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Project Summary

Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water Using XAD-4 Quaternary Resin

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As part of a continuing program to develop methods for the preparation of drinking water concentrates for biological testing, a synthetic resin (Amberlite XAD-4 quaternary) was evaluated as an adsorbent for the concentration/isolation of 22 specific organic solutes at μg/L levels. The adsorption and desorption processes were first developed and tested on a laboratory scale and then adapted for the processing of large volumes of water (pilot scale). Studies determining the effect of humic substances and inorganic salts (sodium bicarbonate at 70 ppm, sodium sulfate at 120 ppm, and calcium chloride at 47 ppm) on the adsorption/desorption of the model compounds were also performed in an effort to simulate drinking water conditions.

Because the method developed under this contract was ultimately intended to produce drinking water concentrates for biological testing, the effect of a 2 ppm chlorine residual on the generation of chlorinated organic compounds was studied.

In general, the XAD-4 quaternary resin in the hydroxide form was efficient in recovering the majority of the model compounds. Glucose, glycine, stearic acid and furfural were among the model compounds that could not be concentrated by the resin. Caffeine which could be concentrated effectively in the bench-scale experiment was not concentrated in the pilot scale runs.

Mass balances developed for each type of the compounds indicated that accountability was generally higher in bench/scale experiments as a drop of 10 to 20% in accountability was observed in the three pilot-plant studies. In the bench-scale studies, flow rates of either 150, or 48 BV/hr were used. In all pilot-plant studies a flow rate of 103 BV/hr was utilized. More importantly the amount of model compounds in the bench-scale studies was 3 mg for 10 cm^3 resin and 1500 mg for 200 cm^3 resin in the pilot-scale runs.

A statistical evaluation of the pilot-scale studies suggested that the presence of humic substances affected the concentration of the model compounds, particularly trimesic acid. While the effect of salts appeared to be significant on 1-chlorododecane and 5-chlorouracil, this was not conclusive because of differences observed between the bench-scale and pilot-plant studies.

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

The field of separation science has made great strides in recent years in de-

veloping techniques for isolating, separating and concentrating organic species in drinking water. One impetus for these advances has been the search for sensitive and accurate analytical methods for trace organic contaminants. A second has been the need for effective concentration and isolation techniques for preparing concentrates for health effects testing since many of the biological tests are not sufficiently sensitive to evaluate drinking water directly. The objective of this project was directed towards the latter application.

Within the realm of analytical separation systems, by far the most fruitful approach has been in the use of solid sorbent techniques. Although other approaches have been studied (reverse osmosis, solvent extraction, foam separation, etc.), none is so versatile and offers so much potential for selectivity, concentration and field-use as adsorption techniques. This project dealt only with the investigation of adsorbents for the isolation of organic substances for toxicological testing. Furthermore, it was limited to the investigation of newly developed synthetic sorbents such as the polymeric XAD-4 quaternary anion exchange resin rather than traditional activated carbons.

Our goal for this project was to develop a system for sampling 500 liters (or more) of drinking water which might contain 1 to 50 ppb concentration of organic compounds. Mass balances for each compound have been determined to reveal the unrecovered amount of each compound. The mass balance determinations were performed in an attempt to determine whether recovery losses were the result of volatilization, adsorption, and/or chemical transformation.

Synthetic solvents are known to contain artifacts in the resin that could be eluted during desorption of the organic compounds concentrated on the resin. Therefore, separate experiments using XAD-4 quaternary resin (OH^- form) were also performed to evaluate the presence of artifacts, either those arising from the interaction of chlorine with the resin or those from the resin itself.

Experimental Procedures

Preparation of Model Compound Test Solutions

Test solutions of the model compounds selected by the U.S. Environmental Protection Agency (EPA) to be used in the bench-scale and pilot-scale studies were prepared by diluting the required volume(s) of stock solution with organic free water containing an inorganic salt matrix. The salt matrix consisted of 77 ppm $NaHCO_3$, 120 ppm Ca_2SO_4 and 47 ppm $CaCl_2 \cdot 2H_20$. Table 1 lists the final concentration at which each model compound was tested. During the experiments, it was noted that there was some precipitation of salt in the reservoir prior to passing the water through the column. The pH was, therefore, adjusted from approximately 8.5 to 7.0 with 1NHCl to correct the problem.

Bench-Scale Column and Resin Preparation

The apparatus used during bench-scale studies for the isolation/concentration of organics from water is shown in Figure 1. The adsorption/desorption column was 37 cm long × 1 cm I.D. In most bench-scale studies, this column was filled with 13 cm of XAD-4 quaternary resin (OH^- form) of 40 to 80 mesh. This was equivalent to approximately 10 cm^3 of wet resin.

The resin clean-up procedure used during this project utilized Soxhlet extraction with the same solvents used for elution. This assured that any impurities would be eluted prior to the actual adsorbent studies. One other solvent, methylene chloride, was also used for resin clean-up, but only during the resin blank study. The XAD-4 quaternary resin was stored in the chloride form under water rather than methanol, since it is not stable when stored under methanol.

The resin is basically an XAD-4 macroreticular crosslinked polystyrene into which a trimethylamine group was introduced. The resin was converted from the chloride form to the hydroxide form before use in the resin sorption experiments.

Table 1. *Summary of Percent Recovery and Percent Total Mass Balance of All Model Compounds in Bench-Scale Studies*[a]

	Conc. (μg/L)	% Recovery[b]	Total % Mass Balance[c]
anthraquinone	500	101	101
biphenyl	596	71.7	71.9
bis(2-ethylhexyl)-phthalate	668	55.2	77.5
caffeine	50.7	31.6	46.4
chloroform	48.7	69.9	83.6
1-chlorododecane	502	42.6	60.0
5-chlorouracil	5,000	91.1[d,e]	91.1[d,e]
2,6-di-tert-cutyl-4-methyl phenol	696	62.2	63.7
2,4'-dichlorobiphenyl	404	66.7	68.8
2,4-dichlorophenol	500, 5000	28.8, 66.1[d]	28.8[d]
furfural	52.4	56.4	75.5
glycine	19,700	0	87.7[e]
glucose	19,800	0	88.9[e]
humic acid[f]	2,000	79.9	79.9
isophorone	500	77.2	77.4
methyl isobutyl ketone	50.5	102	102
phenanthrene	1.0	112	112
quinaldic acid	500, 5000	96.2, 117[d]	96.2, 117[d]
quinoline	48.4	86.7[e]	86.7[e]
stearic acid	50	60.1	81.5
2,5,2',5'-tetrachlorobiphenyl	172	51.9	67.7
trimesic acid	500, 5000	33.6, 53.0[d]	34.5, 53.0[d]

[a] *Studies performed with salts added, without humic acid, and at a flow rate of 150 BV/hr unless otherwise indicated.*

[b] *% Recovery—Represents % of model compound recovered in solvent eluants. Values represent average of 3 determinations.*

[c] *Total % Mass Balance—Represents total % recovered from solvent eluants + column effluent + reservoir rinse.*

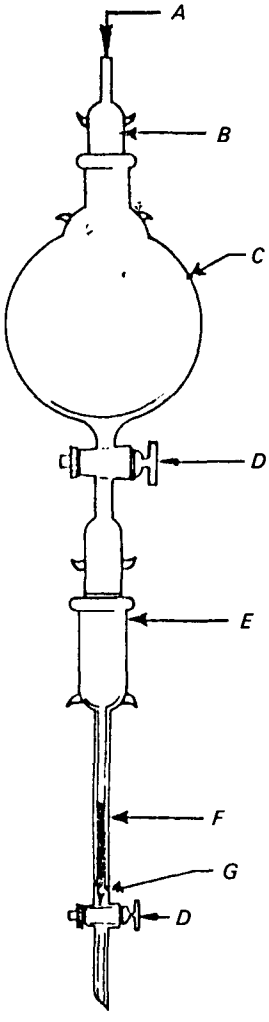
[d] *Flow rate was 48 BV/hr.*

[e] *Value is average of two determinations.*

[f] *Study performed in the presence of salts but the absence of other model compounds.*

Pilot-Plant Design

The design of the pilot plant scale-up was based upon breakthrough studies with quinaldic acid. During scale-up from bench-scale to pilot plant it was decided to keep two factors (residence time and through-put) as close to constant as possible. The first factor controls the rate of adsorption while the through-put controls the capacity of the resin. Experimental conditions were as follows: column dimensions 16" by 1" i.d., residence time 0.57 min, Bed Volume (BV) = 200 cm^3, flow rate = 103 BV/hr.



(A) Pure Inert Gas Pressure Source

(B) Cap

(C) 2-Liter Reservoir

(D) PTFE Stopcock

(E) 24/40

(F) 1.0 cm - I.D. x 37 cm Long Glass Tube Packed with 13 cm Resin

(G) Silanized Glasswool Plug

Figure 1. *Apparatus for extracting organic solutes from water.*

Column Adsorption/Desorption Scheme

Prior to passing the pH 7 test solutions through the columns (1L for bench-scale; 500L for each pilot-plant run) the XAD-4 quaternary resin was changed from the chloride to hydroxide form by passing 75 ml of 0.1N NaOH through the column, followed by organic-free water until the pH of the effluent water was neutral (approximately 100 ml).

In a typical bench-scale study, five columns were set up: one column for control of reagents and glassware; one column for the control of the resin blank; and triplicate columns for model compound studies. Two flow rates were studied in the bench-scale studies. The initial flow rate was 150 BV/hr. A lower flow rate of approximately 48 BV/hr was also evaluated. Flow rates were maintained by nitrogen cylinder pressure. Following passage of the test solution through the column the reservoir was washed with 25 ml of organic-free water and drained through the column.

The desorption was then accomplished with a series of solvents for the elution of neutral, basic and acid compounds. The following steps were used to desorb the different classes of model compounds:

1) Six 25 ml of distilled diethyl ether. The first 25 ml portion of distilled ether was added to the resin column, and the column was agitated to free the resin. The column was then allowed to stand for 5 to 10 minutes before draining. The second through the sixth 25 ml portion of ether eluants were used for desorption by gravity flow without agitation and were combined with the first aliquot.
2) Two 25 ml methanol. This was used for better desorption of caffeine and removal of any remaining water from Step 1.
3) Two 10 ml ether. Used for removal of residual methanol from Step 2 which could interfere in the methylation of acidic compounds.
4) Two 25 ml 0.1N HCl/ether. Used for removal of acidic compounds.
5) Two 25 ml 0.1N HCl/methanol. Used for removal of acidic compounds.
6) Two 25 ml saturated HCl/methanol. Used for removal of humic substances.

Resin Blank Artifacts/Effect of a 2 ppm Chlorine Residual Blank Experiment with Chlorine

This experiment was designed to provide information regarding the effect of chlorine on the production of new chlorinated compounds. Duplicate blank experiments for both pure water and pure water spiked with 2 ppm chlorine residual were performed by the bench-scale resin separation/concentration procedure. This was done for comparative purposes, since only compounds identified in the extract of the chlorine spiked water which are not present in the normal extract from pure blank water were considered as true artifacts caused by the chlorine. In addition, a reagent blank was also concentrated and analyzed.

Clean Water Blank Experiment

This experiment was performed to identify any artifacts that might arise from the resin in the course of normal resin experiments. Four replicate resin blanks were run by the normal column adsorption/desorption scheme.

Results and Discussion

General

The mass balance studies required that analyses be made of the aqueous effluent and column reservoir, as well as the organic eluant from the resin. In order to analyze the aqueous solutions it was usually necessary to extract the model compounds using an organic solvent such as methylene chloride. This is particularly difficult for highly water soluble substances like quinaldic acid, trimesic acid, glycine and glucose and hampers mass balance determinations.

Bench-Scale Study

Resin studies using XAD-4 quaternary resin (OH^- form) were performed several times at 150 BV/hr at various concentrations of the model compounds. Table 1 summarizes the experimental results of the bench-scale experiments. Corrections for extraction efficiency were made for the analysis of aqueous effluent portions of certain model compounds. Twenty-one of the 22 model compounds were evaluated during this

phase (Table 1). It is important to note that quinoline, glycine and glucose were studied at mg/L levels during this phase of the project because of analytical considerations.

Most hydrophobic neutral compounds showed strong concentration by the resin according to the adsorption mechanism (Van der Waals attraction) characteristic of non-ionic polymer resins. In other words, the anionic exchange capacity of the XAD-4 quaternary resin did not seem to affect (either favorably or unfavorably) its capacity to absorb neutral organic compounds.

One hydrophobic neutral compound which showed low recovery in the eluant concentrate was 1-chlorododecane. The reason for the low recovery of this aliphatic hydrocarbon is not clear but one possibility is that it adsorbs onto particulates and passes through the resin in a "micelle" form.

While recoveries of 2,2',5,5'-tetrachlorobiphenyl and bis(2-ethylhexyl)phthalate were both good, a reasonable amount of each compound was also recovered from the water. It is possible that the flow rate for aqueous samples affected the efficiency with which the compounds are sorbed by the resin. Note the improved recoveries for the acidic compounds in Table 1 that were tested at 48 BV/hr.

Acids, in general, have posed problems due to their tendency to form salts. The XAD-4 quaternary resin has the capacity to adsorb acids by two mechanisms, i.e., Van der Waals adsorption and anion exchange. Successful elution with diethyl ether suggests a Van der Waals type adsorption while the necessity of utilizing acidified organic solvents is characteristic of an anion exchange mechanism.

Pilot-Plant Studies

The experimental work involved in pilot-plant studies 1, 2, and 3 was basically the same as the resin blank pilot study. Twenty-one of the 22 model compounds were tested in all three studies, but the inorganic salt matrix was only present in studies 2 and 3. Humic acid was only present in study 3. This order permitted one to evaluate the effect of salts and humic acid on the recovery of the model solutes.

The desorption steps were performed in the columns three times with 150 mL of solvents as in the resin blank pilot-plant study. The resin was shaken each time, then allowed to stand for 20-30 minutes before it was drained. Internal standards were added immediately prior to analysis. Table 2 provides the results of the three runs.

A statistical evaluation of the data using a paired t-test indicated that the lower recoveries observed for study 3 were statistically significant from studies 1 and 2 ($p<0.01$). This was also true when the data for trimesic acid was omitted. No significant difference was observed between studies 1 and 2.

Blank Experiment with Chlorine

This experiment was designed to provide information regarding the effect of chlorine on the production of new chlorinated compounds. Data from this experiment indicated that no new chlorinated compounds were identified as having originated from the addition of chlorine to the blank water.

Clean Water Blank Experiment

This experiment was performed to identify any artifacts that might arise from the resin in the course of normal resin experiments. Based on the results of these tests it was necessary to clean the XAD-4 quaternary resin by batch process with saturated HCl/methanol prior to Soxhlet cleaning by solvents. Artifacts such as benzoic acid were found in the resin blank experiments but the mass of each artifact (per day weight of resin) was considered negligible.

Conclusions

The procedure used in this study for the isolation/concentration of organic compounds in drinking water demonstrated that the XAD-4 quaternary resin (OH^-), is effective for most neutral, acidic and semi-volatile compounds. Because of the quaternary function of this resin, it was possible to concentrate several acidic compounds without any change in the pH of the sampling water. This is an advantage over normal XAD resins for on-site compositing or grab sampling since the problem of continuous acid addition and subsequent pH monitoring is avoided.

Many classes of the organic compounds adsorbed by this resin can be desorbed by solvents such as ethyl ether or acidic methanol and ethyl ether. The acidic solvents can be concentrated to remove inorganic acid, but some residual inorganic acid always remained in the concentrated eluants. The residual acid, or possible trace of water in the concentrated eluants, caused analytical variances when methylation was attempted. Therefore, quinaldic acid, trimesic acid and 5-chlorouracil were analyzed by HPLC rather than GC-FID.

Humic substances were concentrated more than 50-fold on the XAD-4 quaternary resin, but a saturated HCl/methanol solution was required for the desorption. Percent recovery of humic acid, methyl isobutyl ketone, quinoline, phenanthrene, anthraquinone, humic acid, caffeine and 5-chlorouracil were markedly higher in the bench-scale experiments. While the flow rate or linear velocity appeared to affect adsorption for the acidic substances, differences observed here are probably a result of loading capacity since the pilot-plant studies utilized a lower flow rate. The higher percent recoveries for the bench-scale studies were determined to be statistically significant using a paired t-test with a confidence interval of 95 percent.

Recommendations

Future research on the isolation/concentration of organic compounds in water may need to minimize analytical problems by use of radiolabeled compounds.

Based on the results of using several polymeric adsorbents, it appears that the XAD-4 quaternary resin has the best potential for field sampling of natural water. This resin exhibited low blank contamination, and for the most part, was found to concentrate most neutral, acidic and semi-volatile compounds.

Breakthrough experiments should be considered for specific compounds to evaluate the effect of mass transfer due to velocity changes. Breakthrough may not occur for large volumes of water samples with trace organic contaminants due to the high capacity of the XAD-4 resin, but high concentrations of specific compounds may breakthrough.

Future research on the XAD-4 quaternary resin for concentration of trace organics may concern:

1) Several different column dimensions to further evaluate the effect of flow rate for field sampling column size.
2) Utilization of aquatic humic material to more closely simulate drinking water conditions.
3) Experiments with known organic compounds in actual drinking water samples to evaluate the resin efficiency due to suspended matter, and soluble inorganic salts.

Table 2. *Summary of Mass Balance and % Recoveries of All Model Compounds in All Pilot Studies (500L)*

	Amount Spiked (μg)	Pilot Plant Study No. 1		Pilot Plant Study No. 2		Pilot Plant Study No. 3	
		% Recovery	Total % Mass Balance	% Recovery	Total % Mass Balance	% Recovery	Total % Mass Balance
anthraquinone	25,000	50.9	53.2	40.2	44.4	39.5	45.6
biphenyl	25,000	62.6	68.4	51.8	60.4	40.3	52.4
BEHP	25,000	22.2	34.8	22.8	39.8	15.1	22.9
caffeine	25,000	0.9	25.1	0.8	23.7	0.6	28.7
chloroform	25,000	34.8	59.5	42.4	113.8	36	79.2
1-chlorododecane	2,500	34.1	34.4	87.0	87.2	41.8	42.0
5-chlorouracil	25,000	32.9	48.0	43.9	83.2	41.7	65.6
2,6-di-tert-butyl-4-methyl phenol	25,000	52.4	64.8	42.3	48.0	28.0	45.2
2,4'-dichlorobiphenyl	25,000	54.8	60.4	35.3	40.4	37.8	47.2
2,4-dichlorophenol*	25,000	40.6	59.0	34.6	53.4	26.2	66.5
furfural	25,000	49.8	53.6	55.2	57.6	50.2	50.8
glycine	25,000	0	80.7	N.A.	N.A.	N.A.	N.A.
humic acid	1,000,000	N.A.	N.A.	N.A.	N.A.	40.7	85.7
isophorone	25,000	66.4	77.2	52.2	64.4	55.2	67.6
MIBK	25,000	34.5	34.5	28.1	28.1	25.6	25.6
phenanthrene	500	51.0	52.6	55.4	56.6	44.0	44.6
quinaldic acid HPLC	25,000	109.0	109.6	117.2	120.8	95.9	96.4
quinoline	25,000	31.0	31.0	21.4	21.4	21.7	21.7
stearic acid	25,000	<1	<1	<1	<1	<1	32.5
2,5,2',5'-tetrachlorobiphenyl	2,500	47.0	48.8	43.9	44.8	28.7	28.7
trimesic acid	25,000	75.6	75.6	93.1	93.1	22.3	22.3

*These totals are sums of μg found in neutrals analysis for 2,4 DCP and acids analysis for 2,4 DCP (all GC cap FID results).
N.A.—Not analyzed.
% Recovery—Represents % recovered from solvent eluants.
Mass Balance—Represents total % recovered from solvent eluants + column effluent + reservoir rinse.

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***H. Paul Ringhand** is the EPA Project Officer (see below).*
The complete report, entitled "Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water—Using XAD-4 Quarternary Resin," (Order No. PB 86-101 847/AS; Cost: $16.95, subject to change) will be available only from:
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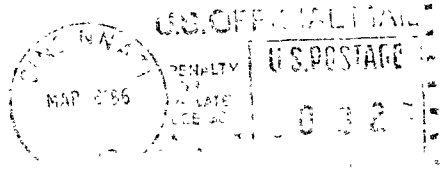

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