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Isolating Organic Water Pollutants: XAD Resins, Urethane Foams, Solvent Extraction

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ISOLATING ORGANIC WATER POLLUTANTS: XAD RESINS, URETHANE FOAMS, SOLVENT EXTRACTION

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ABSTRACT

Isolation, separation, and concentration into an organic solvent are generally required prior to identification and quantitation of organic pollutants in water by gas chromatography or mass spectrometry. These operations can be simplified or improved by the use of XAD-resins (macroreticular resins) and by changes in solvent extraction procedures. XAD-2,4,7, and 8 and mixtures of these resins effectively extracted a broad range of individual industrial pollutants and mixtures typical of paper mill wastewaters, dissolved fuel oil, and textile dyes. Resin recovery efficiencies were typically 65-75% for individual compounds; direct chloroform extraction efficiency was 80%. Polyurethane foams were not effective for extracting these compounds. Chloroform is generally recommended over diethyl ether as an extraction solvent. Drying of chloroform extracts before evaporation was shown to be unnecessary. For typical industrial effluents, extract concentration to 10 ml with a Kuderna-Danish evaporator and to as low as 0.3 ml with a micro-Snyder column is the most quantitative procedure. Extraction with tetralin sometimes allows detection of nonpolar low-boiling pollutants that are usually obscured in gas chromatographic analysis by the solvent peak.

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CONTENTS

SECTION I

CONCLUSIONS

XAD resins extract a broad range of organic compounds from water with slightly lower efficiency than direct chloroform extraction.

The resins may be useful for long-term or composite sampling.

Polyurethane foams are not useful adsorbents for many compounds found in industrial effluents although they function well for PCB's.

Either chloroform or methylene chloride is generally preferable to diethyl ether or hexane as an extraction solvent.

Drying chloroform extracts with sodium sulfate or glass wool results in lower recoveries than direct concentration without drying.

The recoveries of dissolved organics are greater when extracts are concentrated in two stages using Kuderna-Danish and micro-Kuderna-Danish equipment rather than rotating evaporators and airstream-waterbath methods.

Extraction with tetralin sometimes allows detection of low-boiling materials that are usually obscured in gas chromatographic analysis by the solvent peak.

SECTION II

INTRODUCTION

During the last five years, great advances have been made in techniques for identification of small amounts of organic compounds in water. Progress, however, has not kept pace in methods to isolate, separate, and quantitate these materials. Two areas in which research is needed are the development of alternative methods for carbon adsorption for long-term sampling, and improvement in recoveries in solvent extraction. To this end, macroreticular resins and urethane foams were investigated as adsorbents for the isolation of organic pollutants from water. Also, the procedures and reagents for solvent extraction were examined for inefficiencies and changes are proposed in the usual procedures for drying and evaporation.

SECTION III

MACRORETICULAR RESINS

Solvent extraction and carbon filters both have disadvantages for extracting large amounts of water containing small amounts of organic pollutants. For solvent extraction, the labor required for large samples is too great; and carbon filters give incomplete recovery. Recently, macroreticular resins have been proposed for this application.[1]

Macroreticular refers to the relatively large, controlled pore size of the resin beads. Each grain of resin is formed from many microbeads cemented together during the polymerization process. The pores are the spaces left between the cemented-together microspheres. The most popular macroreticular resins are the XAD series made by the Rohm and Haas Co. They are hard insoluble beads of 20-50 mesh, varying from white to light brown in color. Four materials are available, XAD-2,4,7,and 8. XAD-2 and 4 are styrene-divinyl benzene copolymers. XAD-2 has an average area of 330 m^2/g and a nominal pore size of 90 angstroms; XAD-4 has more surface area (750 m^2/g) and smaller pores (50 angstroms).[2] XAD-7 and 8 are chemically similar, both being acrylate esters, but have different physical characteristics; XAD-7 has a 750 m^2/g area and 80 angstrom pores and XAD-8 has an area of 140 m^2/g and a pore size of 250 angstroms.

Adsorption on the surface of the resin is the basis for the separations; no ion exchange mechanisms are involved. In practice, the water sample is passed through a column of XAD resin and the pollutants are adsorbed. Then the organics are desorbed from the resin by elution with a small amount of organic solvent, which is analyzed by gas chromatography or GC-MS.

INDUSTRIAL EFFLUENTS

To be of general utility in water pollution analysis, the resins must be capable of extracting a wide variety of contaminants. A mixture containing 13 materials previously identified in industrial effluents[3] was used to test the resins' extraction ability. To one liter of distilled water was added 1 ml of acetone that contained all the test compounds, each at a concentration of 50 micrograms/ml. The final concentration of each pollutant in the water was therefore 50 micrograms/l (50 ppb). After thorough mixing, the solution was passed through a 1.5 cm x 3 cm column

(i.e., 5 ml of resin) at a flow rate of 20 ml per min (4 bed volumes per min).[4] The pollutants were eluted from the resin with acetone followed by chloroform. The combined eluate was separated from a small amount of water, concentrated in a Kuderna-Danish evaporator and analyzed by GC using a computer-assisted quantitation system. All experiments were done at least in duplicate. The percent recovery of each compound is shown in Table 1.

For this investigation, the best resin was defined as the one that gave the largest value when the recoveries of the individual test compounds were averaged. Eight of the nine resins gave average recoveries of 65-76%, the best being from an equal mixture of XAD-4 and XAD-8. XAD-7 was significantly poorer with an average of only 51%. These recoveries should be compared with an average recovery of 80% for direct chloroform extraction of a similar sample. The difference in recoveries for each compound in duplicate resin extractions was generally less than 10%.

Solvent extraction of the aqueous effluents from the columns revealed measurable amounts of eight of the thirteen test compounds; the phenols, hexadecane, alpha-terpineol and dibenzofuran were in highest concentration. However, although significant amounts of phenols were found to pass through the column, the efficiency of some resins for extraction of phenols was greater than for direct solvent extraction. Paraffins, on the other hand, are more poorly extracted by the resins than by direct solvent extraction, as confirmed by later experiments with fuel oil.

In one experiment, XAD-48 was allowed to completely air-dry in the column for three days before elution. The recoveries from the dry column were only about 12% lower than those from immediate extraction of the wet resin. This suggests that class separations and clean-up of complex mixtures could be made by elution with solvents of varying polarities.

In addition to the classes of compounds in Table 1, alcohols, ketones, acids, and esters are frequently found in industrial effluents. Limited experiments indicate that the resins are reasonably effective in extracting these materials, as shown in Table 2.

Table 1. TABLE OF RECOVERIES

Percent Recovery from 50 µg/l Samples

COMPOUND	XAD Resin									
	7	24[a]	8	27[a]	2	28[a]	2478[a]	4	48[a]	$CHCl_3$[b]
bis-Chloro isopropyl ether	c	74	77	76	76	77	71	80	77	92
sym-Tetrachloroethane	35	58	59	66	61	68	68	72	72	82
n-Hexadecane	3	c	c	8	3	18	14	c	11	36
alpha-Terpineol	36	76	62	77	81	75	75	80	80	92
Naphthalene	64	66	78	77	79	81	82	80	80	87
o-Nitrotoluene	53	75	77	79	82	81	81	83	83	91
2-Methyl naphthalene	63	61	77	72	75	80	81	77	77	86
1-Methyl naphthalene	64	62	80	75	76	82	80	77	79	86
Benzothiazole	40	80	53	75	74	73	77	82	82	96
Phenol	19	30	29	32	14	33	41	38	46	19
p-Cresol	33	58	47	50	44	49	60	69	68	50
Acenaphthene	72	68	20	81	99	85	84	81	81	91
Dibenzofuran	73	70	95	83	93	86	85	82	84	92
Averages excluding n-Hexadecane	51	65	69	70	71	72	74	75	76	80

a - Mixture of equal dry weights of each resin.
b - Sample directly extracted with two 50-ml portions.
c - Peak unsuitable for accurate quantitation.

Table 2. POLAR COMPOUNDS ADSORBED ON XAD RESINS

Percent Recovered from 100 µg/l Sample

Compound	XAD Resin 2	4	7	8
2-Ethylhexanol	85	91	74	79
Isophorone	76	86	46	47
Pentachlorophenol	84	84	83	77
Palmitic acid	67	79	12	16
Dehydroabietic acid	94	86	31	85
2-Ethylhexyl phthalate	33	11	22	13
Average	73	73	45	53

Results were not as reproducible as the earlier studies because of losses in the extra analytical step required (esterification of the eluted acids with diazomethane before GC) and problems with the GC column. The consistently better recovery of dehydroabietic acid, a resin acid, over palmitic acid, a fatty acid, is possibly due to the affinity of the resins for molecules having an aromatic ring. The adsorption of palmitic acid probably would have been more efficient if the test solution had been acidified before adsorption as Junk[5] suggests.

FUEL OIL

The resins were found to be unacceptable for sampling natural waters for oil residues. They sorb the polar and aromatic portions of the oil but they do not remove the aliphatic hydrocarbons that constitute the bulk of most oils. Solvent extraction with carbon tetrachloride removes all the oil components from water and is the preferred method for quantitative analysis.

When No. 2 Fuel Oil (home heating oil) is dispersed in water and the mixture is extracted with carbon tetrachloride, the gas chromatogram of the extract is identical to that of the original oil. In particular the regularly spaced peaks of the straight-chain hydrocarbons are obvious. When a similar mixture is passed through the XAD resins and processed in the usual manner, the chromatographic peaks of the normal hydrocarbons are very small. The peaks corresponding to polar and aromatic materials are of similar intensity as in the original oil. There is no question that the normal hydrocarbons pass through the column because they can be recovered from the effluent by solvent extraction.

TEXTILE DYES

The author of an EPA sponsored study[6] on photodegradation of textile dyes in waste streams pointed out that many of these dyes are difficult to detect when mixed with other colored wastes because they are not extracted from water with the usual organic solvents. Six of his test dyes that do not extract with ether, chloroform, or hexane were tested for extraction by XAD-2 and XAD-7. Dyes tested were Vat Blue 6, Acid Red 18, Direct Red 83, Acid Red 37, Basic Blue 9, and pararosaniline. In general, a few grams of XAD-2 resin would remove all the visible color from 200 ml of 1-10 mg/l solutions of the dyes. Adjustment of the solutions to acid pH was required for the sulfonic acid dyes. The dyes could be eluted with ethanol or aqueous base. XAD-7 was less effective for all dyes, particularly in the elution step. Only Vat Blue 6, an organic base, was not extracted by the resins.

OPERATIONAL NOTES

- The commercial XAD resins require extensive pre-extraction to remove interfering impurities. The best technique seems to be washing large batches in a column with acetone, methanol, and either chloroform or methylene chloride. Batch extraction in shake flasks was not as efficient.

- A water flow rate of 4 bed volumes per minute results in greater extraction efficiency than a rate of 12 bed volumes per minute.

- Direct elution with chloroform or carbon tetrachloride was not efficient. Treatment of the column with a solvent such as acetone or methanol, which is soluble in both water and water-immiscible solvents, elutes the water from the interior of the resin and makes the resin wettable by the chloroform or carbon tetrachloride. On the other hand, Junk *et al.*[5] recommended the direct addition of diethyl ether to the wet column followed by a 10-minute penetration period before drawing off the solvent. He reports excellent recoveries by this procedure.

- Elution by acetone followed by chloroform was more efficient than elution by acetone followed by carbon tetrachloride.

- Two bed volumes of acetone followed by eight of chloroform was as efficient as five of acetone followed by five of chloroform.

- Acetone contains trace amounts of diacetone alcohol and mesityl oxide that are found in the final extract.

- After a resin has been eluted with chloroform it can be washed with acetone and then with water and then used to extract another water sample. Recoveries from re-used columns were not significantly different from the original values. No irreversible adsorption or saturation effect therefore took place during the first cycle.

SECTION IV

POLYURETHANE FOAMS

Polyurethane foam has many everyday uses including seat padding for automobiles and furniture. In the biological laboratory it sometimes replaces cotton balls as closures for culture flasks. In a recent paper[7], Gesser et. al. report that the porous foam can be used to extract polychlorinated biphenyls (PCB's) from water. If the foams are coated with various GC liquid phases such as DC-200, they also extract the DDT class pesticides with high efficiency.[8]

The technique is very similar to that for the XAD-resins. A plug of foam is placed in a column chromatography column, the water sample is passed through, and later the column is stripped of absorbed components with a solvent. In the experiments outlined below, a gram or two of foam was used, usually with a plug about 20 mm in diameter. Two brands of foam were first tested for extraction of PCB's to be sure they behaved as the materials reported[7] and then experiments were done with paper mill wastewater components, fuel oil, and textile dyes. Foam stoppers from Gaymar Industries extracted PCB's from water at 20 micrograms/liter with the same efficiency (84%) as direct extraction with hexane. Foam plugs sold by Analabs, Inc. for PCB extraction also worked well.

PAPER MILL WASTEWATER COMPONENTS

One-liter volumes of test mixtures containing 5 mg/l each of typical materials found in paper mill effluents (camphor, fenchone, fenchyl alcohol, alpha-terpineol, guaiacol, phenol, and para-cresol) were extracted with the foam. In general, no more than 10% of the material was extracted by the foam plug since 90% of the original material was found on analysis of the effluent.

To determine whether the 5 mg of each of the materials had overloaded the column, a one-liter sample containing only 20 micrograms of each solute was extracted. Still no more than 10% of any of the materials was extracted.

The effect of increased contact time was tested by shaking the plug in a jar of the stock cresol solution for several hours. Extraction efficiency was increased only to 20%. The inefficiency of extraction by the urethane foam therefore is probably not a result of insufficient contact time.

Foam plugs were coated with 3% DC-200, DEGS, or Carbowax 20M and a one-liter sample containing 20 micrograms of each solute was extracted. The extraction removed only 10 to 40% of each test compound.

In contrast, the macroreticular resin XAD-2 removed nearly 100% of this test mixture at 0.2 mg/l level and 65% to 80% of each compound was recovered on elution of the resin with acetone and carbon tetrachloride. XAD-7 resin was less satisfactory, with 30% to 45% of the material being extracted and 13% to 40% recovered from the resin.

FUEL OIL

Although urethane foams act as sponges or wicks for oil floating on water, our tests show that for dispersed oil, as opposed to oil slicks, the foams alone or coated with DC-200 are largely ineffective as extraction media. Only 9% of the oil was extracted when a liter of water with 1.6 mg/l No. 2 fuel oil dispersed in it was passed through a 0.7-g foam plug. In a similar experiment using 2.2 g of 4% DC-200 coated foam, 80% of the oil was removed from the water, but only 34% was recovered from the plug by elution with carbon tetrachloride.

TEXTILE DYES

The six textile dyes mentioned earlier that will not extract directly from water with the usual solvents were tested for extraction by polyurethane foam. In general, only part of the color was removed from 200 ml of 1-10 mg/l solutions of the dyes by a gram of foam. The dye that was removed could be only partially recovered from the foam by elution with ethanol even though ethanol dissolves the pure dyes. Alcoholic sodium hydroxide removed the dyes but also disintegrated the foam.

These results indicate that the foams are very limited in their extraction ability. The optimism expressed in a recent paper[9] for their promise as an alternative to carbon adsorption was premature.

SECTION V

SOLVENT EXTRACTION

The most common method for isolating organic water pollutants is direct extraction with a solvent. With the exception of polymers and complex biological molecules, most organic chemicals can be extracted from water by a judicious choice of conditions.

SOLVENTS USED

With EPA analysts, the two most popular solvents for extraction are methylene chloride and chloroform. Diethyl ether, hexane, or mixtures of these solvents[10] are also used frequently. Methylene chloride and chloroform are efficient solvents for a broad range of compounds. They are reasonably insoluble in water so the volumes recovered are nearly equal to those added; they do not require drying with inorganic salts to remove water; their density, which is greater than that of water, makes multiple extractions possible with a minimum of manipulation; they evaporate easily but can be stored without further loss for reasonable periods of time; and they give acceptably narrow solvent peaks on flame detector GC's.

Ether and hexane are poorer in all of these respects. Ether was compared in efficiency with chloroform for extraction of short (C_3-C_4) fatty acids, phenol, p-cresol, and 2-ethyl-1-hexanol. With the exception of phenol, chloroform was the better extractant for each compound. The high solubility of ether in water may be partly responsible for the relatively low efficiency of the ether extraction. When one liter of water was extracted with two 50-ml portions of chloroform, 42 ml and 49 ml of the chloroform were recovered for each fraction, for a total solvent loss of only 9%. In contrast, 100 ml of ether must be added to a liter of water before any separable layer develops. Then when two additional 50-ml portions of ether are used for the extraction, a total volume of only 98 ml is recovered. The "aqueous" layer is then 10% ether by volume and must retain some of the organics.

DRYING CHLOROFORM EXTRACTS

After a water sample is extracted with an organic solvent, the solvent is usually dried to remove dissolved water and then evaporated to a smaller volume before analysis. As shown below, for quantitative recovery of many common industrial pollutants, there is no advantage in drying a

chloroform extract. Fear of losses due to a steam distillation effect in undried extracts is unfounded.

Identical liter samples of water containing 33 micrograms of each of 13 industrial pollutants were extracted with two 50-ml portions of chloroform by the usual separatory funnel technique. The extracts were dried by passing them through a short column of anhydrous sodium sulfate or a short column of glass wool pre-wet with solvent. The extracts were evaporated to about 6 ml in a Kuderna-Danish apparatus and then to 1 ml by blowing a stream of nitrogen over the sample. An undried extract and a reference sample of 100 ml of chloroform spiked with 33 micrograms of each compound were concentrated similarly. The experiments were done in duplicate and each sample was analyzed by GC and quantitated by the computer-assisted data system. The results, tabulated as percent recovery of the amount added to the water, are shown below (listed in order of elution from a Carbowax 20M-TPA column):

	Na_2SO_4	Glass Wool	Undried	Evap. Ref.
bis-Chloro isopropyl ether	87	82	92	91
sym-Tetrachloroethane	76	70	83	89
n-Hexadecane	29	23	36	93
alpha-Terpineol	86	81	92	91
Naphthalene	82	76	87	91
o-Nitrotoluene	84	81	91	93
2-Methyl naphthalene	80	75	86	93
1-Methyl naphthalene	81	77	86	93
Benzothiazole	85	83	96	94
Phenol	19	17	19	91
p-Cresol	46	44	50	83
Acenaphthene	85	82	91	93
Dibenzofuran	84	83	92	92

The last column is the maximum amount that could be recovered if extraction were 100% efficient and indicates the magnitude of losses on evaporation to one ml. Low recoveries of hexadecane, phenol, and p-cresol are due to the inefficiency of extraction rather than the effect of drying. The undried sample gave the best overall results. Recoveries from duplicate experiments differed by an average of only two percentage points for the undried sample. For the sodium sulfate dried sample, the average difference was 6% and for the glass wool samples, it was 16%. The evaporation technique was very reproducible with an average

difference in results of 2%. Even when undried extracts were evaporated to volumes as small as 0.1 ml, no water separated out and recoveries did not differ significantly from those of samples that had not been in contact with water.

A separate experiment showed that undried extracts using hexane or 15% methylene chloride in hexane as the solvent can be analyzed by electron-capture GC without any discernible change in the detector's performance. Samples obtained by extraction of a liter of water with two 50-ml portions of solvent were concentrated with a Kuderna-Danish evaporator to 10 ml and further reduced to 1 ml by the airstream method. Analysis with a Ni-63 detector on a pesticide column showed immediate return to the baseline after elution of the solvent for both undried and sodium sulfate dried samples. Even concentrates with a visible layer of water chromatographed in a normal fashion when the organic layer was sampled.

CONCENTRATION OF ORGANIC EXTRACTS

The common methods for evaporation of organic extracts were also examined. The usual procedure is to concentrate from the original volume (100 ml or more) to 5 or 10 ml in one step and to further reduce the 10-ml volume to about 1 ml in a second step.

First Stage Evaporation

Three methods of evaporation were tested with 100-ml portions of chloroform containing 33 micrograms of each of 13 known pollutants. The beaker method was tested by warming the sample in a 250-ml beaker on a steam bath while directing a gentle stream of air on the surface of the sample. The Rotavapor samples were evaporated from a 250-ml round-bottom flask at a waterbath temperature of 30°C and a pressure of 450 mm mercury. The K-D samples were processed in a 24/25 size evaporator (Figure 1). Each sample was evaporated to 5-10 ml and then transferred to a K-D tube and reduced to 1 ml by the airstream-waterbath method. The experiments were done in duplicate (K-D in quadruplicate).

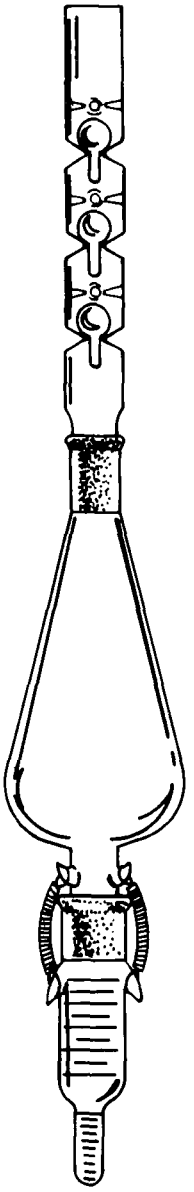

Figure 1. Kuderna-Danish Evaporator

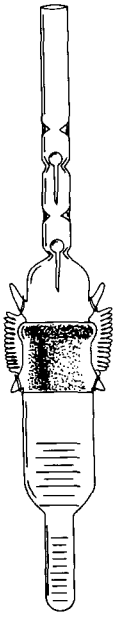

Figure 2. Micro-Snyder Column Evaporator

The average percent recovery of each compound is shown below:

Compounds	Evaporation Method		
	Beaker	Rotavapor	K-D
bis-Chloro isopropyl ether	--	84	91
sym-Tetrachloroethane	76	73	87
n-Hexadecane	88	89	92
alpha-Terpineol	82	85	90
Naphthalene	85	86	91
o-Nitrotoluene	86	86	91
2-Methyl naphthalene	92	90	92
1-Methyl naphthalene	84	86	91
Benzothiazole	82	88	91
Phenol	83	85	90
p-Cresol	78	82	85
Acenaphthene	86	89	91
Dibenzofuran	87	88	92

Each of the methods was reproducible, with duplicate runs showing differences of only about 5 % in recovery for individual compounds. The average recovery of all 13 compounds was 84% for the beaker method, 85% for the RotoVap and 90% for the K-D. Although the K-D method is best, the RotoVap and beaker methods are acceptable. In particular, the beaker method is not nearly as poor as expected. The K-D method is actually nearly 100% efficient since, as shown next, losses of about 10% occur in the final evaporation to 1 ml.

Final Evaporation: Airstream-Waterbath Method

Three methods were tested for the final evaporation step, i.e., evaporation to 1 ml or less. The most used technique is the airstream-waterbath method. Each of eleven people evaporated a 5-ml sample and a 10-ml sample of chloroform, each containing 33 micrograms of the compounds shown above. The samples were all in standard K-D tubes and were all evaporated to 1 ml. The average recovery for all compounds in the 10-ml samples was 90%; in the 5-ml samples it was 92%. The longer exposure time to the air stream was expected to result in significantly lower recoveries for the 10-ml sample, but this was not the case. For 10 out of the 11 people the recovery for each compound was 85-95%. (The other person had recoveries about 12% lower.) The compounds for which more than 10% was lost were tetrachloroethane, 13%; o-nitrotoluene, 13%; benzothiazole, 14%; and p-cresol, 17%. With this set of test compounds, there was no

difference in the recoveries when air was substituted for nitrogen as the evaporating gas.

Block Tube Heater

A variation of the airstream evaporation that is sometimes used in pesticide analysis is a specially designed aluminum block heater.[11,12] The concentrator tube extends through the bottom of the heating block and when the liquid level drops below the heated zone, evaporation immediately slows down. Samples rarely go to dryness unless left unattended for a long time. The one disadvantage mentioned for this system was a tendency for bumping to occur. Boiling chips will not prevent bumping in the block heater because they are not in the heated portion of the solution. The original method for initiating boiling was a small ebullator, but bumping was still a hazard. The introduction of a fine stream of nitrogen bubbles near the bottom of the heated area via a steel capillary inserted from the top of the concentrator tube was recommended as an improvement.[14]

The commercial version of this device gave recoveries ranging from 35-95% in different tests with the industrial pollution test compounds. Poor recoveries always resulted when the solution was allowed to evaporate to less than 1 ml. It was very difficult to know when the volume of solution was approaching the desired point because most of the tube is out of sight. Each evaporation took about three times as long as with the airstream method. For relatively volatile materials (compared to pesticides) there is little to be recommended in this method.

Micro-Snyder Column

A third method, using a two chamber micro-Snyder column (Figure 2) attached directly to a K-D tube containing a few boiling chips and heated by a steam bath, gave better recoveries with less variation in results. Again 5- and 10-ml tests were made. Two sizes of condensers were used, a commercial unit (available from Kontes Glass Co., Vineland, N.J., 08360) with a 19/22 size joint and a locally made unit with a 24/25 size joint. There was no difference in efficiency between the 5- and 10-ml samples with either size condenser. The average recovery for the pollution mixture with a 19/22 condenser was 97% and with the 24/25 condenser, 94%. A commercial 2-chamber 24/25 condenser tested later gave an average recovery of 99.9% in the 10-ml test. Results from all micro-Synder column tests were better than those for the airstream method. In addition, the range of recoveries for tetrachloroethane, o-nitrotoluene, benzothiazole, and p-cresol varied by only 10% or less in

all these experiments as opposed to the 13-17% reported earlier for the airstream-waterbath method.

Sometimes it is necessary to evaporate an extract to less than 1 ml to attain adequate concentrations for analysis. Recovery experiments were done with one-ml samples of the 13 compound pollution mixture that were evaporated to 0.7, 0.5, 0.3, 0.2, and 0.1 ml by the micro-Snyder column and the airstream-waterbath methods. Tests were also made by both methods on spiked water samples that were extracted and then evaporated to these levels.

The micro-K-D was found to be the best way to evaporate a sample to 0.3 ml. Recovery at this volume is 90-95% in comparison to an airstream recovery of 81-87%. Below 0.3 ml the analyst has more control over the final volume with the mild conditions of the airstream-waterbath method. The results become highly variable from sample to sample at these volumes. The airstream method at 0.2 ml gave recoveries of 55-80% for the same compounds in duplicate tests, and 60-80% at 0.1 ml. The micro-Snyder column gave at 0.2 ml, 60-80% recovery and at 0.1 ml, 50-60%.

There are three keys to good micro-Snyder column recoveries. To avoid bumping, the tube must be gently agitated for a few seconds over the steam bath until the boiling chips start bubbling. The condenser must be constructed so that the glass bubbles move freely in their chambers and always maintain a layer of liquid solvent that scrubs the escaping gases. The K-D receiver tube must not be allowed to boil dry. When the receiver tube has almost boiled dry, the entire unit must be removed from the steam bath and allowed to cool and drain. The final volume is 0.3-0.4 ml.

Based on the recovery of dissolved organics, the Kuderna-Danish concentrator is the most efficient method for concentration of large solvent volumes. The use of a rotating vacuum evaporator or open evaporation in a beaker results in lower recoveries. For the final concentration, directly distilling the solvent through a micro-Snyder column is more efficient, more reproducible, and faster than the airstream-waterbath method.

HIGH-BOILING SOLVENTS

Industrial solvents and volatile taste and odor causing compounds are sometimes overlooked in GC analysis because they are obscured by the solvent peak. One proposed solution is to use a high-boiling (and therefore late-eluting) solvent for these applications. The difficulty

lies in finding materials that are pure and are good extractants. The ideal solvent contains no impurities above the microgram/l level. Also, the solvent peak on the GC elutes about ten minutes after injection and returns to baseline quickly, without tailing.

Several solvents have been tested for these characteristics under GC conditions typically used to examine industrial effluent extracts. The best solvent found was tetralin (tetrahydronaphthalene), first recommended by B. F. Dudenbostel of Region II, EPA. This material contained only one major impurity and very few minor materials, leaving considerable "open space" in the baseline. Ortho-dichlorobenzene and one lot of tetradecane were also acceptable.

Several solvents, including the purest commercially available materials (99+%), contained over a dozen impurities at 5-mg/l concentrations. These make the solvent unacceptable. In this class were decane, tridecane, 1,3-cyclooctadiene, chlorobenzene, and 2-ethylnaphthalene. Diethyl terephthalate contained only small impurity peaks but the parent compound and the higher-boiling impurities required an excessively long time to elute.

Tetralin is relatively nonpolar and does not extract highly polar molecules. For example, extraction tests with ethyl-mercaptan, suspected as the odor source in a water supply, were completely unsuccessful. On the other hand, extraction of a liter of landfill leachate with one ml of tetralin revealed the presence of acetone, benzene, chloroform, ethyl-benzene, n-hexane and toluene.

When 2 ml of tetralin was used to extract 1 liter of water spiked with 1 microgram each of chloroform, benzene, and bis-chloroethyl ether, about 1.5 ml of tetralin was recovered. Injection of 1 microliter of this extract on a GC using a 10% SE-30 column produced peaks for each of the three compounds. Enough material was also extracted for interpretable mass spectra using a GC-MS system with a similar GC column and one-microliter injection. Quantitative recovery studies were not made.

SECTION VI

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16. ABSTRACT

Isolation, separation, and concentration into an organic solvent are generally required prior to identification and quantitation of organic pollutants in water by gas chromatography or mass spectrometry. These operations can be simplified or improved by the use of XAD-resins (macroreticular resins) and by changes in solvent extraction procedures. XAD-2,4,7 and 8 and mixtures of these resins effectively extracted a broad range of individual industrial pollutants and mixtures typical of paper mill wastewaters, dissolved fuel oil, and textile dyes. Resin recovery efficiencies were typically 65-75% for individual compounds; direct chloroform extraction efficiency was 80%. Polyurethane foams were not effective for extracting these compounds. Chloroform is generally recommended over diethyl ether as an extraction solvent. Drying of chloroform extracts before evaporation was shown to be unnecessary. For typical industrial effluents, extract concentration to 10 ml with a Kuderna-Danish evaporator and to as low as 0.3 ml with a micro-Snyder column is the most quantitative procedure. Extraction with tetralin sometimes allows detection of nonpolar low-boiling pollutants that are usually obscured in gas chromatographic analysis by the solvent peak.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Separation Techniques, Solvent Extractions, Resins, Adsorption, Chromatography, Drying, Gas Chromatography, Organic Wastes, Oily water, Pulp Wastes, Dyes	Kuderna-Danish Evaporator	05A

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