present study are to evaluate the application of the DOC fractionation scheme to the general characterization of organic materials in an oil shale retort water produced *in situ* and, based on these experiments, to develop a procedure to obtain preparative scale fractions. Retort water, like an organism, is an entity within itself, and the sum of the properties of its constituents does not represent the properties of the mixture. However, emphasis in development of the preparative fractionation was to obtain fractions that are suitable for subsequent biological characterization with minimal adulteration due to the fractionation procedure.

Procedure

Materials

The retort water sample used in this study was obtained from the Laramie Energy Research Center experimental *in situ* oil shale processing facility located near Rock Springs, Wyo., and carries the designation "Omega-9 retort water." The retort water was filtered previously (0.4 μm) to remove suspended material and has been maintained at 4°C. Details as to the acquisition, processing and storage of the large-volume Omega-9 reserve have been published [2]. Analytical data for this sample have been compiled [3].[3]

Unless otherwise noted, reagent grade chemicals and solvents were used throughout the study. If significant blanks in terms of residue or DOC was found, solvents were redistilled before use. Distilled water was used throughout the study and was periodically analyzed to confirm that its DOC content was below 1 mg/litre. Total carbon and organic carbon were determined on both solid and liquid samples with a Coulometrics System 130 carbon analyzer.

The macroreticular resin (XAD-8, Rohm and Haas, Philadelphia, Pa.) used in this study was prepared for use by decantation of fines and sequential 24-h Soxhlet extractions with methanol followed by acetonitrile and ethyl ether [8]. The purified resin was stored in methanol. After packing the columns, methanol was removed from the resin by passing distilled water through the columns until

[3]Important water quality parameters determined include: total organic carbon = 1020 mg/litre, pH = –8.6, $NH_4 \pm N$ = 3470 mg/litre, Na^+ = 4333 mg/litre, HCO_3^- = 15 940 mg/litre, $CO_3^=$ = 500 mg/litre, total Cl = 824 mg/litre, $SO_4^=$ = 1990 mg/litre, S_2O_3 = 2740 mg/litre, $S_4O_6^=$ = 280 mg/litre, SCN^- = 233 mg/litre, total dissolved solids = 14 210 mg/litre.

the eluent contained a DOC of less than 1 mg/litre. The activated carbons used for this study were pretreated by preparing an aqueous slurry and decanting fines before filling the columns. (Filtrasorb-300 and Filtrasorb-400 were obtained from Calgon Corp., Pittsburgh, Pa., Darco-4,000 and Darco-8,000 were obtained from ICI America, Inc., Wilmington, Del.) After the columns were packed, approximately 10 bed volumes of distilled water were passed through the columns before use.

Analytical Fractionation

The DOC fractionation analysis, which characterizes dissolved organic constituents based on their hydrophobic–hydrophilic and acid–base–neutral properties has been described [6]. The analytical procedure is outlined in Fig. 1. Hydrophobic materials are defined as those retained on the macroreticular (XAD-8) resin (DOC 1–DOC 3). Materials passing through the resin are termed hydrophilic (DOC 3). The sample is first passed through the XAD-8 column at its natural basic pH for the adsorption of hydrophobic bases and neutrals. Bases are subsequently eluted from the resin with acid (DOC 2). The sample eluent is then adjusted to pH 2 and again passed through the XAD-8 resin column for
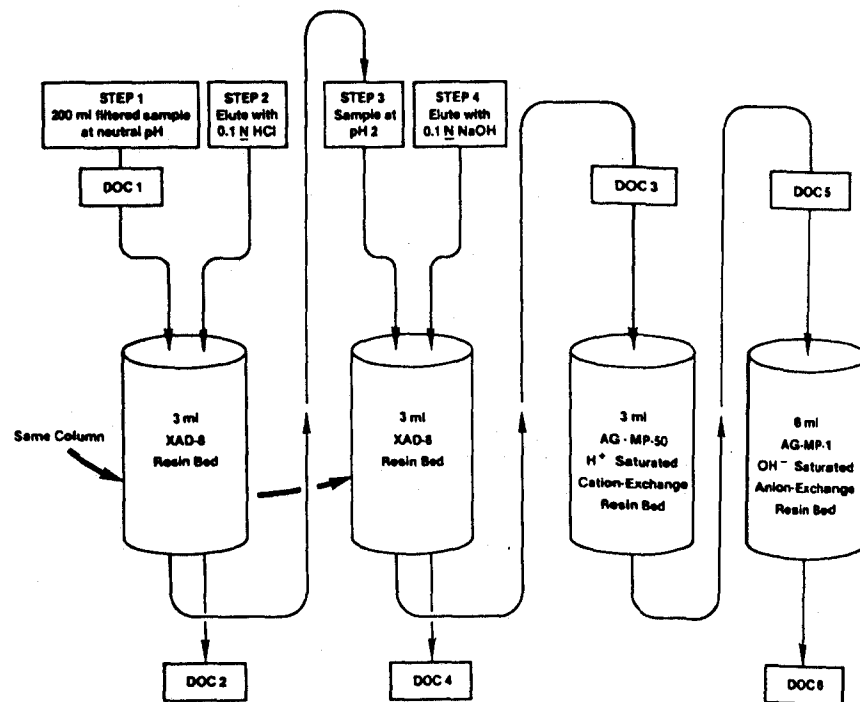

FIG. 1—*Analytical dissolved organic carbon (DOC) fractionation flow diagram.*

adsorption of acids. The adsorbed acids are subsequently eluted from the resin with base (DOC 4). The DOC content of the hydrophobic neutral fraction was determined by the difference between the initial DOC of the sample minus the combined DOC of XAD-8 sample eluent, base fraction, and acid fraction (DOC 1–DOC 3–DOC 2–DOC 4). Hydrophilic acids and bases are adsorbed on cation (Bio Rad AGMP-50) and anion (Bio Rad AGMP-1) exchange resins, respectively. The DOC contents of these hydrophilic fractions are determined by the difference in DOC between the influent and effluent of the respective ion exchange columns (bases, DOC 3–DOC 5; acids, DOC 5–DOC 6). Hydrophilic neutrals are represented by the DOC content of the effluent from the anion exchange resin (DOC 6).

Preliminary Experiments

Several modifications of the analytical DOC fractionation scheme were used for characterization of the dissolved organics and development of a preparative fractionation procedure. The modifications included:

1. The pH of the sample was not adjusted at any point in the procedure (consequently, the acid adsorption recycle, step 3, with the macroreticular resin was omitted).

2. Activated carbon was used in place of the ion exchange resins to adsorb hydrophilic materials.

Glass columns 1.5 cm inside diameter by 34 cm long with fritted glass supports and Teflon stopcocks at the lower end were used. The columns were packed by making a slurry of the appropriate adsorbent in water and filling the column so that a bed volume of 50 ml was obtained.

Preliminary recovery experiments were carried out on the XAD-8 and activated carbon residues after completion of the adsorption step. The XAD-8 resin was air dried for 24 h at room temperature, and the carbon adsorbents were dried in air for 24 h at 40°C. Desorption solvents included: 1,1,1-trichloro-2,2,2-trifluoroethane (freon), ethyl ether, methanol, chloroform, 0.1 N hydrochloric acid, 0.1 N sodium hydroxide, and steam. The acid, base, and steam extractions were performed in glass columns. In the case of the steam extraction, the column was placed in a tube furnace heated to 100°C when the steam was applied. The other extractions were carried out in a Soxhlet extractor. Organic carbon was determined directly on the aqueous desorbing solutions. In the case of organic solvents, a known portion of the extraction solvent was evaporated under a stream of dry nitrogen (purified air was used in a few early experiments). The residue was weighed, and organic carbon was determined on the residue.

Preparative Fractionation

Figure 2 shows the proposed preparative scale retort water fractionation scheme. Preparative fractionations were carried out using glass columns with a
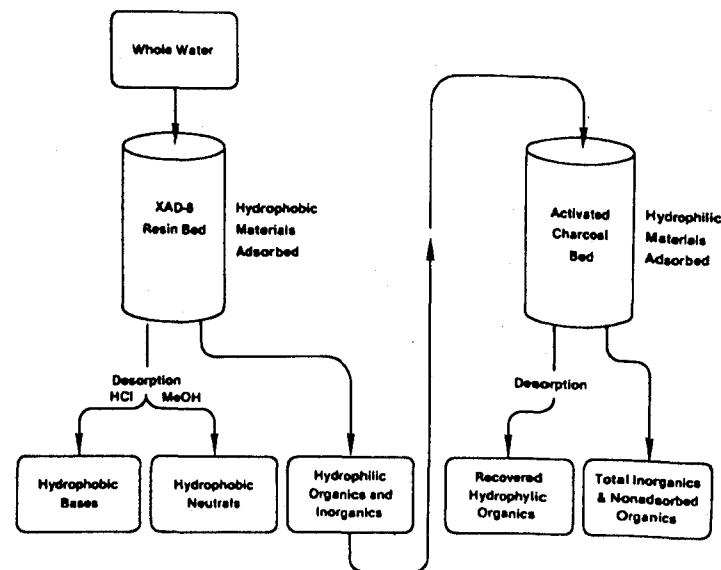
FIG. 2—*Preparative retort water fractionation scheme.*

5.5 cm inside diameter by 1 m long. Glass wool was used to support the adsorbents. Separate columns were packed with a methanol slurry of 1.3 kg of XAD-8 or an aqueous slurry of 1.4 kg of Filtrasorb-300. The columns were rinsed with several litres of distilled water. Eighteen litres of Omega-9 retort water was diluted 1:1 with distilled water in glass carboys and pumped through the XAD-8 column followed by the Filtrasorb-300 column in series at a rate of 50 cm³/min. To determine quantities of organic carbon adsorbed on the Filtrasorb and XAD-8, analytical samples were removed periodically from between the two columns. After the 36 litres of diluted retort water had passed through the two columns, a rinse of 2 litres of 0.05 M sodium carbonate was passed through both columns. The Filtrasorb column was then disconnected and the XAD-8 column eluted with 2 litres of 0.05 N hydrochloric acid.

After the hydrochloric acid elution, the column was allowed to drain, and the XAD-8 resin was spread on aluminum foil and allowed to air dry overnight. The dried XAD-8 resin was Soxhlet extracted for 24 h with methanol. The carbon adsorbent was dried in glass trays at 40°C for 24 h, followed by Soxhlet extraction for 24 h with chloroform.

Dissolved organic carbon was determined directly on the hydrochloric acid eluent of the XAD-8 and the aqueous carbon eluent. A known portion of the methanol and chloroform extracts were evaporated under a dry nitrogen stream at 40°C. The weight and organic carbon content were determined on the residues.

Organic materials adsorbed on the XAD-8 resin are termed hydrophobic. Hydrophobic neutrals are the materials remaining on the XAD-8 resin. The

adsorption of hydrophobic neutrals is calculated from the original DOC of the sample less the combined DOC of the effluent and base fractions. The recovery of hydrophobic neutrals is based on the amount of organic carbon adsorbed.

Materials passing through the XAD-8 resin are termed hydrophilic. Those materials adsorbed on the Filtrasorb-300 are termed adsorbed hydrophilics. The quantity of organic carbon adsorbed is determined from the amount of DOC in the XAD-8 eluent less the DOC of the Filtrasorb-300 eluent. The recovery of the recovered hydrophilic organic fraction is based on the quantity of organic carbon found in the chloroform extract divided by the quantity adsorbed.

Materials passing through the Filtrasorb-300 column are termed nonadsorbables. The volume of the nonadsorbable fraction is approximately 38 litres, and the DOC is determined directly on this fraction.

Results and Discussion

It is desirable to emphasize the definition of terms "hydrophobic" and "hydrophilic" as used in this paper. In all experiments, hydrophobic refers to materials retained on an XAD-8 resin, whereas, hydrophilic refers to materials passing through the XAD-8 resin. Substances may be converted from one classification to another by treatment of the sample. For example, according to the analytical DOC fractionation, hydrophobic acids are hydrophilic at basic pH (that is, the free acid is less soluble than its salt).

Analytical Fractionations

Table 1 shows the results of the analytical DOC fractionation with and without pH adjustment at various sample dilutions. All results are averages of duplicate runs and are given in terms of percentage of the DOC content of the original sample. The maximum range in results at any given dilution was ±3 percent of the total DOC.

TABLE 1—*Analytical dissolved organic carbon (DOC) fractionation at various dilutions with and without pH adjustment (step 3).*

	Total Dissolved Organic Carbon, %				
	With pH Adjustment			Without pH Adjustment	
Fraction	1:100 Dilution	1:20 Dilution	1:10 Dilution	1:100 Dilution	1:20 Dilution
Hydrophobics	53	49	48	35	34
bases	13	13	12	13	13
acids	18	19	19	3	4
neutrals	21	17	17	19	17
Hydrophilics	47	51	52	65	66
bases	9	12	10	12	12
acids	29	28	21	45	48
neutrals	9	10	20	8	6

The results show little effect of dilution in the 1:20 to 1:100 range. One might expect the results to be significantly altered in more concentrated solution due to compound association. It is important to remember that this is a physical separation, and even in the more dilute systems, compound association may still be an important factor.

The apparent low value for acids and consequent high value for neutrals in the 1:10 dilution hydrophilic fraction is due to exceeding the capacity of the anion exchange resin. Obviously, this could be overcome by increasing the quantity of resin. However, this illustrates that a major problem with ion exchange resins for this type of separation is that they must have sufficient exchange capacity for inorganic as well as organic materials in the sample.

As would be expected, the values for hydrophobic bases and neutrals are not affected by the deletion of pH adjustment. The 3 to 4 percent hydrophobic acids may represent either very weak acids, amphoteric compounds, or substances that become more hydrophobic in acid solutions. In this regard, it should be pointed out that there is an equilibrium between substances sorbed on the resin and the substance in the water phase. Depending on the equilibrium constant, various quantities of sorbed materials will equilibrate with the eluents such as the 0.1 N sodium hydroxide eluent. Thurman et al [9] have discussed the equilibrium of various materials with macroreticular resins.

The hydrophilic base and neutral fractions obtained with no pH adjustment are very similar to those obtained by the standard procedure. As expected, the hydrophilic acid fraction contains a quantity of DOC equivalent to both the hydrophobic and hydrophilic acid fractions from the fractionation with pH adjustment.

The effect of concentration on adsorption characteristics was further studied on samples without pH adjustment. Table 2 summarizes the effect of dilution on adsorption of hydrophobic bases and neutrals on XAD-8. At a 1:5 dilution, the results remain quite similar to those obtained at the 1:20 and 1:100 dilutions. In the more concentrated solutions, the adsorption of hydrophobics increases, especially the base fraction.

TABLE 2—*Effect of dilution on adsorption of hydrophobic materials on XAD-8 with no sample pH adjustment.*

	Total Dissolved Organic Carbon, %			
	0 Dilution	1:1 Dilution	1:2 Dilution	1:5 Dilution
Total hydrophobics	45	38	37	34
Hydrophobic bases	21	21	18	14
Hydrophobic neutrals	24	17	19	20

A major problem with the use of ion exchange resins for fractionation of organic constituents is that inorganic materials are also included in the fraction.

Carbon adsorption minimizes adsorption of inorganics but is undesirable in some approaches, because many organic compounds are irreversibly adsorbed by the carbon. In the scheme presented here, it was suspected that materials irreversibly adsorbed by carbon would be adsorbed by the macroreticular resin before the carbon adsorption step.

Table 3 shows results obtained using activated carbon for adsorption of hydrophilics. When the sample is acidified before adsorption, the quantity adsorbed corresponds to the quantity of hydrophilic acids and bases removed by ion

TABLE 3—*Adsorption of hydrophilics (at natural pH) by Filtrasorb-300 with and without adjustment to pH 2 before adsorption.*

Treatment	Hydrophilic Dissolved Organic Carbon Retained on Carbon, %[a]
No pH Adjustment	64 (42)
pH 2	91 (59)

[a]Values in parentheses are percentage of total dissolved organic carbon based on original sample and are comparable with values presented in Tables 1 and 2.

exchange resins. Only 64 percent of the hydrophilics in the unacidified sample are adsorbed by the activated carbon. Table 4 shows the results of an analytical and modified DOC fractionation analysis of the unacidified activated carbon eluent. The total DOC content of the acidified carbon eluent was so low that values obtained from an analytical DOC fractionation were not reliable, however, most of this DOC appeared in the hydrophilic neutral fraction. In the unacidified sample, hydrophilic acids are not adsorbed by activated carbon, and the hydrophilic neutrals are not adsorbed by either ion exchange resins or activated carbon.

TABLE 4—*Analytical dissolved organic carbon fractionation with and without pH adjustment of the organic materials passing through activated carbon without pH adjustment.*

	Total Dissolved Organic Carbon, %	
	Standard Fractionation	No pH Adjustment
Hydrophobics	8	2
bases	0.1	0.1
acids	3	1
neutrals	5	1
Hydrophilics	92	98
bases	6	4
acids	74	73
neutrals	13	21

These results demonstrate the usefulness of the analytical DOC fractionation scheme. We might expect that at the natural pH of the retort water hydrophilic acids would not be adsorbed on carbon. The analytical fractionation confirms this and shows that hydrophilic neutrals are not adsorbed by the carbon.

Preliminary Experiments

In addition to the analytical characterization experiments already described, several experiments were necessary to determine optimum parameters for a preparative scale fractionation procedure.

When the retort water is acidified, thiosulfate [10] decomposes and elemental sulfur precipitates. This precipitation may be accompanied by other reactions and coprecipitation of other materials. It is possible to destroy the thiosulfate with iodate. However, this treatment may cause artifacts in the treated sample that may affect subsequent biological and environmental studies on the isolated fractions. For this reason, the samples were not acidified during the preparative fractionation.

For preparative scale fractionations, dilution can result in copious quantities of material that must be handled. As a compromise between quantities of water to be handled and optimum adsorption characteristics (Table 2), a dilution of 1:1 was selected for preparative experiments.

As discussed previously, ion exchange resins do not distinguish between ionic organic and inorganic species. For this reason, activated carbon was chosen for adsorption of hydrophilics in the preparative fractionation.

Table 5 shows a comparison of adsorption and desorption efficiency of several activated carbons. There was no significant difference in performance between Filtrasorb-300 and Filtrasorb-400. Both adsorption and recovery were lower with the Darco carbons. Filtrasorb-300 was selected for subsequent experiments. It is interesting to note that Filtrasorb-300 is used in a method for recovering organics from water [11].

TABLE 5—*Comparison of various activated carbons for adsorption of hydrophilics and subsequent recovery by extraction with methanol and chloroform (average of duplicate runs).*

Adsorbent	Carbon Adsorbed, %	Adsorbed Carbon Extracted, %
Filtrasorb-300	70	51
Filtrasorb-400	68	50
Darco 4,000	63	47
Darco 8,000	59	40

Figure 3 shows the amount of DOC passing through the XAD-8 and Filtrasorb-300 adsorbents. The curves do not show a sharp breakthrough point, but, rather, a continuous increase. There is an equilibrium constant between the solution and adsorbed phase for each solute [9]. This means that, in a mixture such as
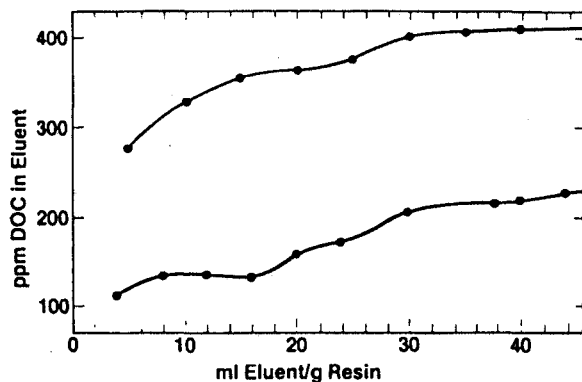
FIG. 3—*Dissolved organic carbon (DOC) breakthrough curves for XAD-8* (top) *and Filtrasorb-300* (bottom). *Initial DOC was 510 ppm.*

retort water, some materials will be strongly adsorbed and others only weakly adsorbed, resulting in the indistinct breakthrough characteristics. Based on the adsorption experiments (Table 1) with 1:100 dilutions, about 35 percent of the DOC should be adsorbed on carbon. Based on the breakthrough curves (Fig. 3), behavior of dilute solutions (Table 1), and the desirability of obtaining maximum adsorbent loadings, a quantity of 1.3 kg of XAD-8 and 1.4 kg of Filtrasorb-300 were chosen for the adsorption of organics from 18 litres of retort water.

The 1:1 dilution of retort water has a pH of about 8.3. If distilled water is used to rinse the column after adsorption, the pH is decreased and some organics are desorbed. To counteract this effect, the adsorbents were rinsed with 0.05 *M* sodium carbonate to remove nonadsorbed materials before recovery of adsorbed materials. In the analytical DOC fractionation, hydrophobic bases are desorbed from XAD-8 with 0.1 *N* hydrochloric acid. To minimize the acid content of the base (acid eluted) fraction, 0.05 *N* hydrochloric acid was used for elution. The 0.05 *N* hydrochloric acid eluted the same quantity of DOC as the 0.1 *N* hydrochloric acid. The use of the sodium carbonate rinse does result in the final recovered base fraction containing approximately 0.03 *N* sodium chloride.

Table 6 summarizes recovery of several organics from XAD-8. Of the solvents evaluated, methanol is the most efficient solvent. A variety of recovery experiments with methanol have shown recoveries of 94 ± 6 percent.

Table 7 summarizes the solvents evaluated for recovery of organics from Filtrasorb-300, and although chloroform only extracted 54 percent of the adsorbed DOC, it is superior to any of the other solvents examined. A variety of recovery experiments have been carried out on analytical carbon adsorption runs. Recoveries have varied from 45 to 68 percent. Reasons for the wide variability in recovery have not been fully elucidated. To obtain best recovery, the carbon should be dried for at least 24 h in thin layers that are occasionally

TABLE 6—*Efficiency of various solvents in removing hydrophobic neutral materials adsorbed on XAD-8 (average of duplicate runs).*

Solvent	Percent Recovery
Freon	23
Ethyl ether	31
Chloroform	90
Methanol	94

TABLE 7—*Efficiency of various solvents in removing adsorbed materials from Filtrasorb-300 (average of duplicate runs).*

Solvent	Percent Recovery
Freon	0.5
Ethyl ether	0.6
Methanol	35
Chloroform	54
0.1 *N* hydrochloric acid	4
0.1 *N* sodium hydroxide	12
Steam	28

stirred. Some of the apparent poor recovery of carbon adsorbables may be due to loss of volatile constituents during removal of solvent for weighing of recovered materials. A sample of raw retort water was dried and the residue redissolved in distilled water. The DOC after this treatment was 65 percent of the original value, suggesting that 35 percent of the total dissolved organics are volatile when taken to dryness. The high recoveries of the hydrophobic neutrals show that less than 5 percent of these materials are volatile. This suggests that the carbon adsorbables may be relatively volatile, accounting for some portion of the low recovery of carbon adsorbables.

Two other approaches were investigated for removal of solvents with minimal volatility losses. Flash evaporation resulted in lower recoveries. Use of a porous polymer trap for volatiles was investigated, but only slight improvements (<3 percent) were obtained.

Preparative Scale Fractionation

Eighteen litres of the retort water containing 18.6 g of dissolved organic carbon yielded the following fractions (deviations represent maximum range from average for two experiments):

1. *Hydrophobic bases*—This material was adsorbed on XAD-8 at the natural pH of the retort water (8.6) and eluted with 0.05 N hydrochloric acid. The 2 litres of 0.05 N hydrochloric acid obtained contains 2.9 g of 16 ± 2 percent of the original organic carbon.

2. *Hydrophobic neutrals*—This material was obtained by Soxhlet extraction of the XAD-8 resin with methanol after elution of bases. Based on adsorption data, the 2 litres of methanol contains 4.1 g or 22 ± 2 percent of the organic carbon from the retort water. Approximately 3.8 g or 20 ± 2 percent of the total organic carbon was recovered from the methanol.

3. *Carbon adsorbables*—This material was obtained by Soxhlet extraction of Filtrasorb-300 with chloroform. Based on adsorption data, the 2 litres of chloroform should contain approximately 8.7 g or 47 ± 3 percent of the organic carbon. However, only 32 ± 4 percent, or approximately 2.8 g, of the adsorbed carbon was recovered.

4. *Nonadsorbables*—This material is the eluent from the activated carbon column. It contains most of the inorganic species and 2.6 g or 14 ± 2 percent of the organic carbon.

Table 8 shows the results of adsorption and recovery of the preparative scale fractions compared to results of the preliminary fractionation experiments. The adsorption and recovery of hydrophobic neutrals and bases is in good agreement with the preliminary results. The agreement with analytical and dilute solution experiments shows that recoveries from the preparative fractions are predictable and reproducible.

TABLE 8—*Comparison of adsorption and recovery efficiencies between analytical and preparative fractionation.*

Fraction	Analytical Fractionation		Preparative Fractionation	
	Percent in Fraction	Percent Recovery	Percent in Fraction	Percent Recovery
Hydrophobic neutrals	21	95	22	88
Hydrophobic bases	17	...[a]	16	...[a]
Carbon adsorbables	42	61	47	32
Nonadsorbables	20	...[b]	14	...[b]

[a]The hydrophobic base fraction is obtained directly by elution with acid. Materials not recovered are included in the hydrophobic neutral fraction.

[b]The nonadsorbables are determined directly on the carbon eluent. Recovery data are not applicable.

A larger quantity of organics was adsorbed on activated carbon in the preparative scale experiment. Consequently, fewer organics were in the nonadsorbed phase. Unfortunately, the quantity of organics recovered from the activated

carbon dropped markedly. Future work will attempt to determine ways to improve recovery from the activated carbon.

Table 9 summarizes results of elemental analysis on the various fractions. The high ash content of the hydrophobic base fraction is due to the sodium carbonate rinse solution. A semiquantitative emission spectrographic analysis showed that sodium was the only significant metal in the ash. The presence of inorganic salt in this fraction represents a significant artifact of the procedure. In light of anticipated biological experiments, the 0.05 N sodium chloride represented the least objectionable of possible choices of recovery methods. Since nitrogen is usually associated with bases, it is interesting to note that the hydrophobic neutral fraction contains a significant nitrogen content. The high ash content of the nonadsorbable fraction is due to the inorganics originally present in the retort water. The hydrophobic neutral fraction and recovered hydrophilics show a low ash content. The forms of sulfur in the various recovered fractions are not known. If elemental sulfur precipitates on the adsorbents, it may be recovered in the extraction, and so these sulfur values may not represent organically bound sulfur.

TABLE 9—*Elemental analysis of the recovered fractions from 38 litres of retort water diluted 1:1.*

Fraction	Percent Recovered					
	Organic Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash
Hydrophobic neutrals	65.80	7.71	14.90	6.50	3.55	0.98
Hydrophobic bases	3.15	0.62	2.03	0.33	0.38	93.50
Recovered hydrophilics	54.50	7.80	22.47	6.63	5.51	0.71
Nonadsorbables	0.30	1.03	33.15	0.29	17.73	82.22

Table 10 shows results of a standard DOC fractionation analysis of the hydrophobic bases, carbon adsorbables, and nonadsorbables. Since the hydrophobic neutral fraction will not redissolve in water, it cannot be subjected to the DOC fractionation analysis.

As expected, the hydrophobic base fraction refractionates predominately into the base fraction. Refractionation of the recovered hydrophilics shows that this fraction contains primarily hydrophobic acids, hydrophilic acids, and hydrophilic neutrals. The nonadsorbables contain predominantly hydrophilic acids and neutrals. It is important to remember in interpreting these results that the percentage figures in the various fractions are based on the DOC of that fraction and not the original sample.

In terms of the criteria for a preparative fractionation procedure presented in the introduction, the procedure developed here meets most of the criteria but has two major shortcomings. The major problem is the poor recovery of adsorbed

organics from carbon. Many conclusions may be reached about the nature of the nonrecovered materials by different techniques. The hydrophobic base fraction contains acid or neutral salt that may be a serious artifact for certain subsequent uses of the fractions. The organic materials in the nonadsorbable fraction are low molecular weight neutral materials, and inclusion of these organics with the inorganics is not unreasonable. In spite of these shortcomings, the procedure provides a superior preparative fractionation scheme for subsequent biological evaluations.

TABLE 10—*Analytical dissolved organic carbon fractionation on recovered fractions.*

Fraction	Total Dissolved Organic Carbon, %		
	Hydrophobic Bases	Carbon Adsorbables	Nonadsorbables
Total hydrophobics	90	39	24
bases	81	1	1
acids	1	33	13
neutrals	9	4	10
Total hydrophilics	8	61	76
bases	6	8	8
acids	1	26	45
neutrals	1	27	23

Conclusions

The DOC fractionation procedure using macroreticular resin and ion exchange resins has been shown to be a reproducible method for characterizing organic materials in an oil shale retort water produced *in situ*. Alteration of pH and use of activated carbon instead of ion exchange resins for adsorption of hydrophilic materials gives predictable results in terms of the original DOC fractionation. Hydrophilic neutrals are not adsorbed by any method used in this study.

A preparative scale procedure for fractionation of an oil shale retort water produced *in situ* capable of producing gram quantities of fractions suitable for further bioenvironmental research has been developed. The four fractions recovered are hydrophobic bases, hydrophobic neutrals, recovered hydrophilics, and hydrophilic nonadsorbables. The procedure yields reproducible and predictable fractions. High recoveries are obtained except for the carbon desorbable fraction, where only 30 percent of the organics adsorbed on the carbon are recovered.

Future research will involve improvement of carbon recoveries as well as subfractionation of the various fractions. Biological assays on the four fractions will dictate which fractions should be further fractionated to delineate biologically active materials. In addition, the basic fractionation procedure should be applicable to other types of wastewaters.

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