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USE OF MACRORETICULAR RESINS IN THE ANALYSIS OF WATER FOR TRACE ORGANIC CONTAMINANTS

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SUMMARY

Organic impurities in water can be isolated by sorption on a small column of a macroreticular resin. The organics are readily eluted by diethyl ether; the eluate is then concentrated by evaporation, and the organics are separated and determined by gas chromatography. Studies on a large number of model compounds added to water in the 10- to 100-ppb range (20 parts per trillion for pesticides) demonstrated that this method is accurate and reliable. An extensive study of the procedure revealed several critical steps where proper technique and conditions are essential to avoid serious error. These include resin purification and handling, preparation of standard samples containing organic impurities, and the technique and apparatus used in concentrating the XAD column eluate.

INTRODUCTION

The best documented and most frequently employed analytical procedures for measuring low levels of organic compounds in water involve solvent extraction and charcoal adsorption. Recently, however, an increasing number of reports have described an additional analytical method which uses porous polymer resins as the sorbing agent for the removal of organics from fresh water[1–4], from salt water[5–7], from waste water[8–10] and from aqueous biological media[11–22]. The most widely used resin has been Rohm and Haas Amberlite XAD-2. This resin is a low-polarity styrene–divinylbenzene copolymer which possesses the macroreticular characteristics[10,23,24] essential for high sorptive capacity.

The recovery efficiency of pesticides[5–8], amino acids[5], aliphatic acids[4,5], and miscellaneous individual compounds[1–5] from water using XAD-2 or the chemically identical XAD-1 and XAD-4 has been reported or suggested. Similar results for bile acids[12], steroids[5,16], alkaloids[15,16] and abuse drugs[13–15,19] in aqueous biological media have also been published. Although these results suggest that the XAD-2 resin has applicability for a wide variety of organic compounds present in an aqueous matrix, no comprehensive study has yet been reported of the efficiency of the resin when employed in a standardized analytical scheme. Such a study is essential for establishing the applicability of the use of the resin for the accurate analyses of organic contami-

nants present at trace levels in natural and processed water supplies. Because of the expected complexity of the contamination profile in water from different localities, the reliability of the standardized analytical scheme must be established by testing the recovery efficiency for a wide variety of different organic compounds.

The substance of this paper is to report the results of such tests not only as they apply to an entire analytical scheme but also individual phases of the scheme. In this way a simple, standardized procedure which is highly effective for analyzing "real" or natural water samples has evolved. The procedure concerns the extraction of organic solutes by passing the contaminated water through a column of clean XAD-2 resin. The contaminants are then desorbed by elution with diethyl ether. This eluate is then concentrated by evaporation and the components in an aliquot of this concentrate are separated by gas chromatography (GC). The GC data provide the information necessary for quantification and a separate aliquot is subjected to GC–MS analyses for identification of the contaminants. An accurate quantitative estimation of organics in water at parts per million to trillion levels requires great care during all phases of the analysis, from sampling to the final chromatographic separation and measurement. For this reason, the techniques and apparatus used in the proposed standardized analytical procedure will be discussed in considerable detail.

EXPERIMENTAL

Material and apparatus

Reagents. Tap water and distilled water were freed of detectable organic matter by passing the water through a column containing clean XAD-2 resin and activated charcoal. Well water used in some of the experiments was obtained from a well whose water contained no detectable organic contaminants.

The organic chemicals used to prepare standard water samples were purchased from Chem. Services (West Chester, Pa., U.S.A.) and were used as received. Anhydrous sodium sulfate was heated in a 400° muffle for 2 h to remove any organic matter.

All solvents used were either spectrograde or analytical grade. The analytical grade solvents were further purified by fractional distillation whenever blank determinations suggested the presence of impurities detectable by flame ionization GC.

The macroreticular resins, XAD-2 and XAD-4, were obtained from Rohm and Haas (Philadelphia, Pa., U.S.A.). The fines were removed by slurrying in methanol and decanting. The remaining resin beads, predominantly 20–60 mesh, were purified by sequential solvent extractions with methanol, acetonitrile and diethyl ether in a Soxhlet extractor for 8 h per solvent. The purified resins were stored in glass-stoppered bottles under methanol to maintain their high purity. In some cases the resins as received from the supplier were ground to smaller particles, sieved and then purified by Soxhlet extraction as described above.

Instruments. A single-column Varian 1200 gas chromatograph equipped with a linear temperature programmer and a flame ionization detector (FID) was used to obtain the GC data from which the results for recovery studies were calculated. All test mixtures and extracts were chromatographed using 6 ft. × 1/8 in. O.D. stainless-steel columns packed with 80–100 mesh acid-washed DMCS-treated Chromosorb W coated with 5% w/w OV-1 liquid phase.

A DuPont 21-490-1 combination gas chromatograph–mass spectrometer (GC–MS) was used to confirm the identity of the organics eluted from the XAD resins.

A Cary Model 14 spectrophotometer using 10-cm cells was used to establish the purity of the eluates and to obtain some of the recovery efficiency results using scans from 220 to 380 nm.

A Chromatronix Model 3100 liquid chromatograph equipped with a Model 220 fixed wavelength spectrophotometric detector and a Model 400 refractive index detector was employed to test the elution efficiency of various solvent systems.

Analytical procedure —overall recovery efficiency studies

1. Column preparation. The apparatus used for removing trace organics from water is shown in Fig. 1. With the upper 2-liter reservoir detached, insert a clean silanized glass wool plug near the stopcock of the glass column. Add the purified XAD resin as a methanol slurry until a resin bed approximately 6 cm high is obtained (1.5–2.0 g dry resin), then insert a second silanized glass wool plug above the resin. Drain the methanol through the stopcock until the level just reaches the top of the resin bed, then wash the resin with three 20-ml portions of pure water. For each portion stop the flow when the liquid level reaches the top of the resin bed.

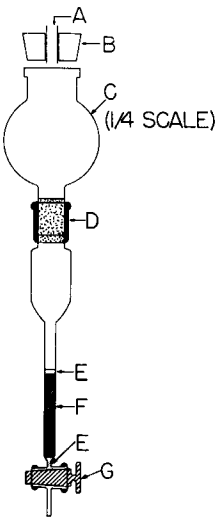

Fig. 1. Scale drawing of apparatus for extracting organic solutes from water. (A) pure inert gas pressure source; (B) cap; (C) 2-liter reservoir relatively scaled by ~1/4; (D) 24/40; (E) silanized glass wool plugs; (F) 0.6-cm-I.D. × 10-cm-long glass tube packed with 20–60 mesh XAD-2 resin; (G) PTFE stopcock.

2. Sample preparation. Attach the 2-liter reservoir to the column (Fig. 1) and add 1000 ml of purified distilled or tap water. Add the organic compound(s) to be tested to the water by injecting a calibrated volume of a standard solution of the organic compound(s) in diethyl ether or methanol. The volume injected and the concentration of the standard is adjusted to achieve the desired amount of the compound(s) in 1 liter of water. In this study, these amounts varied from 50 ppm to 20

parts per trillion. Any additional pretreatment of the water such as adding acid, base or salt is done immediately after the injection of the standard organic solution.

3. Column extraction. Cap the reservoir with a one-hole stopper connected to a nitrogen source and allow the water to pass through the XAD resin column by gravity flow at a rate of 30 to 50 ml/min. If the flow-rate is slower than this, apply a pressure of about 1 p.s.i. to the reservoir using organic-free nitrogen. When most of the sample has passed through the column and the liquid level is at the top of the resin, wash the reservoir walls carefully with a 20-ml portion of pure water and drain through the column until the level reaches the top of the resin bed. Repeat this wash twice, letting the water drain completely only after the last wash.

4. Elution and regeneration. Wash the reservoir walls with two 10-ml portions of diethyl ether and allow each wash to drain into the XAD resin but not through the column. Remove the reservoir, cap the column with a 24/40 glass stopper, and allow the diethyl ether to equilibrate with the resin for 10 min. Then remove the cap, open the stopcock and allow the ether to flow through the column into a 30-ml test tube. Add an additional 5 ml of diethyl ether to the column and immediately allow it to flow through the resin into the receiver. The elution is complete when the gravity flow ceases even though the last traces of ether have not been removed from the resin.

Regenerate the XAD resin column immediately after the ether elution. Add methanol, shake to remove any air bubbles, then pass a total of 30 ml of methanol through the column. Close the stopcock, add an additional 15 ml of methanol and cap the column with a 24/40 glass stopper. It is now ready for subsequent analyses without any further treatment beyond wetting the resin with pure water as outlined above in step 1.

5. Drying. Remove the residual water (0.5 to 2 ml) from the diethyl ether eluate by immersing the test tube receiver in liquid nitrogen for two 10-sec intervals. Immediately decant the ether into the concentration vessel shown in Fig. 2. Wash the

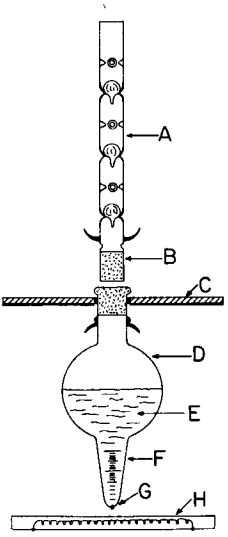

Fig. 2. Scale drawing of concentration apparatus. (A) Snyder distillation column; (B) 14/20; (C) bakelite heat shield covered with Al foil; (D) ~50 ml vessel; (E) ether solution; (F) graduated and calibrated taper; (G) small boiling chip; (H) hot plate.

ice in the test tube with 1 ml of diethyl ether, dip briefly in the liquid nitrogen to freeze any ice which may have melted and add this ether to the concentration vessel.

Anhydrous sodium sulfate and petroleum ether (b.p. 30–60°) may also be used to dry the ether eluate. Collect the ether eluate from the column in a 60-ml separatory funnel and reject the water layer. Add 15 ml of petroleum ether (30–60°) and 2 g of anhydrous sodium sulfate to the ether. Shake vigorously until a clear solution is obtained and transfer the ether to the concentration vessel.

6. Concentration of eluate. Add a small boiling chip to the concentration vessel and attach a three-cavity Snyder column as shown in Fig. 2. Add about 2 ml of diethyl ether to the top of the Snyder column and tap gently to distribute the ether into the three cavities. Apply heat from a hot plate or steam bath so that the boiling action is vigorous enough to agitate the balls of the Snyder column continuously. A solvent evaporation rate of 0.5 to 2.0 ml/min should be attained. When the volume of solution in the calibrated appendage of the concentration vessel is about 0.5 ml, remove the apparatus from the heat and immediately spray acetone over the outside walls of the concentration vessel. The condensation of the ether vapor causes an automatic sequential washing of the inside walls of the vessel with the ether held in the three cavities of the Snyder column. The volume of liquid in the calibrated section of the concentration vessel should now be ≤ 1.0 ml. Remove the Snyder column and add ether if necessary so that the solution volume is exactly 1.00 ml. Cap the vessel with a 14/20 stopper and swirl to mix the solution. Proceed with the GC analysis of the concentrate as soon as possible.

7. Separation and quantification. Inject a 2.0-μl aliquot of the 1.00-ml concentrate into the gas chromatograph with a syringe. When the GC separation of the organic compound(s) in the concentrate is completed, immediately repeat the GC separation using a 2.0-μl aliquot of a 1.00-ml standard ether solution containing the same organic compound(s) at a concentration identical to that expected in the 1.00-ml concentrate assuming complete recovery of solute(s) from the water sample. The GC conditions are held rigidly constant for both sample and standard during these tests and the percentage recovery of the organic solutes is calculated directly from a comparison of the chromatogram peak heights.

8. Identification. Further concentrate the 1.00-ml ether solution to 0.1 ml after completion of step 7. Subject a 2.0-μl aliquot of this 0.1-ml solution to GC–MS analysis to confirm positively that no chemical transformation has occurred during any of the previous steps.

Analytical procedure —real water samples

The results of tests of the overall recovery efficiency of the procedure outlined above for pure water spiked with known organic compounds have led to a standardized analytical procedure applicable to real water samples. This standardized procedure is exactly as given above except for appropriate changes in steps 2, 7 and 8.

For natural or treated water samples, spiking with known compounds (step 2) is unnecessary and sample preparation involves only transfer of the water sample from its source to the reservoir of the extraction apparatus (Fig. 1). Actual water samples of unknown organic content may be collected if necessary in 1-gal amber "solvent" bottles with PTFE-lined screw caps. Prior to use, the bottles should be carefully washed with a detergent, rinsed several times with "pure" distilled water,

and then several times with methanol. After pouring off the last methanol rinse, the bottle is immediately capped, thus trapping a small amount of methanol in the bottle. Fill the bottle with the water sample and cap tightly. As soon as possible, preferably within 30 h, transfer 1000 ml of the water sample to the extraction apparatus reservoir and proceed immediately with the analysis. Errors which can easily occur due to sorption, vaporization and other losses during sample storage in bottles can be obviated by taking the extraction apparatus to the water sampling site where an appropriate volume is sampled directly onto the XAD-2 resin without delay or contact with any sample or transfer containers.

Separation and quantification (step 7) of components in mixtures extracted from real samples is accomplished by using standard quantitative GC procedures. The amounts of separated components are determined from peak area measurements and the volume of water used in step 2.

Finally, the GC–MS assay (step 8) of components from real water samples is much more complicated than from standard solutions. Interpretation of the mass spectra of various unknown components must be done properly, taking advantage of whatever aids or confirmatory techniques are available, in order to make positive identification. However, once this is accomplished for a particular water supply, GC retention times on two different liquid phases are usually sufficient for future monitoring of samples of the water supply. Further use of the GC–MS is unnecessary except for periodic spot checks or when an extraneous GC peak occurs.

RESULTS AND DISCUSSION

Recovery studies

The recovery efficiency of the entire analytical scheme, hereafter referred to as the porous polymer method, was tested by analyzing water samples to which known concentrations of model organic compounds were added. The test compounds included alcohols, aldehydes, acids, aromatic halides, alkylbenzenes, phenols, chlorinated phenols, esters, ethers, ketones, polynuclear aromatics, herbicides, pesticides, and various compounds containing halogens, nitrogen or sulfur. These are considered to represent a cross-section of organic chemicals rather than those chemicals currently most apt to be found as environmental contaminants. The results of these studies are tabulated in Table I.

Most of the model compounds were tested both individually and as mixtures of components from within and outside a particular homologous series. Most frequently the test compounds were added to purified distilled water, but in a number of cases tap water was used as the sample matrix. The recovery values given in the table are average values and represent the work of four or five different analysts. The results are considered to be the lower limits of recovery since conditions were not always optimized for each compound or class of compounds. For 110 individual determinations by a single analyst on samples of many different types the average recovery of organics was 78%. The average deviation was 6.1% and the standard deviation was 6.3%.

The results indicate that the procedure is reliable and accurate, and the porous polymer method can be used with confidence for analysis of natural waters of unknown composition. However, considerable research was necessary to develop the final

TABLE I

OVER-ALL RECOVERY EFFICIENCY OF THE POROUS POLYMER METHOD OF ANALYSIS FOR ORGANICS IN WATER AT THE 10- TO 100-ppb LEVEL*

Compounds tested	*Efficiency (% recovery)***	*Compounds tested*	*Efficiency (% recovery)*
Alcohols		Acids (acidified)****	
Hexyl	93	Octanoic	108
2-Ethylhexanol	99	Decanoic	90
2-Octanol	100	Palmitic	101
Decyl	91	Oleic	100
Dodecyl	93	Benzoic	107
Benzyl	91		
Cinnamyl	85	Phenols****	
2-Phenoxyethanol	102	Phenol	40
		o-Cresol	73
Aldehydes + ketones		3,5-Xylenol	79
2,6-Dimethyl-4-heptanone	93	*o*-Chlorophenol	96
2-Undecanone	88	*p*-Chlorophenol	95
Acetophenone	92	2,4,6-Trichlorophenol	99
Benzophenone	93	1-Naphthol	91
Benzil	97		
Benzaldehyde	101	Ethers	
Salicylaldehyde	100	Hexyl	75
		Benzyl	99
Esters		Anisole	87
Benzyl acetate	100	2-Methoxynaphthalene	97
Dimethoxyethyl phthalate	94	Phenyl	91
Dimethyl phthalate	91		
Diethyl phthalate	92	Halogen compounds	
Dibutyl phthalate	99	Benzyl chloride	88
Di-2-ethylhexyl phthalate	88	Chlorobenzene	95
Diethyl fumarate	86	Iodobenzene	81
Dibutyl fumarate	92	*o*-Dichlorobenzene	88
Di-2-ethylhexyl fumarate	84	*m*-Dichlorobenzene	93
Diethyl malonate	103	1,2,4,5-Tetrachlorobenzene	74
Methyl benzoate	101	α-*o*-Dichlorotoluene	96
Methyl decanoate	95	*m*-Chlorotoluene	80
Methyl octanoate	98	2,4-Dichlorotoluene	71
Methyl palmitate	70	1,2,4-Trichlorobenzene	99
Methyl salicylate	96		
Methyl methacrylate	35	Nitrogen compounds	
		Hexadecylamine	94
Polynuclear aromatics		Nitrobenzene	91
Naphthalene	98	Indole	89
2-Methylnaphthalene	95	*o*-Nitrotoluene	80
1-Methylnaphthalene	87	N-Methylaniline	84
Biphenyl	101	Benzothiazole	100
Fluorene	84	Quinoline	84
Anthracene	83	Isoquinoline	83
Acenaphthene	92	Benzonitrile	88
Tetrahydronaphthalene	62	Benzoxazole	92
Alkyl benzenes			
Ethylbenzene	81		
Cumene	93		
p-Cymene	92		

(Continued on p. 752)

TABLE I *(continued)*

Compounds tested	*Efficiency (% Recovery)*
Pesticides + herbicides[§]	
Atrazine	83
Lindan	95
Aldrin	47
Dieldrin	93
DDT	96
DDE	81

[*] The ppb designation corresponds to parts of organic solute by weight. Thus 10 ppb corresponds to 10 μg/l of water.

[**] The average reproducibility of these values is $\pm 12\%$. This uncertainty is high because it includes results accumulated by a number of different analysts and results where rigid procedural control was not yet established. With dedicated control of all variables discussed in the text the reproducibility limit may be decreased to $\pm\sim 5\%$.

[***] The water was acidified by adding 5 ml of concentrated HCl prior to adding the organic solute. XAD-4 resin was used.

[§] All pesticides and herbicides except atrazine were tested at a concentration of 20 parts per trillion in water.

procedure. With an earlier procedure, recoveries of model compounds were quite good in some cases but in other instances recoveries were sometimes low and erratic. This led to a detailed examination of the various parts of the procedure to determine the effect of variations in apparatus, technique and experimental conditions on the efficiency of the method.

Development of analytical procedure

Resin clean-up and handling. Three procedures were tested for cleaning the XAD resins as received from the suppliers. The most effective method is sequential Soxhlet solvent extraction with methanol, acetonitrile and diethyl ether. Resin treated in this manner and stored under methanol has a very low blank level and this is the recommended clean-up technique.

The other two clean-up procedures tried were vacuum degassing at 225° under 10^{-7} torr and heat desorption in an inert gas train at 200°. Neither of these techniques are as effective as Soxhlet solvent extraction because naphthalene, ethylbenzene and benzoic acid appear as major constituents in the blank obtained for XAD-2 and XAD-4. These major contaminants plus other unidentified minor constituents are apparently trapped interstitially within the resin during the polymer bead formation process. Their origin is probably as impurities present in the starting materials used to make the resin. Although the resin surfaces are cleaned of these contaminants using either vacuum degassing or Soxhlet extraction, it is virtually impossible to avoid exposing new surfaces when the system is vented and the resin is cooled in the vacuum degassing technique. The resins are somewhat friable and the temperature gradient during the cool-down causes ruptures which expose new pockets of contaminants. In addition, unless the venting procedure is extremely slow, some implosions occur that also lead to fresh contamination. These problems are so severe that even shelf storage of the cleaned resins in the dry form can appreciably increase the blank level.

The Soxhlet extraction technique avoids these problems because of the very low temperature gradient and the continuously wet nature of the process. The cleaned, wet resin is easily transferred to a storage vessel and methanol added to maintain a wetted condition. Resins that have been properly cleaned by Soxhlet solvent extraction and kept under methanol may be stored for many months. If a high blank level develops because of inadvertent drying of the resin or mechanical cracking of the beads, it is necessary to repeat the Soxhlet extraction to obtain low blank levels.

The clean resin in the column must also be kept wet. After elution of the organics with diethyl ether, methanol should be added to the column before the residual ether has had time to evaporate, as is described in the experimental procedure. If desired, strong or weak acidic and basic washings of the column may be incorporated into the recycling scheme without any adverse effects. We have found acidic washings to be particularly helpful for removing metallic oxide deposits that often occur when large quantities of high mineral content water are passed through a resin bed.

The resin most frequently employed for the recovery efficiency tests was Rohm and Haas XAD-2, a polystyrene–divinylbenzene copolymer of low polarity, of 300 m^2/g active surface area and 90 Å average pore diameter. Some of the values quoted in Table I were obtained, however, using XAD-4, which is chemically identical to XAD-2 but has a surface area of 784 m^2/g and an average pore diameter of 50 Å. Since the results showed no significant differences between these two low polarity resins, the results for XAD-2 and XAD-4 are not specified and are used interchangeably in this report.

The effect of varying the particle size of the resin was also investigated. Spherical resin beads, mostly 20–60 mesh, as well as resin ground and sieved to particle sizes as small as 150 mesh were tested. There appears to be no clear-cut advantage in any particular size range. Therefore the approximately 20–60 mesh spherical resin, as received, is recommended.

Preparation of standard samples. In the development of the porous polymer method during the past two years, fluctuations in the recovery efficiency results by various analysts was for a time very disturbing. Gradually the importance of subtle features of the analytical scheme emerged as each phase of the scheme was carefully checked. One of the most critical features involves the method employed to add known amounts of organic impurities to water when preparing standards. This is particularly true for solutes of limited solubility in water. To illustrate the potential errors attributable to preparation of standard samples, the efficiency of the entire analytical scheme for cumene standards prepared by two slightly different techniques is cited.

The two procedures used and the rest of the analytical scheme were identical with the exception that the cap shown in Fig. 1 was not employed in one of the methods. When the cap was employed in the second method, the recovery efficiency for cumene showed a dramatic increase from 40% with the uncapped reservoir to 92% with the capped reservoir. The explanation for this difference is related to the solubility, volatility, and density of cumene. When this material is added to water from a standard solution of diethyl ether, an appreciable quantity of the very slightly soluble cumene rises to the surface of the water thereby exposing a large surface area from which evaporation occurs. Thus a significant amount of cumene vaporizes and is lost from the open reservoir during the time it takes for the water solution to flow by gravity through the resin. Although supporting data are not available, it is highly probable

that the evaporative losses from a water surface are greater than that which would occur were the same amount of cumene distributed over an equivalent non-polar surface area. These results for cumene are representative of what generally occurs with alkylbenzenes and many other organic compounds of very low solubility.

Thus errors in the observed recovery efficiency due solely to the manner of adding organic impurities are most probable whenever the concentration level exceeds the solubility of the organic compound in water, the compound is less dense than water and thus rises to the surface, and the volatility of the compound is appreciable. The results for alkylbenzenes demonstrate this effect most dramatically but the same situation exists for many other compounds tested and listed in Table I. Although solute losses can easily occur due to inadequate techniques during other phases of the analytical scheme, the method of preparing standard solutions is the most suspect and could well lead to erroneous conclusions about the recovery efficiency.

Results of tests of the recovery efficiency for alkanes are not included in Table I because effects similar to those discussed above for cumene are operative with alkanes plus an additional effect that is probably related to adsorption on apparatus surfaces. This problem is still under investigation and positive results should be forthcoming in the future. Our tests presently suggest that the resin is nearly 100% efficient in extracting alkanes truly present as a solution in water and that ether quantitatively elutes the sorbed alkanes from the resin.

This isolation and documentation of losses incurred in preparing solutions is of concern whenever natural water samples are assayed. For some contaminated natural waters, not all the organic molecules will be in true solution. Some may be present as part of microscopic globules suspended in the water and some may be sorbed on particulate matter. Whenever this occurs, a snatch sampling procedure could well lead to inaccurate results caused by non-representative sampling as well as evaporative losses that far exceed those expected solely on the basis of vapor pressure and Raoult's law considerations.

Concentration limits of standard samples. Our interpretation of the data already presented in Table I suggests that no change in over-all recovery efficiency occurs for non-dissociative solutes in water at the concentration range of 10–100 ppb. This range has been extended by a factor of ~ 1000 by results of extraction and elution efficiency tests of various polyaromatics, aromatic esters and aromatic ketones using a Cary 14 spectrophotometer for detection of the eluted solutes. These results for non-dissociated compounds are tabulated in Table II.

The apparent quantitative recovery at both concentration levels proves that the concentration range for accurate analytical results, divorced from any losses associated with the separation scheme, extends over at least a factor of 1000 and possibly more. For example, 50 ppm is certainly not the upper limit for the analytical scheme because that limit is determined by the capacity of the resin employed. Of course, if very highly polluted waters are to be tested, the size of the water sample or the amount of resin can be readily adjusted to accommodate the amount of contamination. Likewise, 50 ppb is certainly not the lower limit for quantitative results. Although this lower limit undoubtedly varies for different compounds, the limited data from this laboratory (see Pesticides in Table I and ref. 7) and elsewhere[6–8] suggest that the lower limit extends to the 5 parts per trillion level in favorable cases. Thus it appears

TABLE II

COMPARATIVE EXTRACTION AND ELUTION EFFICIENCY AT DIFFERENT CONCENTRATION LEVELS

Compound type	*% Recovery —extraction and elution*	
	~50 ppb	*~50 ppm*
Polyaromatics	105	100
Ketones	102	100
Esters	100	98

that the concentration range for accurate analyses covers a factor of 10^7 or more, from ~5 ppt to ~50 ppm.

For organic solutes that dissociate in water these concentration limits must be qualified. The ionic form of all but the largest organic molecules is apt to prefer the aqueous phase and pass through the resin column. Partially dissociated organic compounds are often weakly sorbed by the resin, but the percentage retained by the resin is apt to be less in very dilute solutions where the organic is more completely dissociated. This effect is illustrated by *p*-chlorophenol, which is 16% retained by a XAD-2 resin column from tap water solutions at 50 ppb, but is 0% retained at 2 ppb. Likewise 1-naphthol is 44% retained at 50 ppb but 0% at 2 ppb. While acidification of the water sample increases the retention of phenols and naphthols by XAD resin, the situation is still not comparable to that achieved for non-dissociating solutes and the lower concentration limit for dissociating solutes does not approach the low part per trillion level.

Column extraction. The effect of pH on recovery of organic acids and phenols was tested by adding 5 ml of concentrated hydrochloric acid per liter of standard water sample prior to passage through the XAD-2 column. Results are shown in Table III. These results include not only the possible errors associated with the entire analytical scheme but also errors associated with an additional chemical conversion of the acids to methyl esters prior to GC analysis. This esterification using the BF_3–methanol reagent was done to simplify the chromatographic problems associated with the detection of small amounts of acids.

TABLE III

COMPARISON OF THE RECOVERY EFFICIENCY OF XAD-2 FOR ACIDS AND XAD-4 FOR PHENOLS IN DISTILLED WATER AND ACIDIFIED DISTILLED WATER SPIKED AT THE 10- TO 50-ppb LEVEL

Acids	*% Recovery*		*Phenols*	*% Recovery*	
	Untreated	*5 ml HCl*		*Untreated*	*5 ml HCl*
Octanoic	22	108	Phenol	41	40
Decanoic	8	90	*o*-Cresol	62	73
Palmitic	32	101	3,5-Xylenol	71	79
Oleic	32	100	*o*-Chlorophenol	70	96
Benzoic	7	107	*p*-Chlorophenol	75	95
			2,4,6-Trichlorophenol	72	99
			1-Naphthol	43	91

The observed increase in recovery efficiency suggests that pH adjustment is necessary to achieve good analytical accuracy for acidic compounds present in water. Although no detrimental effects caused by the addition of acid have been observed concerning the recovery efficiency for non-dissociated solutes in water, the most reliable procedure for natural water samples is to divide the sample and make two simultaneous extractions, one at the ambient pH and a second under acidified conditions.

Up to 50 g/l of sodium chloride was added to standard water samples to determine whether sorption of the organic solutes by XAD-2 resin would be improved. The results indicated no significant advantage. Likewise variations in flow-rate through the column produced no significant change in recovery. Column dimensions are not very critical although a height-to-diameter ratio of about 6 is recommended.

The extraction efficiency of the XAD-2 resin column for several model organic compounds in water was tested by collecting the column effluent water and assaying it for the organic solutes using conventional extraction techniques. For all non-dissociating organics no solute could be detected in the effluent water. Within the limits of the solvent extraction sensitivity, this proves that sorption by the XAD-2 column is complete. For compounds that dissociate in water, such as phenols and acids, the extraction efficiency of the resin is less than 100% and is related approximately to the water solubility and/or the ionization constant of the compounds.

Elution efficiency. The comparative elution efficiencies of diethyl ether and methanol for a wide variety of organic solutes sorbed on the XAD resins were measured individually and are given in Table IV. For brevity the individual measurements of the elution volumes were averaged. These values were obtained by sorbing 40 μg of each solute on a 0.5-g column of XAD-2 and then determining the required elution volumes using a liquid chromatograph equipped with an ultraviolet or refractive index detector.

In every case tested, diethyl ether was about twice as effective as methanol in stripping all the sorbed components from the resin. Diethyl ether is therefore recom-

TABLE IV

COMPARISON OF ELUTION EFFICIENCY OF DIETHYL ETHER AND METHANOL FOR ORGANICS SORBED ON A 0.5-g COLUMN OF XAD-2

Compound type	*No. tested*	*ml for quantitative elution*	
		Methanol	*Diethyl ether*
Acids	17	5.9	4.0
Alcohols	8	6.0	5.9
Aldehydes	3	10.0	6.5
Alkanes	5	5.0	6.0
Amines	5	10.2	6.3
Aromatics	19	22.0	7.1
Esters	12	6.3	5.5
Ethers	3	7.3	5.3
Organic halides	11	8.9	5.5
Ketones	8	15.1	6.0
Sulfur compounds	12	9.9	5.1
Total = 103		Ave. = 9.7	Ave. = 5.7

mended as the eluting agent in our standard porous polymer method. It is also more advantageous for the concentration and GC detection steps in the analytical procedure.

Although ~7 ml or less of diethyl ether is sufficient for complete elution of the compounds tested as determined on the liquid chromatograph, 25 ml of diethyl ether is recommended in our standard procedure where a somewhat larger column is employed.

The elution capability of aqueous acids and bases was also tested for some organic solutes sorbed on XAD-2 (see Table V). The results show that many acidic compounds are effectively eluted from an XAD-2 column with aqueous base without disturbing the sorbed neutral compounds. However, the elution of some substituted phenols is slow or incomplete. In general, only basic compounds are eluted with aqueous acid, although indole is not eluted. Thus the standard procedure can be modified to include on-column separation into acidic and basic fractions by sequential elution with 0.05 *N* NaOH and then 1 *N* HCl prior to the elution with ether to collect the neutral fraction.

TABLE V

ELUTION OF ORGANIC SOLUTES FROM A 0.2-g COLUMN OF XAD-2 WITH AQUEOUS ACID OR BASE

Compound	*Elution capability**	
	0.05 M NaOH	*1.0 M HCl*
2,3,6-Trimethylphenol	~25 ml	
3,5-Dimethylphenol	~18 ml	
4-Chlorophenol	+	
3,5-Dichlorophenol	~15 ml	
Phenol	+	−
Benzoic aicd	+	−
Benzenesulfonic acid	+	−
2-Naphthalenesulfonic acid	+	−
Dibutyl phthalate	−	−
Benzothiazole	−	
Acetophenone	−	
Pyridine	~22 ml	+
Indole	−	−
Aniline	−	+
N-Methylaniline	−	+
N,N-Dimethylaniline	−	+

* + indicates almost immediate elution with eluent solvent front; − indicates no elution with 25 ml of eluent.

Some additional tests of the eluting capability of purified tap water for neutral organics sorbed on XAD-2 were also made to determine if the water matrix would elute the neutral organics present at very low concentrations. For these tests 10 μg of each solute was sorbed on XAD-2 resin from a 1-liter water solution. Then 100 l of purified tap water at pH 8 were passed through the resin before the neutral organics were eluted with diethyl ether. The percentage recovery was then compared to that achieved when the elution with 100 l of tap water was deleted from the scheme. These

results are tabulated in Table VI. The decrease in recovery is representative of the eluting capability of tap water for the compounds tested. Only a slight decrease that is within the reproducibility limits of the measurements was observed for three of the compounds tested.

The fourth column of Table VI lists the solubility of the compounds tested and shows that a crude relationship appears to exist between solubility and detectability limits that can be achieved by increasing the volume of water sampled. Although other factors[10] certainly influence the sorption and desorption character of the resins, solubility alone seems to explain the observed decrease in the percentage recovery for dimethyl and possibly for dibutyl phthalate.

TABLE VI

ELUTION CAPABILITY OF PURIFIED TAP WATER AND ESTIMATION OF THE ABILITY TO ANALYZE NEUTRAL ORGANICS AT THE PARTS PER TRILLION LEVEL IN WATER

Component	*% Recovery*		*Solubility (g/100 g of water)*
	10 ppb in 1 l	*10 ppb in 1 l, then 100 l*	
1-Methylnaphthalene	93	89	insol.
Benzil	97	91	insol.
Dibutyl phthalate	101	90	0.4
Dimethyl phthalate	91	63	0.5

Unfortunately accurate solubility data for organic compounds slightly soluble in water are not available to test further the possible inverse relationship between solubility and recovery efficiency at very low contamination levels. Nevertheless, the decrease from 91% to 63% for dimethyl phthalate is attributed here to the relatively higher solubility of the dimethyl ester compared with the other compounds used in these experiments.

In a recent report[25] additional organic eluants such as carbon tetrachloride, ethanol and hexane have been shown to be effective eluting agents for desorbing a variety of organics from XAD-4 resin but no exacting comparative study of these solvents with diethyl ether is currently available. Carbon disulfide is probably an even more desirable eluting solvent because of its low vapor pressure which aids in concentration of the eluate and its insensitivity to flame ionization, which is helpful in detecting small amounts of solutes that appear near the solvent peak in the gas chromatogram. Although limited tests of carbon disulfide suggest that it compares very favorably with diethyl ether, we currently do not recommend its use because of the incomplete nature of the tests on a variety of sorbed solutes as well as olfactory and safety considerations.

Drying. The residual water in the XAD-2 column is eluted by the diethyl ether so that the 25 ml of ether eluate contains about 1 ml of water. This water must be removed to achieve smooth concentration of the eluate and to ensure trouble-free GC. Several drying methods were tested. Refrigeration for 24 h is easy but unduly delays the analytical process and can lead to significant evaporative and/or irreversible surface adsorption losses. The salt bath and CO_2–acetone slush techniques yield almost negligible losses for most solutes but both techniques are messy and generally incon-

venient. Both the Na_2SO_4 drying and the liquid nitrogen freeze-out of water are completely effective. The liquid nitrogen freeze-out is the recommended technique because it is convenient to employ and does not involve addition of any component that might contaminate the sample or sorb some solutes on a surface. For all solutes tested, no losses occurred that could be attributed to either the liquid nitrogen freeze-out or the Na_2SO_4 drying procedures.

Concentration of eluate. The controllable variables in concentrating the ether eluate to a small volume were tested separately with respect to possible losses of solute.

The heat sources tested were hot plate, steam and boiling water. No losses of solute could be attributed to the source of heat employed. The hot plate is recommended for convenience although safety may dictate the use of steam in some laboratories.

The solvent evaporation rate has no effect on losses provided it is maintained within the range of 0.5 to 2 ml/min.

The solvents tested were carbon disulfide, diethyl ether, pentane, hexane and benzene. No solute loss could be attributed to solvent effects. The recommended solvent is diethyl ether for reasons discussed above.

Glassware surface activity was tested using a variety of pretreatment techniques which included: (1) sequential solvent washings using acetone, methanol and ether; (2) detergent washing prior to organic solvent washings; (3) detergent washing and drying; (4) silanization of all glass surfaces; (5) bake-out for 16 h at 400°; and (6) reduced surface area by substituting Clear-seal for ground glass joints. No effects related to surface activity could be isolated. For this reason, sequential solvent washings is the recommended pretreatment procedure for all glassware.

Small boiling chips do not occupy any significant volume nor do they sorb any organic solutes. Their use is recommended to prevent bumping and losses that can occur due to violent eruptions, particularly when a Vigreux column is used.

Two types of distillation columns were tested. Both retain the solutes with near 100% efficiency. The Snyder column is recommended because it is less susceptible to losses when vigorous eruptions occur, it is easily saturated with solvent prior to the start of the distillation, and it provides automatic sequential washing of the inside walls when the heat source is removed as discussed earlier. Since no appreciable liquid hold-up exists in the Vigreux column, it is the column of choice when concentration to less than 0.6 ml is desired; concentration to below this level is impossible with the Snyder column.

The two parameters that can cause appreciable losses during the concentration step involve the use of a nitrogen stream to adjust the final solution volume by free evaporation and the shape of the concentration vessel. These parameters are discussed separately below.

A standard evaporative concentration technique is to concentrate by distillation to slightly above a desired level and then to use free evaporation aided by a stream of nitrogen or other gas to adjust exactly the final solution volume. Our experiments show that from 10 to 80% of all but the extremely low vapor pressure solutes are lost using this technique. No solute is lost provided the vessel shape is as described below and the free evaporation step is eliminated. If an exact pre-selected solution volume is desired, it can be readily attained by distillation to just below this volume and then adding ether to the desired final volume. The explanation for the losses during the

free evaporation is related to ineffective washing of the exposed glass surface of the concentration vessel which inevitably becomes coated with solute during the solvent removal. Also some nebulization with subsequent losses from deposits can occur if a fast stream of nitrogen gas is focussed directly over the solution surface.

The shape of the concentration vessel is also critical. The most effective shape based on our studies is shown in Fig. 3A. Vessel shapes B and C as well as slight variations of these shapes were also tested, and these yielded solute losses from 10 to 60%. For comparison, the losses using vessel A were a maximum of 6%. These vessels are conveniently made from 50-ml round-bottom flasks by attaching the conical ~2-ml end of 10-ml graduated centrifuge tubes to the bottom of the flask, being careful to maintain a smooth surface at the point of attachment.

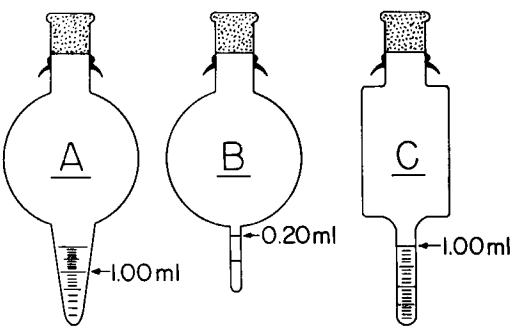

Fig. 3. Scale drawings of the concentration vessels. (A) is recommended, (B) is unsatisfactory, (C) is questionable.

The chief reason for negligible loss of solute with vessel is the effective solvent and/or solution washing of the exposed walls of the vessel during the distillation and immediately after the heat source is removed and the vessel cooled. A second reason is the maximum exposed solution surface consistent with the accurate reading of the solution volume. Vessel B is particularly ineffective because comparatively violent eruptions occur with subsequent spattering when the solution level approaches ~1 ml. With this vessel it is also necessary to use the highly questionable free evaporation technique to adjust the final solution volume so that is it within the calibrated range of the narrow-bore appendage. Vessels similar in shape to C are readily available from laboratory glassware suppliers but the washing action of the surfaces is not as effective as with vessel A.

Several solutes in ether solution were tested for losses using vessel A and the Snyder distillation column. The results of these tests are given in Table VII. The procedure employed was to add 25 ml of diethyl ether to a 1-ml volume of a standard solution containing the solute to be tested. The volume of this diluted standard solution was then concentrated back to 1.0 ml and the efficiency of concentration calculated from the GC solute peaks observed before and after the concentration. The random uncertainty in these efficiency values is ±5%. The most unfavorable components tested were alkylbenzenes but even in these cases results show near 100% recovery for the concentration procedure employed.

TABLE VII

RECOVERY EFFICIENCY FOR SOLUTES IN 25 ml OF DIETHYL ETHER DURING CONCENTRATION TO 1.0 AND 0.6 ml

Sample	*% Recovery*	
	25 ml to 1.0 ml	*25 ml to 0.6 ml*
Naphthalene	94	95
Methylnaphthalene	105	102
Dimethylnaphthalene	93	101
Acenaphthene	99	96
Biphenyl	101	97
Octane	96	
Dodecane	103	
Cumene	99	
p-Cymene	101	
Toluene	91	
Ethylbenzene	98	
Decalin	97	
Tetralin	101	

CONCLUSIONS

The porous polymer resins are best cleaned by Soxhlet solvent extraction and they must be kept in a continuously wetted condition to ensure a very low blank.

The procedure used for preparing standard solutions of organic solutes in water is critical and can result in considerable loss of solute if proper techniques are not employed.

These porous polymer resins are completely effective in extracting neutral organic solutes from water. Many dissociated solutes are also extracted provided the acidity of the water sample is adjusted prior to the extraction. No significant improvements or detrimental effects can be definitely attributed to salting-out, flow-rate variations, pore diameter, bead size, resin bed volume, and mixtures *vs.* single component contaminations.

The sorbed organic compounds are quantitatively and easily eluted from the resin without any chemical transformations using 25 ml of ether, which is a more effective and universal eluant than methanol.

Acidic and basic eluants may be employed to achieve separations into basic and acidic fractions prior to elution of the neutral fraction with diethyl ether.

The eluate is effectively freed of residual water by cooling with liquid nitrogen or by adding excess anhydrous Na_2SO_4 and 10 ml of petroleum ether.

Conventional concentration techniques must be modified to ensure 100% retention of the solutes in the ether solution. Vessel shape is critical and free evaporation aided by a stream of nitrogen or other gas is detrimental.

Regeneration of the resin for subsequent analyses is simple and rapid.

The porous polymer resins can be used for the accurate analyses of organic solutes in water covering a concentration range of 50 ppm to 20 parts per trillion. Upper and lower limits may actually exceed these values but no tests have been made beyond these levels.

The porous polymer procedure as described in this report appears to be quan-

titative for all classes of organic compounds provided these compounds are amenable to GC processing. To accommodate those organic compounds which are not gas chromatographable, the procedure is readily adaptable to other means of separation and quantification.

The porous polymer procedure also accommodates well to on-site composite sampling of large water volumes.

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