## Extraction of Organic Compounds from Aqueous Media by Amberlite XAD Resins

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Three Amberlite polymeric resins, XAD-2, XAD-4 and XAD-7, were evaluated for extraction efficiency from aqueous media of several organic compounds representing pesticides, polyaromatic hydrocarbons, phenols and phthalate esters. The three resins exhibited different extraction characteristics. The extraction efficiency of the resins was found to be dependent on pH conditions and, on the average, was best at pH 7. At this pH the XAD-2 and XAD-4 resins yielded quantitative recoveries in the 90–100% range for most compounds at the 20–200 ppb level. Recoveries by XAD-7 resins were lower for several compounds. The recovery of aldrin and o,p DDT under all conditions was relatively low ( <68%) and showed a higher degree of variability than that obtained for the other compounds. Alkaline pH conditions were generally unfavourable for the extraction of phenolic compounds but acidification to pH 2 was not found to be a necessary step for the quantitative extraction of the phenolic compounds. Acidification to pH 2 further led to a decrease in the recovery of most compounds for XAD-4 resins. A combined resin column yielded extraction efficiencies comparable to the XAD-2 column at pH 7, but since the three resins possess different extraction characteristics, a mixture comprising all three is recommended for the preconcentration of organic compounds from environmental water samples containing a wide range of compounds.

KEY WORDS: Extraction, organic, XAD resin, water.

## INTRODUCTION

The applicability of the Amberlite polymeric resins for the extraction of organic compounds from water has been the subject of many reports. Junk and coworkers studied the extraction of a cross-section

of organic chemicals by the resins and highlighted the critical steps for obtaining reliable quantitative analyses in a standardized analytical scheme employing these resins.[1] Burham demonstrated the quantitative recovery by XAD-2 of methyl isobutyl ketone, benzene, ethyl butyrate, naphthalene, benzoic acid, aniline and several phenols in the parts per billion range.[2] Other workers have applied these resins to the extraction of several classes of compounds and some have compared their extraction capabilities to those of other adsorbants such as carbon.[3-5] In most cases higher recoveries were obtained for XAD-resin sorption than for carbon sorption techniques.

Many reports detail the application of the Amberlite resins to the extraction of specific compounds or groups of compounds from distilled water, wastewaters, and drinking water. Polychlorinated biphenyls and many pesticides and pesticide residues have been successfully recovered and analysed from fortified water samples as well as natural waters from different parts of the world.[6,7] The isolation and preconcentration of chlorophenoxy acetic acid herbicides from water with XAD-2 and XAD-7 resins was studied by Niederschultz and Ballschmiter.[8] Halogenated hydrocarbons in water have been quantified by methods based on extractions by resins.[9] Other specific applications of the Amberlite resins to the analysis of organic compounds in water include the recovery of nitrosamines[10] and phenols.[11]

Amberlite resins are hard, insoluble, polymerized copolymer beads.[12] Each bead is formed from microbeads cemented together during polymerization, giving the resin a macroreticular structure which results in a high surface area in each bead. The resins are available in a variety of polarities and are usually provided in a nominal mesh size of 20–60 mesh. Amberlite XAD-2 and XAD-4 are styrene-divinylbenzene copolymers and function as non-polar, hydrophobic adsorbents. Amberlite XAD-7 is an acrylic ester polymer, which is more polar and has a somewhat more hydrophilic structure than the XAD-2 and XAD-4 resins. The adsorption of organic compounds onto the homogeneous surface of these resins is a low energy binding process involving van der Waal's forces, which allows for easy desorption of the adsorbed molecules.

The work reported here is an integral part of a study on organic pollution in the Caroni River, Trinidad. One of the major objectives

of the study is the development of simple and reliable methods for the broad-spectrum monitoring of organic compounds present in this river.[13] The extraction efficiency of Amberlite XAD-2, XAD-4 and XAD-7 was evaluated for several pesticides, polyaromatic hydrocarbons, phenols and phthalate esters under different pH conditions in order to establish whether pH adjustment is required prior to extraction of water samples. These compounds are representative of the classes of compounds found in the Caroni River. Although other workers have studied the extraction of organic compounds by the XAD resins, a systematic study of the simultaneous extraction of this group of compounds has not been done. This study was, therefore, required as a basis for the development of an optimal methodology for the quantitative extraction and analysis of the samples from the Caroni River, for use in future monitoring programs. The variability of extraction with pH conditions is especially important since requirements for pH control will influence the design of extraction equipment and the time needed for analyses. The procedures used for extraction and concentration of compounds from aqueous media were essentially those outlined by Junk with a few modifications.[1] Losses of compounds incurred through evaporation of organic extracts in a preconcentration step with a Kuderna Danish evaporator followed by further concentration with a stream of nitrogen gas were also evaluated.

## EXPERIMENTAL

### Instrumental analysis

Quantitative gas chromatographic analyses were performed with a Hewlett-Packard (HP) 5880A gas chromatograph equipped with a level 4 integrator, a flame ionization detector, cool on-column injection system and a widebore (0.32 mm × 30 m) DB-1701 fused silica capillary column (J & W Scientific Inc. Rancho Cardova, CA. U.S.A.). The GC conditions were: injection port 40°C; column temperature programmed from 40°C to 250°C at a rate of 4°C/min; detector temperature 300°C; helium carrier gas flow rate measured at 40°C, 2 mL/min; injection volumes 0.4 $\mu$L or 0.6 $\mu$L.

Capillary gas chromatographic/mass spectrometric analysis

employing a Hewlett-Packard 5992A GC/MS/Calculator equipped with the same column was used to verify the identities of compounds corresponding to each gas chromatographic peak.

## Sorbents and reagents

Amberlite XAD-2, XAD-4 and XAD-7 resins (Rohm and Haas, Philadelphia) were purified by sequential twelve hour Soxhlet extractions with methanol, acetonitrile and diethyl ether. The purified resins were stored under methanol.

Purified water was prepared by extracting distilled water sequentially with previously cleaned XAD-2 and XAD-7 resins.

Diethyl ether was subjected to a clean-up procedure involving four solvent extractions with sodium hydroxide solution (0.05 M) in order to remove a contaminant which was identified in earlier chromatographic analyses of ether extracts. This contaminant was identified as isobutyric acid. Equal volumes of sodium hydroxide and diethyl ether were used in each extraction.

All solvents were distilled-in-glass grade obtained from Caledon Laboratories, Canada. Sodium hydroxide pellets and hydrochloric acid were ACS grade (J. T. Baker Chemical Co.).

## Standard compounds

Standard organic compounds were obtained from the U.S. Environment Protection Agency Reference Standards Repository; The Polyscience Corporation U.S.A.; Chem. Service Inc. Pa.; and Aldrich Chemical Company, Inc., Wisconsin, U.S.A.

## Glasswool preparation

Silanized glasswool (Chromatographic Specialities, Canada) was soaked in purified water for several minutes, placed in a glass column fitted with a teflon stopcock and extracted with several mL of clean ether followed by a few mL of purified water.

## Column preparation

Glass columns, 25 cm in length, i.d. 1.0 cm, fitted with teflon

stopcocks were employed. A plug of pre-extracted silanized glasswool was inserted at the bottom of the column and a slurry of the resin in methanol added to the column. Approximately 2 g of resin were used to produce a resin column 8 cm long. Another plug of pre-extracted glasswool was inserted into the column at the top of the resin bed and the methanol was drained through the stopcock until the liquid level just reached the top of the resin bed. The resin was then washed with 50 mL of diethyl ether followed by three 20 mL portions of purified water. For each portion the flow was stopped when the liquid level reached the top of the resin bed.

## Efficiency tests

Figure 1 outlines the approach used in these studies. A two-litre glass reservoir was attached to the top of each column, care being taken to ensure that the quickfit joint between the reservoir and column was leakproof. To 500 mL of water was added 100 μL of a test solution containing the following standard compounds in concentrations ranging between 100 and 1000 ppm: methyl tetradecanoate, methyl hendecanoate, 1-naphthol, phenyl phenol, endrin, biphenyl, α-BHC, γ-BHC, dieldrin, aldrin, fluoranthene, 1 methyl-phenanthrene, o,p, DDT, phenanthrene, 2,3 dimethyl naphthalene, methoxychlor, 1,6 dimethyl naphthalene, o-ethyl phenol, n-hexyl benzene, dibutyl phthalate, benzyl benzoate. Pentachlorophenol, diphenyl mercury, chlordane and arochlor 1254 were also included in the test solution but the FID response for the compounds was too low to allow their quantification. The test solution was introduced into the water via a microsyringe, the needle of the syringe being kept beneath the water surface while the solution was being delivered. The resulting aqueous solution of the standards whose concentrations ranged from 20 to 200 ppb was carefully added to the reservoir and allowed to pass through the resin column by gravity flow at 30 mL/min. When the solution level reached the top of the resin bed the wall of the reservoir was washed with three 25 mL portions of purified water, each portion being allowed to drain through the column to the top of the resin bed. The last wash was allowed to drain completely through the column.

The sorbed organics were then eluted with 25 mL of purified diethyl ether. The reservoir wall was washed with two 10 mL

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STEP 1

```
┌─────────────────────┐
│    500 mL H₂0       │
│    spiked with      │        SPIKED SOLUTION
│  100 µL of test     │
│     mixture         │
└─────────┬───────────┘
          │  STEP 2
┌─────────┴───────────┐
│   XAD resin         │
│     column          │        EXTRACTION
│                     │
└─────────┬───────────┘
          │  STEP 3
┌─────────┴───────────┐
│    Diethyl          │
│     ether           │        ELUTION
│    eluate           │
└─────────┬───────────┘
          │  STEP 4
┌─────────┴───────────┐
│  Concentrate        │        SOLVENT REDUCTION
│    organic          │
│    extract          │
└─────────┬───────────┘
          │  STEP 5
┌─────────┴───────────┐
│      GC             │        QUANTITATIVE ANALYSIS
│                     │
└─────────┬───────────┘
          │  STEP 6
┌─────────┴───────────┐
│    GC/MS            │        PEAK VERIFICATION
│                     │
└─────────────────────┘
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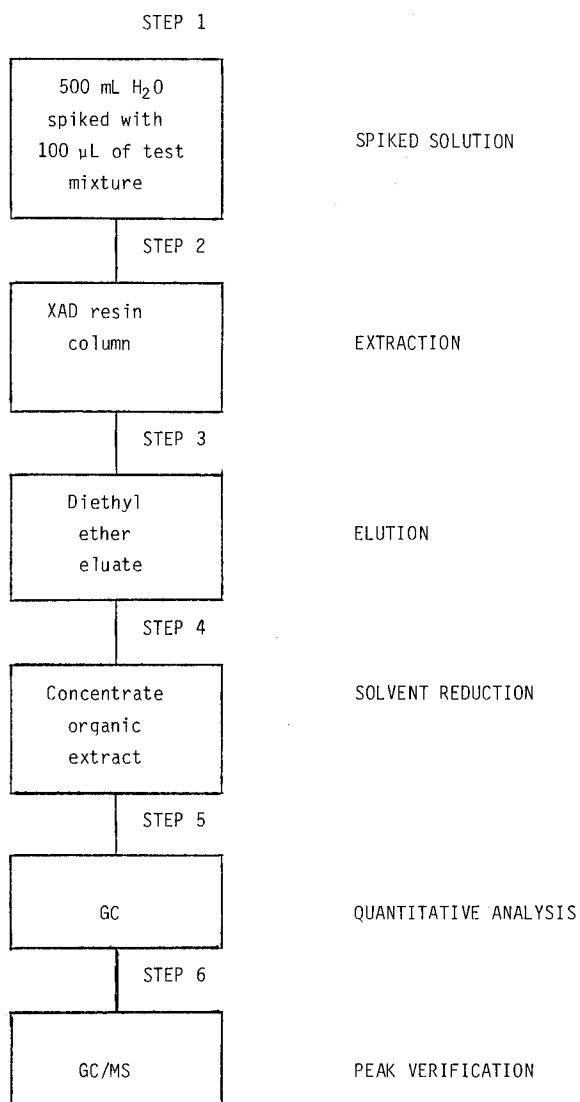
FIGURE 1   Block diagram illustrating the procedure used from study of resin efficiency.

portions of diethyl ether and each wash allowed to drain into the resin but not through the column. The reservoir was removed, the column capped and left to stand for fifteen minutes. The ether was then allowed to drain through the column and the eluate collected into a 25 mm diameter thick-walled test-tube. A further 5 mL of ether was added to the column and allowed to flow through immediately into the receiving test-tube.

Residual water was removed from the diethyl ether by immersing the test-tube in liquid nitrogen for several seconds to freeze the water (lower layer). The supernatant diethyl ether solution was decanted into the concentration vessel of the Kuderna Danish (K–D) evaporator. The ice in the test-tube was washed with 5 ml of ether, the test-tube briefly re-immersed in liquid nitrogen and the ether decanted into the concentration vessel.

The organic extract of $\simeq 35$ ml volume was concentrated to 1.5 mL using the K–D evaporator. The volume was then adjusted to 0.1 mL with a stream of nitrogen and the recoveries of the various compounds determined by gas chromatography. The final volume adjustment was done by evaporating the solution to the 0.1 mL mark of factory-calibrated 1 mL Pierce® Reacti-vials (Chromatographic Specialities, Canada). All chromatographic peak areas of the concentrated extracts were corrected for error in the factory-calibration of the vials. The correction factor for each vial was obtained through recalibration of the vial using a 100 $\mu$L syringe with gradations of 1 $\mu$L. For a series of 10 calibrations of the same vial a relative standard deviation of 2.3% was obtained. Extraction efficiencies of XAD-2, XAD-4 and XAD-7 resins were determined for aqueous solutions of the standards at pH 7, 2 and 12. Solutions of pH values 2 and 12 were obtained by adding 5 mL of concentrated HCl and 5 mL of a 1 M solution of sodium hydroxide respectively to the 500 mL of water used for preparing the standard. All experiments were performed in triplicate.

## Evaporative losses

100 $\mu$L of the test solution was injected via a microsyringe into 50 mL of diethyl ether contained in the concentration vessel of a K–D evaporator. The solution was evaporated to $\approx 1.5$ mL, then further concentrated to 1.0 mL with a stream of nitrogen. The

resultant solution was then analysed by gas chromatography and evaporative losses of each compound determined in triplicate experiments.

## Injection technique

All gas chromatographic injections were performed using the modified technique for cool-on-column injection described by Tong.[14] A Hamilton 701 RN $10\,\mu L$ microsyringe, with a fused-silica needle ($0.18\,m$ O.D., $0.4\,\mu L$ needle dead volume; Hewlett-Packard) was used. In this technique, approximately $0.8\,\mu L$ of pure solvent is taken into the syringe, followed by an air space ($\simeq 0.8\,\mu L$), then the desired volume of sample solution. The entire column solvent-air-sample is withdrawn into the barrel of the syringe leaving the needle empty and the volume of sample accurately read. The entire sample is delivered onto the chromatographic column with minimal pre-evaporation of the sample on injection. This technique affords good reproducibility in the injection of small volumes of solution. For a series of five injections of $0.4\,\mu L$ of the test solution an average relative standard deviation of 6% was obtained for the areas of the 22 peaks with values ranging from 3 to 8%. With one exception, higher precisions were associated with the earlier-eluting peaks. These values reflect uncertainties due to the injection technique as well as the instrumental detector response.

## RESULTS AND DISCUSSION

A gas chromatogram of the test mixture under the conditions used for the efficiency and evaporative studies is shown in Figure 2. Baseline resolution for virtually all components of the mixture was attained under these chromatographic conditions. GC/MS analysis employing similar chromatographic conditions was performed to verify the identities of all peaks. The identities of the peaks shown in Figure 2 are listed in Table II. All quantification in these studies were based on the area of these peaks in the recovered extracts relative to those of the original test solution injected under identical GC conditions. The volume of solution injected for all chromatographic analyses was $0.4\,\mu L$.
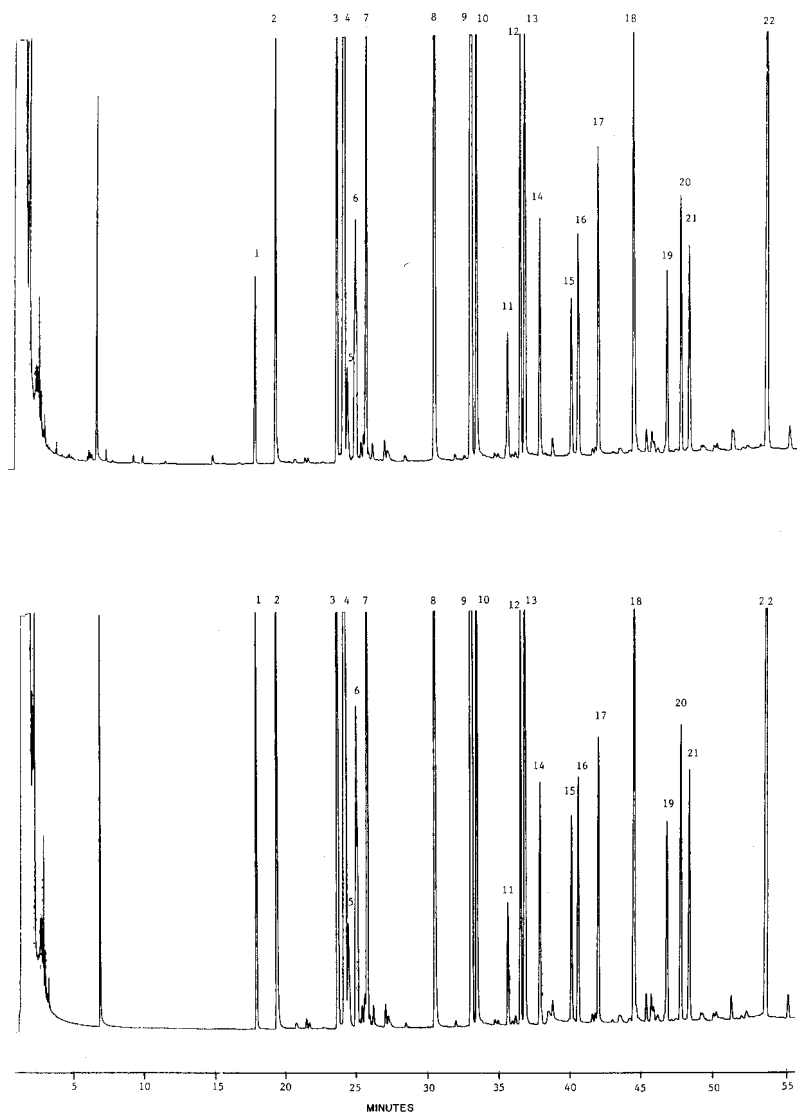
FIGURE 2   Gas chromatogram of test solution and recovered extract.
Lower trace—test solution.
Upper trace—extract, XAD-4, pH 7.
GC conditions: 30 m × 0.32 mm i.d. DB 1701 fused silica capillary column; flame ionization detector; cool on-column injection at 40°C, temperature programmed to 250°C at 4°C/min: 0.4 μL injection of solution; carrier gas—helium, 2 mL/min @ 40°C.

Evaporative losses for the compounds corresponding to the seven earliest eluting peaks are shown in Table I. The average relative standard deviation was 7% based on triplicate analyses and ranged from 4 to 9%. The remaining compounds used in the study suffered no evaporative losses.

TABLE I

Evaporative losses of test compounds.

| [a]Pk no. | Compound | % lost on evaporation |
|---|---|---|
| 1 | N-hexyl benzene | 30 |
| 2 | Ethyl phenol | 20 |
| 3 | Biphenyl | 16 |
| 4 | Methyl hendecanoate | 10 |
| 5 | 2,3 Dimethyl naphthalene | 12 |
| 6 | 2,3 Dimethyl naphthalene | 13 |
| 7 | 1,6 Dimethyl naphthalene | 13 |

[a]Peak number as indicated in Figure 2.

The results of studies on extraction efficiencies of the resins under various pH conditions are shown in Table II. The recovery values shown in this table have not been corrected for evaporative losses and are intended to reflect the recoveries obtained for the compounds on application of the entire described procedure. Losses of compounds evident from Table II can therefore be attributable to several causes: adsorption on glasswool and glassware surfaces; failure to be quantitatively adsorbed by the resin; inefficient desorption from the resin; volatilization in the evaporative step. Except for the latter, no attempt has been made to identify and quantify the factors responsible for losses of compounds.

XAD-2 resin extraction at pH 7 gave essentially quantitative recoveries for all compounds except methyl tetradecanoate (63%), aldrin (67%) and o,p DDT (62%). Similar results were obtained for XAD-4 extraction under the same pH conditions, but recovery of n-hexyl benzene was considerably lower (42%). XAD-7 extraction under these conditions yielded lower recoveries for most compounds, especially the early-eluting ones. The recoveries for methyl

TABLE II

Extraction efficiency of XAD resins under various pH conditions. % recovered (average relative std. deviation = 7%; range 4% to 9%).

| Pk[a] | R.T. | Compound | pH ≃ 7 | | | pH ≃ 2 | | | pH ≃ 12 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | XAD-2 | XAD-4 | XAD-7 | XAD-2 | XAD-4 | XAD-7 | XAD-2 | XAD-7 | XAD-7 |
| 1 | 17.89 | N-hexyl benzene | 62 | 42 | 35 | 47 | 31 | 33 | 51 | 43 | 38 |
| 2 | 19.28 | Ethyl phenol | 75 | 76 | 51 | 72 | 54 | 54 | 16 | 38 | 22 |
| 3 | 23.54 | Biphenyl | 90 | 79 | 59 | 77 | 51 | 59 | 75 | 78 | 62 |
| 4 | 24.11 | Methyl hendacanoate | 84 | 76 | 57 | 75 | 51 | 57 | 55[b] | 57 | 33 |
| 5 | 24.23 | Dimethyl naphthalene | 88 | 76 | 55 | 78 | 50 | 57 | 78 | 76 | 58 |
| 6 | 24.82 | Dimethyl naphthalene | 89 | 78 | 59 | 78 | 52 | 61 | 75 | 76 | 61 |
| 7 | 25.59 | Dimethyl naphthalene | 91 | 80 | 61 | 80 | 54 | 64 | 79 | 81 | 66 |
| 8 | 30.26 | Phenyl phenol | 104 | 102 | 85 | 97 | 78 | 86 | 65 | 99 | 66 |
| 9 | 32.85 | Methyl tetradecanoate | 63 | — | 34 | 67 | 28[b] | 49[b] | 46 | 44 | 34 |
| 10 | 33.13 | 1-Naphthol | 93 | 88 | 72 | 96 | 70 | 86 | 16 | 43 | 15 |
| 11 | 35.27 | α-BHC | 107 | 105 | 90 | 101 | 73 | 94 | 76 | 91 | 69 |
| 12 | 36.16 | Benzyl benzoate | 104 | 99 | 87 | 96 | 70 | 92 | 68 | 81 | 46 |
| 13 | 36.47 | Phenanthrene | 110 | 97 | 90 | 96 | 69 | 94 | 89 | 98 | 90 |
| 14 | 37.49 | γ-BHC | 107 | 101 | 91 | 101 | 75 | 95 | 80 | 94 | 70 |
| 15 | 39.65 | Aldrin | 67 | 67 | 51 | 67 | 28[b] | 52[b] | 52 | 53 | 50 |
| 16 | 40.12 | 1 Methyl phenanthrene | 104 | 97 | — | 85 | 60 | — | 81 | — | — |
| 17 | 41.50 | Dibutyl phthalate | 107 | 101 | 93 | 104 | 74 | 95 | 87 | 101 | 80 |
| 18 | 43.99 | Fluoranthene | 101 | 88 | 94 | 92 | 54 | 93 | 81 | 89 | 91 |
| 19 | 46.28 | Dieldrin | 101 | 92 | 91 | 93 | 58 | 91 | 84 | 89 | 88 |
| 20 | 47.25 | Endrin | 97 | 86 | 89 | 90 | 54 | 89 | 82 | 87 | 85 |
| 21 | 47.83 | o,p DDT | 62 | 67 | 31 | 65 | 23[b] | 48[b] | 43[b] | 37 | 33 |
| 22 | 53.53 | Methoxychlor | 92 | 86 | 94 | 91 | 48 | 91 | 91 | 93 | 88 |

[a]Peak number as indicated in Figure 2.
[b]Relative standard deviation 12–15%.

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tetradecanoate (34%) and o,p DDT (31%) were particularly low for XAD-7 extraction.

Acidification to pH 2 has been recommended by Junk for the improved extraction of phenolic compounds.[1] For extractions at pH 2, XAD-2 resins yielded recoveries greater than 75% for most compounds, many being in excess of 90%. The recovery of n-hexyl benzene was low (48%). The XAD-4 extraction at pH 2 gave lower recoveries than XAD-2 extractions at this pH, most recoveries ranging between 50 and 75%. On the whole, XAD-4 extraction efficiency was lower for all compounds at pH 2 than it was at pH 7; at pH 2 its extraction efficiency was especially low for methyl tetradecanoate (28%), aldrin (28%), and o,p DDT (23%). For most compounds, the XAD-7 resin gave similar recoveries at pH 2 as those for its extraction at pH 7. However, improved recoveries were obtained for methyl tetradecanoate and o,p DDT.

XAD-2 resin extractions at pH 12 resulted in particularly low recoveries of 1-naphthol and ethyl phenol (both 16%), but recovery of phenyl phenol was fairly good (65%). Recovery of methyl hendecanoate was 65%, aldrin, o,p DDT and methyl tetradecanoate yielded recoveries in the vicinity of 50%; recoveries of the other compounds were ≈75% or higher. Recoveries obtained for XAD-4 resin extraction under these conditions were similar to those of XAD-2, but recovery of phenyl phenol was quantitative for the XAD-4 extraction and this resin also yielded improved extraction of naphthol, ethyl phenol, benzyl benzoate, and α- and γ-BHC. The results obtained for XAD-7 at pH 12 were much the same as those obtained for XAD-2 extraction except that recoveries for n-hexyl benzene, methyl hendecanoate and benzyl benzoate were somewhat lower.

These preliminary studies indicate that basic pH conditions are generally unfavourable for extraction of phenolic compounds in aqueous samples by the XAD resins and provide no advantage for the extraction of the other compounds investigated. Aqueous bases convert the phenols to their salts which can be expected to have more unfavourable distribution coefficients for the relatively non-polar resins than the free phenols. The high affinity of XAD-4 resin for phenyl phenol in basic solution is somewhat surprising. Although the recovery of ethyl phenol and 1-naphthol by XAD-4 lower than that for phenyl phenol, these compounds were also better extracted

by XAD-4 than XAD-2 and XAD-7. Contrary to previous reports[1] acidification of the sample did not seem necessary for the quantitative extraction of the phenolic compounds used in this study, and generally led to decreased extraction efficiency for most compounds in the case of XAD-4 resins.

The degree of variability in the recovery was observed to be much higher in several cases for aldrin, o,p DDT, methyl hendecanoate than for the other compounds employed in this study. For the latter, the relative standard deviation in the mean recovery ranged from 4% to 9%, but for the aforementioned compounds standard deviations as high as 15% were obtained, notably for some extractions from basic and acidic solutions. The recovery of these compounds appear to be very sensitive to experimental conditions, especially to the pH of the aqueous solution. Hence, for reproducible results, extraction conditions need to be stringently controlled for the quantification of these compounds.

For the extractions at pH 7, no one resin seemed to possess an advantage over the other with respect to extraction efficiency. XAD-7 resins are reported to be superior for extraction of carboxylic acids and phenols from aqueous samples but no representatives of the former were included in this study.[1] The extraction efficiency of the XAD-7 resin for the phenolic compounds was marginally lower than that of the XAD-2 and XAD-4 resins.

Since the three resins possess different characteristics, a mixture comprising all three may be best suited for the preconcentration of organics from environmental water samples containing a wide range of compounds. The extraction efficiency of a combined resin column, $\simeq 8$ cm long and containing equal volumes of the three resins, was evaluated (Table III). Except in the case of n-hexyl benzene (recovery 38%) extraction efficiencies of this column paralleled those of the XAD-2 column at pH 7. Extraction efficiencies of the combined resin column for three additional compounds—2 isopropyl phenol, 2,3,5 trimethyl phenol and the pesticide carbaryl—were also excellent (84%) at this pH. These results indicate that the combined resin column and the XAD-2 column are equally effective for the extraction of the compounds studied. Nevertheless, because of the differences in the extractive properties exhibited by the resins, the combined resin column is recommended for initial screening surveys in water systems for which one has no prior knowledge of the

TABLE III

Extraction efficiency of column containing combination of XAD-2, XAD-4, and XAD-7 resins.

| Compound | % recovered[a] | |
| --- | --- | --- |
| | pH 7 | pH 2 |
| N-hexyl benzene | 38 | 32 |
| Ethyl phenol | 83 | 61 |
| 2 isopropyl phenol | 84 | 65 |
| 2,3,5 trimethyl phenol | 90 | 70 |
| Biphenyl | 87 | 65 |
| Methyl hendecanoate | 71 | 64 |
| Dimethyl naphthalene | 82 | 63 |
| Phenyl phenol | 101 | 90 |
| Methyl tetradecanoate | 68 | 71 |
| 1-napththol | 101 | 77 |
| α-BHC | 103 | 87 |
| Benzyl benzoate | 100 | 86 |
| phenanthrene | 98 | 94 |
| γ-BHC | 102 | 93 |
| Aldrin | 66 | 67[b] |
| Dibutyl phthalate | 101 | 104 |
| Carbaryl | 100 | 100 |
| Fluoranthene | 92 | 80 |
| Dieldrin | 93 | 85 |
| Endrin | 94 | 85 |
| o,p DDT | 68 | 66[b] |
| Methoxychlor | 99 | 99 |

[a]Values are not corrected for evaporative losses. Average relative standard deviation 5% based on triplicate analyses (range 4% to 7%).
[b]Relative standard deviation 11%.

pollutant profile. Acidification to pH 2 decreased the extraction efficiency of the combined resin column for many compounds. Acidification of water samples prior to extraction by the combined resin column is, therefore, not recommended, except in those cases for which the quantitative determination of organic acids is of interest.

Extraction of large volumes of water is often one of the slowest steps in the sample preparation procedures for water analysis. It is therefore desirable to extract such samples at a high level of efficiency for all components using one composite extraction matrix.

If necessary, the sample can be simplified prior to instrumental analysis, through fractionation in the elution step. Alternatively, a single eluent which will efficiently desorb all compounds from the resin may be used and fractionation of the sample then carried out on a more suitable matrix. The efficiency of the processing of large volumes of water is greatly enhanced through the use of semi-automated sampling/extraction devices employing adsorbent columns for on-site or in-situ sampling.[15] The adjustment of the pH of the influent water is usually impracticable in such cases, hence a matrix capable of effectively concentrating a wide range of organics from water at ambient pH proves highly advantageous for these applications. The results of this study confirm that a combined XAD-resin column or simple XAD-2 column provides an extraction matrix which meets this requirement for the classes of compounds identified in the Caroni River.[13] Other components of the natural water samples can be expected to influence the extraction capabilities of the resin; this aspect will be investigated in future studies.

## Acknowledgement

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