



Project Summary

Isolation and Concentration of Organic Substances from Water Using Synthetic Resins and Graphitized Carbon Black

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This study describes the evaluation of an integrated adsorption system for the isolation and concentration, not less than 50 fold, of 22 specified organic compounds at $\mu\text{g/L}$ levels. The system was first developed and tested on a laboratory scale and then adapted for the processing of large volumes of water (pilot scale).

With this system, dissolved organics were separated into fractions by adsorption onto Amberlite XAD-8, AG MP-50 cation exchange resin, and graphitized carbon black (GCB) under varying pH conditions. Model compounds used in the evaluation covered a broad spectrum of physical and chemical properties, so that comparisons between this and other concentration/isolation techniques could be made.

A substantial effort was made to establish analytical techniques for monitoring model compound recovery in the proposed system. Quantification was performed using GC, GC/MS and HPLC.

In the laboratory-scale studies, 15 of the 22 model compounds exhibited recoveries varying from 30% to 90%. In general, poorer recoveries were observed for the more volatile, polar, or water soluble compounds. Recoveries of model solutes appeared to be virtually unaffected by the presence of humic acid (2 ppm) and inorganic salts.

The results of the final pilot experiments with five 100-L test solutions confirmed those of the bench-scale studies. However, some difficulties with column flow and lower recoveries

were encountered. These problems were attributed to humic acid breakthrough on the XAD-8 column and the subsequent coprecipitation of calcium salts, humic acid and possibly other organic substances at high pH.

This Project Summary was developed by EPA's Health Effects Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project report ordering information at back).

Introduction

In recent years, organic waterborne pollutants have been identified as potential health hazards. Epidemiological studies have suggested a relationship between the ingestion of these pollutants in drinking water and carcinogenic and teratogenic effects. Although hundreds of organic compounds have been detected and quantified in drinking water, the majority of organic material, i.e. the nonvolatile fraction, cannot be identified using currently available technology. Therefore, the direct concentration/isolation of organic contaminants in aqueous samples for biological testing offers a practical solution to the determination of health risks associated with trace organic contaminants.

The Health Effects Research Laboratory has funded several independent studies in an effort to determine the effectiveness of different isolation/concentration techniques. Systems or techniques investigated were reverse osmosis,

vacuum distillation, solid adsorbents, and supercritical fluid CO₂ extraction. The necessity of concentrating aqueous samples before an assessment of potential health risks can be made, stems from the lack of sensitivity for existing *in vitro* and *in vivo* biological test systems.

The following criteria must be considered when attempting to concentrate organic substances from potable water for biological testing: 1) the aqueous organic concentrate prepared by the selected concentration scheme should have the same relative abundance of the individual components as the original water sample; 2) introduction of artifacts and constituent alteration by the concentration method should be kept to a minimum; 3) alteration of the organic constituents after preparation of concentrates and before biological testing and chemical analysis must be avoided; 4) the effect of humic material, which constitutes the bulk of the organic fraction, on the recovery of trace solutes has to be taken into account; 5) co-recovery of toxic inorganic constituents by the concentration scheme should be avoided and 6) effect of chlorine residual on the material used in the concentration scheme — resins, graphitized carbon black, etc., must be assessed.

These considerations, as well as the necessity for a comprehensive approach toward the isolation and concentration of dissolved organic carbon in water, led to the investigation of an isolation scheme in which organic compounds with different functionalities and sorption parameters were separated and concentrated. A mixture of 22 model compounds proposed by the Health Effects Research Laboratory was chosen for process evaluation. The proposed isolation scheme was first tested on a laboratory scale and then adapted for processing several hundred liters of water.

Procedure

Preparation of Model Compound Test Solutions

As shown in Table 1 stock solutions of quinaldic acid, glycine and glucose were prepared in organic-free water (OFW). Humic acid was dissolved in 0.02N NaOH, 5-chlorouracil in 2N NH₄OH, and the remaining compounds in methanol except for phenanthrene; 1-chlorododecane; 2,4'-dichlorobiphenyl; and 2,2',5,5'-tetrachlorobiphenyl. The spiking of the test solution with the latter compounds required successive solubilization and evaporation in hexane and acetone prior to the addition of OFW. The test solutions for the other model solutes were prepared by simply diluting the required volume of

stock solutions in OFW containing 70 ppm NaHCO₃, 120 ppm CaSO₄ and 47 ppm CaCl₂·2H₂O. The salts were included to simulate inorganic levels found in a typical drinking water.

Preparation of Resins and Graphitized Carbon Black (GCB)

The XAD-8 resin was air-dried and sieved through 20- and 50-mesh size sieves, sequentially. The 20-50 mesh size fraction was washed and then stored in 0.1N NaOH for 24 hours. The remaining fines were removed by decanting. The resin was soxhlet - extracted for 24 hours each with acetone, hexane and methylene chloride. The cleaned resin was stored in methanol. In the laboratory-scale experiments, glass columns (200 x 13 mm I.D.) with Teflon stopcock were packed with 15 mL bed volumes (B.V.) of XAD-8. In order to process 100 L of test solution, larger glass columns (500 x 34 mm I.D.) with 250 mL B.V. of XAD-8 were prepared. Immediately before passage of the test solution, the resin bed was rinsed with 0.1N NaOH, 0.1N HCl and OFW in order to eliminate methanol and stabilize the column. The samples were processed at a flow rate of approximately 15 B.V./hour.

AG MP-50 (20-50 mesh, H⁺-form) was purified by Soxhlet-extraction with methanol (24 hrs) and stored in fresh solvent. Glass column dimensions were the same as for the XAD-8 resins in both the laboratory-scale and 100-liter pilot-scale experiments. Just prior to use, the AG MP-50 resin was rinsed with 3N NH₄OH, until breakthrough of ammonia was observed, followed by four B.V. of 2N HCl, and finally with OFW until the effluent was Cl⁻ free.

GCB was washed with acetone, methylene chloride, and OFW prior to column packing. Since this material is fragile, care was taken to avoid any mechanical stress which might cause particle rupture and consequently generate flow-rate problems. In the laboratory-scale experiments, 200 mg of GCB were packed in a glass column (200 x 5 mm I.D.) with a Teflon stopcock. In the large scale experiments, 10 g of GCB were packed in a glass column (300 x 35 mm I.D.) fitted with a Teflon rotaflo valve.

Isolation Scheme

The flow schematic of the isolation scheme devised and evaluated in the bench-scale phase of the study is shown in Figure 1. The test solution was first acidified to pH 2 and passed through the XAD-8 column by gravity flow at a rate of approximately 15 B.V. hr⁻¹. The final

portion of test solution was displaced from the resin with 1 B.V. of 0.01N HCl rinse and combined with the initial column effluent. Next, the hydrophobic acid fraction was desorbed with 0.25 B.V. of 0.1N NaOH followed by 1.5 B.V. of OFW.

Following elution of the hydrophobic acid fraction, the XAD-8 effluent plus rinse was adjusted to pH 10 with 1N NaOH. This solution was then recycled through the XAD-8 column at a rate of approximately 15 B.V. hr⁻¹ followed by 2.5 B.V. of OFW which was combined with the test solution effluent. The hydrophobic base fraction was eluted with 0.25 B.V. of 0.1N HCl followed by 1.5 B.V. of 0.01N HCl. The hydrophobic neutral fraction was recovered by transferring the XAD-8 resin from the column to a separatory funnel and extracting with three 50 mL aliquots of methylene chloride.

The test solution effluent, which should now contain only hydrophilic substances, was readjusted to pH 2 with 1N HCl and passed through the AG MP-50 cation exchange column at a flow rate of approximately 15 B.V. hr⁻¹. Desorption and elution of the hydrophilic base fraction was accomplished with 1N NH₄OH. Finally, the test solution effluent containing primarily hydrophilic acids and neutrals, was adjusted to pH 7 and passed through the graphitized carbon black column at a rate which allowed a 0.5-minute contact time. Elution of the adsorbed hydrophilic solutes was accomplished with methylene chloride.

In the pilot-scale experiments, two XAD-8 columns, one for each pH condition were used, rather than recycling the pH-adjusted effluent through the same column. Extraction of the hydrophobic neutral fraction from XAD-8 was accomplished by shaking the resin with methylene chloride in the glass column.

Results and Discussion

Bench-Scale Studies

The original scheme proposed for the trace enrichment of model organic solutes consisted of Amberlite XAD-8 resin, AG MP-50 cation exchange resin and Duolite A-7 anion exchange resin in series followed by reverse osmosis. However, initial testing indicated that Duolite A-7, as utilized in this system, did not significantly increase model solute recovery and it was eliminated from further study. Reverse osmosis was shown to recover a substantial amount of hydrophobic neutrals.

Table 1 shows the average recoveries obtained from six repetitive experiments

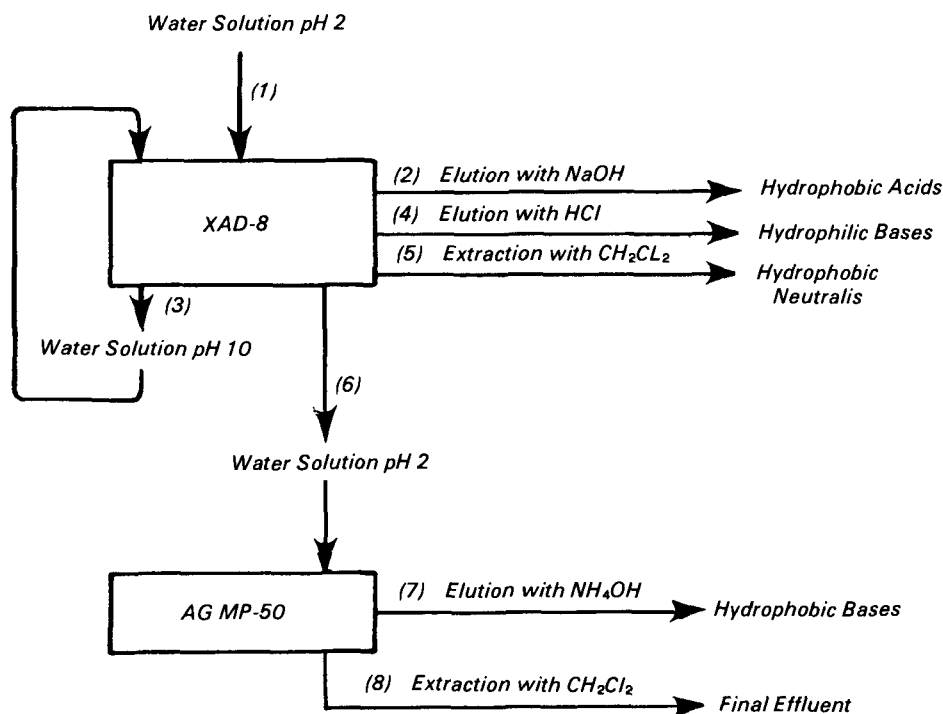


Figure 1. Flow schematic of resin fractionation scheme at laboratory scale.

at the bench-scale level. The test solutions were prepared in 500-mL batches with the following salt composition: 70 ppm of NaHCO_3 , 120 ppm of CaSO_4 , and 47 ppm of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Of the 22 model organic compounds, the following 15 were effectively recovered: stearic acid; trimesic acid; isophorone; biphenyl; 1-chlorododecane; 2,6-di-tert-butyl-4-methylphenol; 2,4'-dichlorobiphenyl; 2,2',5,5'-tetrachlorobiphenyl; anthraquinone; phenanthrene; bis(2-ethylhexyl)phthalate; quinoline; humic acid; caffeine and glycine. The 2,4-dichlorophenol was partially recovered in the hydrophilic base fraction, presumably because of an adsorptive affinity to the styrene divinylbenzene lattice of the cation exchange resin. Quinoline was partitioned between the hydrophobic base and the hydrophobic neutral fractions. Therefore, the acid used to elute the hydrophobic base fraction did not quantitatively desorb quinoline, suggesting that different adsorption mechanisms are responsible for its removal from aqueous solution onto XAD-8 resin. The presence of bis-(2-ethylhexyl)phthalate in several fractions suggested nonspecific adsorption on both macroreticular and ion-exchange resins. Chloroform not detected in the

Table 1. Average Recovery of Model Compounds From Bench-Scale Study

| Compound | Detections (number) | Concentrations (ppb) | % Recovery (S.D.) | | | |
|----------------------------------|---------------------|----------------------|-----------------------------------|-----------------------------------|--------------------------------------|--------------------------------------|
| | | | Hydrophobic Acid Fraction (XAD-8) | Hydrophobic Base Fraction (XAD-8) | Hydrophobic Neutral Fraction (XAD-8) | Hydrophobic Base Fraction (AG MP-50) |
| Stearic Acid | 3 | 50 | 32.4 (16.5) | | | |
| Trimesic Acid | 2 | 50 | 41.8 (13.1) | | | |
| 2,4-Dichlorophenol | 6 | 50 | | | | 13.8 (11.1) |
| Quinaldic Acid | 6 | 50 | NA | | | |
| Isophorone | 6 | 50 | | | 80.6 (18.5) | |
| Biphenyl | 6 | 50 | | | 82.7 (5.8) | |
| 1-Chlorododecane | 6 | 5 | | | 33.8 (6.8) | |
| 2,6-di-tert-Butyl 4-Methylphenol | 6 | 50 | | | 50.3 (8.6) | |
| 2,4'-Dichlorobiphenyl | 6 | 50 | | | 74.2 (5.3) | |
| 2,2',5,5'-Tetrachlorobiphenyl | 6 | 5 | | | 44.4 (22.1) | |
| Anthraquinone | 6 | 50 | | | 58.0 (13.3) | |
| Phenanthrene | 6 | 1 | | | 77.8 (27.8) | |
| bis(2-Ethylhexyl) phthalate | 4 | 50 | 1.8 (1.5) | | 37.6 (7.9) | 2.3 (1.6) |
| Glucose | 0 | 50 | | | | |
| Furfural | 6 | 50 | | | | ND |
| Quinoline | 6 | 50 | | 22.1 (10.6) | ND | |
| 5-Chlorouracil | 6 | 50 | ND | ND | 5.2 (1.9) | |
| Caffeine | 2 | 50 | | | 16.4 (5.4) | 3.7 (2.2) |
| Glycine | 4 | 50 | | | | 56.5 (19.6) |
| Humic Acid | 6 | 2000 | 85.1 (6.5) | | | |
| Chloroform | 6 | 50 | | | ND | ND |
| MIBK | 6 | 50 | | | ND | ND |

NA = Not Analyzed
ND = Not Detected

hydrophobic neutral fraction was presumed lost by the volatilization associated with the concentration and analytical procedures.

Because numerous model solutes were only partially adsorbed on XAD-8 and AG MP-50, adsorption studies were also conducted with graphitized carbon black (GCB). Recovery data for this adsorbent are provided in Table 2.

Pilot-Scale Studies

The average recoveries of the model compounds from five 100-L batches of test solution are shown in Table 3. The

majority of the model compounds demonstrated lower recoveries than those observed in the bench-scale experiments. Part of the failure was attributed to humic acid breakthrough on the XAD-8 column at pH 2. This breakthrough of humic acid resulted in the formation of solid calcium-humate upon adjustment of the effluent to pH 10. This affected column flow characteristics and may have caused some coprecipitation of other model solutes.

Incomplete humic acid adsorption was attributed to insufficient quantities of XAD-8. The decision to utilize a resin bed

volume of 250 ml, in the pilot study, was based on the following factors: known capacity of XAD-8 for aquatic humic material, the requirement of a 50-fold or greater concentration of solutes and a desire to minimize resin artifacts. Unfortunately, the capacity of XAD-8 resin for commercially available humic acid (soil origin) differed appreciably from the reported values for aquatic humic material.

The low recovery of 2,6-di-tert-butyl-4-methylphenol was attributed to partial oxidation, since 2,5-bis-cyclohexadiene,1,4-dione-bis(1,1-dimethylethyl) was tentatively identified in the test solution and in the hydrophobic neutral fraction. Further evidence was obtained from the observed continuous decrease of this compound in the organic standard solution used for GC analysis. Glycine was also found in considerably lower amounts in the hydrophilic base fraction, since the amount of Ca^{++} ions present in 100 L of test solution exceeded the exchange capacity volume of the AG MP-50 resin (1.7 meq/mL).

Conclusions

1. A method for the isolation and concentration of 22 model organic compounds from water (Table 1) was developed. The process separates the organic solutes into several fractions based on adsorption on

Table 2. Recovery of Model Compounds on Graphitized Carbon Black

| Compound | Desorbed from GCB | Extracted from water after GCB |
|-------------------------------|-------------------|--------------------------------|
| 2,4-Dichlorophenol | 115.2 | NF |
| Quinoline | 97.5 | NF |
| Isophorone | 16.3 | 92.4 |
| 1-Chlorododecane | 51.2 | NF |
| 2,4'-Dichlorobiphenyl | 48.6 | 0.9 |
| 2,2',5,5'-Tetrachlorobiphenyl | 54.1 | 3.7 |
| Anthraquinone | 92.1 | NF |
| bis-(2-Ethylhexyl)phthalate | 51.1 | 64.3 |
| Phenanthrene | 114.0 | NF |
| Caffeine | 92.1 | NF |
| Furfural | NF | 26.0 |
| MIBK | 6.7 | 65.5 |

NF = Not found

Table 3. Average Recovery of Model Compounds From Pilot-Scale Study

| Compound | Hydrophobic Acid Fraction (XAD-8) | Hydrophobic Base Fraction (XAD-8) | % Recovery (S.D.) | | GCB Fraction |
|----------------------------------|-----------------------------------|-----------------------------------|--------------------------------------|--------------------------------------|--------------|
| | | | Hydrophobic Neutral Fraction (XAD-8) | Hydrophobic Base Fraction (AG MP-50) | |
| Stearic Acid | 7.8 (9.1) | | | | |
| Trimesic Acid | 47.6 (19.8) | | | | |
| 2,4-Dichlorophenol | 11.3 (11.3) | | | | |
| Quinaldic Acid | ND | ND | | | |
| Isophorone | | | 37.4 (3.4) | | 3.9 (7.3) |
| Biphenyl | | | 56.8 (14.4) | | |
| 1-Chlorododecane | | | 94.7 (3.5) | | |
| 2,6-di-tert-Butyl 4-Methylphenol | | | 8.4 (12.6) | | |
| 2,4'-Dichlorobiphenyl | | | 70.1 (10.3) | | |
| 2,2',5,5'-Tetrachlorobiphenyl | | | 64.8 (14.7) | | |
| Anthraquinone | | | 59.9 (13.8) | | |
| Phenanthrene | | | 38.6 (6.9) | | |
| bis(2-Ethylhexyl)phthalate | 2.0 (1.9) | | 60.9 (17.8) | | |
| Glucose ^{NA} | | | | | |
| Furfural | | | ND | | ND |
| Quinoline | | 61.6 (25.6) | | | |
| 5-Chlorouracil | | | | 27.8 (10.7) | |
| Caffeine | | | | 4.8 (1.9) | 43.2 (28.4) |
| Glycine | | | | | |
| Humic Acids | 34.0 (4.6) | | | | |
| Chloroform | | | ND | | |
| MIBK | | | 3.3 (2.7) | | |

ND = Not Detected

NA = Not Analyzed

- Amberlite XAD-8 resin, AG-MP-50 cation exchange, and graphitized carbon black under varying pH conditions. Out of the 22 model compounds evaluated, the following fifteen compounds showed average recoveries between 30% and 90%: stearic acid; trimesic acid; isophorone; biphenyl; 1-chlorododecane; quinoline; 2,4'-dichlorobiphenyl; 2,6-di-tert-butyl-4-methylphenol; 2,2',5,5'-tetrachlorobiphenyl; anthraquinone; phenanthrene; bis-(2-ethylhexyl)phthalate; caffeine; humic acid; and glycine.
2. The fractionation system in general gave unsatisfactory recovery results for the more polar, water soluble and/or volatile solutes 5-chlorouracil, glucose, quinaldic acid, furfural, chloroform, and methyl isobutylketone. The lone exceptions were glycine and trimesic acid which were recovered on the cation exchange resin (AG MP-50) and XAD-8 resin, respectively.
 3. The majority of the compounds displayed a 15% or greater decline in adsorption in the pilot-scale study, as compared to the bench-scale experiment. This difference presumably resulted from undersized resin beds.
 4. The adsorption of the model solutes was found to be unaffected by the presence of humic acid.
 5. The introduction of artifacts by the resins appeared to be within reasonable limits (only three impurities were detected at levels comparable to that of the model compounds).
 6. The presence of a 2 ppm free chlorine residual carried through the adsorption scheme did not produce any major GC detectable artifacts.

column concentrations should be evaluated since solute breakthrough is a function of the column distribution coefficient as well as resin capacity.

4. To provide increased recovery of a broader spectrum of organic compounds, resin columns should be used in combination with reverse osmosis.

Recommendations

1. To improve mass balance determinations, future evaluation studies should include the use of radiolabeled model compounds where possible.
2. Aquatic humic acid, isolated from a major drinking water source, should be substituted for commercially available humic acid in future method evaluations, despite the increased cost.
3. Both resin capacity (batch studies) and column breakthrough data should be used to establish column dimensions for processing large volumes of test solutions. Where an increased concentration factor is necessary, the use of multiple

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H. P. Ringhand is the EPA Project Officer (see below).

The complete report, entitled "Isolation and Concentration of Organic Substances from Water—Using Synthetic Resins and Graphitized Carbon Black," (Order No. PB 85-125 672; Cost: \$13.00, subject to change) will be available only from:

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