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MINI-COLUMN PROCEDURE FOR CONCENTRATING ORGANIC CONTAMINANTS FROM WATER

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SUMMARY

A mini-column 1.2–1.8 mm × 25 mm containing XAD-4 resin or Spherocharb effectively sorbs most organic contaminants from a 50–100-ml water sample. The sorbed organics are eluted by 50–100 μ l of an organic solvent and the organic solutes separated by gas chromatography. The procedure is simple, it requires no evaporation step, and gives excellent recoveries of model organic compounds added to water. The sorption properties of XAD-4 and Spherocharb are compared. The procedure developed is applicable for the analysis of waste water and for badly contaminated drinking water.

INTRODUCTION

To measure low levels of organic compounds in drinking water and waste water, concentration methods must be used before analysis. Macroreticular resins are an effective sorbent^{1–6}; a standard method using XAD-2 has been thoroughly tested on a large number of model organic compounds added to water⁵. Activated carbon has also been used successfully as an analytical sorbent^{7,8}. Comparative studies of macroreticular resins and activated carbon have been performed^{9,10}. A difficulty of these methods is that some volatile organics are lost during the solvent evaporation step. Another drawback is that in the leading method⁵ only about 2 μ l of the 1000- μ l solvent concentrate is used for the chromatographic analysis.

In the present study a “mini-column” has been tested for concentration of low concentrations of organic contaminants from water. The column is packed with a sorbent bed 1.2–1.8 mm × 25 mm. Organics from a 50–100-ml water sample are effectively sorbed; the organics can be eluted from the column with 50–100 μ l of an appropriate organic solvent. A 2- μ l aliquot of the eluate is taken for gas chromatographic (GC) analysis. There is no evaporation step in this procedure, and the fraction

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of the sample concentrate actually taken for the final GC analysis is 10–20 times that of the earlier procedure⁵. For this reason, significantly smaller water samples are needed for the mini-column procedure. A drawback of the mini-column method is that the water sample size is limited, and this in turn limits the sensitivity of the method to about 2 ppb* of each organic compound in water.

Amberlite XAD-4 resin and Spherocharb, a hard, spherical carbon molecular sieve, are shown to be effective sorbents. The comparative advantages and drawbacks of these two sorbents are studied and compared.

EXPERIMENTAL

Instruments

A Hewlett-Packard Model 5711 gas chromatograph equipped with a linear temperature programmer and a flame ionization detector was used. One GC column was 6 ft. \times 1/8 in. O.D. stainless steel packed with 10% FFAP on Chromosorb W AW DMCS (80–100 mesh). Another column was 6 ft. \times 1/8 in. O.D. stainless steel packed with Tenax G.C. (60–80 mesh). A third 6 ft. \times 1/8 in. O.D. stainless steel column was packed with 3% OV-17 on Gas-Chrom Q.

Sorbents and reagents

Amberlite XAD-4 from Rohm & Haas (Philadelphia, Pa., U.S.A.) was ground and sieved to 150–200 mesh. This was purified according to the procedure described by Junk *et al.*⁵. The purified resin was stored in glass-stoppered bottles under methanol to maintain its purity. Spherocharb (100–120 mesh) was obtained from Analabs (North Haven, Conn., U.S.A.) and purified with several solvent washings just before use.

Distilled water was freed from interfering chromatographic peaks by passing the distilled water through an activated charcoal column and followed by a XAD-2 column. Model compounds were checked chromatographically for purity. Methanol and acetone were spectrograded and purchased from Burdick & Jackson Labs. (Muskegon, Mich., U.S.A.). Carbon disulfide was c.p. grade.

Column preparations

Disposable transfer pipets used for the sorption columns and for the collecting vessels of eluates were obtained from Fisher Scientific (Pittsburgh, Pa., U.S.A.; Cat. No. 13-678-5A). Disposable pipets (overall length approximately 15 cm; capillary 3.5 cm \times 1.2 mm I.D.; body 7 mm O.D.) were cut in the body portion and adjusted to an overall length of 8–9 cm. The resultant glass tubes were used as resin columns. A small plug of clean glass wool was inserted near the end of each capillary. The purified XAD-4 as a methanol slurry was added to the tube until a resin bed of 2.5 cm length was obtained. Then a plug of clean glass wool was inserted above the resin. In Spherocharb columns, dry Spherocharb was put into a tube which was already filled with acetone. The resin bed was adjusted to 2.5 cm length. Both columns were washed with 3–5 ml acetone and methanol. The excess organic solvent was drained until the level just reaches the top of the resins. In the sorption experiments for low-molecular-weight compounds, columns were washed with 3–5 ml acetone and carbon disulfide,

* Throughout the article the American billion (10⁹) is meant.

and the carbon disulfide removed by pressing with a rubber bulb until the resins looked dry.

The XAD-4 or Sphero carb columns were washed with several milliliters of pure water. The columns were then filled with pure water and attached to the stem of a separatory funnel with a PTFE connector already filled with pure water. The columns were washed with another 20–30 ml of pure water.

The apparatus prepared for the sorption of organic compounds from a sample solutions is shown in Fig. 1. The XAD-4 was freshly prepared from purified XAD-4 and new Sphero carb was used in every sorption experiment.

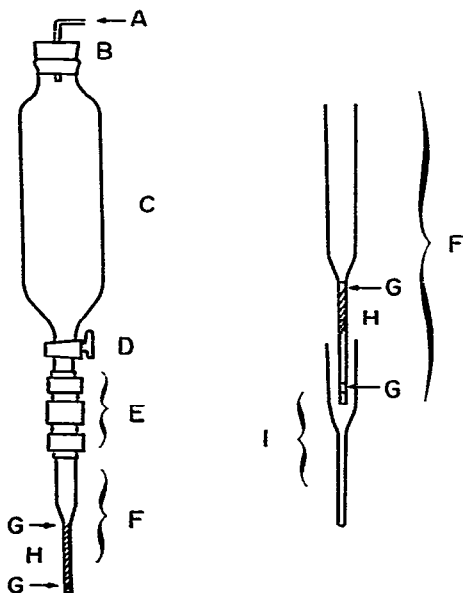


Fig. 1. Adsorption apparatus of organic compounds by mini-column and collecting vessel for eluate. A, air inlet; B, rubber cap covered with PTFE tape; C, separatory funnel; D, PTFE stopcock; E, PTFE connector; F, mini-column, G, glass wool; H, XAD-4 or Sphero carb; I, collecting vessel eluate.

Sorption procedures

In the recovery experiments for model compounds, the organic compounds to be tested were added directly into 50 ml of the sample solution in a separatory funnel by injecting a calibrated volume of standard solutions of the organic compounds dissolved in acetone or mixed acetone–carbon disulfide or pure water.

The separatory funnel was capped with a one-hole rubber stopper which was covered with PTFE tape and connected to clean air. The sample solution was passed through the resin column under air pressure at a flow-rate of 0.8–1.2 ml/min. When the level of the sample solution just reached the inlet of a stopcock, the stopcock was shut off, 5 ml of pure water was added, and the funnel contents shaken together. The washing solution was drained through the column.

When the last drop of washing solution had passed through, the column was

removed from the connector. The residual water in the resin and glass wool was removed by pressing with a rubber bulb. The water can be easily removed by repeated blotting with tiny pieces of filter paper inserted into the outlet of the tube.

Elution procedures

Three kinds of solvents were employed to desorb the organic compounds from resins. In the recovery experiments with XAD-4, elution is performed with acetone: add 15–20 μl of acetone to the column with a syringe, allow to diffuse into the resin for several minutes and push back and forth slightly with the rubber bulb to remove the air in the resin phase. Add more acetone and continue the elution by gravity flow until 50 μl of acetone has been collected in a collecting vessel.

In the comparison experiments of Spherocharb and XAD-4, elution is performed with acetone and carbon disulfide: add 5–10 μl of acetone and 20–30 μl of carbon disulfide, allow to stand for 5 min and add more carbon disulfide until the volume of eluate has reached 100 μl . At this point, elute by pressing with the rubber bulb.

In the recovery experiments for low molecular weight and water soluble compounds, elution is performed with carbon disulfide: add 20 μl of carbon disulfide, allow to stand for 5–10 min and add more carbon disulfide until the volume of eluate has reached 100 μl .

The collecting vessels as shown in Fig. 1 were made of disposable pipets by cutting both ends of the body and the capillary and by shielding the end of capillary. The vessel is 4–5 cm overall length and is half the length of the capillary. This size is convenient to handle because the syringe needle must be approximately 5 cm long to reach the bottom of the vessel.

Separations and quantifications

The eluate in the collecting vessel was analyzed immediately or stored in the freezer with a cap. The eluate was mixed well by using a 10- μl syringe. A 1.0–2.0- μl aliquot of the eluate was injected into the gas chromatograph. A similar aliquot of the standard was also injected into the chromatograph. The conditions were held rigidly constant for the sample and standard during these tests. The percentage recovery of the organic compounds is calculated directly from a comparison of the chromatogram peak heights or peak areas. Recoveries were calculated as average values and represent more than two different analyses.

RESULTS AND DISCUSSIONS

Recovery of model compounds by XAD-4

Thirty different compounds including alcohols, ketones, halogen compounds, esters, alkylbenzenes and phenols were added to water or water-organic solvent mixtures and used to test recovery by the mini-column method.

The recovery of model compounds by using XAD-4 at concentrations of 2–10 ppb and 100 ppb is shown in Tables I and II. Acetone was used as an eluent in the desorption of organic compounds from XAD-4. Diethyl ether was used as the eluent in the earlier resin sorption method⁵. However, a low-boiling-point solvent such as diethyl ether is not needed because the evaporation step is omitted in the

TABLE I
RECOVERY OF MODEL ORGANIC COMPOUNDS FROM XAD-4 AT 2-10-ppb LEVELS

Compound	Recovery (%)		
	Water	10% Methanol	20% Methanol
<i>Alcohols</i>			
1-Hexanol	95	74	30
1-Octanol	103	100	93
1-Decanol	93	96	86
Cinnamylalcohol	93	93	75
<i>Esters</i>			
Diethylmalonate	91	94	59
Methyldecanoate	95	91	
Methylbenzoate	96	96	96
Methylpalmitate	35	53	79
Diethylphthalate	99	97	99
Dibutylphthalate	96	93	98
<i>Ketones and aldehydes</i>			
2-Nonanone	93	98	89
2-Undecanone	105	102	97
Acetophenone	96	90	59
Benzophenone	98	92	100
Benzaldehyde	92	83	34
<i>Alkylbenzenes</i>			
Benzene	65		
Toluene	70		
Ethylbenzene	73	69	62
<i>p</i> -Cymene	80	70	70
<i>Polynuclear aromatics</i>			
Naphthalene	83	83	83
Biphenyl	87	81	87
<i>Phenols*</i>			
<i>o</i> -Cresol	64		
3,5-Dimethylphenol	88		
2,4,6-Trimethylphenol	93		
2-Naphthol	105		
<i>Chloro compounds</i>			
Chlorobenzene	85	87	83
<i>o</i> -Dichlorobenzene	91	93	96
1,2,4-Trichlorobenzene	87	85	84
<i>p</i> -Chlorotoluene	86	80	
Benzylchloride	93	102	

* The water was acidified by adding conc. HCl prior to adding the organic solute.

mini-column method and a more water-soluble solvent such as acetone works quite well.

The recoveries for model compounds from pure water by the mini-column method are similar to those in an earlier paper dealing with the resin sorption of organic pollutants⁵. The average recovery is 89% at 2-10-ppb levels and 83% at the 100-ppb level. The average recovery of the same compounds in earlier results was 92% at 10-100-ppb levels⁵. The average standard deviation is 6.3%. Errors other than sorption and desorption would be included, like evaporation losses from the

TABLE II
RECOVERY OF MODEL ORGANIC COMPOUNDS FROM XAD-4 AT 100-PPB LEVEL

Compound	Recovery (%)		
	Water	10% Methanol	20% Methanol
<i>Alcohols</i>			
1-Hexanol	91	47	15
1-Octanol	100	101	96
1-Decanol	98	94	89
Cinnamylalcohol	103	88	70
<i>Esters</i>			
Diethylmalonate	84	86	46
Methyldecanoate	77	88	88
Methylbenzoate	82	90	92
Methylpalmitate	4	10	22
Diethylphthalate	85	81	82
Dibutylphthalate	92	92	90
<i>Ketones and aldehydes</i>			
2-Nonanone	97	94	89
2-Undecanone	95	91	86
Acetophenone	95	87	66
Benzophenone	82	79	79
Benzaldehyde	84	62	36
<i>Alkylbenzenes</i>			
Benzene	65	37	29
Toluene	87	82	85
Ethylbenzene	71	68	76
<i>p</i> -Cymene	85	83	82
<i>Polynuclear aromatics</i>			
Naphthalene	85	90	89
Biphenyl	85	88	87
<i>Phenols*</i>			
<i>o</i> -Cresol	40		
3,5-Dimethylphenol	67		
2,4,6-Trimethylphenol	88		
<i>Chloro compounds</i>			
Chlorobenzene	77	86	73
<i>o</i> -Dichlorobenzene	84	92	82
1,2,4-Trichlorobenzene	88	97	89
<i>p</i> -Chlorotoluene	80	87	76
Benzylchloride	86	91	84

* The water was acidified by adding conc. HCl prior to adding the organic solute.

sample, decomposition, sorption on glassware, calibration of eluate volume, and errors in the GC determination.

The low solubility of some compounds in water makes standard sample preparation difficult. Also, actual water samples may be heterogeneous and contain visible or invisible tiny particles of organic contaminants. It was felt that addition of an organic solvent such as methanol or acetone might solubilize the organic solutes and improve their recovery. Tables I and II show that 10% and 20% methanol (by volume) have little effect for many compounds tested, but the more soluble organic compounds show lower recovery. Methyl palmitate was the only compound tested that showed

TABLE III
RECOVERY FROM ACETONE-WATER SOLUTIONS BY XAD-4

Compound	Recovery (%)					
	100 ppb*			10 ppb*		
	Percentage acetone in sample					
	0%	5%	10%	0%	5%	10%
Chlorobenzene	71	76	43	86	78	54
1-Hexanol	91	< 5	0	95	< 5	< 5
2-Nonanone	97	85	84	93	100	95
<i>o</i> -Dichlorobenzene	84	83	81	91	93	91
Benzaldehyde	88	< 5	0	92	< 5	< 5
Diethylmalonate	84	< 5	0	91	< 5	< 5
Methyldecanoate	77	66	68	95	90	80
Acetophenone	95	12	< 5	91	15	5
1-Decanol	98	80	83	93	100	99
Methylpalmitate	4	15	16	35	40	45

* Concentrations of organic compounds.

marked improvement with methanol addition. In this case the methanol improves the solubility in water and thus increases the recovery efficiency.

Similar effects as with methanol can be seen in the recovery from acetone-water solutions for selected organic compounds at 10- and 100-ppb levels. The results are shown in Table III.

Tests were performed to determine whether the column length affected the recovery of organic compounds. The results for insoluble compounds in water at the 10-ppb level in Table IV show the same recovery within experimental error for both the 25-mm and 30-mm length, but lower results for 20-mm length. Therefore a column 25 mm in length was employed in these experiments.

Tests were also performed to determine whether the sample volume affected the recovery of organic compounds (see Table V). In general recoveries are somewhat decreased in going from 50 to 100 to 200 ml of water, especially for the relatively water-soluble compounds. However, recovery for most compounds is satisfactory for a 100-ml sample and is reasonably good in most cases for 200 ml.

TABLE IV
EFFECTS OF COLUMN LENGTH FOR XAD-4 AT 10-PPB LEVEL

Compound	Recovery (%)					
	Water			10% Methanol		
	20 mm	25 mm	30 mm	20 mm	25 mm	30 mm
Chlorobenzene	78	87	85	87	80	82
2-Nonanone	86	97	98	90	90	95
<i>o</i> -Dichlorobenzene	83	79	80	84	83	85
Acetophenone	81	97	95	70	83	83
1-Decanol	80	93	98	91	94	94

TABLE V
EFFECTS OF SAMPLE VOLUMES FOR XAD-4

Compound	Recovery (%)			
	5 ppb in 100 ml	2.5 ppb in 200 ml	10 ppb in 50 ml, then 50 ml water	10 ppb in 50 ml, then 150 ml water
Chlorobenzene	72	57	72	57
1-Hexanol	83	74	74	43
2-Nonanone	90	90	94	90
<i>o</i> -Dichlorobenzene	75	64	87	73
Benzaldehyde	79	60	77	43
Diethylmalonate	90	90	97	84
Methyldecanoate	75	75	82	77
Acetophenone	86	88	92	79
1-Decanol	91	80	97	90

Recovery of model compounds by Spherocarb

Spherocarb is a strong, spherical carbon molecular sieve with a very large surface area ($\approx 1200 \text{ m}^2/\text{g}$). It is convenient to use in small columns and sorbs organic compounds very strongly. To compare Spherocarb with XAD-4 for concentration of organics from water, the same model compounds were tested. After sorption onto Spherocarb, acetone, methanol, diethyl ether, acetonitrile, methylene chloride, pentane and carbon disulfide were evaluated as eluting solvents. In general the elution process was found to be very slow and a large volume of the organic solvent was required for complete desorption of the organic compounds. However, carbon disulfide was found to be satisfactory and the best of the solvents tested; 100 μl of carbon disulfide will elute most organic compounds except for phenols and some strongly sorbed compounds like naphthalene.

Several experiments with column length using Spherocarb showed the same results with 20-mm and 25-mm column lengths. The 25-mm length was chosen so that direct comparison with XAD-4 could be obtained. Results of this comparison at the 100-ppb concentration level are shown in Table VI. The average recoveries with Spherocarb are 77% from both water and from 10% methanol. Under similar conditions the average recovery with XAD-4 was 79% from water and 76% from 10% methanol. The average standard deviation was 5.1% for Spherocarb and 4.0% for XAD-4. If results under 10% recovery are omitted, the average recovery with Spherocarb is 86% from both water and 10% methanol, and with XAD-4 is 89% and 85% from water and 10% methanol, respectively.

The recovery of several compounds from Spherocarb is very poor because of incomplete elution, even though sorption appears to be excellent. For example, some naphthalene, biphenyl and 2-naphthol were found in every 100- μl fraction of carbon disulfide eluate, but elution was still incomplete after 500 μl . Chu found strong uptake of naphthalene by Spherocarb even from 100% methanol¹¹. The elution of phenols from Spherocarb with carbon disulfide was very poor. A mixture of acetone and carbon disulfide gave recoveries ranging from 38 to 88% for various phenols, but reproducibility was poor.

Spherocarb has one major advantage over XAD-4 for analytical use: stronger retention of low-molecular-weight polar organic compounds. Compare especially

TABLE VI
COMPARISON OF RECOVERY EFFICIENCY AT 100-ppb LEVEL FROM SPHEROCARB AND XAD-4

Compound	Recovery (%)			
	Spherocarb		XAD-4	
	Water	10% Methanol	Water	10% Methanol
1-Butanol	10	0	0	0
1-Pentanol	67	66	9	6
1-Hexanol	81	83	81	47
1-Octanol	85	90	85	99
1-Decanol	90	92	85	90
Chlorobenzene	87	82	90	78
<i>o</i> -Dichlorobenzene	89	88	90	84
1,2,4-Trichlorobenzene	90	87	80	80
<i>p</i> -Chlorotoluene	86	83	86	83
2-Heptanone	83	87	89	89
2-Octanone	85	92	88	88
2-Nonanone	87	93	87	86
Methylhexanoate	88	90	96	88
Methyloctanoate	87	91	95	89
Diethylmalonate	0	0	87	90
Methyldecanoate	89	89	96	83
Methylbenzoate	98	94	100	97

1-pentanol recoveries with Spherocarb and XAD-4 in Table VI. Additional data shown in Table VII demonstrate that Spherocarb generally gives higher or equivalent recoveries than XAD-4 for these polar compounds. In other experiments recoveries with sample volumes of 100 and 200 ml were almost identical using Spherocarb but were sometimes lower with 200 ml using XAD-4.

Combination of the mini-column method with a larger-scale sorption method

The mini-column method, while directly applicable for waste water analysis,

TABLE VII
COMPARISON OF RECOVERY FOR WATER-SOLUBLE AND LOW-MOLECULAR-WEIGHT ORGANIC COMPOUNDS AT 100- AND 10-ppb LEVELS FROM SPHEROCARB AND XAD-4

Compound	Recovery (%)			
	100 ppb		10 ppb	
	Spherocarb	XAD-4	Spherocarb	XAD-4
2-Butanone	35	0	0	0
Methylpropionate	51	0	<5	0
2-Pentanone	83	22	83	8
Methylbutyrate	80	73	76	72
Methylisobutylketone	93	86	82	80
Butylacetate	90	87	82	80
1-Butanol	25	<5	24	0
1-Hexanol	66	80	50	80

does not have the sensitivity needed for analysis of organics in most drinking water or other relatively pure water. The larger-scale sorption method⁵ has better sensitivity but suffers from the small fraction of the sample used for the final GC analysis (2 μ l of the 1000- μ l ether concentrate). The two procedures were combined by adding 1 ml of the ether concentrate from the larger-scale procedure to 50 ml of pure water, and then proceeding according to the mini-column procedure. A large fraction of the sample is thus taken for analysis (2 μ l of the 100- μ l carbondisulfide eluate) so that the original ether concentrate is further concentrated by a factor of 10.

Recovery for known standards is listed in Table VIII. The average recovery excluding 1-butanol is 9% lower for Spherocarb than without ether. With XAD-4 the results are good for some compounds tried but low for some polar compounds.

A practical use of this combination procedure is shown in Fig. 2. By standard procedure curve a shows only small peaks. Spherocarb (curve b) shows much larger peaks at the same attenuation (10×8) but peak 7 is missing and peak 6 is much lower than expected. With XAD-4 (curve c) most peaks are close to the expected 10-fold increase in peak height, including peaks 6 and 7.

TABLE VIII

EFFECTS OF ETHER BY ADDING 1 ml TO 50 ml WATER

The concentrations of the organic compounds are 10 ppb.

Compound	Recovery (%)	
	Spherocarb	XAD-4
1-Butanol	0	0
Methylhexanoate	78	30
Chlorobenzene	80	60
<i>p</i> -Chlorotoluene	78	73
Methyloctanoate	85	89
<i>o</i> -Dichlorobenzene	82	87
Methyldecanoate	73	97
Methylbenzoate	90	20

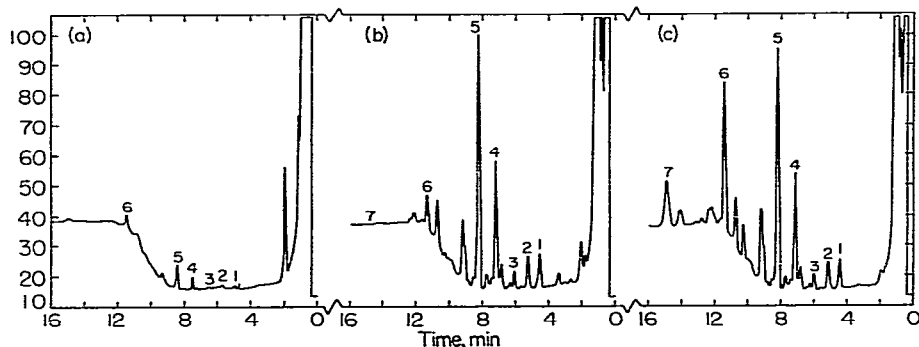


Fig. 2. Chromatograms of Iowa State University tap water. (a) Ether concentrate by large-scale sorption method; (b) Eluate from Spherocarb; (c) Eluate from XAD-4. Column 6 ft. \times $\frac{1}{8}$ in. 10% FFAP; temperature, 60–200° at 16°/min; initial temperature hold, 2 min; final temperature hold, 8 min; temperature of injector and detector, 300°; carrier gas flow-rate, 20 ml/min.

Application of the mini-column method to real samples

The sensitivity of the mini-column method for most organic compounds is about 2 ppb ($2 \mu\text{g/l}$) which is quite adequate for analysis of waste water and badly contaminated drinking water.

Fig. 3 shows the results of analysis of only 100 ml of raw water from a municipal well that had to be used during a severe drouth². XAD-4 appears to be the better sorbent because many of the later-eluting peaks are attenuated or missing from Spherocarb.

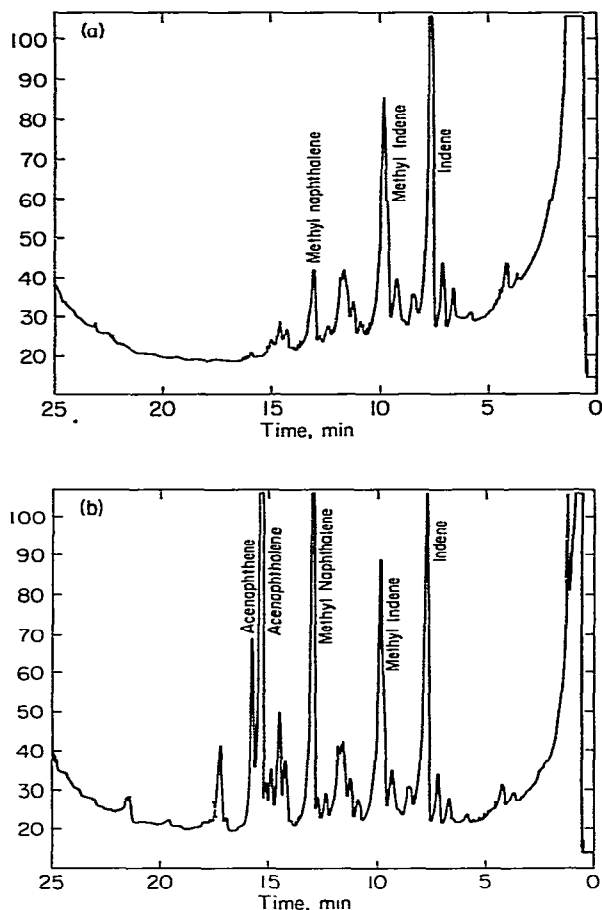


Fig. 3. Chromatograms of well water in Ames, Iowa. (a) Eluate from Spherocarb; (b) eluate from XAD-4. Column, $\frac{1}{8}$ in. \times 6 ft. 3% OV-17; temperature, 30–240° at 8°/min; temperature of injector and detector, 350°; carrier gas flow-rate, 20 ml/min.

The major components in the well water are indene, methyl indene, methyl-naphthalene, acenaphthalene and acenaphthene¹. The other peaks were not identified. Using naphthalene as a standard the total concentration of the five major peaks in the well water was estimated to be 260 ppb. The total concentration of all peaks was roughly 325 ppb.

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