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ISOLATION OF ORGANIC WATER POLLUTANTS BY XAD RESINS AND CARBON

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SUMMARY

The recovery efficiencies of XAD resins -2, -4, -7, and -8 and of resin mixtures were measured using distilled water samples containing 13 organic pollutants. An equal-weight mixture of XAD-4 and XAD-8 was most efficient. XAD-2 and XAD-4/8 were further tested and found effective using tapwater. Carbon was tested as a sorbent for materials not well retained by the resins. In-column solvent washing before sample sorption was found to be as effective as Soxhlet extraction for removing background impurities. Some compounds can be desorbed from carbon by in-column solvent elution; others require Soxhlet extraction. An XAD-4/8 column in series with a carbon column was used to sample 1000 l of tapwater. Halomethanes, *n*-hydrocarbons, polynuclear aromatic compounds and dibenzofuran in the order of ng/l were identified using a gas chromatograph-mass spectrometer-computer system.

INTRODUCTION

Solvent extraction and carbon-filter methods both have disadvantages for extracting large amounts of water containing small amounts of organic pollutants. For solvent extraction, the labour required for large samples is too great; carbon filters frequently have unacceptable backgrounds (blanks) or give incomplete recovery. Recently, macro-reticular resins have been proposed for this application¹. In this study, all available resins² in the XAD series were tested to find the best resin or combination of resins for a wide variety of known water pollutants. Because several classes of compounds were inadequately recovered by the resins, carbon was investigated for

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sorbing them. The two systems were tested in series for isolation of organics from a municipal drinking water.

EXPERIMENTAL

Gas chromatography

A non-polar column of SE-30 or SP-2100 was used to analyze the Athens tap-water extracts, some of the carbon column blanks and the following test compounds: 2,4,6-trichlorophenol, dimethyl phthalate, hexachlorobenzene, dibutyl phthalate, fluoranthene, pyrene, and di-(2-ethylhexyl) phthalate. All other test compounds were chromatographed on the polar substrate, Carbowax 20M-TPA. All analyses were done with the flame ionization detector and all quantitation was performed by the internal standard method. Depending on the other materials in the test mixture, the internal standards were isoborneol, *o*-nitrotoluene, or *n*-octadecane.

Preparation of XAD-resins

The resins used were a gift of the Rohm and Haas Co. (Philadelphia, Pa., U.S.A.), or were supplied by Chemical Dynamics Corporation (South Plainsfield, N.J., U.S.A.). The resins require extensive extraction to remove impurities. Batches of 100 g were placed in 5-cm I.D. columns and washed successively with 1.5 l of acetone, methanol, and methylene chloride or chloroform. A portion of the chloroform effluent was evaporated (150:1) and checked for interferences by gas chromatography. If necessary the chloroform washing was repeated. When the blank chromatogram showed no interferences, the resin was removed from the column and stored under methanol.

Efficiency tests of XAD resins

To 1 l of distilled water was added 1 ml of acetone that contained all the test compounds, each at a concentration of 50 $\mu\text{g/ml}$. After thorough mixing, the solution was passed through a 3×1.5 cm column (*i.e.*, 5 ml of resin) at a flow-rate of 20 ml/min (4 bed volumes per min)³. The column was not allowed to run dry. The fully wet column was eluted with 10 ml of acetone followed by 40 ml of chloroform. The combined eluate was separated from a small amount of water, concentrated in a Kuderna-Danish evaporator, and with an air stream to 1 ml and analyzed by gas chromatography (GC) using a computer-assisted quantitation system. All experiments were done at least in duplicate.

The mixed resins, *i.e.*, XAD-4/8, were prepared by drying the individual resins and mixing equal dry weights. The mixed resins were stored under methanol. A glass-wool plug on top of the column was essential to keep the lighter resins from floating and separating during elution or washing with dense solvents.

The tapwater experiments utilized 6.5×1.2 cm columns of resin. The 1-l sample containing 50 μg of each test component was passed through the column at 20 ml/min (2.7 bed-volumes). The wet column was eluted with 15 ml of acetone followed by 40 ml of chloroform. After separation of the water, the extract was concentrated to 1 ml with a Kuderna-Danish evaporator and a micro-Kuderna-Danish apparatus. The 2-l separatory funnel used as the original sample reservoir was rinsed with 30 ml of chloroform, which was similarly concentrated to 1 ml. The water effluent from the column

was extracted with three 25-ml portions of chloroform, which was concentrated to 1 ml.

Preparation of activated carbon

Filtrisorb 300, a coal-based carbon made by Pittsburgh Activated Carbon (Pittsburgh, Pa., U.S.A.), was Soxhlet extracted (60 g) with 400 ml of chloroform for 190 cycles (11 h). No thimble was used; the siphon was plugged with glass wool. The carbon was dried in an oven at 110° overnight. The carbon was cooled in a desiccator and stored in a glass stoppered bottle. This cycle was repeated a second time. Each chloroform extract was concentrated to 1 ml and analyzed by GC. In most experiments the dry carbon (8–30 mesh) was ground in a mortar and sieved to 20–40 mesh to parallel the experiments with XAD resins. Just before use, it was washed with distilled water or tapwater to remove fines and then packed wet into a 6.5 × 1.2 cm column.

The tests with model compounds were carried out using the same conditions as the tapwater XAD studies.

Isolation of organics from tapwater

Stock carbon was prepared by grinding and sieving to 20–40 mesh. The fines were washed out with tapwater in a beaker. The tapwater was replaced by acetone by decanting and filling the beaker four times; this removed most of the sorbed gases. To a glass column (2.3 cm I.D.) containing a 10-ml plug of glass wool was added 40 ml of the carbon topped by another 10-ml glass-wool plug. On top of this was placed 40 ml of XAD-4/8 with a 20-ml plug of glass wool at the top of the column. The column was washed with three bed volumes (120 ml each) of acetone, three of chloroform, three of acetone and two of methanol. The last bed volume of acetone, chloroform and acetone were collected separately, concentrated to 1 ml and each analyzed by GC using a non-polar column.

The top of the column was fitted with a modified glass wash bottle mouthpiece and delivery tube that allowed a constant water supply and overflow without exposure of the column to the atmosphere. The supply tubing from the faucet to the column was made of teflon. A uniform flow through the column was maintained by drawing the water through with a peristaltic pump at a rate of 80 ml/min. Tapwater from the Athens (Ga., U.S.A.) water system was drawn continuously through the column until 1000 l had been sampled over 9 days in April 1976.

RESULTS AND DISCUSSION

Although the macro-reticular resin XAD-2 has been most often reported for isolation of organics, no systematic study of the XAD series has been reported. Four materials are available, XAD-2, -4, -7, and -8. Adsorption on the surface of the resin is the basis for the separations; no ion exchange or pore exclusion mechanisms are involved.

To be of general utility in water pollution analysis, the resins must be capable of extracting a wide variety of contaminants. A mixture containing thirteen materials previously identified in industrial effluents⁴ was used to test the extraction abilities of the resins (Table I). For this investigation, the best resin or resin mixture was defined as the one that gave the largest value when the recoveries of the individual test com-

TABLE I
PERCENT RECOVERY FROM 50 $\mu\text{g/l}$ DISTILLED WATER SAMPLES
The mixtures are of equal dry weights of each resin.

| Compound | XAD Resins and Mixtures | | | | | | | | | |
|--|-------------------------|-----|----|-----|----|-----|---------|----|-----|-------------------|
| | 7 | 2/4 | 8 | 2/7 | 2 | 2/8 | 2/4/7/8 | 4 | 4/8 | CHCl_3^* |
| Acenaphthene | 72 | 68 | 20 | 81 | 99 | 85 | 84 | 81 | 81 | 91 |
| 2-Benzothiazole | 40 | 80 | 53 | 75 | 74 | 73 | 77 | 82 | 82 | 96 |
| bis (2-Chloroisopropyl)ether | —** | 74 | 77 | 76 | 76 | 77 | 71 | 80 | 77 | 92 |
| <i>p</i> -Cresol | 33 | 58 | 47 | 50 | 44 | 49 | 60 | 69 | 68 | 50 |
| Dibenzofuran | 73 | 70 | 95 | 83 | 93 | 86 | 85 | 82 | 84 | 92 |
| <i>n</i> -Hexadecane | 3 | — | — | 8 | 3 | 18 | 14 | — | 11 | 36 |
| 1-Methyl naphthalene | 64 | 62 | 80 | 75 | 76 | 82 | 80 | 77 | 79 | 86 |
| 2-Methyl naphthalene | 63 | 61 | 77 | 72 | 75 | 80 | 81 | 77 | 77 | 86 |
| <i>o</i> -Nitrotoluene | 53 | 75 | 77 | 79 | 82 | 81 | 81 | 83 | 83 | 91 |
| Naphthalene | 64 | 66 | 78 | 77 | 79 | 81 | 82 | 80 | 80 | 87 |
| Phenol | 19 | 30 | 29 | 32 | 14 | 33 | 41 | 38 | 46 | 19 |
| α -Terpineol | 36 | 76 | 62 | 77 | 81 | 75 | 75 | 80 | 80 | 92 |
| <i>sym</i> -Tetrachloroethane | 35 | 58 | 59 | 66 | 61 | 68 | 68 | 72 | 72 | 82 |
| Averages excluding <i>n</i> -Hexadecane | 51 | 65 | 69 | 70 | 71 | 72 | 74 | 75 | 76 | 80 |

* Sample transferred from a beaker to a separatory funnel to simulate adsorption on reservoir wall and then directly extracted with two 50 ml portions.

** Peak unsuitable for accurate quantitation.

pounds were averaged. Eight of the nine resins or resin mixtures tested gave average recoveries of 65–76%, the best being from an equal mixture of XAD-4 and XAD-8. XAD-7 provided significantly lower recoveries with an average of only 51%. These recoveries should be compared with an average 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, α -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 by direct solvent extraction.

TABLE II
PERCENT RECOVERY FROM 100 $\mu\text{g/l}$ DISTILLED WATER SAMPLES

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

In addition to the classes of compounds in Table I, 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 II. These 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 dehydroabiatic acid, a resin acid, over palmitic acid, a fatty acid, is possibly caused by 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^{1,5}.

Resin elution

The most popular method for elution of the adsorbed compounds is direct addition of ether to the wet column followed by a 10-min penetration period before drawing off the solvent⁵. In this laboratory, however, the use of ether is discouraged because of its flammability and its contamination with impurities, peroxides, and preservatives. Direct elution with chloroform or carbon tetrachloride was found to be inefficient. Treatment of the column with a solvent such as acetone or methanol,

TABLE III
PERCENT RECOVERY FROM 50 µg/l TAPWATER SAMPLES

Values in parentheses are for distilled water.

| Compound | Retained on Reservoir Wall | | Recovered from Resin | | In Aqueous Effluent from Column | |
|--------------------------------|----------------------------|---------|----------------------|---------|---------------------------------|---------|
| | XAD-2 | XAD-4/8 | XAD-2 | XAD-4/8 | XAD-2 | XAD-4/8 |
| Acenaphthene | 0 | 2 | 79 | 80 | 0 | 0 |
| Acenaphthylene | 0 | 0 | 38 (84) | 42 (83) | 0 | 0 |
| 2-Benzothiazole | 0 | 0 | 69 | 77 | 26 | 30 |
| Camphor | 0 | 0 | 83 | 87 | 5 | 2 |
| bis (2-chloroethyl) ether | 0 | 0 | 41 (110) | 79 (94) | 47 | 11 |
| bis(2-chloroisopropyl) ether | 0 | 0 | 85 | 90 | 8 | 0 |
| Di- <i>n</i> -butyl phthalate | 4 | 4 | 91 | 92 | 0 | — |
| Di-(2-ethylhexyl) phthalate | 22 | 19 | 19 | 26 | 43 | — |
| <i>p</i> -Dichlorobenzene | 6 | 6 | 71 | 75 | 0 | 0 |
| Dimethyl phthalate | 0 | 0 | 116 | 113 | 0 | — |
| Fluoranthene | 0 | 0 | 85 | 85 | 0 | — |
| Hexachlorobenzene | 15 | 11 | 39 | 47 | 28 | — |
| Hexachlorobutadiene | 27 | 30 | 47 | 49 | 0 | 0 |
| Hexachloroethane | 11 | 12 | 66 | 69 | 0 | 0 |
| <i>n</i> -Hexadecane | 10 | 19 | 16 | 28 | 42 | 31 |
| Naphthalene | 10 | 0 | 84 | 86 | 0 | 0 |
| <i>o</i> -Nitrotoluene | 0 | 0 | 80 | 87 | 0 | 0 |
| Phenol | 0 | 0 | 0 (34) | 9 (70) | 6 | 0 |
| Pyrene | 5 | 0 | 64 | 68 | 11 | — |
| α -Terpineol | 0 | 0 | 5 (84) | 5 (88) | 0 | 0 |
| 1,1,3,3-Tetrachloroacetone | 0 | 0 | 0 (22) | 0 (53) | 0 | 0 |
| Tri- <i>n</i> -butyl phosphate | 4 | 12 | 85 | 72 | 0 | 0 |
| 2,4,6-Trichlorophenol | 0 | 0 | 20 | 25 | 0 | 0 |
| <i>n</i> -Tridecane | 37 | 43 | 4 (5) | 9 (6) | 18 | 15 |

which is soluble in both water and water-immiscible solvents, causes elution of the water from the interior of the resin and makes it wettable by the chloroform or carbon tetrachloride. Elution with two bed volumes of acetone followed by eight of chloroform gives excellent results, but the ratio is not critical. In some cases, acetone contributes traces of diacetone alcohol and mesityl oxide to the final concentrate. One advantage of this elution procedure is that after separation of the free water from the water-acetone-chloroform mixture, no further drying of the solvent is necessary, because the water is apparently removed as an azeotrope during the evaporation step. Other experiments show that acetone-methylene chloride give equivalent results to acetone-chloroform. Drying the extract is unnecessary here also. Methylene chloride is now recommended because of its lower inhalation toxicity over that of chloroform.

Tapwater matrix

The data of Table I differs from a real situation in two major respects: the fact that distilled water rather than tapwater, river water, *etc.*, was used and the fact that the compounds tested had a predominantly aromatic character. Therefore, some of the compounds from Table I and an additional group of compounds that were recently found in drinking waters⁶ and industrial effluents were sorbed from a matrix of local tapwater by XAD-2 and XAD-4/8. The results are given in Table III. The values for the material retained on the reservoir wall and in the column effluent were determined by extraction with chloroform. Separate experiments indicate that most chloroform recoveries are about 90% except for tridecane and hexadecane, 30-50%; hexachloroethane, 50%; and phenol, 25%. The values in the table are uncorrected for differences in chloroform extractibility. On the average, XAD-4/8 is 5% better than XAD-2.

Previous experience had shown that some of these compounds were recovered better from distilled water than tapwater, presumably because of reaction of the compounds with the hypochlorous acid (chlorine residual) and other materials in the tapwater. Several compounds that gave low recoveries in the tapwater experiments were retested in distilled water and most of them gave significantly higher recoveries (values in parenthesis in Table III). The products of aqueous chlorination of one of these materials, α -terpineol, have recently been identified⁷.

In general, the XAD resins seem applicable to a broad range of materials found in drinking waters and industrial effluents. However, because of the incomplete sorption of some materials, as indicated by the column effluent data in Table III, it seemed desirable to investigate carbon, in spite of its limitations, as a scavenger for these materials.

Carbon adsorption

The carbon-chloroform extraction (CCE) method originated by Braus *et al.*⁸, was designed as a gross guideline to determine the efficiency of drinking water treatment plants much as biochemical oxygen demand is for sewage treatment. The official description of the CCE method⁹ points out that carbon does not adsorb all organic compounds and that chloroform does not desorb all that are sorbed. Three main problems must be overcome in applying carbon to isolation of trace pollutants for the purpose of specific identification and quantitation: finding a carbon with broad sorption power, obtaining a carbon with an acceptable blank and finding methods of desorption that remove most classes of compounds.

TABLE IV
EFFICIENCY OF PRE-CLEANED AND STOCK CARBON, PERCENT RECOVERIES

| Compound | Retained on Reservoir Wall | | Recovered from Carbon | | In Aqueous Effluent from Column | |
|--------------------------------|----------------------------|-------|-----------------------|-------|---------------------------------|-------|
| | Soxhlet Pre-clean | Stock | Soxhlet Pre-clean | Stock | Soxhlet Pre-clean | Stock |
| Acenaphthene | 0 | 0 | 0 | 0 | 5 | 4 |
| 2-Benzothiazole | 0 | 0 | 0 | 0 | 6 | 5 |
| bis (2-chloroethyl) ether | 0 | 0 | 82 | 85 | 0 | 3 |
| Hexachlorobutadiene | 21 | 21 | 45 | 48 | 0 | 0 |
| Hexachloroethane | 9 | 15 | 59 | 61 | 0 | 0 |
| <i>n</i> -Hexadecane | 12 | 12 | 3 | 14 | 42 | 34 |
| Phenol | 0 | 0 | 7 | 9 | 4 | 0 |
| Tri- <i>n</i> -butyl phosphate | 12 | 14 | 80 | 82 | 7 | 7 |
| <i>n</i> -Tridecane | 24 | 24 | 9 | 14 | 44 | 27 |

Carbon background levels

Even with the strictest quality control, manufacturers find it impossible to prepare lot after lot of exactly identical activated carbons. For this study, the carbon used in recent 10-city National Organics Reconnaissance Survey (NORS) of the Environmental Protection Agency, was chosen. An extraction blank is usually run before using a particular batch of carbon in a CCE system in order to determine whether there would be a significant interference from the carbon when the sample is chromatographed. It is not common practice to attempt to clean the carbon before use, apparently out of fear that the adsorptive power (activation) would be impaired.

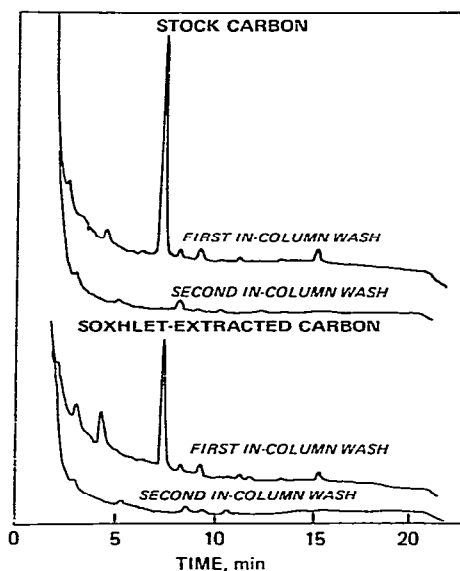


Fig. 1. Determination of background impurity levels of carbon by GC on Carbowax 20M-TPA, 3 min at 80°, 8°/min to 170°.

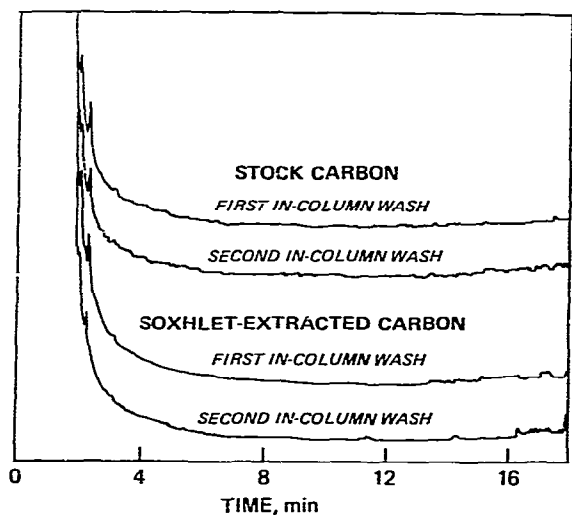


Fig. 2. Determination of background impurity levels of carbon by GC on SE-30, 100–225° at 7°/min.

Pre-cleaning carbon

Whether pre-cleaning carbon actually causes a deterioration in its ability to sorb organics from water is not discussed in the literature. The data of Table IV show that there is no appreciable difference in the ability to sorb and desorb organics between stock carbon and carbon that was Soxhlet pre-extracted with chloroform and dried.

The compounds given in Table IV elute from the GC in areas where there is no interference with the many impurities in this carbon. With an unknown sample there is no assurance that this would be the case, and it is desirable to find as simple a method as possible for removing the background impurities. A better method than Soxhlet extraction for producing acceptable backgrounds in this carbon was a simple in-column wash with several solvents just before passing the water sample through. Columns of stock carbon and the Soxhlet extracted material were washed with one bed volume of acetone followed by three bed volumes of chloroform. GC examination of the concentrated organic effluent, using a Carbowax column, (Fig. 1, first wash) shows, surprisingly, that the level of impurities removed from carbon that has already been through 400 cycles of chloroform Soxhlet extraction is nearly the same as that from the stock carbon. Further elution of the columns with three additional bed volumes of chloroform gave acceptable blank chromatograms (Fig. 1, second wash). Therefore, the time-consuming Soxhlet step is unnecessary for any phase of cleaning this particular carbon, particularly when a water-sampling system is used that requires small amounts of carbon and solvent, relative to the usual CCE procedure.

It is very revealing to examine the SE-30 chromatograms (Fig. 2) of these same extracts. The first extract contained no appreciable contamination and for an analysis that would only be done on SE-30, no pre-cleaning at all would have been necessary. The same situation probably holds for the large carbon samples used in the 10-city survey (NORS). That is, the blank of this same carbon was apparently acceptable by analysis with the non-polar GC substrate used in that survey but, as shown earlier,

TABLE V

EFFECT OF COLUMN PRE-CLEANING ON EFFICIENCY OF IN-COLUMN DESORPTION

The percent recoveries are corrected for sample sorbed on reservoir wall.

| Compound | Stock Carbon | | Twice CHCl ₃ Soxhlet Extracted | |
|-------------------------------|---------------------------|------------------------------|---|------------------------------|
| | With In-Column Prewashing | Without In-Column Prewashing | With In-Column Prewashing | Without In-Column Prewashing |
| Acenaphthene | 0 | 0 | 0 | 0 |
| 2-Benzothiazole | 0 | 0 | 0 | 0 |
| bis(2-Chloroethyl) ether | 102 | 83 | 106 | 85 |
| Hexachlorobutadiene | 74 | 57 | 87 | 61 |
| Hexachloroethane | 85 | 65 | 90 | 72 |
| <i>n</i> -Hexadecane | 20 | 3 | 22 | 16 |
| Tri- <i>n</i> -butylphosphate | 85 | 91 | 95 | 95 |
| <i>n</i> -Tridecane | 24 | 12 | 32 | 18 |

would have been unacceptable for polar-column GC analysis. Carbon, therefore, cannot be defined as absolutely clean or dirty but only as acceptable or unacceptable for a given analytical scheme in which such parameters as the GC substrate and detector are specified.

After the carbon has been cleaned by in-column washing with chloroform, it must be washed with one or two bed volumes of a water-miscible solvent such as methanol or acetone before the sample is applied.

Carbon desorption methods

If carbon is to be used in routine water monitoring surveys, it would be desirable to have a quicker method of desorption than drying the carbon and Soxhlet extraction. The acetone-chloroform desorbing method used for the XAD resin was tested on tapwater samples sorbed on carbon columns prepared in four ways: stock carbon with and without in-column pre-washing and Soxhlet extracted carbon with and without in-column washing. The results of Table V show that the in-column pre-washed carbon desorbs better than the unwashed material. These results closely follow the

TABLE VI

DESORPTION BY IN-COLUMN WASHING FOLLOWED BY SOXHLET EXTRACTION, PERCENT RECOVERIES

| Compound | In-Column Desorption | | | Soxhlet Chloroform | Soxhlet Benzene |
|-------------------------------|----------------------|--------------|-----------|--------------------|-----------------|
| | Wet Carbon | Freeze Dried | Air Dried | Air Dried | Air Dried |
| Di- <i>n</i> -butyl phthalate | 41 | 47 | 38 | 32 | 0 |
| Di-(2-ethylhexyl)phthalate | 28 | 15 | 9 | 27 | 2 |
| Dimethyl phthalate | 0 | 19 | 27 | 45 | 9 |
| Fluoranthene | 0 | 0 | 0 | 0 | 18 |
| Hexachlorobenzene | 0 | 0 | 0 | 0 | 16 |
| Pyrene | 0 | 0 | 0 | 0 | 14 |
| 2,4,6-Trichlorophenol | 0 | 0 | 0 | 0 | 11 |

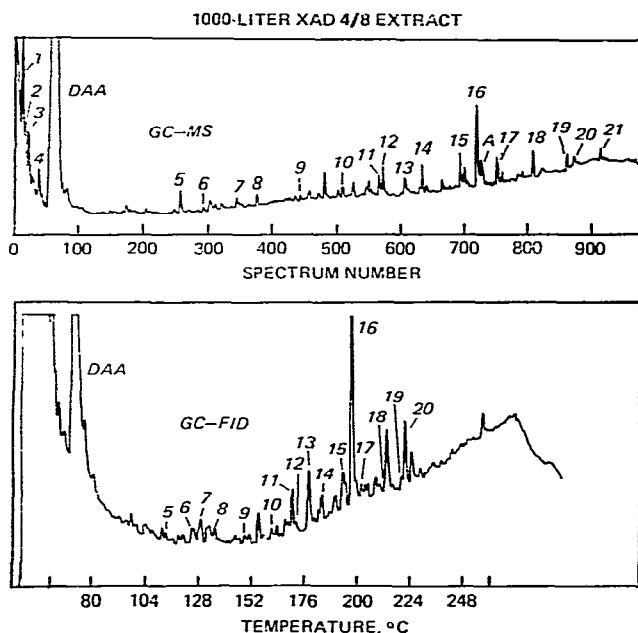


Fig. 3. Upper: MS total ion current integration of the resin extract of Athens tapwater chromatographed on an SP-2100 capillary column. Lower: FID response of the extract chromatographed on a packed SP-2100 column. The numbered peaks are listed in Table VII.

recoveries from the XAD resins shown in Table III, except for acenaphthene and benzothiazole.

Because the in-column elution procedure did not give uniformly high recoveries, the classical Soxhlet elution method was tried in conjunction with it. Three columns of stock carbon were in-column pre-washed and a sample was sorbed on each. One wet column was immediately in-column eluted with acetone and chloroform. The wet carbon was removed from the other two columns and one sample was air dried for three days and the other freeze dried and held under vacuum for three days. The dried carbons were returned to their columns and eluted with acetone and chloroform. Table VI shows that only portions of the phthalates in the test mixture were recovered. The solvent-wet carbon from the air-dried sample was transferred to a Soxhlet extractor and successively extracted with chloroform (again only phthalates eluted) and benzene (some of all the other materials eluted) (Table VI). The total recoveries for each compound are less than the corresponding results for XAD resins (Table III).

Based on recovery values and the labour involved in the analysis — particularly the desorption step where carbon may require a Soxhlet extraction— XAD-2 or 4/8 is better in every respect than carbon. Because the resins do not completely sorb all materials, however, it seemed useful to sample with a system in which the water first passes through resin and then through carbon. In addition to the improvement in quantitation, there is always a nagging concern that the model set of compounds was not broad enough and that carbon might catch something in the sample completely unretained by the resins.

TABLE VII

COMPOUNDS IDENTIFIED IN XAD-4/8 EXTRACT OF 1000 l OF TAPWATER

Compounds are listed in order of elution from SP-2100 column.

| <i>Compound</i> | <i>Conc. ($\mu\text{g/l}$)</i> | <i>Compound</i> | <i>Conc. ($\mu\text{g/l}$)</i> |
|--------------------------|---|-------------------------|---|
| 1 Toluene* | — | 12 <i>n</i> -C15 | — |
| 2 Chloropicrin* | — | 13 Fluorene | 0.031 |
| 3 Dibromochloromethane* | — | 14 <i>n</i> -C16 | — |
| 4 Dichloriodomethane* | — | 15 <i>n</i> -C17 | — |
| 5 Hexachloroethane | 0.010 | 16 Phenanthrene | 0.255 |
| 6 <i>n</i> -Undecane | 0.009 | 17 <i>n</i> -Octadecane | 0.008 |
| 7 Naphthalene | 0.009 | 18 <i>n</i> -C19 | — |
| 8 <i>n</i> -Dodecane | 0.009 | 19 <i>n</i> -C20* | — |
| 9 <i>n</i> -Tridecane | 0.006 | 20 Fluoranthene | 0.023 |
| 10 <i>n</i> -Tetradecane | 0.006 | 21 <i>n</i> -C21* | — |
| 11 Dibenzofuran | 0.032 | | |

* Identification from mass spectra only; all others confirmed by co-injection retention time.

Application to drinking waters

The accumulator column for the tapwater sample consisted of a bed of XAD-4/8 over a bed of carbon. The total column was solvent-rinsed and produced acceptable background when solvent concentrates were examined with the non-polar GC column. When 1000 l of unspiked Athens tapwater had been sampled, the glass wool, which had trapped some black waxy-appearing sediment, and the resin were removed from the column and eluted with acetone and chloroform. The carbon layer, together with the middle and bottom plugs of glass wool were eluted separately, in the original glass column, with acetone and chloroform.

Fig. 3 shows the total ion monitor tracing from the mass spectrometer and the flame ionization detector chromatogram for the material isolated from the XAD resin. Fig. 4 shows similar data for the carbon extract. The materials identified in the XAD extract are given in Table VII. The halomethanes, which are found in virtually all chlorinated water supplies, were not quantitated because they elute on the side of the solvent peak and because they broke through to the carbon column. The only other materials in the XAD extract that could be found in the carbon extract were the long chain *n*-hydrocarbons and diacetone alcohol (DAA), a contaminant from the elution solvent. The only new materials from the carbon extract that careful computer-aided MS search suggested were a couple of complex alcohols, for example, 4-methyl-4-hexanol, eluting in the very early part of the chromatogram, and sulfur, marked S in Fig. 4. The peak marked A in each figure is a GC-MS system artifact.

The carbon was also Soxhlet extracted with toluene but nothing was identified that might not arise from solvent impurities. In particular, there was no breakthrough from the resin of any of the polynuclear organic materials. Table VI indicates that fluoranthene, for example, should be found by aromatic solvent extraction of the carbon.

The data from the model compound studies suggest that the *n*-hydrocarbon concentrations may be much higher than actually measured because their collection efficiency on both sorbents is very low. In addition, the identification of alcohols in the

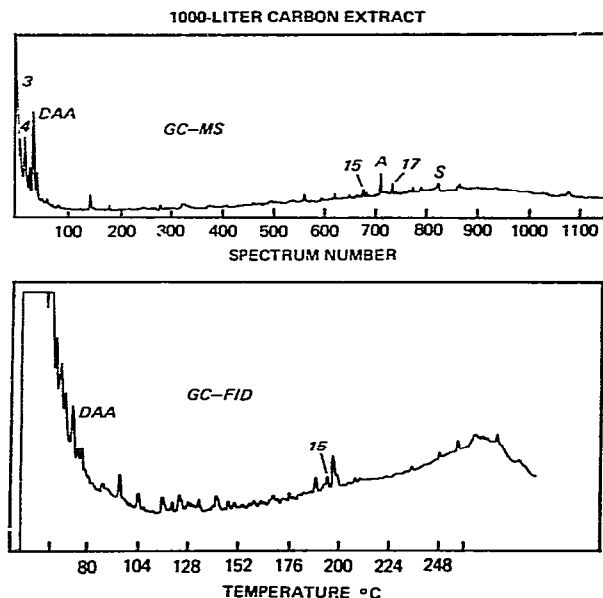


Fig. 4. Upper: MS total ion current integration of the carbon extract of Athens tapwater chromatographed on an SP-2100 capillary column. Lower: FID response of the extract chromatographed on a packed SP-2100 column. The numbered peaks are listed in Table VII.

carbon extract but not in the XAD is suspect because the model compound, 2-ethylhexanol, is efficiently collected by XAD-4 (Table II). The approximately 10 times lower concentrations of hydrocarbons, naphthalene, and hexachloroethane that are found here relative to New Orleans and the NORS study⁶ may reflect either a cleaner river water source or the carbon filter polishing step used in the Athens water filtration system.

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