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Isolation of Organic Material from Water

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More than 2000 chemicals have been identified in the aquatic environment, more than 700 of these in drinking water (Kraybill 1981, Bedding et al. 1982). It is estimated that only 10 to 20 % of the total organic matter in drinking water are identified by current methods. The great majority of the compounds is present in minute concentrations, frequently in the nanogram/liter region (Bedding et al. 1982). These facts have lead to efforts in recent years to recover the totality of chemicals, particulary organics, from water for biological screening tests.

Numerous methods are described in the literature for concentrating or isolating organics from water samples (reviewed by Jolley, 1981). Adsorption on XAD resins is widely used because it can easily be adapted to large sample volumes and also to continuous sampling. XAD 2 was tested extensively (Burnham et al. 1972, Junk et al. 1974) and good recovery of many types of compounds was reported. However, for some polar compounds XAD 7 was found more effective (Stepan and Smith 1977). Van Rossum and Webb (1978) reported a combination of XAD 4 and XAD 8 to be superior to XAD 2. Besides the resin methods, freeze concentration (Baker 1967) has been used successfully in our institute for concentrating e.g. nitrosamines (Hartmetz and Slemrova 1980) and phenols (Rübelt et al. 1982). Lyophilization was considered as a supplementory method for recovery of compounds which are not sorbed on resins.

The object of our study was to compare the above mentioned methods with respect to recovery of total organic matter from water using dissolved organic carbon (DOC) as a criterion of effectivity. UV absorbance, gas chromatography (GC), and recovery of added chemicals were used for additional information.

MATERIALS AND METHODS

Samples of river water were taken from the Rhine and the Main Rivers near Mainz, Germany, in 10 l stainless steel vessels. Tap water was obtained in the laboratory directly from the tap. In those experiments where chemicals were added distilled water was used.

Solvents were analytical grade and were obtained from E. Merck AG (Darmstadt). They were distilled before use. Resins: Amberlite XAD 2, XAD 4, XAD 7, XAD 8, and IRA 401S, analytical grade, were supplied by Serva GmbH & Co (Heidelberg). Activated carbon, granular, 1.5 mm, from E. Merck AG (Darmstadt).

Glass columns with teflon stopcocks, 9 or 15 mm i.d. were filled with either a combination of 3 cm XAD 7 and 7 cm XAD 2 or with 10 cm of a mixture of equal parts of XAD 4 and XAD 8. They were washed with acetone, dichloromethane and methanol, then rinsed with distilled water. Samples from 6 to 10 liters were pumped through the resins at a flowrate of 3 to 6 bed volumes/min. In the pump and the pipes water came in contact only with stainless steel and teflon. Flow rate could be regulated from 5 to 200 ml/min. Tap water from the laboratory (up to 200 l) was fed to the column directly. The sorbed material was eluted with 2 bed volumes of acetone and 8 bed volumes of dichloromethane. The Amberlite 401S, filled into the column to a height of 10 cm, was washed with 0.1 M sodium hydroxide solution, methanol, 0.1 M hydrochloric acid and distilled water, and the sorbed material was eluted with methanol. Activated carbon was treated in the same way as XAD resins.

Resin column blanks were eluted immediately after rinsing with distilled water and the eluate concentrated and injected into a gas chromatograph. No peaks were discovered using a 3 % OV 17 column with temperature programming from 333 to 523 K and FID detection.

Batches of 3 l of water in a 4 l round bottom flask were rotated in a cooling bath at 261 K for 2 hours. The liquid phase, approximately 500 ml, was then poured off into a 1 l round bottom flask and rotated in the bath for another 30 min. 50 to 60 ml concentrate was recovered from the second stage.

Lyophilization was carried out in stainless steel trays in a lyophilizer with 12 l capacity (Martin Christ GmbH & Co, Osterode). Final temperature was kept below 303 K.

For the determination of DOC a Maihak (Hamburg) analyzer Model UV-DOC UNOR was used. Lyophilized material was dissolved in distilled water with the addition of sulfuric acid and diluted to original volume. Distilled water with an appropriate amount of sulfuric acid was used as a blank. To estimate DOC recovery in XAD eluates and in organic extracts of lyophilized material the following procedure was adopted: the solvents were completely removed by evaporation and the residue suspended in distilled water with ultrasonication. The suspension was then diluted to original volume with distilled water which yielded a clear liquid.

RESULTS AND DISCUSSION

Table 1 shows the recovery rates of added chemicals obtained with four different sorption procedures: (a) a combination of XAD 2 and XAD 7 and neutral pH of the sample, (b) the same, followed, after acidification to pH 2 to 3, by a second column of the same material, (c) followed, after acidification, by a column with Amberlite IRA 401S, (d) a mixture of XAD 4 + XAD 8 at neutral and acid pH. The variations between the methods were not significant and were within the range of scatter. The results indicate that an additional adsorption step does not significantly improve the recovery rates. Therefore in later experiments the one stage procedure was adopted. It greatly facilitates continuous sampling e.g. directly from the tap or in water works.

Table 1. Recovery of organics from 10 l of water with different combinations of resins.

	% Recovery			
Compound	XAD 2+7 pH 7	XAD 2+7 pH 7 and pH 3	XAD 2+7 pH 7 IRA 401S pH 3	XAD 4+8 pH 7 and pH 3
Diethylphthalate[a]	99	82	64	66
4-Methylanisole[a]	43	34	-	28
γ-Hexachlorocyclohexane[a]	80	77	62	59
DDT[a]	3	5	5	n.d.
Dieldrin[a]	22	30	31	16
Tetrachlorobenzene[a]	10	15	7	13
4-Nitroaniline[a]	18	43	18	75
Indole[a]	52	52	43	42
2,4-Dichlorophenol[a]	74	65	63	59
1,2-Dihydroxybenzene[a]	72	62	58	61
2,6-Di-tert.butyl-4-methylphenol[a]	22	29	11	29
Fluoranthene[b]	88	81	100	86
Benzo(b)fluoranthene[b]	34	16	30	8
Benzo(k)fluoranthene	29	13	26	7
Benzo(a)pyrene[b]	14	12	17	5
Average	44	41	36	37

[a] concentration 4 and 40 µg/l
[b] concentration 0.1 and 0.01 µg/l
n.d. = not detected

With an average between 36 and 44 %, our recovery rates are generally lower than those reported by Junk et al. (1974, 1976). These authors used 1 l-samples, whereas we chose 10 l to be closer to real conditions. Losses could be due to adsorption on the large surface area of the containers and pipes and also to evaporation during the time it takes for the 10 l to pass through the column as has been observed by Fritz (1977). Also, in their

earlier work Junk et al. (1974) report higher recovery rates - typically between 80 and 100 % - than in the later work (Junk et al. 1976) where an average recovery of 59 % was found with a "normalized scheme for sorption".

The recovery experiments with added chemicals are valuable in assessing the possibilities of a method but they give no information about the recovery of the large amount of unidentified organic material in water. DOC was determined to assess the portion of organic carbon in river water which is not retained by XAD 2 + 7, or IRA 401S, or activated carbon. For additional information UV absorbance was measured and gas chromatograms were recorded from the dichloromethane extracts of the original water and the column effluents and from the eluates of the columns. Total peak area was measured. Table 2 shows the results.

Table 2. DOC, UV absorbance and GC peak total in river water passed through different sorbents.

	% in column effluent			% recovered
	DOC	UV	GC	GC
XAD 2+7, exp. 1	91	85	47	36
exp. 2	93	67	26	11
IRA 401S	53	42	35	5
Activated Carbon	124	88	37	2

Although the Amberlite IRA 401S seemed to be superior in retaining organic material as indicated by DOC and UV-absorbance the recovery with respect to material being detectable by GC was lower than from the XAD resin. The reason probably is that humic substances are preferably sorbed on the IRA 401S resin which are not completely desorbed and are not detected by GC. Also, the apparently low retention on XAD resin was, in later experiments, shown to be due to remaining solvents from the cleaning procedure. When rinsing was improved only 70 to 80 % of DOC was found in the column effluent. This means that at least 20 to 30 % of the organic carbon are retained on the XAD column. This is in agreement with the results of Baird et al. (1981) who found that 28 % was retained.

In experiments using tap water 35 % of the DOC was recovered from XAD 2+7 resin columns. It is rather difficult to determine the organic carbon of the material eluted from the column because elution is done with organic solvents. We tried to overcome the difficulty by complete removal of solvents and preparing an aqueous solution as described under methods. To check for completeness of solvent removal and other interferences we prepared blanks from eluents of unloaded XAD columns. In about half of these, low DOC concentrations were detected, and appropriate correction was made. Similar difficulties are encountered with the residue from lyophilization. Due to the large amount of inorganic salts which could interfere with biological tests, the

separation of the organic material by extraction with organic solvents is necessary. We used the same solvents as for the elution of the XAD resins.

A recovery rate of 87 % is found for lyophilized material if dissolved in total but only 33 % if an organic extract of this material is prepared. This disadvantage has also been reported by Jolley (1981). The efficiency of freeze concentration is 78 % at a concentration factor of 6 but decreases to 35 % with 50-fold concentration, and in addition the high concentration of inorganic salts may affect biological tests.

The results of the study show that about 35 % of the organic carbon in water can be recovered by a simple XAD resin adsorption procedure. This is comparable to the recovery rates obtained with freeze concentration at a concentration factor of 50, and with lyophilization, if the organic material is extracted.

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REFERENCES

Baird RB, Jacks CA, Jenkins RL, Gute JP, Neisess L, Scheybeler B (1981) A high performance macroporous resin concentration system for trace organic residues in water. Chem Water Reuse 2:149-169

Baker RA (1967) Trace organic contaminant concentration by freezing. I. Low inorganic aqueous solutions. II. Inorganic aqueous solutions. Water Res 1:61-77; 97-113

Bedding ND, McIntyre AE, Perry R, Lester N (1982) Organic contaminants in the aquatic environment. I. Sources and occurence. Sci Total Environ 25:143-167

Burnham AK, Calder GV, Fritz JS, Junk GA, Svec HJ, Willis R (1972) Identification and estimation of neutral organic contaminants in potable water. Anal Chem 44:139-142

Fritz JS (1977) Concentration of solutes from aqueous solution. Acc Chem Res 10:67-72

Hartmetz G, Slemrova J (1980) Detection of volatile nitrosamines in waste water from chemical plants by combined capillary gas chromatography-mass spectrometry. Bull Environ Contam Toxicol 25:106-112

Jolley RL (1981) Concentrating organics in water for biological testing. Environ Sci Technol 15:874-880

Junk GA, Richard JJ, Grieser MD, Witiak D, Witiak JL, Arguello MD, Vick R, Svec HJ, Fritz JS, Calder GV (1974) Use of macroreticular resins in the analysis of water for organic contaminants. J Chromatog 99:745-762

Junk GA, Chriswell CD, Chang RC, Kissinger LD, Richard JJ, Fritz JS, Svec HJ (1976) Applications of resins for extracting organic components from water. Z Anal Chem 282:331-337

Kraybill HF (1981) Carcinogenesis of synthetic organic chemicals in drinking water. J. Am Water Works Assoc 73:370-372

Rübelt C, Dietz F, Kickuth R, Koppe P, Kunte H, Peschel G, Sonneborn M (1982) Schadstoffe im Wasser. II. Phenole. Forschungsbericht Dt Forschungsgemeinschaft, Boldt, Boppard 168 pp

Stepan SF, Smith JF (1977) Some conditions for use of macroreticular resins in the quantitative analysis of organic pollutants in water. Water Res 11:339-342

Van Rossum P, Webb RG (1978) Isolation of organic water pollutants by XAD resins and carbon. J Chromatog 150:381-392
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