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COMPARISON OF SORPTION AND EXTRACTION METHODS FOR RECOVERY OF TRACE ORGANICS FROM WATER

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ABSTRACT

Several commercially available adsorbents were compared with solvent extraction methods for their utility in recovering trace organics from water. The adsorbents examined included Amberlite XAD-2, XAD-4 and XAD-8, Ambersorb XE340 and XE348 and Tenax-GC. All were found to produce high artifact levels, even after extensive clean-up, making them unsuitable for the analysis of trace organics in water. Quantitatively, Likens-Nickerson or continuous liquid-liquid extraction with methylene chloride gave better recoveries than the adsorbents. Qualitatively, extractive methods were preferred as they yielded much lower levels of impurities than the adsorbents.

These methods of recovering trace organics were evaluated using a standard mixture of compounds added to the water at a level of 55 µg/l. Likens-Nickerson extraction gave comparable recoveries of this mixture at 55 µg/l and 11 µg/l.

KEYWORDS

Amberlite XAD-2,4,8; XE-340, 348; Tenax GC, Likens-Nickerson extraction; continuous liquid-liquid extraction, trace organics, water.

INTRODUCTION

A comparison of several sorption and extraction methods was made by the authors to find one suitable for the analysis of trace organics contributing to tastes and odours in water. A variety of methods for recovering trace organics from water have been published including the purge and trap technique (Bellar and Lichtenberg, 1974), closed loop stripping (Grob, 1973), adsorption-thermal desorption (Pankow and Isabelle, 1982), adsorption-solvent desorption (van Rossum and Webb, 1978), reverse osmosis (Lin and coworkers, 1979) and liquid-liquid extraction (Yohe and coworkers, 1979). Our study was limited to an evaluation of several adsorbents for use in adsorption-solvent desorption (including Amberlite XAD-2, XAD-4 and XAD-8, Ambersorb XE340 and XE348 and Tenax-GC), continuous liquid-liquid extraction using dichloromethane or pentane and Likens-Nickerson extraction with dichloromethane, pentane or ether.

Compounds such as geosmin and 2-methylisoborneol, which are frequently associated with off-flavours in water, have threshold odour concentrations in the 10-200 ng/l range (Persson, 1980). To monitor and identify trace organics such as these using a capillary gas chromatograph equipped with a flame ionization detector or capillary GC/MS, preconcentration of the organics is required to attain sample concentrations within the sensitivity range of these instruments. Two requirements of a preconcentration method are acceptable quantitative recoveries for a broad range of organic compounds in the µg/l to ng/l range and absence of background impurities arising from the recovery procedure which could interfere with the identification of organics recovered from the water.

In the past, activated charcoal was used extensively for recovering trace organics from water: however; problems such as high levels of background impurities, inconsistent quality, difficulties in desorption of some compounds and alteration of sample components (Chriswell and coworkers, 1977; Dressler, 1979) which are associated with this adsorbent have reduced its use although it is used in closed loop stripping procedures (Grob, 1973). Porous polymeric adsorbents such as the Amberlite XAD series (Junk and coworkers, 1974; Thurman and coworkers, 1978; Van Rossum and Webb, 1978; Budde and Eichelberger, 1979) and Tenax-GC (Leoni and coworkers, 1976), carbonaceous Amberlite XE adsorbents (Hunt and Pangaio, 1982) and polyurethane foam (Uthe and coworkers, 1972; Musty and Nickless, 1977) are now available for use in adsorbent-solvent desorption methods. Tenax-GC is also used in the purge and trap method (Bellar and Lichtenberg, 1974) which Jüttner and Wurster (1979) have used to identify metabolites of the alga Cyanidium caldarium.

Liquid-liquid extraction has been used to extract organics from water by shaking a small amount of solvent with the water for rapid extraction (Musty and Nickless, 1973; Grob and coworkers, 1975) or with a continuous liquid-liquid extractor which permits unattended operation (Yohe and coworkers, 1979). Gerber (1968, 1969) and Tabachek and Yurkowski (1976) used solvent extraction to recover and identify geosmin and 2-methylisoborneol from distillates of culture media of actinomycetes and blue-green algae. Solvent choice is a critical factor in attaining good recoveries and freedom from solvent impurities (Grob and coworkers, 1975; Dressler, 1979).

The Likens-Nickerson apparatus (Likens and Nickerson, 1964) uses a combination of steam distillation and continuous liquid-liquid extraction for the recovery of steam volatile compounds. In this apparatus the water sample and extracting solvent are boiled in separate flasks and the vapours condensed in a central chamber which allows solvent and water to separate and return to their respective containers. Although this method has not been used previously to isolate odourous compounds from water, it has been used in isolating volatile compounds from such diverse material as carrots (Buttery and coworkers, 1968), hop oil (Likens and Nickerson, 1966), Douglas Fir needles (Maarse and Kepner, 1970), lipids (Flath and coworkers, 1973) and eggs (Macleod and Cave, 1975). High recoveries (80-100%) for model compounds in water at concentrations of 0.21-210 mg/l (Schultz and coworkers, 1977) have been reported. Because only steam volatile compounds are recovered, a less complex extract would be expected hence simplifying the analysis for taste and odour causing compounds.

The concentration methods included in this report were evaluated based on quantitative and qualitative recoveries of an aqueous mixture of 18 compounds at 55 µg/l and 11 µg/l. The compounds (Table 1) were selected on the basis of their similarity to compounds previously identified in water, their functional groups, range of volatility and their compatibility for simultaneous gas chromatography. Quantitative recoveries were determined using the internal standard method.

EXPERIMENTAL

The solvents used were purified by double distillation as described elsewhere (Slater and Blok, 1983). If required the collected distillate was redistilled until sufficiently purified. However; this was usually only necessary for ether.

TABLE 1 Properties of Compounds in Standard Mixture

		Molecular Weight	b.p. °C
1.	1,1,1-Trichloroethane	133.4	74
2.	Methylisobutyl ketone	100.2	118
3.	n-Octane	133.4	126
4.	Cyclohexanone	98.1	156
5.	α-Pinene	136.2	156
6.	Benzyl Alcohol	108.2	205
7.	Acetophenone	120.1	202
8.	Benzyl Cyanide	117.1	234
9.	Naphthalene	228.3	218
10.	p-Chloroacetophenone	154.6	237
11.	Tridecane[1]	184.4	234
12.	Biphenyl	154.2	255
13.	Biphenyl Ether	170.2	259
14.	BHT[2]	220.3	265
15.	Diethylphthalate	222.2	295
16.	Methyl Myristate	242.4	300
17.	Anthracene	178.2	342
18.	Nonadecane	268.5	330
19.	Methyl Stearate	298.5	360

[1] Internal standard.
[2] BHT = butylated hydroxytoluene (2,6-di-t-butyl-4-methylphenol)

All glassware was cleaned in chromic acid and rinsed with distilled water, dichloromethane and methanol prior to use and dried at 130°C.

The standard compounds (Table 1) were prepared in distilled acetonitrile at a concentration of 1 g/l per compound. A 0.25 ml aliquot of this standard mixture was used in the recovery experiments (4.5 l per experiment). The water was deionized, glass distilled and passed through cleaned XAD-2 resin (Yohe and coworkers, 1979).

Amberlite XAD-2, XAD-4 and XAD-8 and Ambersorb XE340 and XE348 adsorbents were obtained from Rohm and Haas (Philadelphia, Pa., U.S.A.), and Tenax-GC from Applied Science (State College, PA., U.S.A.). The XAD-2, XE340 and XE348 resins were purified by soxhlet extraction for 24 h successively with dichloromethane, water, methanol and dichloromethane and stored under methanol. The final dichloromethane extract was concentrated and subjected to gas chromatography as a check on impurities leached from the resins. The XAD-4 resin was treated similarly and given an additional methanol and dichloromethane soxhlet extraction; however, many impurities were still evident in the final solvent concentrate. XAD-8 was purified according to Junk and coworkers, (1974). Methanol slurries of the resins were transferred to glass columns fitted with glass sinters at their base, below which was a Teflon stopper and a threaded Teflon flow controller. Resin bed volumes of

20 ml were used giving height:width ratios of approximately 4 (column i.d. ∿1.8 cm and column height 8 cm). A methanol-extracted cotton plug was placed on top of the resin bed.

Tenax-GC was used as provided by the manufacturer but was rinsed with 80 ml methanol before use. The column used was similar to that described above. A methanol-extracted cotton plug was placed between the sintered glass and the Tenax-GC (1.5 gm) and glass beads (2 cm) were placed above the adsorbent followed by another cotton plug (Leoni and coworkers, 1976). The Tenax-GC was kept under methanol.

Methanol was displaced from the resins by successive 40 ml washes of methanol and purified water in ratios of 1:1, 1:3, 1:7 and 1:15 and then 80 ml of water. The spiked water was then passed through the resins at a flow rate of 50 ml/min using a vacuum pump when necessary to achieve the desired flow rate. The water was drained to the top of the resin bed, then 20 ml of freshly distilled ether added and drained into the column. The ether was allowed to remain in contact with the resin for 10 min, another 20 ml of ether added and drained into the column. This was repeated once more. A second column rinse with 3x20 ml ether as above was done and the water reservoir was rinsed with 3x20 ml of ether.

Likens-Nickerson extractions were performed for 24 h on spiked water using 60 ml of solvent. After 24 h the solvent was collected, replaced with fresh solvent and the extraction continued for another 24 h. Continuous liquid-liquid extraction with pentane (125 ml) were performed for 24 h with continuous magnetic stirring. Solvent was replaced with fresh solvent after 24 h and extraction continued for another 24 h. The apparatus used for continuous liquid-liquid extraction with dichloromethane could only accommodate a 1.5 l sample. Extractions were carried out for 24 h, then the water was replaced with another 1.5 l sample without changing solvent and the process repeated until all 4.5 l was used. All recovery experiments were performed in duplicate and results shown are averages of the two determinations.

Extracts from recovery experiments were dried and concentrated as described elsewhere (Slater and Blok, 1983). A small Vigreux column equipped with Teflon-faced connectors (Wheaton Scientific, Millville, N.J., U.S.A.) was used to further concentrate the residue to below 5 ml in a threaded 5 ml volumetric flask. Internal standard solution (1 ml, tridecane, 0.25 g/l) and solvent were added to bring the sample to volume.

Solvent extracts were analyzed on a Hewlett Packard 5700 gas chromatograph as previously described (Slater and Blok, 1983). Peak identification and recoveries relative to the internal standard were determined using the Hewlett Packard 3350 Lab Data System.

DISCUSSION

The recovery results for the six adsorbents are shown in Table 2 and chromatograms of the compounds recovered using XAD-2 and the extraction methods are shown in Fig. 1. Values for three of the compounds in the standard mixture (Table 1), 1,1,1-trichloroethane, octane and benzyl alcohol are not included. Recoveries of 1,1,1-trichloroethane were very erratic due to its high volatility and it was not always possible to reliably identify this compound (Fig. 1A). Octane concentrations used were not consistent throughout the experiments thus results for this compound were not strictly comparable and tailing of the benzyl alcohol peak occurred sporadically hindering its quantitation (Fig. 1C).

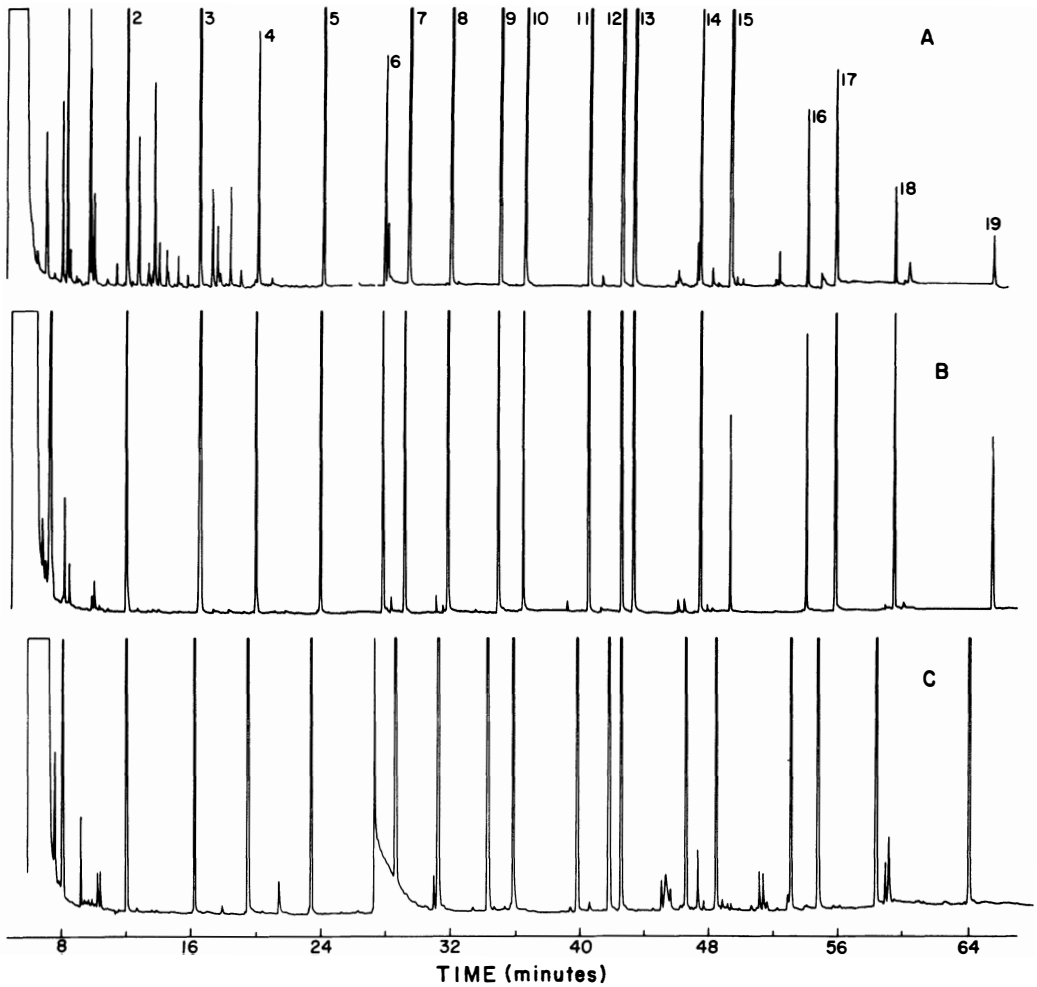

Fig. 1. Chromatogram of: A) compounds recovered using XAD-2 resin;
B) compounds recovered by Likens-Nickerson extraction;
C) compounds recovered by continuous liquid-liquid extraction.

The results presented in Table 2 indicate that of all the adsorbents tested, XAD-4 gave the best overall recovery of the fifteen remaining compounds in the standard mixture. The other Amberlite styrene-divinyl benzene resin, XAD-2, and Tenax-GC gave somewhat lower recoveries, followed by XAD-8. The poorest recoveries were obtained with the two Ambersorb resins, XE340 and XE348. XAD-8 is a polar adsorbent of an acrylic ester composition which has larger pore diameters than XAD-2 or XAD-4 (Table 3). It is reported to be particularly good for recovering low molecular weight solutes and natural organic polyelectrolytes (Dressler, 1979) and has been combined with XAD-4 to yield better recoveries of organic compounds in drinking water than were possible with XAD-4 alone (Thurston, 1978). Individually

TABLE 2 Comparison of Adsorbents Showing % Recovery of Standard Compounds Relative to Internal Standard

Compound	XAD-2	XAD-4	XAD-8	XE-340	XE-348	Tenax GC
Methylisobutyl ketone	49.1	79.6	20.7	9.7	69.5	35.7
Cyclohexanone	26.0	71.0	10.9	12.6	59.4	10.5
α-Pinene	54.8	56.3	61.4	22.8	50.8	39.6
Acetophenone	76.1	83.9	61.1	30.5	5.0	64.6
Benzyl Cyanide	79.6	86.9	64.1	27.9	6.3	68.5
Naphthalene	86.2	82.4	83.7	35.7	1.4	75.7
p-Chloroacetophenone	86.6	87.9	83.1	26.0	2.0	73.3
Biphenyl	96.2	80.2	81.6	49.6	0.9	76.2
Diphenyl Ether	100.8	85.2	84.5	58.3	12.1	83.1
BHT	46.5	65.2	53.8	18.8	21.8	56.6
Diethylphthalate	102.4	78.4	77.9	41.6	19.9	92.6
Methyl Myristate	17.8	43.2	33.5	30.4	8.4	38.6
Anthracene	40.4	49.0	51.2	18.5	1.4	57.5
Nonadecane	12.6	43.5	25.2	16.9	6.3	48.2
Methyl Stearate	16.5	44.1	24.8	27.1	5.9	46.5
% Mean Recovery	59.4	69.1	54.5	28.4	18.1	57.8

XAD-8 generally gave lower recoveries than XAD-4 for most compounds (Table 2). Leoni and coworkers (1975, 1976) initiated the use of Tenax-GC for recovering organic compounds from water. Results presented in Table 2 indicate that it gave overall recoveries of the compounds in the standard mixture similar to those using XAD-2.

The two Ambersorb resins, XE340 and XE348 were developed as alternatives to activated charcoal and the polymeric adsorbents (Table 3). Neither performed as well as the Amberlite resins.

The values expressed in Table 4 represent the total recovery from elution of the column and from a solvent rinse of the reservoir which contained the standard aqueous solution. As indicated in Table 4, elution of the columns with three bed volumes of ether recovered 85-95% of adsorbed material, except for the XE-resins which still retained an appreciable fraction (16-23%) of the total amount recovered.

The concentration of the eluate from the column is a potential source of losses, especially if volatile compounds are involved. Junk and coworkers (1974) recommended a round bottom flask with a drawn out tip fitted with a three-ball Snyder column. Solvent was distilled from a steam-bath at a rate of 0.5-2.0 ml/min. and resulted in losses of up to 5%. This method, and concentration using the same distillation apparatus as for solvent purification, were tested with a standard solution of the test mixture in dichloromethane. Using either method losses were less than 5%.

It became apparent during GC analysis of the concentrated ether eluents of the adsorbents that impurities were arising from the resins in spite of rigorous clean-up procedures recommended for reducing artifacts from the manufacturing process remaining in the resins (Fig. 1A). These impurities were not seen in the purified solvent, initial ether rinses of the resins, or when the water was

TABLE 3 Physical Properties of Synthetic Adsorbents

Adsorbent	Chemical Structure	Polarity	Surface Area m^2/g	Pore Vol. cm^3/g	Pore Diam. A°
Amberlite XAD-2[1]	Styrene-Divinylbenzene Copolymer	Nonpolar Hydrophobic	300	0.854	90
Amberlite XAD-4[1]	Styrene-Divinylbenzene Copolymer	Nonpolar Hydrophobic	725	1.145	40
Amberlite XAD-8[1]	acrylic ester	Polar	51.9	0.822	235
Ambersorb 340[2]	Carbonaceous composition similar to adsorbents	Nonpolar Hydrophobic	400	0.34	100-300
Ambersorb 348[2]	Carbonaceous composition similar to charcoal	Polar Hydrophilic	500	0.58	100-300
Tenax-GC[3]	(2,6-Diphenyl-p-phenylene oxide)	Nonpolar Hydrophobic	19-30	0.667	720

[1] Amberlite XAD-2, Amberlite XAD-4 and Amberlite XAD-8, Technical Bulletins.

[2] Ambersorb Carbonaceous Adsorbents, Technical Bulletin.

[3] Sakodynskii and coworkers (1974).

extracted using the Likens-Nickerson method and hence are believed to arise from the resins either during solvent changes, or the passage of water through the resin. These impurities are shown in the chromatogram of the XAD-2 ether eluate (Fig. 1A). They interfered with the identification of 1,1,1-trichloroethane and would be unacceptable for the analysis of trace organics in authentic water samples in the μg/l to ng/l range. Similar impurities were seen in the XAD-4 ether eluate. A previous report (Hunt and Pangaro, 1982) identified these impurities as alkyl derivatives of benzene, styrene, naphthalene and biphenyl which are related to the parent material of the adsorbents. The high levels of impurities released by XAD-8 and Tenax GC also rendered these adsorbents unsuitable for use. The Ambersorb resins showed improvement with repeated use but they also were unacceptable for analysis of water for trace organics for the same reasons as the XAD resins.

James and coworkers (1981) also encountered impurities when using adsorbents and suggested that these originated from fracturing of the resin beads in conjunction with expansion of the beads during solvent changes. Their method involves displacement of the methanol with ether prior to adding the water sample which did reduce the amount of impurities. However their continued presence even at lower levels led us to look at other methods for water analysis.

Dichloromethane gave better overall recoveries than pentane during both Likens-Nickerson and continuous liquid-liquid extractions (Table 5 and 6) (Figs. 1B and 1C). Two major factors affecting the recovery of aqueous organics using solvent extraction methods are the choice of solvent and the amount of solvent relative to water used. Solvent solubility influences the amount of solvent

TABLE 4 % Recovery of 15 Standard Compounds Relative to Internal Standard During Recovery of Compounds from Adsorbents

Adsorbent	1st Elution	2nd Elution	Reservoir Rinse	Total
XAD-2	54.8 (93.2)[1]	2.5 (4.3)	1.6 (2.7)	58.8
XAD-4	59.0 (85.4)	6.5 (9.4)	4.6 (6.7)	69.1
XAD-8	49.5 (90.8)	2.4 (4.4)	2.6 (4.8)	54.5
XE 340	22.1 (77.8)	4.5 (15.8)	1.8 (6.3)	28.4
XE 348	13.1 (72.4)	4.1 (22.7)	0.9 (5.0)	18.1
Tenax-GC	54.8 (94.8)	0.7 (1.2)	2.5 (4.3)	57.8

[1] Figures in brackets are percentages of total recovery.

TABLE 5 Comparison of Extraction Methods Showing % Recovery of Standard Compounds Relative to Internal Standard

	Likens-Nickersons Extraction				Continuous Liq-Liq Extraction	
Compound	CH_2Cl_2	Pentane	Ether	CH_2Cl_2[1]	CH_2Cl_2[2]	Pentane
Methylisobutyl ketone	79.5	53.7	55.4	88.3	77.9	24.1
Cyclohexanone	96.3	56.6	58.0	126.5	89.5	18.9
α-Pinene	79.8	69.6	49.7	35.8	35.0	29.0
Acetophenone	85.3	78.4	61.1	96.0	91.5	52.9
Benzyl Cyanide	86.9	74.4	62.4	97.5	92.5	10.2
Naphthalene	82.1	88.5	58.9	78.3	80.0	76.2
p-Chloroacetophenone	92.4	81.8	59.1	106.0	102.2	44.8
Biphenyl	77.2	88.1	59.8	84.0	91.0	75.7
Diphenyl Ether	79.4	96.6	71.1	84.3	90.2	63.6
BHT	99.2	91.0	34.6	42.0	90.7	33.9
Diethylphthalate	28.4	36.4	36.2	47.3	107.4	33.3
Methyl Myristate	47.5	36.9	31.4	61.3	95.7	37.4
Anthracene	69.3	66.4	21.7	72.8	96.5	33.0
Nonadecane	54.9	58.7	64.3	69.5	98.8	67.6
Methyl stearate	72.9	59.4	54.8	73.0	99.0	32.8
% mean recovery	75.4	69.1	51.9	77.5	89.2	42.3

[1] Individual compounds of aqueous concentration of 55 μg/l except for this extraction with methylene chloride at 11 μg/l.

[2] All extracts for 2x24 hours except this extraction. See text for explanation.

recovered from the water and can have a solubilizing effect on certain compounds. The solubilities of n-pentane, dichloromethane, and diethyl ether in water are 0.04, 13.0 and 60.0 g/l respectively (Riddick and Bunger, 1970). Dichloromethane, though more water soluble than pentane gave better recoveries in Likens-Nickerson and continuous liquid-liquid extraction. Similarly, Yohe and coworkers (1979) found chloroform gave better recoveries than hexane or ether during continuous liquid-liquid extraction.

TABLE 6 % Recovery of 15 Standard Compounds Relative to Internal Standard from Successive 24 h Extractions Using Fresh Solvent

Method	Solvent	1st Extraction	2nd Extraction	Total
Likens-Nickerson	CH_2Cl_2	74.7 (99.1)[1]	0.7 (0.9)	75.4
	pentane	68.6 (99.3)	0.5 (0.7)	69.1
	ether	49.9 (96.1)	2.0 (3.9)	51.9
	CH_2Cl_2[2]	70.5 (91.0)	7.0 (9.0)	77.5
Continuous liquid/liquid	pentane	39.0 (92.2)	3.3 (7.8)	42.3

[1] Figures in brackets are percentages of total recoveries.

[2] Individual compounds at aqueous concentration of 55 μg/l except this extraction with methylene chloride at 11 μg/l.

Recoveries of the standard mixture at aqueous concentrations of 55 μg/l and 11 μg/l gave similar total recoveries with Likens-Nickerson extraction using dichloromethane (Table 5). However, the proportions of the total recovery obtained during the first and second extractions differed (Table 6) and were lower for the first 24 h extraction period at the 11 μg/l level. This suggests that recoveries of trace organics in the μg/l to ng/l range may not be as good as observed for the standard mixture at the 55 μg/l level. Ether did not perform well as a solvent for Likens-Nickerson extraction because of its high water solubility. Water accumulated in the solvent flask interfering with the continuous distillation of the ether. Also, recoveries were found to be much more variable with this solvent as previously reported by Yohe and coworkers (1978).

The best overall recoveries obtained to date were achieved with continuous liquid-liquid extraction using dichloromethane (Table 5). This method was particularly effective in recovering the less volatile, higher molecular weight compounds in the standard mixture. The Likens-Nickerson method using the same solvent gave somewhat better recoveries of the more volatile lower molecular weight compounds. Despite the lower overall recoveries obtained with the Likens-Nickerson method, its specificity for steam volatile compounds and effectiveness in recovering low molecular weight compounds makes it particularly suitable for the isolation of compounds causing tastes and odours in water.

CONCLUSION

Continuous liquid-liquid extraction of a standard aqueous solution (55 μg/l) of organic compounds using dichloromethane as solvent gave better recovery (89%) than Likens-Nickerson extraction (75%) with the same solvent. Other solvents such as ether or pentane were not as efficient as dichloromethane in either extraction procedure.

XAD-2, XAD-4, XAD-8, XE-340, XE-348, and Tenax GC were found to be unsuitable because impurities from these adsorbents interfered with the capillary GC analysis of the lower boiling compounds in the standard mixture.

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