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SYSTEMATIC APPROACH TO ADSORPTION ON XAD-2 RESIN FOR THE CONCENTRATION AND ANALYSIS OF TRACE ORGANICS IN WATER BELOW THE μg/l LEVEL

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SUMMARY

The adsorption on XAD-2 resin of trace organics in water has been optimized and evaluated step-by-step at concentration levels below 1 μg/l and in the presence of organic substances that may interfere with the adsorption. Two solvent sequences, methanol–diethyl ether–water (sample) and methanol–acetone–water (sample), gave satisfactory blank levels without reducing the adsorption capacity. Separate studies of the adsorption, desorption and evaporation steps showed that for a great number of non-polar compounds with different functional groups the recovery was mainly limited by losses in the evaporation step. For polar compounds such as certain alcohols and phenols the adsorption efficiency was the most critical factor. Losses during the desorption step could be made negligible except for naphthalene and anthracene. A study of interaction effects between humic substances in the water sample and the low-molecular-weight compounds to be analysed by gas chromatography did not give any evidence of a decrease in recovery or increase in breakthrough for any of the surface-water samples. Comparisons with dichloromethane extraction and stripping enrichment showed that adsorption on XAD-2 can give blank levels and recoveries which are in some respects superior. Furthermore, the XAD-2 technique and dichloromethane extraction were less sensitive to interaction effects from humic substances and less sensitive than the stripping technique.

INTRODUCTION

During the past 15 years, porous macroreticular resins have been widely used for the concentration of trace organics in water. This is particularly true for the polystyrene–divinylbenzene resins XAD-2 and XAD-4. In addition to the chemical analysis of pesticides and other trace organics[1–9], adsorption on XAD has become

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one of the standard techniques for the preparation of extracts in connection with short-term bioassays[10–14].

The first comprehensive study of the XAD-2 technique was carried out in 1974 by Junk *et al.*[1], who proposed that adsorption on XAD-2 was a suitable method for concentrating a large number of compounds in the concentration range 0.02–50 000 ppb. They also made comparisons with other adsorption techniques by determining recoveries for a large number of model compounds[3]. In recent years, Zygmunt *et al.*[8] have shown that adsorption on XAD-2 is a feasible technique for the analysis of selected pollutants in industrial waste water. However, several critical reports have also been published[15–20] in which it has been suggested that a high blank level due to impurities from the resin and a low recovery due to incomplete adsorption and desorption make the XAD-2 technique unsuitable for the detection and quantification of organic compounds below the ppb level. In the present study, however, it is demonstrated that an optimization of each step in this technique can eliminate most of its drawbacks. Furthermore, it is shown that the gas chromatographic (GC) quantification of compounds from surface-water samples may be less affected by the presence of other organic material when using the XAD technique than when using alternative concentration techniques. The fact that the technique is convenient to use, especially when large volumes of water are to be processed, is an extra advantage.

James *et al.*[21] showed that the blank level could be improved substantially by a change in solvent sequence from methanol–water (sample) to methanol–diethyl ether–water (sample). In the present study, the effects of solvent changes are investigated further. The remaining drawbacks of the XAD-2 technique are minimized and illustrated by a series of experiments in which the efficiency of the adsorption, desorption and evaporation steps is studied separately. Throughout the study, all experiments were performed in the concentration range of 20–200 ng/l, *i.e.*, a range in which the XAD adsorption technique has been suggested to be inappropriate. Comparisons are made with dichloromethane extraction and a modified stripping technique.

MATERIALS AND METHODS

Materials

All solvents were of analytical grade, and additionally purified by distillation in an all-glass apparatus. Distillation was repeated until the gas chromatograms showed no further improvement of the blank level. One distillation was usually sufficient. The adsorbent XAD-2 (20–50 mesh), was obtained from Fluka (Buchs, Switzerland). Fines were removed by decanting after slurrying in water. The resin was washed sequentially in a Soxhlet extractor with methanol, acetonitrile, diethyl ether and, finally, with methanol again. The extraction time for each solvent was 8–12 h. The purified adsorbent was stored under methanol.

Concentration by XAD

A 25-ml volume of methanol-slurried XAD-2 was poured into a glass column (500 mm × 50 mm) equipped with a No. 2 glass filter and a PTFE stopcock. Before introducing the water sample, the resin was washed with 25 ml of methanol and 2 × 25 ml of diethyl ether. When studying the recovery of model compounds, the adsorbent was treated with 500 ml of tap-water prior to the introduction of the sample, in order to avoid losses due to instantaneous elution by the ether remaining in the pores. The water sample (10–20 l) was then passed through the column at a flow-rate of 25–75 ml/min. For desorption, 25 ml of freshly distilled diethyl ether were carefully poured over the water–resin mixture. The remaining water was drained, and the resin was left to equilibrate with the ether. After 20 min, the ether was drained completely by applying pressure at the top of the column. The same procedure was repeated with 20 ml of diethyl ether and, finally, 15 ml of diethyl ether were flushed through the column. The ether fractions were pooled, residual water was eliminated by freezing and the ether phase was decanted.

Concentration by dichloromethane extraction

The water sample (10 l) was mixed with dichloromethane in a glass bottle at a ratio of 12:1. The mixture was stirred vigorously with a magnet bar for 90 min. After separation of the layers, the organic phase was dried by freezing out the water. In certain experiments a second extraction was performed in the same way.

Concentration by stripping

Stripping was performed in an open system at 60°C as described by Borén and co-workers[22,23]. The charcoal filters were extracted by carbon disulphide–acetone (90:10).

Evaporation

The organic phase obtained by liquid–liquid extraction was transferred to a 1000-ml round-bottomed flask equipped with a Vigreux column, and the solvent was evaporated at 50°C without using boiling chips. When the volume had been reduced to 50 ml, the extract was transferred to a 100-ml round-bottomed flask in a similar distillation apparatus. The 1000-ml flask was rinsed with a small portion of pure solvent. After reducing the volume of the extract to approximately 1 ml, the flask was cooled and the extract was transferred to a conical test-tube. The 100-ml flask was rinsed with pure solvent. The final concentration was accomplished by directing a very gentle stream of nitrogen (20 ml/min) onto the surface of the extract, while the test-tube was kept in ice–water. The nitrogen gas was purified by an activated carbon filter as is done in the stripping analysis. At a volume of approximately 100 μl, the evaporation was stopped and the extract was transferred to a 200-μl vial. The walls of the test-tube were carefully rinsed by 2 × 25 μl pure solvent. The XAD-2 extracts were evaporated by the same procedure but with the omission of the first distillation.

Quantification of recovery

A standard solution containing 32 neutral organic compounds in acetone was prepared (see Tables I and II). The water samples (tap-water and river-water) were spiked with this standard solution to give a concentration of 200 ng/l of each model compound. After applying the different concentration procedures to the spiked water samples, an internal standard, 1-chloroundecane, was added to the evaporated extracts, and a standardized peak area was determined for each model compound by analyzing these extracts by gas chromatography. Finally, each standardized peak area was divided by a response factor that was determined by adding the internal standard directly to a standard solution of the model compounds and then injecting this solution into the gas chromatograph. A correction was made for those peaks originating from the water that coincided with any of the standard compounds. The same procedure was repeated for a mixture of nine phenols (see Table II).

Gas chromatography

An Hewlett-Packard 5880 gas chromatograph was equipped with a flame ionization detector, and fused-silica columns DB-1 (J&W) 0.25 μm (60 m × 0.32 mm I.D.) and ULTRA 1 (Hewlett-Packard) 0.17 μm (25 m × 0.31 mm I.D.). The carrier gas (helium) flow-rate was 40 cm/s; on-column injection was used for all quantifications. For certain other chromatograms the splitless injection technique with the split valve closed for 60 s was utilized. Volume injected; 1.5 μl. Temperature programme: 40°C for 5 min, then raised at 5°/min to 230°C, finally kept at 230°C for 10 min.

RESULTS

The blank problem

As pointed out in the Introduction, the blank level is dramatically reduced if all methanol is removed from the XAD resin by diethyl ether before introducing the water sample. James *et al.*[21] suggested that it was the mixture of methanol and water in contact with the XAD resin that generated impurities. An alternative explanation for the improvement in the blank level by the initial removal of methanol could be a reduction of the effective contact surface between the water and the resin when methanol, which is highly soluble in water, is replaced by diethyl ether, which is poorly soluble in water. This, in turn, would lead to a decrease in adsorption capacity. In order to test the latter hypothesis, the adsorption capacity of the resin was compared for three different solvent sequences: methanol–water, methanol–diethyl ether–water and methanol–acetone–water. Tap-water samples spiked with 10 mg each of four compounds that are relatively insoluble in water, 1-decanol, 2-methoxynaphthalene, methyl dodecanoate and benzophenone, and 1 g each of three water-soluble compounds, 1,3-dichloroacetone, 1-hexanol and 2,5-hexanedione, were passed through XAD columns. Despite the very high loading of the resin, no significant difference in recovery could be detected, thus indicating that the adsorption capacity does not decrease when methanol is replaced by diethyl ether. The strong positive effect on the blank level created by the initial removal of methanol by diethyl ether (or acetone) is demonstrated by the chromatograms in Fig. 1.

James *et al.*[21] described the blank problem as a leakage of a series of hydrocarbons from the resin, and estimated that the standard methanol–water procedure gave rise to about 2.5 μg of impurities per gram resin used (1 μg for *n*-undecane and *n*-dodecane, respectively). Similar values, about 3 μg/g resin, were obtained in the present study. However, according to our results and in agreement with Melton *et al.*[15], most of the blank peaks were caused by different substituted aromatic compounds, even though *n*-undecane was the largest single peak in the chromatograms from the blank extracts. When the solvent sequence methanol–diethyl ether–water or methanol–acetone–water was applied the amount of impurities in the blanks was reduced from about 3 μg/g resin to about 0.1 μg/g, *i.e.*, by a factor of 30.

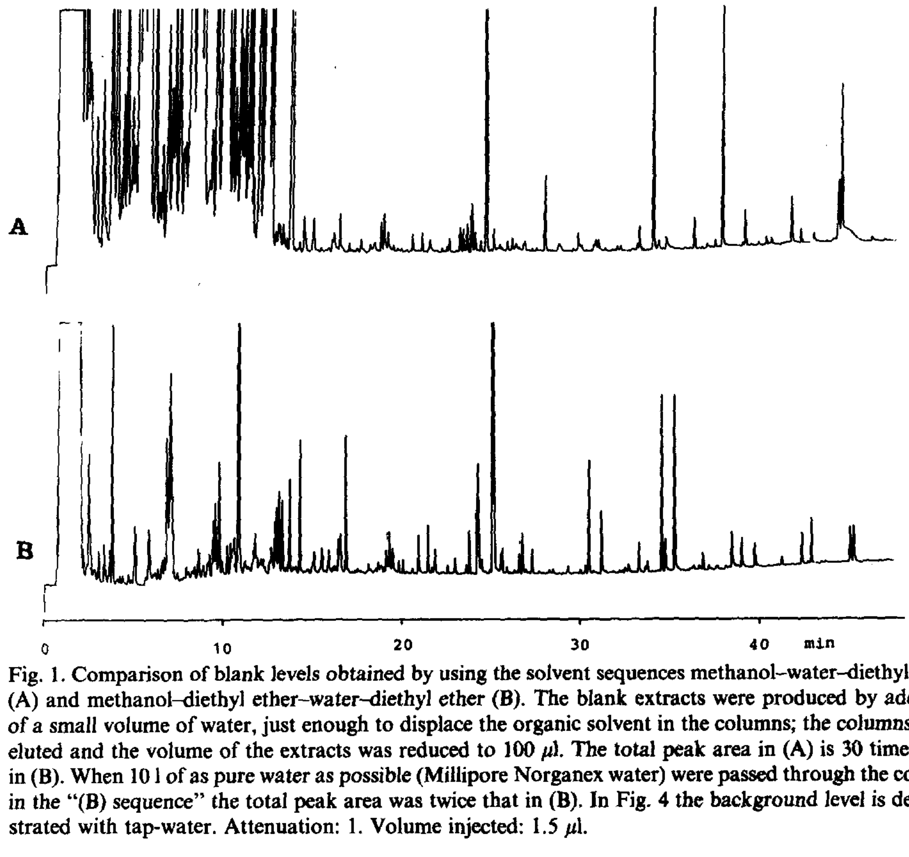

Fig. 1. Comparison of blank levels obtained by using the solvent sequences methanol–water–diethyl ether (A) and methanol–diethyl ether–water–diethyl ether (B). The blank extracts were produced by addition of a small volume of water, just enough to displace the organic solvent in the columns; the columns were eluted and the volume of the extracts was reduced to 100 μl. The total peak area in (A) is 30 times that in (B). When 10 l of as pure water as possible (Millipore Norganex water) were passed through the column in the "(B) sequence" the total peak area was twice that in (B). In Fig. 4 the background level is demonstrated with tap-water. Attenuation: 1. Volume injected: 1.5 μl.

Recovery studies

The three main steps of the XAD technique — adsorption, desorption and evaporation — may all give rise to losses or contamination, making careful and exact laboratory techniques extremely important. In the present study, each step was evaluated and optimized individually, using tap-water samples (10 l) spiked with 32 different organic compounds (see Experimental and Table I). For quantification of the recoveries, experiments were performed at a concentration of 200 ng/l. For investigation of detection limits, the XAD technique was applied to samples containing model compounds at a concentration of 20 ng/l. After optimization, the XAD-2 technique was also evaluated on authentic river-water samples with different contents of organic material.

Adsorption. The adsorption efficiency of the XAD-2 resin was studied in experiments in which adsorption was performed on up to four columns in series. Water containing 200 ng/l of each compound of the 32-component mixture and water containing nine phenols was passed through the first column, then through the second column and so on. The eluate from each column was analysed separately.

The results showed that all compounds were sufficiently adsorbed to allow GC analysis with flame ionization detection. For most compounds, the total recovery

TABLE I

MEAN RECOVERIES FROM THE EVAPORATION STEP FOR THE COMPOUNDS IN THE 32-COMPONENT MIXTURE

The 32-component mixture contained 2000 ng of each compound in 50 ml diethyl ether; final volume 100 μl; *n* = 3. The average relative standard deviation (R.S.D.) was 3%.

No.	*Compound*	*Recovery (%)*
1	3-Hexanone	73
2	Butyl acetate	74
3	Chlorobenzene	75
4	1-Chlorohexane	75
5	1-Hexanol	79
6	Anisole	77
7	Amyl acetate	76
8	Propylbenzene	76
9	*p*-Dichlorobenzene	76
10	Acetophenone	77
11	1-Chlorooctane	76
12	1-Octanol	77
13	Benzyl acetate	79
14	Naphthalene	78
15	2,6-Dichloroanisole	78
16	3-Phenyl-1-propanol	79
17	1-Chlorodecane	79
18	1-Decanol	80
19	1,2,3,5-Tetrachlorobenzene	79
20	Methyl decanoate	80
21	2,3,6-Trichloroanisole	80
22	Diphenyl ether	81
23	2-Methoxynaphthalene	82
24	Ethyl cinnamate	81
25	1-Chlorododecane	84
26	Pentachlorobenzene	–*
27	Methyl dodecanoate	82
28	1-Chlorotetradecane	83
29	Anthracene	84
30	*n*-Octadecane	83
31	1-Chlorohexadecane	83
32	1-Chlorooctadecane	83

* Coelution with blank peak.

from the first column was at least ten times higher than the recovery from the subsequent column. For more polar compounds such as 1-hexanol, 3-phenyl-1-propanol and some phenols, there was a marked but reproducible breakthrough, resulting in exponentially decreasing recoveries from the first to the last column. A third recovery pattern could be seen for the long-chain hydrocarbons and for the very polar phenols. These compounds were poorly adsorbed, resulting in a low and almost constant recovery from all columns. The different recovery patterns are illustrated in Fig. 2.

The negligible or at least reproducible breakthrough for all model compounds except the long-chain hydrocarbons and polar phenols shows that the adsorption

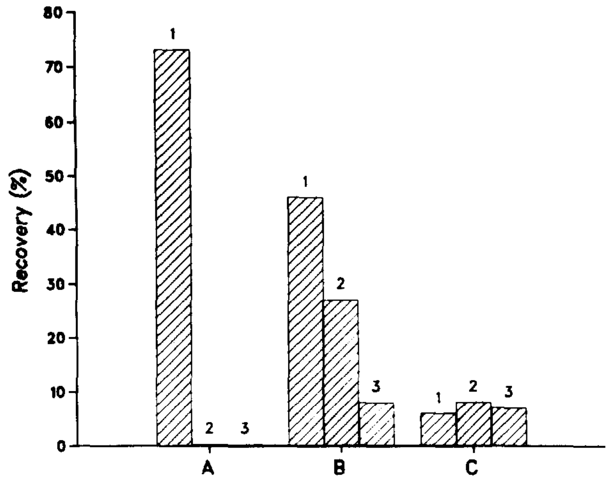

Fig. 2. Different types of adsorption patterns. Total recovery (after losses in the adsorption, desorption and evaporation steps) from three XAD-2 columns in series for (A) 2,6-dichloroanisole, (B) 1-hexanol and (C) *n*-octadecane.

efficiency of XAD-2 is sufficient for a quantitative analysis of a large number of compounds with different functional groups. The low adsorption efficiency for the long-chain hydrocarbons is somewhat surprising, considering the non-polar character of both these compounds and the XAD-2 resin. This type of molecule does not appear to fit into the lattice of the XAD-2 material.

Desorption. The desorption studies focused on the draining of the resin between the three sequential elutions of the column. The results clearly showed that optimum recovery was obtained when each portion of the solvent (diethyl ether) was completely removed from the resin by applying pressure at the top of the column. Fig. 3, which shows chromatograms from the first and second portions of the solvent, illustrates the good desorption efficiency with this procedure. With the exception of some aromatic compounds, the losses due to incomplete desorption were negligible. For anthracene, which had the lowest desorption efficiency among the compounds tested, the loss may reach 10%. Fig. 3 also shows that there is no reason to fear a higher blank level if the resin dries between the elutions.

Evaporation. After eluting the XAD column, further concentration of the extract was necessary to obtain sufficient sensitivity in the GC analysis. Evaporation of the solvent may be performed in many different ways[1,24]. In the present study, care was taken to prevent losses in the final, very critical, evaporation step; this was accomplished by using a very gentle stream of nitrogen gas (see Experimental).

The recoveries in the evaporation step were in complete accordance with the volatility of the model compounds (see Table I). The most volatile compound gave the lowest recovery (73%), and thereafter the recoveries increased continually up to the least volatile compound which gave the highest recovery (84%). When interpreting Table I it should be emphasized that the recovery is highly dependent on the concentration of the compounds and the final volume of the extract; lower concen-

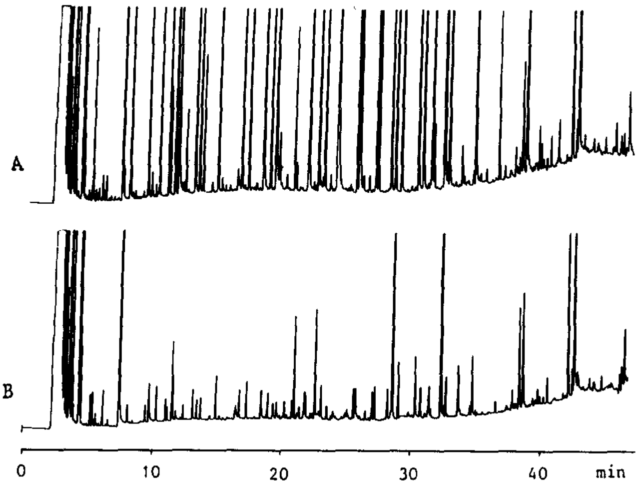

Fig. 3. Repeated elution of a XAD-2 column. Chromatograms of extracts from the first (A) and second (B) elution, respectively, carried out according to the standard procedure. Attenuation: 1. Volume injected: 1.5 μl.

trations result in lower recoveries, as do lower final volumes. The concentration levels in the present study (20–200 ng/l) and the final volume of the extract (100 μl) were lower by, at least, a factor of ten in comparison to previous reports on the evaporation of XAD extracts[1,24].

By comparing the recoveries in Table I with those from the total concentration procedure (see next section), one can easily see that the losses during the evaporation step greatly affect the recovery of most compounds in the test mixture.

Interaction effects. When analysing natural water samples, the presence of high-molecular-weight organic material in the water can affect the recovery of low-molecular-weight compounds to be analysed by GC. Several authors have shown that (a) humic substances can complex low-molecular-weight organic compounds and thereby affect the physico-chemical state and the analytical availability of these compounds[25–27]. When using resin adsorption methods for the concentration of trace organics in water one also expects two other interaction effects: (b) macromolecules may occupy sites on the resin surface and decrease the capacity of the adsorbent; (c) macromolecules that are adsorbed on the resin may reduce the desorption efficiency.

To investigate whether any of these mechanisms have any practical influence on recovery, tap-water samples (chemical oxygen demand, COD_{Mn}, 2 mg/l; colour, 5 mg Pt/l) and river-water samples (COD_{Mn}, 9 mg/l; colour, 45 mg Pt/l) were spiked with the same 32-component mixture at a concentration of 200 ng/l. The water samples were passed through two XAD columns in series, and the recovery from each column was determined. If interaction effects of type (b) were important, river-water samples would give a comparatively higher recovery from the second column than tap-water samples. Interaction effects of type (a) or (c) would most likely give a lower recovery from both columns for samples with high contents of humic material. However, no significant differences in recovery or breakthrough between tap-water and river-water were observed for any of the model compounds. The average recovery was 50 % for tap-water and 47% for river-water. The breakthrough, measured as the average recovery from the second column, was 3 and 2% respectively. Thus, interaction effects between different organic compounds seem to be of minor importance for the analysis of normal surface-water samples by the XAD-2 technique. Previous reports on interaction effects between humus and low-molecular-weight compounds have invariably dealt with water samples of higher humic load than in the present study[25,26,28]. It should also be emphasized that, in order to avoid confounding effects of microbial degradation, all water samples in this study were processed immediately after the model compounds had been shaken with the water for half an hour. The conclusions about interaction effects are therefore restricted to rather rapid interaction processes[26,28].

Comparison of adsorption on XAD-2 with other concentration techniques

Blank levels. Under the conditions of the present study (25 ml of XAD to 10 l water), the XAD-2 technique could be refined to give about the same blank level as liquid–liquid extraction by distilled analytical grade dichloromethane. However, as regards blank levels, stripping with an open system is superior to both adsorption on XAD and liquid–liquid extraction. When comparing the blank level of the XAD technique with that of liquid–liquid extraction, certain fundamental differences must be considered. In the XAD method the leakage from the resin and the amount of solvents used is proportional to the amount of resin, i.e., with a constant bed volume, the blank level is almost independent of the volume of the water sample. In the liquid–liquid extraction technique, the blank level is essentially determined by the impurities in the extraction solvent, and thus proportional to the volume of the water sample. The small volume of solvent used for the extraction of the carbon filter in the stripping procedure makes the presence of solvent impurities less critical for this concentration method. For all three methods, laboratory air can be a major source of contamination, unless the contact between the water sample and the air is reduced as much as possible.

Total recoveries. Table II lists the recoveries for 41 model compounds by adsorption on XAD-2, dichloromethane extraction and stripping. In the experiments with XAD-2 and liquid–liquid extraction with dichloromethane, the samples consisted of 10 l of spiked tap-water; in the stripping experiments, the sample volume was 1 l. The concentration of model compounds was 200 ng/l in all experiments.

According to Table II, the highest overall recoveries were obtained by liquid–liquid extraction, even though the differences between adsorption on XAD and liquid–liquid extraction were quite small. As for adsorption on XAD, the final evaporation step was also responsible for a large part of the losses in the dichloromethane extraction procedure. (Experiments with repeated extractions showed that, for all neutral model compounds, the extraction efficiency was greater than 90% at the first extraction. For phenols the extraction efficiency was considerably lower.) The stripping technique resulted in slightly lower recoveries, in particular for more polar compounds (see Table II). However, due to the very low blank level of this method, it is still more sensitive than both adsorption on XAD and liquid–liquid extraction. The standard deviation of the recovery is also smaller for the stripping technique, since this technique does not include any evaporation step. For com-

TABLE II

TOTAL RECOVERIES OF THE COMPOUNDS IN THE 32-COMPONENT MIXTURE AND THE PHENOL MIXTURE FROM THREE CONCENTRATION METHODS

XAD-2 and dichloromethane extraction: 10 l water containing 200 ng/l of each compound. Stripping: 1 l of water containing 200 ng of each compound. The average R.S.D. for the compounds with a recovery > 20% was 6% (n = 5) for the XAD-2 technique and 3% (n = 3) for the stripping technique. The stripping of phenols was performed at 90°C and the carbon filter was extracted with carbon disulphide–benzene–methanol (65:30:5). tr = Traces; n.d. = not detected.

No.	*Compound*	*Recovery (%)*		
		XAD-2	*Dichloromethane extraction*	*Stripping*
1	3-Hexanone	56	43	24
2	Butyl acetate	66	48	42
3	Chlorobenzene	62	42	29
4	1-Chlorohexane	61	42	39
5	1-Hexanol	46	26	18
6	Anisole	65	43	46
7	Amyl acetate	66	45	58
8	Propylbenzene	62	44	46
9	*p*-Dichlorobenzene	67	50	45
10	Acetophenone	68	51	8
11	1-Chlorooctane	51	51	48
12	1-Octanol	68	56	41
13	Benzyl acetate	64	56	12
14	Naphthalene	63	60	24
15	2,6-Dichloroanisole	73	63	54
16	3-Phenyl-1-propanol	50	47	n.d.
17	1-Chlorodecane	47	61	52
18	1-Decanol	70	—*	55
19	1,2,3,5-Tetrachlorobenzene	59	66	43
20	Methyl decanoate	56	65	57
21	2,3,6-Trichloroanisole	61	71	45
22	Diphenyl ether	60	68	56
23	2-Methoxynaphthalene	58	69	7
24	Ethyl cinnamate	66	68	7
25	1-Chlorododecane	42	78	63
26	Pentachlorobenzene	—*	77	39
27	Methyl dodecanoate	46	74	56
28	1-Chlorotetradecane	23	79	61
29	Anthracene	63	—*	2
30	*n*-Octadecane	6	84	56
31	1-Chlorohexadecane	9	87	54
32	1-Chlorooctadecane	5	87	49
33	Phenol	5	tr	4
34	2-Methoxyphenol	42	14	12
35	2,6-Dimethylphenol	64	16	40
36	2-Ethylphenol	56	19	23
37	2-*tert.*-Butylphenol	63	29	65
38	3-Chloro-5-methoxyphenol	3	7	tr
39	2-Hydroxybiphenyl	61	—*	7
40	4-Octylphenol	65	—*	—*
41	Pentachlorophenol	7	—*	5

* Coelution with blank peak.

pounds with a recovery exceeding 20%, the average relative standard deviation (R.S.D.) for the stripping technique is 3% and for the XAD-2 technique is 6% (based on three and five consecutive experiments respectively).

The satisfactory detection level of the optimized XAD-2 adsorption technique is demonstrated by Fig. 4, which shows a chromatogram of an XAD-2 extract of 10 l of water with a concentration of 20 ng/l for each of the neutral compounds. Almost all model compounds except the long-chain hydrocarbons gave rise to distinct peaks. The detection limit for these compounds is therefore below 20 ng/l. By increasing the volume of the water sample, the signal-to-noise ratio can be increased, and the detection limit can thereby also be lowered.

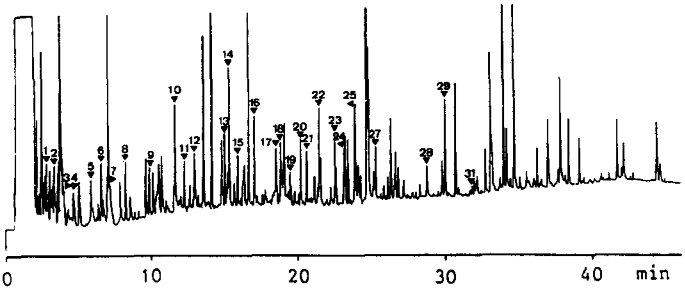

Fig. 4. Chromatogram of an XAD-2 extract of a 10-l water sample containing neutral model compounds at a concentration of 20 ng/l. Peaks corresponding to the model compounds are marked with arrows and numbered according to Table I. Final volume of extract: 100 µl. Attenuation 1. Volume injected: 1.5 µl.

Thus far the comparison of the three concentration methods has been concerned with the recovery of model compounds. With the exception of the poor adsorption of long-chain hydrocarbons on XAD-2 and the invariably low recovery of more polar phenols, all three methods were found to be suitable for the analysis of all the compounds tested. When applying these methods to authentic water samples containing a large number of unknown compounds, however, there were large differences in recoveries between the stripping technique and the two other techniques. This is illustrated in Fig. 5, which shows chromatograms of extracts from the same river-water sample prepared by XAD-2 adsorption, dichloromethane extraction and stripping. A closer analysis of the chromatograms also showed that the XAD-2 extracts contained several compounds not found by dichloromethane extraction and *vice versa*. Finally, due to the lower background, there were certain peaks in the stripping chromatograms that were not found in the other two extracts.

Interaction effects. As stated previously, when using adsorption on XAD-2, the presence of organic material of high molecular weight in the water samples used in this study had little effect on the recovery of compounds to be analysed by GC. Also in the dichloromethane extraction technique, the extraction efficiency of the added model compounds (200 ng/l in 10 l of water of the previously mentioned mixture) was almost the same for tap-water samples as for surface-water samples. Among the model compounds tested only the long-chain hydrocarbons were somewhat less efficiently extracted from surface-water samples.

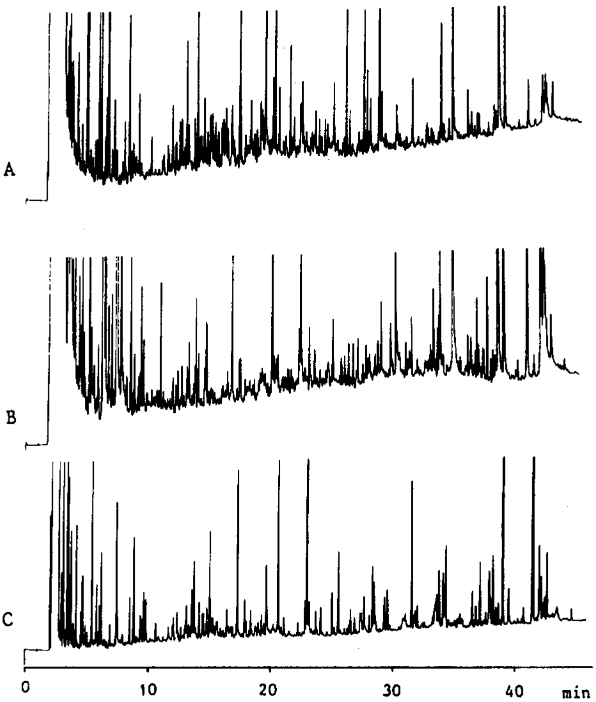

Fig. 5. Chromatograms of extracts produced with (A) XAD-2, (B) dichloromethane extraction and (C) stripping. The water samples were three aliquots (10, 10, 1 l) of the same river-water. Final volume of extracts: XAD-2 and dichloromethane extraction, 100 µl; stripping, 10 µl. Attenuation: 1. Volume injected: 1.5 µl.

When using the dichloromethane extraction technique, material of high molecular weight can also cause problems in the final step of the evaporation procedure. There is a much greater yield of such material with this technique than with the XAD-2 technique (when the resin is extracted by diethyl ether), yielding quite viscous extracts at the concentration factors used in this study. This makes evaporation down to very small volumes difficult.

The large yield of high-molecular-weight organics when using dichloromethane extraction can also cause serious problems during GC analysis. The organic material that is not volatile enough will remain in the column (or in the inlet system) and cause increased column activity. It will also shorten the life of the column, especially when on-column injection is utilized.

The stripping technique was more sensitive to interaction effects than were both liquid–liquid extraction and adsorption on XAD-2. For the long-chain hydrocarbons, the recovery from the spiked surface-water samples was only about half compared to that from the spiked tap-water samples. A decreased recovery from the surface-water samples was also recorded for practically all other compounds in the test mixture, although the effects were smaller than for the hydrocarbons.

CONCLUSIONS

In contrast to several previous reports, it has been shown that adsorption on XAD-2 is a suitable method for the concentration and analysis of organic compounds in water, even far below the μg/l level. If the adsorption, desorption and evaporation steps are carried out optimally, the limit of detection for XAD-GC with flame ionization detection is in general below 20 ng/l for a sample volume of about 10 l. By increasing the volume of the water sample the detection limit may be lowered further.

As long as the resin is not exposed to a mixture of water and methanol, acceptable blank levels can be obtained by at least two different solvent sequences (methanol–diethyl ether–water or methanol–acetone–water). The adsorption efficiency is satisfactory for most low-molecular-weight organic substances. Compounds such as long-chain hydrocarbons and polar phenols, however, are poorly adsorbed.

The study of interaction effects between humic substances in the water sample and the low-molecular-weight compounds to be analysed by GC did not give any evidence of a decrease in recovery or an increase in breakthrough for the surface-water samples. It should, however, be emphasized that the studies were restricted to relatively rapid interaction processes.

In some papers, adsorption on XAD-2 has been described as inferior to liquid–liquid extraction[16,29]. In this study, the two techniques were found to be almost equally efficient in concentrating a large number of model compounds. When applying them to authentic water samples, however, the resulting chromatograms differ considerably. The XAD-2 extracts contain compounds not found in extracts obtained by liquid–liquid extraction, and *vice versa*. Thus, the two concentration techniques should be considered as complementary rather than alternative methods.

Contrary to expectation, the XAD-2 technique is not more sensitive than dichloromethane extraction and less sensitive than the stripping technique to interaction effects from high-molecular-weight material in normal surface-water samples. It is also worth mentioning that XAD-2 extracts obtained by ether elution affect the GC columns less than corresponding dichloromethane extracts of normal surface waters. The fact that large water volumes can more readily be processed by XAD adsorption than by alternative techniques is of course an additional advantage.

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