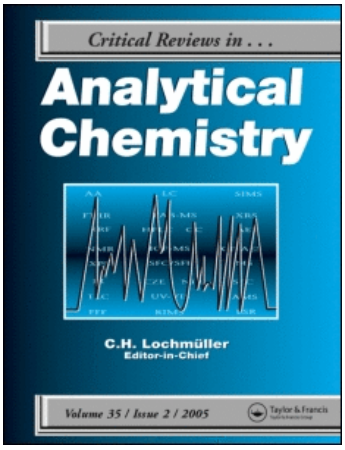
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Sampling and Preconcentration Methods for the Analysis of Polycyclic Aromatic Hydrocarbons in Water Systems

S. Ruven Smith; John Tanaka; David J. Futoma; Trudy E. Smith; Jerry A. Leenheer; Earl M. Thurman; Ronald Malcolm

To cite this Article Smith, S. Ruven , Tanaka, John , Futoma, David J. , Smith, Trudy E. , Leenheer, Jerry A. , Thurman, Earl M. and Malcolm, Ronald(1981) 'Sampling and Preconcentration Methods for the Analysis of Polycyclic Aromatic Hydrocarbons in Water Systems', Critical Reviews in Analytical Chemistry, 10: 4, 375 — 425
To link to this Article: DOI: 10.1080/10408348108542730
URL: http://dx.doi.org/10.1080/10408348108542730

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SAMPLING AND PRECONCENTRATION METHODS FOR THE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER SYSTEMS

Authors: S. Ruven Smith
John Tanaka
Department of Chemistry and Institute of Materials Science
University of Connecticut
Storrs, Connecticut

David J. Futoma
Department of Chemistry
University of Connecticut
Storrs, Connecticut

Trudy E. Smith
Department of Chemistry
Connecticut College
New London, Connecticut

Referees: Jerry A. Leenheer
Earl M. Thurman
Ronald Malcolm
Water Resources Division
U.S. Geological Survey
Denver, Colorado

Downloaded At: 16:07 17 January 2011

TABLE OF CONTENTS

Downloaded At: 16:07 17 January 2011

I. INTRODUCTION

The determination of polycyclic aromatic hydrocarbons (PAH) in water systems is at present being studied with great interest since a large number of PAH have been shown to be highly carcinogenic. The analyst is confronted by a number of problems in the analysis of PAH in water samples.

The first problem is that the concentration of individual PAH range from less than 1 ppt (pg/g) in pure groundwater supplies to greater than 1 ppm (μg/g) in heavily contaminated sewage. These concentrations necessitate the application of some extraction or preconcentration technique to raise the concentrations to a level at which identifications can be made and quantitative analyses carried out.

The second problem occurs when handling solutions where the concentrations of the solute are in a range less than 1 ppm. Serious errors can arise from losses or contamination in sampling or indeed in any step of the analytical process. Practically any surface with which the sample comes in contact can become a source of contamination, or a surface on which the trace pollutant can be lost by adsorption, reaction, etc.

The third problem is that the PAH may represent as little as 0.01% of the organic fraction present in the water sample. Thus, the analytical scheme must be devised so that the PAH can be analyzed without interference from other pollutants.

The literature relating to the extraction and preconcentration of PAH in water has been carefully evaluated in this review. Many of the studies reported in the literature have been carried out with model solutions of PAH, thus necessitating careful consideration before applying the results to an environmental ("real") sample which may contain a large number of other organics at concentrations which may mask the PAH present in the sample. Some of the procedures are accurate and relatively simple, enabling a large number of samples to be rapidly and inexpensively treated by nonprofessional personnel. Other collection and concentration methods are examples of superb analytical techniques, but are very time consuming and involve complex equipment that require the skills of a very highly trained chemist.

The techniques reviewed here that have been used to extract and concentrate the PAH from water samples include adsorption methods, solvent extraction, headspace analysis, steam-distillation, and coupled-column chromatography.

II. COLLECTION AND STORAGE OF WATER SAMPLES

Two approaches are available to the analyst for the collection and separation of the PAH. Samples can be collected in the field and returned to the laboratory for working-up or they can be preconcentrated on site. In the cases where the samples are stored prior to extraction in the laboratory, a number of processes can occur that contribute

to the loss of PAH. Contaminants may be introduced from the container and the container caps. In such cases where the samples must be stored prior to the extraction of the PAH, they must be stored in glass containers with metal liners in the plastic cap. Furthermore, they should be stored in the dark at subzero temperatures (°C) to minimize reactions leading to the loss of PAH.

Several groups of investigators have studied this problem quantitatively. Hertz et al.[1] working with stirred solutions of PAH at the 1-ppb level, showed that adsorption losses of 80% occurred in glass containers after 4 hr of stirring and that these losses increased to 95% after 40 hr of stirring. Hertz et al. also observed that the freeze drying of samples for preservation resulted in the loss of volatile components. Strup et al.[2] obtained low recoveries from water samples spiked in the parts per billion range and showed that these low recoveries were due to adsorption losses on the walls of the glass container used in their experimental set-up. Recovery factors were 50% higher when the PAH were directly spiked into the sampling module rather than when the PAH first passed through the water reservoir being studied before entering the sampling module. Basu and Saxena[3] have followed the losses for six PAH used in the preparation of 60-*l* standard water solutions where the PAH concentrations were in the parts per billion range. The adsorption losses ranged from 44.3% in the case of fluoranthene to 77.4% for benzo(ghi)perylene and are listed in Table 1. Acheson et al.[4] also studied the effect of a 6-hr mixing on the recovery of PAH from water solutions, both with and without added solids. The added solids did not appear to affect the extraction efficiency. They concluded that losses were due either to the adsorption of PAH on the glass of the mixing and extraction vessels or to chemical or biological degradation within the vessels.

Glassware used in PAH analyses is generally cleaned by either detergents or organic solvents or both. Some workers have followed this treatment by heating the glassware to 400°C to ensure the removal of traces of organic matter (see Section III.B). Ogan et al.[5,6] (see Section V) have noted that silanization of glassware and flushing of all components of the system with the sample improved recoveries. The desirability of further studies with a view to the development of a standard procedure for the treatment of sampling apparatus is indicated.

The important conclusion from all of these observations is that where possible one should sample directly into the extraction vessel and carry out the extraction as soon as possible after sample collection.

III. SOLID ADSORBENTS

A. Tenax-GC®

Tenax-GC® is a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide. It has found use as a packing material in gc work and has been used for the collection of PAH from water and air samples.[5] The outstanding advantages in using Tenax-GC® are that (1) the adsorption and recovery of organics from the polymer are almost complete, (2) the polymer is impervious to water, and (3) the polymer has excellent thermal stability.

Leoni et al.[6] have studied Tenax-GC® for the extraction of PAH and pesticides from surface and drinking waters. They examined a number of parameters of the sampling system such as (1) the amount of Tenax-GC® in the sampling column, (2) the effect of pH, (3) the flow rate of the water sampled on the collection efficiency, and (4) the volume of solvent required to elute the hydrocarbons from the Tenax-GC®. On the basis of their studies, they selected a column 7.5 × 1 cm containing 1.5 g of 60 to 80-mesh Tenax-GC®. The column was used to sample up to 20 *l* of water at the

Downloaded At: 16:07 17 January 2011

Table 1
AMOUNT OF PAH UNACCOUNTED FOR AS A RESULT OF MIXING WITH WATER IN A GLASS BOTTLE (WATER VOLUME: 60 *l*)

Compound	Conc on basis of amount added to water (ng/*l*)	Conc found in aqueous phse (ng/*l*)	PAH losses (%)
Fluoranthene	500	278.6	44.3
Benzo(j)fluoranthene	100	48.3	51.7
Benzo(k)fluoranthene	100	51.7	48.3
Benzo(*a*)pyrene	100	36.4	63.6
Indeno(1,2,3-cd)pyrene	100	25.5	74.5
Benzo(ghi)perylene	100	22.6	77.4

rate of 3 *l*/hr. The optimum pH of the water was between 6.8 and 7.2. Under these conditions, analysis of the column effluent showed no traces of PAH or pesticides, with the exception of small amounts of hexachlorobenzene. The adsorbed pollutants were extracted from the Tenax-GC® with 30 m*l* of acetone. Leoni et al. give results for the addition of five different PAH to 25 to 30 *l* of drinking water at levels of 0.08 to 0.13 ppb and report recoveries that average 95%. They note that the adsorption of pollutants by polymers can be adversely affected by the presence of surfactants and fatty substances and recommend the use of a Celite® 545 prefilter when working with natural waters. We note that the removal of interfering substances such as particulate matter, fats, etc. poses serious problems since, as we discuss below (Section IV), in the presence of small particulate matter about 50% of the PAH may be lost from the water by adsorption.

Downloaded At: 16:07 17 January 2011

B. Amberlite® Resins

The Amberlite® resins have received a great deal of attention as adsorbents of organic species in water. The XAD 1-5 resins are polystyrenedivinyl benzene copolymers and are nonpolar; whereas XAD-7 and XAD-8 are polar polymethacrylate resins.[7,8]

Prior to their use in the collection and concentration of organic compounds from water systems, the Amberlite® resins must be cleaned to remove impurities or nonpolymerized material that will be extracted when the water pollutants are desorbed from the resin. All investigators who have used Amberlite® resins to extract pollutants from water systems have used essentially the same clean-up procedure. Stepan and Smith[7] have used a 6-hr Soxhlet extraction with methanol followed by a 6-hr Soxhlet extraction with diethyl ether. After the second extraction, the resin is equilibrated with 20 m*l* of diethyl ether for 10 min, and the diethyl ether eluate is analyzed by gas chromatography to check the effectiveness of the clean-up. If the blank chromatogram indicates that the resin is clean, the resin is stored under methanol in a glass bottle until it is to be used. Storage of the resin under methanol prevents adsorption of organic pollutants from the atmosphere and also prevents the resin from drying out. It has been shown that the dried resin develops cracks, allowing more impurities to leach out of the resin.[9] Fritz, Junk, and co-workers, who have used Amberlite® resins in a number of studies of water systems, use essentially this same clean-up procedure.[9-13]

Strup et al.[2] have carefully studied the resin blank problems associated with the use of XAD-2 resins. In their clean-up procedure, the resins were cleaned with 5 to 6 washes of water followed by 24-hr Soxhlet extractions with methanol, diethyl ether, pentane, and methylene chloride. One batch of the cleaned resin was dried and stored

under nitrogen; a second batch was washed with methanol and stored as a methanol slurry. Each of these resin samples was used to analyze 4-*l* portions of the same batch of distilled water. The adsorbed solutes were eluted from the resins by an 8-hr Soxhlet extraction with methylene chloride, and the volume was reduced in a Kuderna-Danish evaporation apparatus. The gc traces (Figures 1 and 2) show the superiority of the slurry storage method over the dry storage method. Our own studies with Amberlite® XAD-2 and XAD-4 also indicate that sequential 24-hr Soxhlet extractions with methanol, acetronitrile, and diethyl ether with subsequent storage under methanol is necessary in order to obtain a satisfactory gc blank.

The selection of a particular XAD resin for the extraction of PAH from water systems appears to be determined by the personal bias of the investigator. Fritz and coworkers have used both XAD-2 and XAD-4 at various times.[10,14] The recovery efficiencies of the XAD-2, 4, 7, and 8 resins and resin mixtures have been studied by Van Rossum and Webb.[15] In their comparative study, they used distilled water samples spiked with 13 organic pollutants. For tap water samples, they found XAD-2 and an equal-weight mixture of XAD-4 and XAD-8 to be about equally effective. The average recovery was about 80% for acenaphthene, acenaphthylene, fluoranthene, and pyrene. However, for extracting chlorinated insecticides and polychlorinated biphenyls from water, Musty and Nickless[16] have shown that XAD-4 is far superior to XAD-2.

Thurman et al.[17] have studied the capacity factors for organic solutes in water systems when adsorbed on Amberlite® XAD-8 resin. Their results can be used as a basis for estimating the size of the resin column required to sample PAH from water. Factors in addition to the resin type can affect the efficiency with which organic pollutants are extracted from water systems. Stepan and Smith[7] have shown that the recovery factor of naphthalene decreases when the rate of flow of water through the adsorption column is increased from 20 to 200 m*l*/min. The extraction efficiency of the column for nonpolar compounds such as PAH are independent of the pH of the water; however, the extraction of organic acids is strongly pH dependent.[10] Junk et al.[10] have investigated the effect of varying the particle size of the resin. They tested spherical resin beads, 20 to 60 mesh, as well as resin samples that had been ground to meshes as small as 150. No advantage to any particular size range was found, and they recommend the 20 to 60 mesh spherical resin.

For sampling, Stepan and Smith[7] filled the glass adsorption tube with a slurry of Amberlite® in methanol and plugged the ends of the tube with either sintered glass or glass wool. Then 30 m*l* of methanol were passed through the adsorption tube, and before the methanol had completely drained, the tube was stoppered with glass stoppers until it was to be used. Immediately before sampling, two 100-m*l* portions of distilled water were passed through the adsorption tube to remove the methanol.

For the study of model samples in the laboratory and the analysis of grab samples collected in the field, Junk and co-workers[10,11] used the apparatus shown in Figure 3. A silanized glass wool plug (E) is inserted near the stopcock. The methanol slurry of XAD resin (F) is added to form a bed approximately 6 cm high containing 1.5 to 2 g of dry resin. A second plug of silanized glass wool (E) is placed over the resin, the methanol is drained, and the resin is washed with three 20-m*l* portions of water. During this step, care is taken to drain the wash liquids only to the top of the resin bed. The reservoir flask (C) of the apparatus shown in Figure 3 has a capacity of either 2 or 5 *l*. The water sample is placed in the reservoir and the top of the reservoir is connected to a cylinder containing organic-free nitrogen. The water sample is passed through the resin bed at a rate of 30 to 50 m*l*/min. If the water flow falls below this rate, nitrogen at about 1 psi is applied to the reservoir to increase the flow rate. When most of the sample has drained through the resin, the walls of the reservoir are washed

Downloaded At: 16:07 17 January 2011

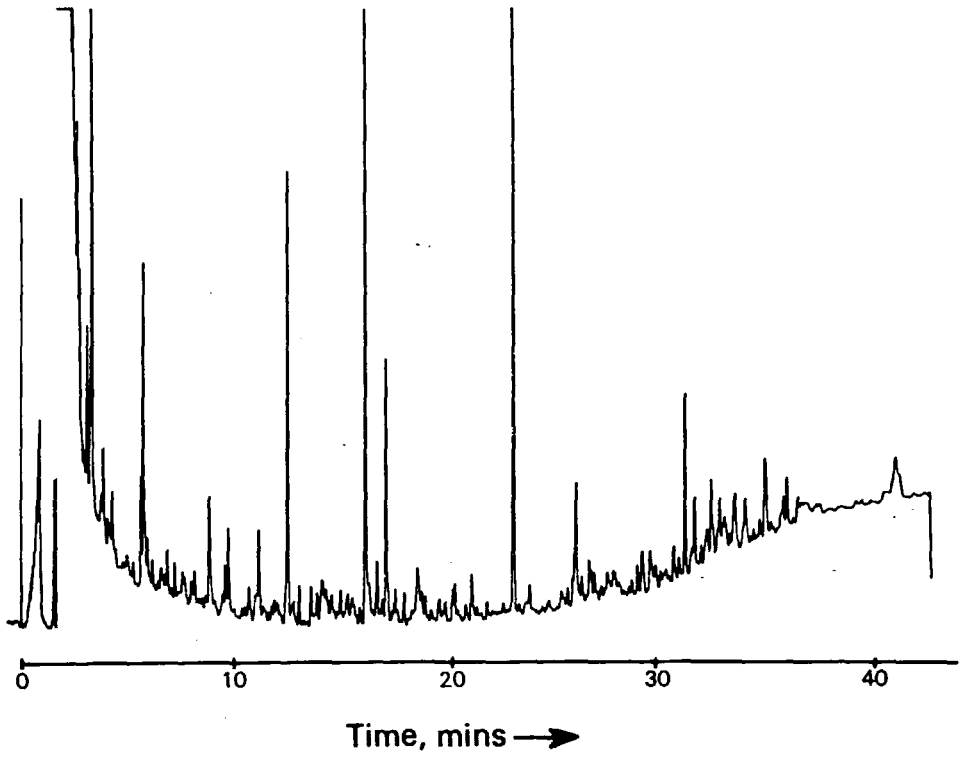


FIGURE 1. Gas chromatographic scan of the eluent from an XAD-2 blank after dry storage and dry packing.

Downloaded At: 16:07 17 January 2011

with two 20-mℓ portions of pure water, and the liquid level is allowed to drop below the level of the resin only after the last wash. After the water has drained from the column, the sample is extracted with diethyl ether. First the reservoir is washed with two 10-mℓ portions of diethyl ether which are allowed to drain into the column and are retained there for about 10 min. During this period, the reservoir is removed and the column is capped with a 24/40 glass stopper. After the 10-min equilibration period, the ether is drained into a test tube and an additional 5 mℓ of diethyl ether is passed through the column.

Immediately after the sample extraction, the column is regenerated by passing 30 mℓ of methanol through the column and shaking the column to remove entrapped air bubbles. The stopcock is then closed, 15 mℓ of methanol is added, and the column is ready for use again without any additional preparation.

For composite sampling over a 24-hr period, Junk et al.[12,13] used the column shown in Figure 4. The glass tube was filled with XAD-2 resin as described for the column in Figure 3 and connected to a standard garden hose coupling with a short length of polytetrafluoroethylene (PTFE) tubing. The water is sampled through this extractor at the rate of 150 mℓ/min so that over a 24-hr period, 200 ℓ of water are sampled. After the sampling, the garden hose coupling is replaced by a 25-mℓ bulb, retaining the same piece of PTFE, and a PTFE stopcock is attached to the bottom of the column with another piece of PTFE tubing. The PAH are eluted with diethyl ether as described above.

Strup et al.[2] have modified a commercially available 400 × 25 mm liquid chromatography column (Fischer Porter Co.) to serve as a composite sampling tube. The water sample is drawn through the tube with either an aspirator or a pump.

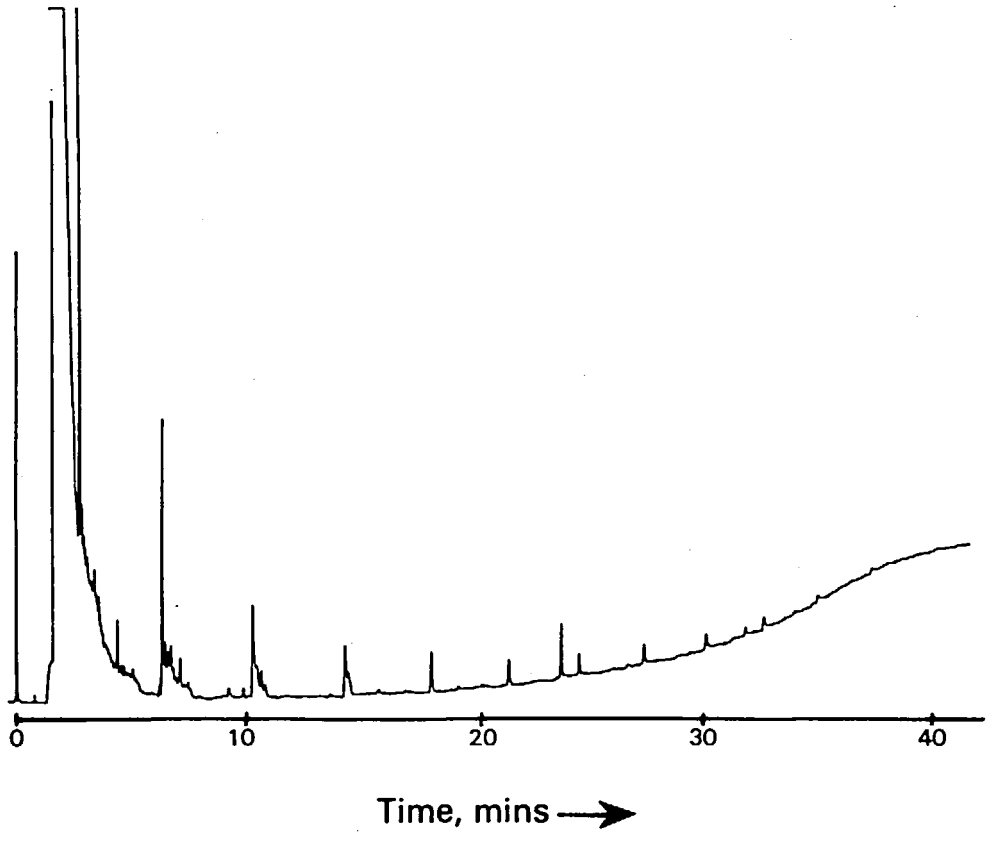


FIGURE 2. Gas chromatographic scan of the same XAD-2 blank used in Figure 1, but with methanol storage and slurry packing. All other conditions and chromatographic parameters were the same as in Figure 1.

After the adsorbed sample has been eluted from the adsorption column, the 20 to 30 m*l* of eluate is generally reduced in volume to about 1 m*l*. To ensure both a smooth volume reduction and to avoid the introduction of water into the gc, the eluted sample is first dried. Stepan and Smith[7] used magnesium sulfate as the drying agent. Junk et al.[10] have investigated a number of alternatives for removing the water from the eluate obtained from the column. They stated that placing the eluates in a refrigerator for a 24-hr period introduced evaporative and irreversible adsorption losses. They also noted that although rapid cooling with ice-salt or dry ice-acetone slush baths did not result in losses of PAH, the handling and preparation of these baths is inconvenient. They found that a sodium sulfate drying procedure or a liquid nitrogen freeze-out was completely satisfactory. The liquid nitrogen freeze-out for two 10-sec intervals is the recommended technique since it avoids the addition of an extraneous component to the eluate which might contaminate the solution or serve as a surface on which the solute can be adsorbed.

For samples in which the PAH concentration in the eluate is too low for reliable determination, volume reduction is necessary prior to gc. Our experience and the experience of other workers[9] has shown that the concentration step is a critical step where serious solute losses can occur. Junk et al.[10] recommend a distillation technique to concentrate the sample. They have used the apparatus shown in Figure 5 with a Snyder

Downloaded At: 16:07 17 January 2011

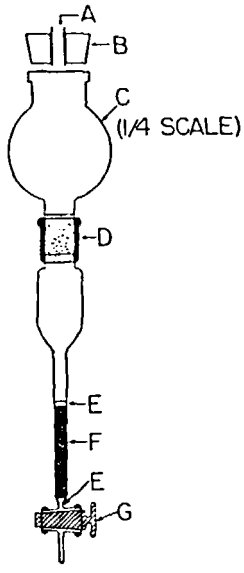


FIGURE 3. Apparatus for extracting organic solutes from water. A, Purified inert gas pressure source; B, cap; C, 2-ℓ reservoir; D, 24/40; E silanized glass wool plugs; F, 0.6-cm I.D. × 10 cm-long glass tube packed with 20- to 60-mesh XAD-2 resin; G, PTFE stopcock.

Downloaded At: 16:07 17 January 2011

column when the sample volume is to be reduced to 1 mℓ and with a Vigreux column when the sample is to be reduced to 0.6 mℓ. The Snyder column is less likely to lead to losses when bumping occurs; on the other hand, the Vigreux column has negligible holdup. They use a boiling chip and an evaporation rate of between 0.5 to 2.0 mℓ/min. They state that small boiling chips do not sorb organic solutes. Smith et al.[18] have used a rotary evaporator for concentrating solutions of PAH. They found that with a little experience, the concentration proceeds smoothly.

Junk et al.[10] examined a number of pretreatment techniques to test glassware activity. They tested (1) sequential solvent washing with acetone, methanol, and ether; (2) detergent washing followed by the organic solvent washings; (3) detergent washing and drying; (4) silanization of the glass surfaces; (5) baking the glassware at 400°C for 16 hr; and (6) substitution of Clear-seal for ground-glass joints. They were unable to correlate any of these treatments with surface activity. For this reason they settled on and recommend sequential solvent washing for all glassware.

Junk et al.[10] have also investigated the shape of the vessel in which the concentration step is carried out. They have studied a number of configurations of concentration vessels. Several of the shapes that were studied are shown in Figure 6. When vessels B and C were used, solute losses from 10 to 60% were noted, whereas losses from vessels of shape A were at the most 6%. The vessels of shape A are constructed by sealing a graduated centrifuge tube to a round-bottom ground-glass joint flask, taking care to

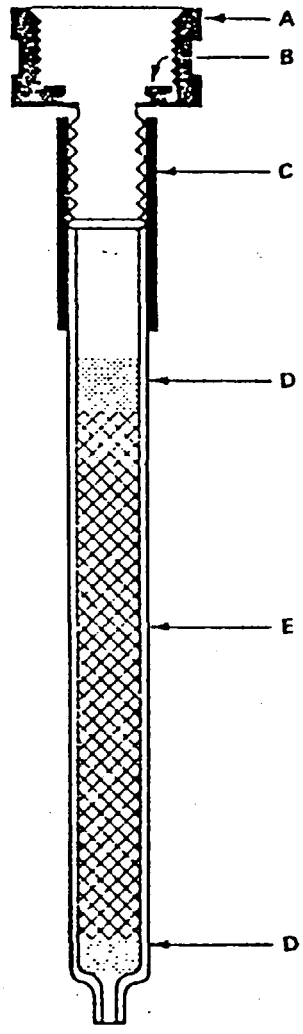


FIGURE 4. Illustration of composite sample extraction device. A, Standard garden hose coupling; B, PTFE washer; C, 12.7-mm I.D. PTFE tubing; D, glass-wool plugs; E, 12.7-mm O.D. × 9-cm-long glass tube packed with approximately 2 g of 40- to 60-mesh XAD-2 resin.

produce a smooth seal. This configuration gives an effective solution washing of the sides of the flask during the volume reduction step.

Junk et al.[10] have also investigated volume reduction by using a stream of nitrogen or another inert gas. Their results show that this method leads to serious solute losses and should be avoided. They point out that 10 to 80% of all solutes except those of extremely low volatility are lost by using a gas stream to concentrate the sample. Shinohara et al.[19] have compared the recovery factors for the nitrogen gas stream method

Downloaded At: 16:07 17 January 2011

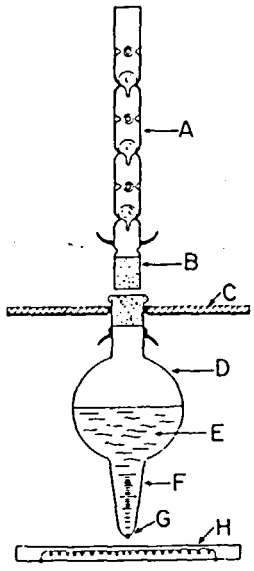


FIGURE 5. Sketch of a concentration apparatus. A, Snyder® distillation column; B, 14/20 ground glass connection; C, Bakelite® heat shield covered with aluminum foil; D, approximately 50-mℓ vessel; E, ether solution; F, graduated and calibrated taper; G, small boiling chip; H, hot plate.

Downloaded At: 16:07 17 January 2011

and the micro-Snyder distillation method of volume reduction for benzene and ether solutions of PAH. They found that the average recovery from the distillation method was about 5 to 7% higher than that for the nitrogen gas stream method.

Both investigations show that the micro-Snyder distillation method is superior to the nitrogen gas stream method, but losses by the nitrogen gas stream method are dependent on the individual investigator. The problem of reducing the volume of the sample to a predetermined final volume (1 mℓ) is not a simple one. Junk et al.[10] suggest that in order to arrive at a desired final volume, the volume of the solution be reduced below this level and then brought up to volume by the addition of ether. Smith et al.[18] have used this same approach but they adjusted the final volume with isooctane. The higher boiling point of the isooctane reduced solvent losses during the handling of the sample.

Tateda and Fritz[14] have recently reported a procedure that uses a minicolumn requiring only a small water sample. In this way, the volume-reduction step is eliminated. The minicolumn, constructed of a disposable pipet, was packed with an adsorbent bed 1.2 to 1.8 × 25 mm consisting of XAD-4 or Spherocarb® (Analabs, New Haven, Ct.) By using this column, the volume of water sampled could be reduced from 2 to 5 ℓ to 50 to 100 mℓ and the volume of eluent reduced to 50 to 100 μℓ. Thus, without resorting to a volume reduction, the concentration of the PAH in the minicolumn eluate is 10 to 20 times greater than that obtained after the eluate from the larger column has been

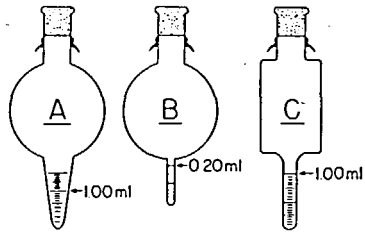


FIGURE 6. Various configurations of concentration vessels tested. (A) Recomended, (B) unsatisfactory, (C) questionable.

reduced from 25 to 1 mℓ. However with the smaller volume of adsorbent, the sensitivity of the minicolumn method is limited to 2 ppb for each organic solute in the water.

Sampling with the minicolumn is carried out in the same way as with the larger columns, but at a flow rate between 0.8 to 1.2 mℓ/min. Since the volume-reduction step is eliminated in the XAD-4 minicolumn method, the more volatile diethyl ether that is used to elute the sample from the larger column can be replaced by acetone. Then 15 to 20 $\mu\ell$ of acetone are added at a time and forced back and forth through the resin bed with a rubber bulb until a total of 50 $\mu\ell$ of acetone has been added. For low molecular weight and water-soluble compounds, the elution is carried out with carbon disulfide added in 20-$\mu\ell$ portions. For the minicolumn, the average recovery was 89% at the 2-ppb level and 83% at the 100-ppb level; this compares favorably with the average recovery of 92% for the same compounds with the larger apparatus.

The same model compounds that were used to test the minicolumn packed with XAD-4 were used to test the minicolumn packed with Spherocarb®. Elution of the solutes from the Spherocarb® column was both slow and difficult. Carbon disulfide was the best eluent, superior to acetone, methanol, diethyl ether, acetonitrile, methylene chloride, and pentane; however, even with carbon disulfide, a number of compounds were difficult to elute. Five successive 100-$\mu\ell$ portions of carbon disulfide failed to completely elute naphthalene, biphenyl, and 2-naphthol from Spherocarb®. Thus, the Spherocarb® appears to have a stronger retention for low molecular weight organic compounds than XAD-4.

The sensitivity of the minicolumn is 2 ppb for each solute, and this sensitivity is adequate for the analysis of raw water and wastewater. The result of the analysis of 100 mℓ of raw water with the minicolumn using both Spherocarb® and XAD-4 are shown in Figure 7.

Tateda and Fritz[14] have combined the minicolumn and the large-scale adsorption method to take advantage of the best features of both. Whereas the large-scale apparatus has good sensitivity, only a small fraction of the final concentrate (2 $\mu\ell$ out of 1 mℓ) is used for the gc analysis. The minicolumn does not have adequate sensitivity for the determination of pollutants in pure water, but the eluate from the column is 50 to 100 $\mu\ell$. The best features of both methods were combined by taking the 1-mℓ ether concentrate from the larger column, adding it to 50 mℓ of pure water, and processing this sample in the minicolumn. When 2 $\mu\ell$ of the 100-$\mu\ell$ carbon disulfide extract from the minicolumn is analyzed, a further improvement by a factor of 10 in sensitivity is achieved. The enhancement in sensitivity resulting from the second concentration by the minicolumn is shown in Figure 8.

Malcolm, Thurman, and Aiken[20,21] have quantitatively related the separation of organic solutes on XAD resins into hydrophobic and hydrophilic fractions. Their papers

Downloaded At: 16:07 17 January 2011

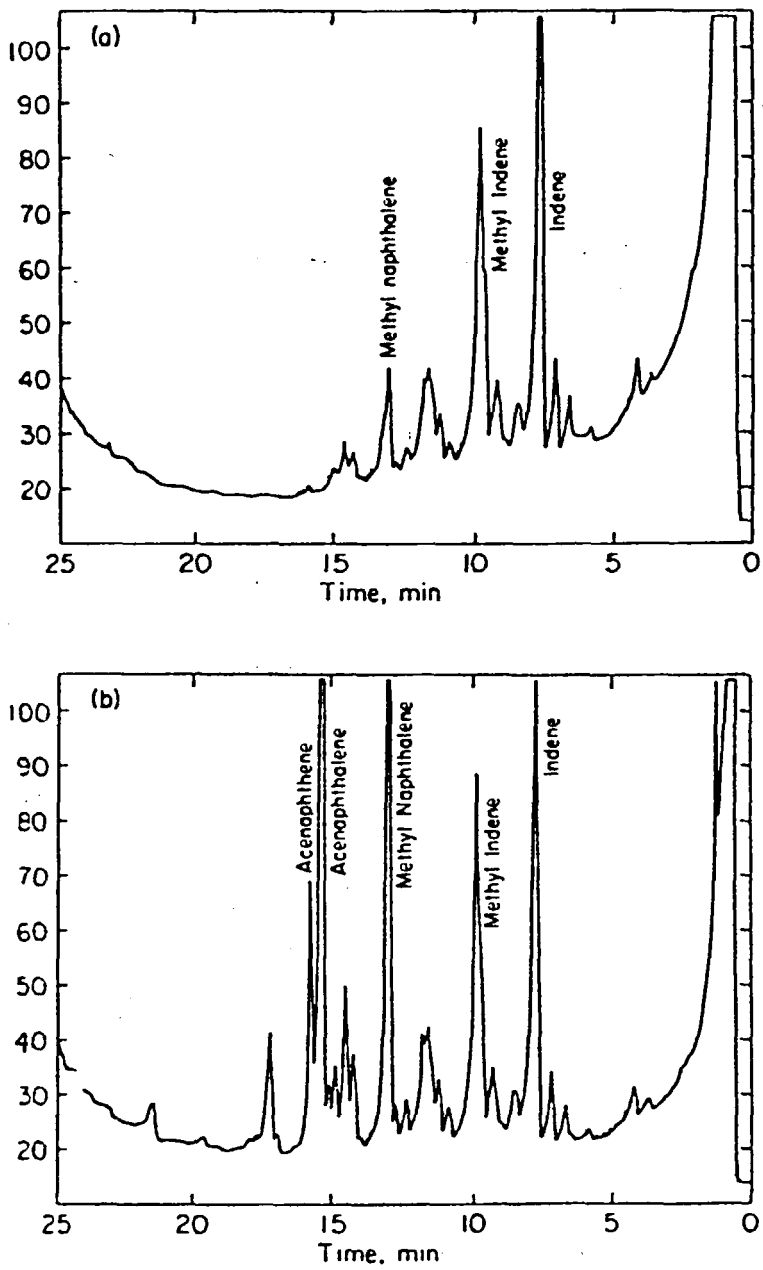


FIGURE 7. Chromatograms of well water in Ames, Iowa collected on Spherocarb® and XAD-4. (A) Eluate from Spherocarb®; (b) eluate from XAD-4. Gas chromatographic column, 1/8 in. × 6 ft, 3% OV-17; temperature, 30 to 240° at 8°/min; temperature of injector and FID detector, 350°; carrier gas flow rate, 20 ml/min.

deal with the hydrophobic fraction which contains the PAH compounds. Although they have not tested PAH compounds, the classification is pertinent to this review. They have selected XAD-8 for their study, having found it the most effective adsorbent for both high and low molecular weight organic solutes in natural waters. XAD-8 was

Downloaded At: 16:07 17 January 2011

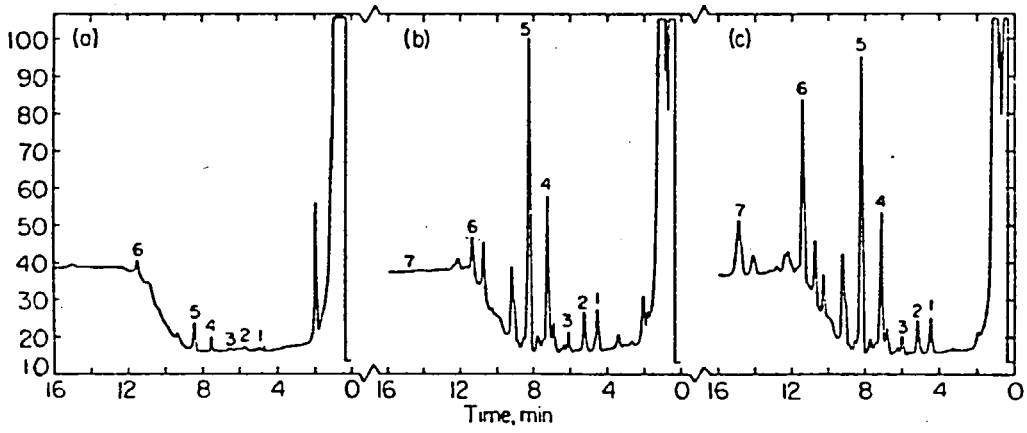


FIGURE 8. Chromatograms of Iowa State University tap water after concentration by (1) large-scale sorption and (2) large-scale sorption followed by minicolumn sorption (see text). (A) Ether concentrate by large-scale sorption method (1); (B) elute from Spherocarb® method (2); (C) Eluate from XAD-4 method (2). Gas chromatographic column 6 ft × 1/8 in., 10% FFAP; temperature, 60 to 200° at 16°/min; initial temperature hold, 2 min; final temperature hold, 8 min; temperature of injector and FID detector, 300°; carrier gas flow-rate, 20 m*l*/min.

Downloaded At: 16:07 17 January 2011

chosen in preference to XAD-2, since the latter resin shows a tendency to become clogged by natural polyelectrolytes which results in a reduced retentive capacity of the adsorption column.

The major factor that influences the retention of organic solutes on XAD-8 is the solvent-solute interaction rather than the solute-resin interaction. Solvent-solute interaction can be related to the formation or disruption of the hydrogen-bonded cage structure of the water molecules and can be expressed quantitatively as the solubility of the organic solutes in water. Thurman et al.[17] have correlated the logarithm of the column distribution coefficient, k', with the logarithm of the solubility as shown in Figure 9. With a knowledge of the solubility, the retention of an organic solute can be predicted to within 10%. The column distribution can be defined as:

$$k' = \frac{\text{mass of solute in stationary phase}}{\text{mass of solute in mobile phase}} \qquad (1)$$

From the graph it can be seen that for a homologous series, the amount of material adsorbed by the resin column increases as the molecular weight increases or as the aqueous solubility decreases.[8,22] Since the molecular weight of PAH is generally higher and their aqueous solubilities are lower than most other organic solutes, the Amberlite® resins will serve as an excellent matrix for the adsorption of PAH from water.

Leenheer and Huffman[23] have proposed the use of macroreticular resins as both a classification and adsorption tool. The macroreticular resins are used to concentrate and separate the dissolved organic carbon into a hydrophobic and hydrophilic fraction. The hydrophobic/hydrophilic break is defined for a $k' = 110$ on XAD-8. In the analytical dissolved organic carbon (DOC) fractionation,[23a] the hydrophobic solutes are adsorbed on a nonionic resin of low polarity (XAD-8) and the hydrophilic fraction is collected on macroreticular ion-exchange resins. The solutes are subsequently desorbed from the resins and separated into acidic, basic, and neutral fractions. The technique merits attention since it bridges the gap between the analysis of total dissolved organic carbon and the specific compound identification of all organic species dissolved in

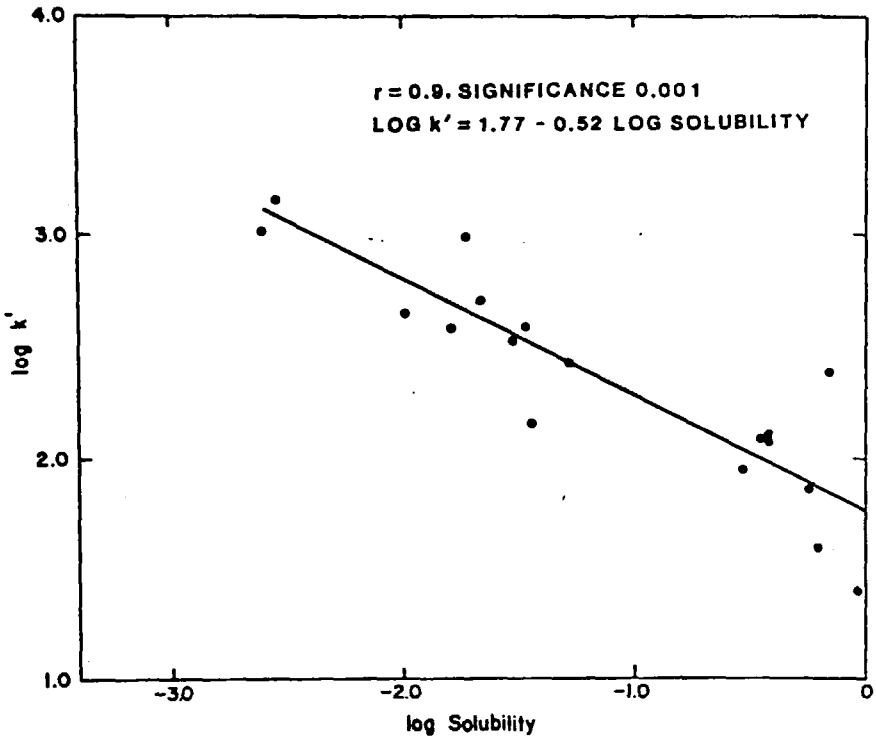


FIGURE 9. Log k' vs. log solubility for 18 organic solutes.

Downloaded At: 16:07 17 January 2011

water that one would obtain with a gc/ms system. The technique is presented by Leenheer and Huffman as a total classification scheme for DOC. Of special interest in this review is that the procedure can be used to separate the PAH (which are a part of the neutral hydrophobic fraction) from the acidic and basic hydrophobic fractions and the hydrophilic compounds.

Leenheer and Huffman[23] define hydrophobic solutes as the organic compounds that are adsorbed on resin surfaces of low and intermediate polarity. The polarity requirement is met by XAD-2, 4, and 8 resins. The hydrophobic solutes repel water and are attracted to the hydrocarbon surface of the resin by van der Waals forces. The hydrophilic solutes have water-attracting oxygen, nitrogen, or sulfur functional groups such that these solutes interact with water through hydrogen bonding.

In the "analytical DOC fractionation" procedure outlined by Leenheer and Huffman,[23a] samples are collected in organic-free glass containers. Then, 200 m*l* are filtered on-site through a 0.45-μm porosity silver membrane filter to remove particulate and colloidal material; chilling to 4°C is the recommended method of sample preservation.

The method is applicable to water samples with DOC concentrations between 5 and 25 mg/*l* and whose specific conductance is less than 2000 μmhos/cm at 25°C. Water samples with a DOC less than 5 mg/*l* can be freeze dried to the specific conductance limit; samples with DOC concentrations greater than 25 mg/*l* should be diluted with organic-carbon-free water to a DOC of 25 mg/*l* prior to analysis. If the sample has a pH less than 6.5, the pH is adjusted to 7 by dropwise addition of 1.0 *M* sodium hydroxide, since the hydrophobic bases become protonated in acid solution and these protonated bases will not adsorb on XAD resins.

The first step in the analysis is the measurement of the total DOC on a 10-mℓ aliquot of the water sample. The sample is adjusted to a pH of 7 and is then pumped at 2 mℓ/min through an XAD-8 column containing 3 mℓ of XAD-8 resin, and the hydrophobic bases and neutral solutes are removed from the sample. After the sample has been passed through the XAD-8 column, 0.1 *M* hydrochloric acid is pumped through the column to elute the hydrophobic bases. The procedure that is followed after the bases have been removed from the XAD-8 column is as follows: (1) the XAD-8 column is connected in series with a column containing 3 mℓ of AG-MP-50 BioRad® H^+-saturated cation-exchange resin (to adsorb hydrophilic bases) and 6 mℓ of AG-MP-1 BioRad® OH^--saturated anion-exchange resin (to adsorb hydrophilic acids), (2) the pH of the water sample is adjusted to a pH of 2 with concentrated hydrochloric acid, and (3) the sample is pumped through all three columns. The hydrophobic acids (now in the nonionized form) are adsorbed on the XAD resin in this step and are subsequently eluted from the XAD-8 with 0.1 *M* sodium hydroxide and the DOC is determined. The hydrophilic acids and bases are eluted from the ion-exchange resins and their DOC is determined. The DOC of the hydrophilic neutrals is determined from the sample that has passed through all three columns. In this procedure the neutral hydrophobic fraction is not eluted from the XAD-8 column and is determined by difference. For the analyst who wishes to extend this method and characterize the individual components of the hydrophobic neutral fraction which contains the PAH, this fraction can be eluted from the XAD-8 with an organic solvent such as diethyl ether, methanol, or acetonitrile. The procedure can serve not only to separate the DOC into characteristic fractions but also to isolate the PAH, which are normally only a small fraction of the organic solutes found in water systems. Stuber and Leenheer[23b] have used preparative scale DOC fractionation to study sorption of oil-shale retort-water organic solutes on processed oil shale.

The column distribution coefficient k^1 defined by Thurman et al.[17] can also be used to estimate the concentration factor achieved by using Amberlite® XAD-8 columns and assuming elution with three pore volumes of eluent (which proved sufficient to elute the solute from all test solutions). The calculation is made with the following equation:

$$\text{Concentration factor from original solution} = k^1/7.5 \qquad (2)$$

Malcolm et al.[21] also use k^1 in the following empirical equation to calculate the complete retention of any solute

$$\frac{6(x)}{y} = k^1 \qquad (3)$$

where x = volume of sample in milliliters, y = bed volume of the column in milliliters, and 6 is an empirically determined constant for XAD-8. Using this equation, the analyst can vary both the bed volume and the sample size, depending on experimental conditions. For example, the following calculation is used to determine the volume of sample from which fluorene can be completely removed using a 20-mℓ bed volume of XAD-8. The solubility of fluorene is 1.69 mg/ℓ[24] = 1.0×10^{-5} mol/ℓ and log solubility is −5.0. Extrapolating the data in Figure 9, log k^1 = 4.4 and $k^1 = 2.3 \times 10^4$. From Equation 3, $x = 7.7 \times 10^4$ mℓ or 77 ℓ.

Since fluorene is one of the most water-soluble PAH that will be encountered in water analysis, a bed volume of 20 mℓ that corresponds to ~6 g of XAD-8 is more than adequate to collect the PAH and other hydrophobic solutes from a 100-ℓ sample

Downloaded At: 16:07 17 January 2011

of water. Natural water may have a DOC value as high as 20 mg/ℓ and if the hydrophobic fraction is about one half of this value, the PAH must compete with other organic solutes for adsorption sites.

Another advantage of using the XAD resins is their ability to serve also as a desalting agent for isolating the hydrophobic fraction from inorganic salts which might interfere with certain instrumental methods.

As mentioned earlier, on-site extraction of pollutants from a water system has several advantages over collection of samples in the field which are then returned to the laboratory for analysis. The problems of transporting large sample volumes that are eliminated are the possibilities of chemical alteration and adsorption losses on the container surface. In addition, the continuous sampling of a water system should be expected to give a more representative sample than a grab sample. Stepan and Smith[7] have shown that in order to obtain quantitatively reproducible results when sampling with XAD resins, it is necessary to control the pH of the water. This is obviously impractical with on-site sampling, but the pH of the water will usually remain constant during sampling and can be measured with a pH meter. However, depending on the pH of the water system, some of the acidic or basic components may not be collected on the resin.

Downloaded At: 16:07 17 January 2011

The XAD resin adsorption method has been widely tested by a number of workers both in the laboratory and in the field for the analysis of PAH and other organic pollutants in water systems. Shinohara et al.[19] have obtained recoveries of 95% using model systems containing 2,3 dimethylnaphthalene, fluorene, phenanthrene, pyrene, chrysene, and benzo(*a*)pyrene, (B(*a*)P), at the parts per trillion (pg/g) level using XAD-2 in an extraction system. By passing 200 ℓ of water through an XAD-2 column, they were readily able to detect and analyze PAH and hydrocarbons at the parts per trillion level. With a 200-ℓ water sample, the detection limits are biphenyl, 0.05 ppt; acenaphthene, 1.5 ppt; benzo(*a*)fluorene, 0.1 ppt; dimethylnaphthalene 1.0 ppt; fluorene, 0.02 ppt; phenanthrene + anthracene, 0.05 ppt; benz(*a*)anthracene + chrysene + triphenylene, 0.5 ppt; and benzo(*a*)pyrene, 2.0 ppt.

The research group of Fritz, Junk and co-workers at Iowa State University have studied trace organics in a number of water systems using both the laboratory and on-site extraction apparatus described in Section III.B.[10,11,25,26] They use either sampling procedure, depending on whether an instantaneous or an average concentration over a period of time is the point of interest. Composite sampling has the advantage that large volumes of water can be sampled, which is important when more of the contaminant is needed for identification purposes. The grab sample for laboratory extraction suffers the drawback of losses on the container walls during storage and transportation. In both of these samplers, the eluant that is used to remove the adsorbed organics from the XAD must be reduced in volume, and the volatile organic solutes are lost during this step, and even those that are not lost are generally masked by the solvent peak during gc analysis. The loss of volatile compounds can be reduced by use of the XAD minisampler. With the minisampler only 100 mℓ of water are sampled with 80 mg of resin (as opposed to 100 ℓ with 2 g of resin), and the sample can be eluted with 100 μℓ of solvent, and no volume reduction is necessary. A second approach that can be used with the minisampler is to use the XAD column directly in a thermal desorption procedure. The EPA *Procedure for Analyzing Priority Pollutants* calls for headspace analysis to determine the low molecular weight volatile pollutants, and we concur that this is the best procedure for recovering the highest percentage of these materials.

A number of specialized on-site sampling devices have been developed using XAD resins or Tenax-GC. One such apparatus is that developed by Stepan et al.[27] The apparatus consists of a sampling module with two peristaltic pumps and a lead storage

battery to power them. The operation of the pumps is controlled by an electronic timer so that the sampler can be operated either in the intermittent or continuous mode. A voltage stabilizer circuit allows the operator to vary the pumping speed between 0 to 60 mℓ/min. A 15 × 2 cm stainless steel cartridge contains the XAD-2 or XAD-7 resin. The resin is treated as described previously (Section III.B) and 20 mℓ of the methanol slurry is loaded into the cartridge which is securely capped until it is installed in the sampler. In the field the cartridges are fitted into the sample holder. The sample holder serves to protect the cartridge from damage. A stainless steel mesh screen at the base of the cartridge prevents clogging of the resin by particulate matter. To avoid contamination from the connecting tubing and the pump, the cartridge is placed at the inlet of the sampling system and submerged. At the end of the sampling period, the cartridge is removed from the sampler, resealed, returned to the laboratory, and the solutes are eluted, concentrated, and analyzed. Tests carried out to compare the results of on-site extraction with grab samples showed the results to be identical to within 10%.

Since peristaltic pumps are equally effective with gases and liquids, the Stepan et al.[27] field sampler was also used for low-volume on-site extraction of organic compounds from air. For air sampling, Tenax-GC® was used as the adsorbent. The Tenax-GC® was contained in a 3 × 1 cm glass tube and kept in place by sintered glass discs. The Tenax-GC® was conditioned by passing helium through the Tenax-GC® while the cartridge was maintained at 200°C. After sampling, the adsorbed organics were eluted from the Tenax-GC® with 40 mℓ of hexane. The eluent was concentrated and analyzed by gas chromatography.

Downloaded At: 16:07 17 January 2011

C. Open-Pore Polyurethane

Polyurethane foams have been used by a number of investigators to recover PCB, pesticides,[28-30] and phthalate esters from water.[31] These applications have prompted the investigation of the retentive properties of PAH on these foams.

Two groups have studied the removal of PAH from water systems with open-pore polyurethane (OPP) foams. In their studies, Navratil et al.[32,33] prepared the OPP foam by polymerization directly in the sampling column, whereas Saxena et al.[3,34] have used commercially available foam plugs: diSPo® plugs (Scientifc Products, Inc.), Identi® plugs (VWR Scientific), and plugs cut from UU34 foam sheets (Thomas C. Forrest Co., Inc.).

Navratil et al.[33] describe in detail the *in situ* preparation of the OPP columns. The OPP tubes are prepared by mixing 60 to 40 volume percent solutions of an isocyanate and polyol into a glass column 5 or 10 cm long and 3.2 mm in diameter and allowing the polymerization to take place in the tube. The isocyanate used was Mondur MR® (Mobay Chemical Co.) which is a mixture of 4,4′-diphenylmethane-diisocyanate and some tri-, tetra-, and pentaisocyanates. The polyol used was LA-475® (Union Carbide Co.), and it is primarily a pentahydroxy compound formed by the total oxypropylation of diethylenetriamine.

Navratil et al.[33] investigated a number of variables in the polymerization process. They investigated monomer formulations with OH/NCO ratios of 1.0 and 2.2 and concluded, on the basis of breakthrough studies with pyrene, that the OPP prepared with OH/NCO = 2.2 had a much higher capacity than OPP with an OH/NCO = 1.0. Data were also presented to show that OPP polymerized at 0°C permitted a higher flow rate than the OPP polymerized at 25°C. Larger microspheres were formed when the reactants were polymerized at the lower temperature. We have used OPP tubes prepared according to the directions of Navratil et al. and have found, in addition, that the foam polymerized at 0°C maintains a better OPP-to-glass bond than those polymerized at 25°C.

The breakthrough capacity of the OPP columns was tested with pyrene test solutions and found to be superior to a number of resin-packed columns. The OPP formed from the OH/NCO = 2.2 formlation had a higher breakthrough capacity than Bio-Rad® AG-MP-50 (Bio-Rad Laboratories) and Amberlite® XAD-2.

Navratil et al.[33] eluted the PAH test compounds from the OPP columns with methanol. For a test solution containing B(*a*)P, fluoranthene, and pyrene, 90 to 98% recoveries were obtained.

Saxena et al.[34] studied the optimum parameters for the extraction of PAH from water using polyurethane foam plugs. In their studies, C^{14}-labeled B(*a*)P was employed as a means of avoiding the necessity of determining the background levels of B(*a*)P in the water samples studied.

The extraction columns were prepared by wetting polyurethane foam plugs and inserting them in 25-mm Chromoflex® columns (Kontes Glass Co.). The prepared columns were washed successively with acetone, benzene, acetone, and distilled water. The columns were tested with a model sample of spiked water which was drawn through the column at a constant rate of 250 ± 10 m*l*/min at 25°C. The recovery data showed that the three types of foam plugs tested (diSPo®, Identi®, and plugs cut from UU34 foam sheets) performed equally well.

With the 25-mm columns, the retention efficiency of B(*a*)P at ambient temperature remained unaltered for flow rates between 130 to 520 m*l*/min. A flow rate of 250 m*l*/min was selected, since at higher flow rates the plugs had a tendency to slip to the bottom of the Chromoflex column. Larger diameter columns were investigated, but it was found that when the column diameter was increased from 20 to 50 mm, the recovery of B(*a*)P decreased by 20%. Retention efficiency as a function of pH was studied using spiked tap water samples. At pH 3.0 the retention efficiency was 59%, at pH 6.7 it was 62 to 65%, and it increased to 76% at pH 10.0. When the foam plugs are used to extract PAH from water samples in the laboratory, the pH of the water can readily be adjusted for maximum efficiency; however, for on-site extractions, this is not convenient and the pH of the water must be measured so that the appropriate correction factor can be applied.

The effect of water temperature on extraction efficiency is most interesting (Figure 10). The retention efficiency of the foam plugs increased with temperature up to 40°C, decreased, and then increased again with a further increase in temperature, reaching a plateau at 60°C. On the basis of these measurements, water samples were heated to 60°C prior to passage through the polyurethane packed column.

The possibility of increasing the retention efficiency of the foam plugs by coating them with a number of chromatographic phases was investigated.[34] The plugs were coated with DC-200, SE-30, and a nematic liquid crystal [N,N′ bis(*p*-methoxybenzylidine) - α,α' -bi-*p*-toluidine]. Improvements in retention efficiency of 4 to 9% were obtained. However, these improvements are nullified by the fact that when the sample is eluted from the foam plug, the chromatographic coating is also eluted, thus complicating further concentration and analysis.

Retention studies as a function of B(*a*)P concentrations between 0.002 and 25 ppb were carried out using 4-*l* samples of spiked water, and the recovery factory remained between 84 to 87% over this range of concentrations.

The retention efficiency of the foam plugs remained constant with increasing volume of water sample when distilled water, which is free of extraneous solids or dissolved matter, was sampled. However, when successive increments in volume of tap water spiked with 0.05 ppb B(*a*)P were passed through a single plug, a steady decrease in retention efficiency was observed. The retention efficiencies for 4, 10, 20, and 40 *l* of water were 87, 73, 67, and 49%, respectively. To overcome this drop in retention effi-

Downloaded At: 16:07 17 January 2011

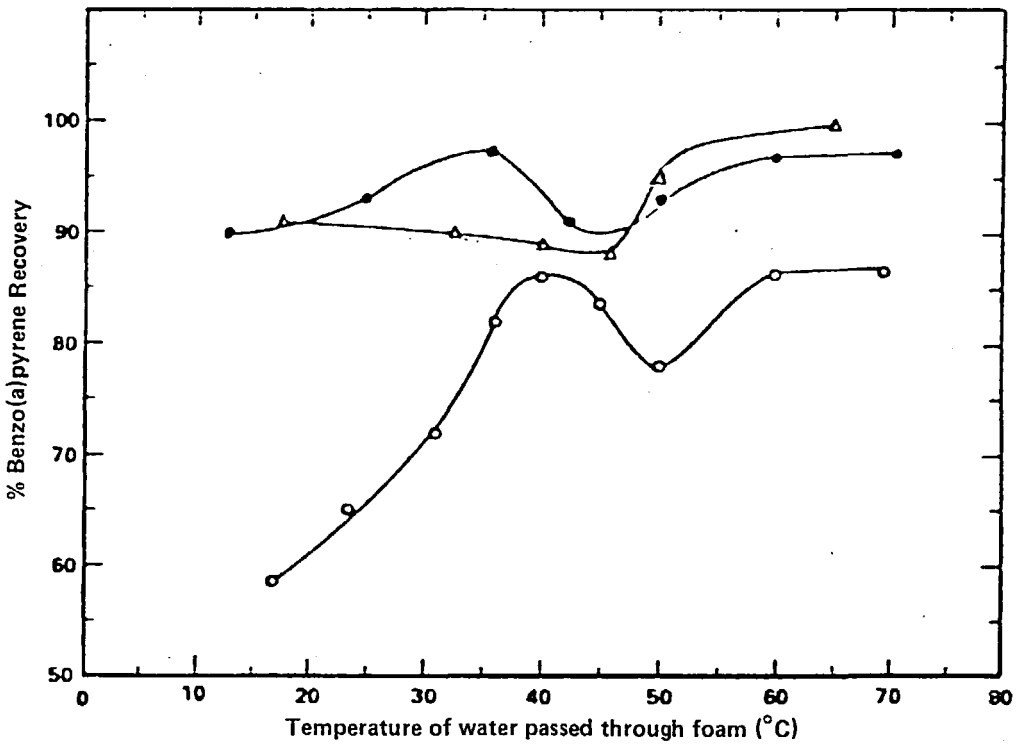


FIGURE 10. Effect of water temperature on extraction efficiency of PAH from polyurethane foam plugs. Water volume, 4 *l*; B(*a*)P concentration, 0.1 ppb; flow rate, 250 ± 10 m*l*/min. O, Tap water (unfiltered); •, filtered tap water; Δ, distilled water.

Downloaded At: 16:07 17 January 2011

ciency, the number of foam plugs was increased. When four foam plugs (two each in two different columns) were used, the retention efficiency for a 20-*l* sample of spiked tap water was raised to 85%. The "four foam plug" sampler was tested with raw drinking water that contained 102 mg/*l* of total suspended solids and 2.4 mg/*l* of total dissolved solids and was spiked with 0.1 ppb B(*a*)P. When 4 *l* was sampled with one foam plug, the retention efficiency was 69%, which was increased to 81% when two foam plugs were used. On the basis of these experiments, Saxena et al.[34] concluded that two columns, each containing two foam plugs, should be adequate to concentrate the B(*a*)P from 20 *l* of finished water, and this configuration should also be used for sampling B(*a*)P from 10 *l* of raw water. When the foam plugs were stored at 4°C for 7 days,[34] no effect on the recovery of B(*a*)P was observed, but only 82% of the B(*a*)P was recovered when the plugs were stored at room temperature for the same period of time.

Basu and Saxena[3] extended these pilot studies with ^{14}C-labeled B(*a*)P to the six PAH recommended for monitoring by the World Health Organization.[35] Using the extraction column configuration described above, the sampling efficiencies for benzo(*a*)pyrene, fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and benzo(ghi)perylene were evaluated with model solutions.

When the foam plugs were used for sampling environmental samples (rather than isotopically labeled spiked water samples), it was necessary to preclean the plugs to remove contaminants that would be eluted with the trace pollutants. The foam plugs were cleaned with cyclohexane and/or benzene by batch or Soxhlet extraction. How-

ever, even after this cleaning, the foam plugs contained 6 ng of fluoranthene and 1 ng of benzo(ghi)perylene per foam plug which necessitated the running of blank determinations with each batch of foam.

When foam plugs or any other adsorbent are used for the sampling of environmental samples, other organic pollutants in addition to the PAH are adsorbed and are subsequently eluted during the extraction step. Some of these compounds interfere with the PAH analysis and a clean-up step is required. The separation scheme used by Basu and Saxena to isolate the PAH is shown in Table 2.

A 60-*l* sample of drinking water was passed through six columns, each containing two foam plugs. After sampling, each column was eluted with 30 m*l* of acetone and 125 m*l* of cyclohexane. The extracts from each column were combined, concentrated, and the solutes were separated as described in Table 2 and analyzed.

The retention efficiency of the polyurethane foam plugs was also investigated with laboratory tap water spiked with PAH at the 25-ppb level.[3] The results of this experiment are shown in Table 3. The plugs maintained the same high efficiency when heavily polluted surface waters were sampled. The limit of detection of the six PAH when 60 *l* of water were sampled using gc/fid is about 5 ng/*l*.

For on-site sampling, Basu and Saxena[36] have employed a portable version of the polyurethane foam plug sampler to analyze ground, raw, and treated waters. The field apparatus consisted of a pumping unit, a thermostated water circulator to maintain the water at 60°C, two columns each containing two foam plugs, and temperature and water flow monitoring devices. In this manner, the flow rate and water temperature conditions optimized in the laboratory could be maintained in the field. The columns were changed after every 20 *l* when sampling treated waters and after every 10 *l* when sampling raw water.

^{14}C-Benzo(a)pyrene was added to the foam plugs as an internal standard before the extraction step. The recovery factor determined for this standard was used to correct the final results for losses in the elution and clean-up steps. The final result must also be corrected for the traces of PAH contributed by the foam plugs. Concentrations of individual PAH as low as 0.2 ng/*l* were determined in drinking water, and concentrations as high as 600 ng/*l* were observed in raw waters.

The use of labeled PAH is a direct and effective technique for testing the efficiency of an adsorbent for extracting PAH from water samples. The data presented by Basu and Saxena show that polyurethane foam plugs are effective in removing PAH from water, however, the nuisance of exchanging columns during sampling and the large volumes of solvents required to elute the PAH from the foam plugs does not make this procedure attractive.

D. Carbon

The carbon-chloroform extraction method was developed by Braus et al.[37] to determine the efficiency of organic solute cleanup in drinking water plants. Carbon has been used for concentrating chlorinated insecticides and biphenyls. Rosen and Middleton[38] used activated carbon filters for determining the concentration of pesticides and found that the results may be low by a factor of two. Hoak[39] studied the adsorption of phenol on activated carbon and found that while the adsorption efficiency was about 94%, the subsequent desorption was as low as 22%. Hoak also noted that chemical changes in the adsorbed phenol could have affected the apparent efficiency of the carbon adsorption method. Eichelberger and Lichtenberg[40] have examined the carbon adsorption method for the recovery of organochlorine and organophosphorous pesticides from water samples. They recovered less than 10% of the fenthion and methyl parathion and were not able to recover any of the malathion, ethion, or methyl tri-

Downloaded At: 16:07 17 January 2011

Table 2
STEPS IN THE SEPARATION OF PAH FROM POLYURETHANE FOAM EXTRACT

Concentrated foam extract in cyclohexane (10 m*l*)
- Wash with two 60-m*l* portions of 4:1 methanol/water
  - Retain cyclohexane layer
  - Discard methanol/water layer
- Wash with two 60-m*l* portions of distilled water
  - Retain cyclohexane layer
  - Discard aqueous layer
- Extract with three 20-m*l* portions of DMSO
  - Retain combined DMSO layer
  - Discard cyclohexane layers
- Add 120 m*l* of distilled water, then extract with two 40-m*l* portions of cyclohexane
  - Retain cyclohexane layers
  - Discard DMSO/water layer
- Dry the cyclohexane layer by passage through anhydrous Na_2SO_4
- Concentrate to 5 m*l*
- Put on the Florisil® column and elute with 125 m*l* of benzene
- Concentrate the eluate to 0.5 m*l*

Downloaded At: 16:07 17 January 2011

Table 3
FOAM RETENTION EFFICIENCIES FOR PAH FROM TREATED WATER

Compound	Amount added to water (μg)	Retention (%)
Fluoranthene	100	100
Benzo(j)fluoranthene	100	88*
Benzo(k)fluoranthene	100	
Benzo(*a*)pyrene	100	81
Indeno(1,2,3-cd)pyrene	100	89
Benzo(ghi)perylene	100	91

Note: Water source, laboratory tap water; water volume, 4 *l*; concentration of each PAH, 25 ppb; detection method, GLC-FID.

* Combined value given since the compounds could not be separated on the GLC column.

thion. Booth[41] found that closely reproducible results could be obtained for the comparison of total chloroform extractables using the carbon adsorption method. However, the *Standard Methods for Examination of Water and Wastewater,* 13th ed., notes that not all organic compounds are adsorbed on carbon and of those adsorbed, not all are desorbed by chloroform.

Van Rossum and Webb[15] have recently carried out a careful investigation of the use of carbon alone and carbon in conjunction with XAD resins for the adsorption of organic pollutants from water. They included several PAH in their model systems. The problem of removing background impurities received careful attention in this study. The carbon used as the adsorbent was Filtrasorb 300® (Pittsburgh Activated Carbon, Pittsburgh, Pa.)

The stock carbon was compared to carbon that had been cleaned by 400 chloroform extraction cycles in a Soxhlet extractor. The results of an in-column wash of one bed volume of acetone and three bed volumes of chloroform of these two carbon samples are shown in Figure 11 ("first wash"), and it can be seen that the results are almost identical. A second wash with three bed volumes of chloroform gave the acceptable blanks shown in Figure 11 ("second wash"). Van Rossum and Webb point out that the time-consuming Soxhlet extraction step is unnecessary for the Filtrasorb 300® when only small amounts of carbon and solvents are used in a water sampling system. The chromatograms shown in Figure 11 were obtained using a polar Carbowax® column. When the same precleaning rinses that were used to obtain the chromatograms in Figure 11 were analyzed on a nonpolar SE-30 column, the chromatogram shown in Figure 12 was obtained. This chromatogram indicates that no precleaning of the carbon is necessary if the solutes extracted from the water sample are to be determined on an SE-30 column. These experiments show that clean or unclean carbon must be defined in terms of the analytical system used. Van Rossum and Webb present data that shows that higher recoveries are obtained from carbon columns prepared with in-column, prewashed material than with unwashed material. Acenaphthene was not recovered from a spiked tap water from either the washed or unwashed carbon when the carbon was extracted with a mixture of acetone and chloroform. In another experiment using carbon adsorbers, the carbon was extracted with benzene in a Soxhlet extractor and less than 20% of the fluoranthene and pyrene were recovered.

On the basis of these experiments, Van Rossum and Webb[15] concluded that XAD-2 or a mixture of XAD-4/8 "...is better in every respect than carbon." However, they used a carbon column as a back-up for an XAD-4/8 column to sample 1000 ℓ of tap water to check if the carbon might retain some compounds that were not adsorbed by the XAD resin. The resin and carbon adsorption traps were eluted separately with acetone and chloroform and the eluates were analyzed by gc/ms. The analyses showed that only some halomethanes and long-chain n-hydrocarbons broke through the XAD column. The carbon was further extracted with toluene in a Soxhlet extraction apparatus. This extraction confirmed that there was no breakthrough of PAH materials from the XAD resin. In spite of these negative results with carbon, Grob[43] has successfully used carbon pellets for the adsorption of organic pollutants including PAH in conjunction with headspace extraction (see Section VI).

IV. LIQUID EXTRACTION

Mieure and Dietrich[44] have examined liquid extraction of organic pollutants from water systems in addition to headspace extraction and thermal desorption methods. They selected methylene chloride as the extraction solvent for the liquid extractions and cited the following advantages: (1) it is available in highly purified form, (2) it is relatively chemically inert, (3) it will dissolve many compounds at low concentration, and (4) since it is denser than water, it is readily separated from the water phase in a separatory funnel.

In the Mieure and Dietrich procedure, a 500-mℓ sample of water is placed in a separatory funnel and 150 g of sodium chloride added to form an almost saturated solution. The high concentration of the electrolyte in the water improves the extraction efficiency of water soluble compounds by a salting-out effect. Then 15 mℓ of methylene chloride is added, the funnel is shaken and when the phases have separated, the methylene chloride phase is drained through a cotton plug into a receiving vessel. Allowing for the solubility of methylene chloride in water, about 10.0 ± 0.3 mℓ are recovered, and if the extraction is complete a 50-fold concentration of the organic pollutants in the water has been achieved. The enrichment can be further enhanced by

Downloaded At: 16:07 17 January 2011

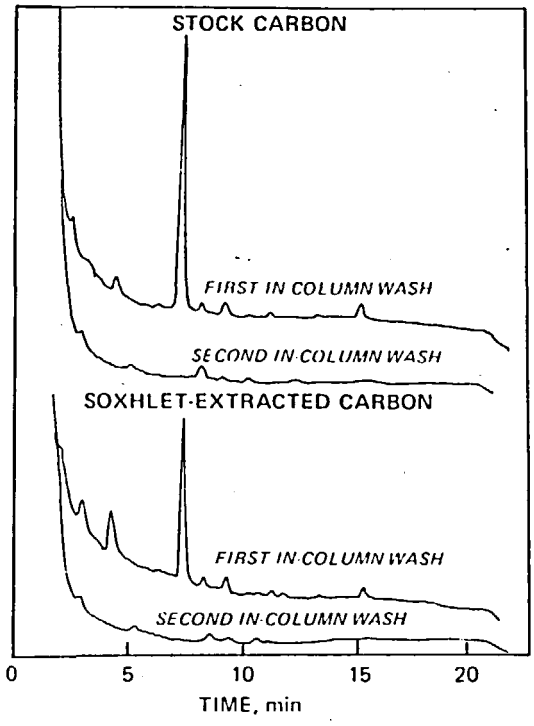


FIGURE 11. Comparison of background impurity levels of stock carbon and Soxhlet-extracted carbon by gas chromatography. Column: Carbowax® 20M-TPA; temperature, 3 min at 80° C; 8°C/min to 170°C.

Downloaded At: 16:07 17 January 2011

evaporating the methylene chloride, but this step involves the risk of losing volatile compounds.

Some organic compounds can be almost completely extracted from water with methylene chloride in one extraction step, while others are quite soluble in water and are only incompletely extracted. Pancirov et al.[45] have measured the efficiency of the direct extraction of PAH from a wastewater sample spiked with ^{14}C B(*a*)A and ^{14}C B(*a*)P using methylene chlorid as the extraction solvent. The first extraction recovered 88% of the PAH and by the third extraction, 98% of the PAH had been recovered.

When quantitative analytical results are needed, a correction must be applied to account for incomplete extractions. The most direct way to arrive at this correction is to run two sequential extractions on the same water sample. The second addition of methylene chloride can be reduced to 10.0 m*l* since the water is already saturated with methylene chloride. If the chromatographic peak area for a component in the first and second extractions are represented by A_1 and A_2 and the extraction efficiency is assumed to be the same for the first and second extraction, the total amount of A in the water sample can be calculated from the equation

$$\text{Total A in water sample} = \frac{A_1^2}{A_1 - A_2} \qquad (4)$$

When samples of spiked tap water were extracted twice and analyzed, and Equation 4 was applied, satisfactory results were obtained at the parts per million level, even

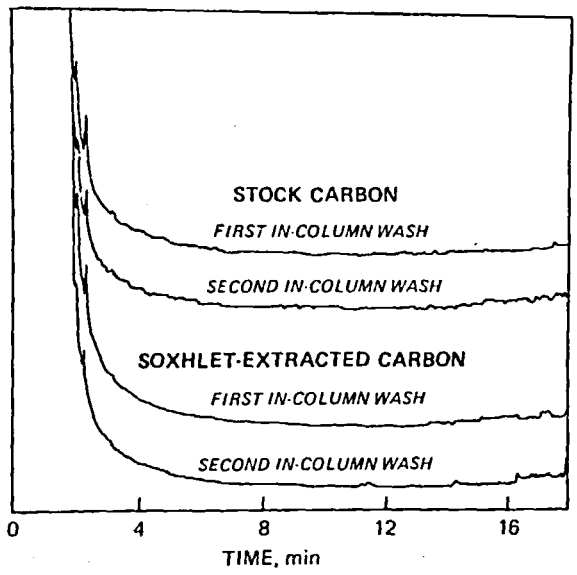


FIGURE 12. Comparison of background impurity levels on stock carbon and Soxhlet-extracted carbon by gas chromatography with SE-30 column. Temperature 100 to 225°C at 7°C/min.

Downloaded At: 16:07 17 January 2011

when the percentage recovered in the first extraction was less than 30%. A second approach to determine the total amount of A in the water sample is to extract the sample several times, combine the extracts, and analyze them. A third approach is to prepare and analyze standard samples. The latter method can be very time consuming for multicomponent solutions.

Grob et al.[46] have also examined the potential of liquid extraction for the recovery of organic pollutants from water at concentrations of 10 ppt (10 pg/g). As an example, a 1-*l* sample is extracted with 100 m*l* of an organic solvent. If the extraction efficiency is assumed to be 100% and if the extract is then reduced to 2μ*l* for a single injection onto a capillary column, the solvent is concentrated by a factor of 50,000. However, impurities in the solvent are also concentrated by this factor so that the resulting chromatogram contains both the original impurities in the water and in the solvent. Grob et al.[46] conclude that the combined effect of the losses of the pollutants and the enrichment of the solvent impurities make this procedure impractical. To avoid the problems created by large volume reductions, they developed a unique liquid extraction method. In this method, 1 *l* of water is extracted by 200 μ*l* of solvent, so that very little if any further concentration is required before the sample is injected into the gc. To achieve a reasonable extraction with so small a volume of solvent, a solvent of very low aqueous solubility is necessary, so that the fraction of solvent remaining in the aqueous phase is minimized. Furthermore, any solvent dissolved in water solubilizes trace levels of organic material. This effect becomes the important factor in the distribution of organic substances between the phases at extreme trace level concentrations. As a result, distributions that cannot be predicted from simple distribution coefficient considerations may occur. The solvents that best meet these requirements are the higher alkanes; however, pentane was selected as the best compromise between low solubility, reasonable equilibration time, and a low gas chromatographic retention time, which allows the more volatile water pollutants to be detected without solvent masking.

Grob et al.[46] used a series of even-numbered 1-chloroalkanes as internal standards and these were added to the water samples containing the unknown pollutants. The advantages of using this homologous series as internal standards are twofold: (1) the compounds of the series are generally absent in polluted waters and are readily identified on the gas chromatogram, and (2) recovery factors as a function of the varying volatility of extracted substances can be interpreted. To carry out the extraction, 0.6 mℓ of pentane is added to 900 mℓ of the water sample at 12°C in a 1-ℓ volumetric flask and the flask is shaken vigorously by hand for 2 min. More water is added to raise the liquid level into the narrow neck. Then 1 mℓ, containing the pentane and some water, is removed and transferred to a 15 × 4 mm glass tube. The organic phase, which is about 200 $\mu\ell$, is transferred from this tube into a conical test tube. In the case of heavily polluted waters, the extract can be analyzed directly, or in the case of very pure waters, the volume of the extract is reduced to 3 $\mu\ell$ by evaporation. The losses of volatile solutes are gauged by the internal standards.

The results of this liquid extraction procedure are compared with the results obtained from headspace analysis (see Section VI) using a water sample spiked with 2.5 ppb of diesel oil. As might be expected, liquid extraction is only one third as efficient as headspace analysis for low to medium molecular weight substances; at C_{20} (eicosane), both methods are equivalent, and for high molecular weight substances, liquid extraction is more efficient.

Murray[46a] has developed an extraction flask for liquid extractions with small volumes of solvent using Grob's method.[46] In place of the 1-ℓ volumetric flask, Murray has used a two-neck 1-ℓ flask with a capillary tube sealed to a shortened center neck. Then 980 mℓ of water and 200 $\mu\ell$ of hexane are shaken manually for 2 min. The extraction flask is then tilted, so that by the addition of more water through the sidearm, the solvent layer is forced into the capillary and can be readily recovered.

Acheson et al.[4] have compared conventional liquid extraction using a separatory funnel, continuous solvent extraction, and the Ultra-Turrax® (an ultrasonic mixer/homogenizer) method. They found that extraction in a separatory funnel gave low results and rejected this method.

For water samples free of suspended solids, the Ultra-Turrax® method and continuous solvent extraction method gave comparable recoveries (~84%) for pyrene at a concentration of 0.3 $\mu g/\ell$. For benzo(ghi)perylene at a concentration of 0.1 $\mu g/\ell$, the Ultra-Turrax® method gave a recovery of 82%, but only 55% was recovered by continuous solvent extraction. When Fuller's earth was added to the water as a suspended solid, the extraction efficiency by both methods dropped, but the recovery by the Ultra-Turrax® method was significantly better than by solvent extraction. On the basis of these experiments, Acheson et al. selected the Ultra-Turrax® method for all their tests.

Acheson et al. investigated several factors that influence the extraction and analysis of PAH in environmental water samples spiked with pyrene and benzo(ghi)perylene. Their results showed that extraction efficiency varies with both the concentration of the PAH in the water sample and with the amount of suspended solids in the water.

The effect of prolonged mixing of water samples, both with and without suspended solids, spiked with PAH and stirred in the dark for 6 hr, was investigated. The 6-hr mixing lowered the extraction efficiency equally for samples with and without suspended solids. Acheson et al.[4] postulate, and we concur, that these results can be explained by adsorption of PAH onto the walls of the mixing vessel. They conclude, as we have noted previously (Section II), that it is important to sample water directly into the extraction vessel and to carry out the extraction as quickly as possible.

Harrison et al.[47] have studied the effect of water chlorination on the levels of some PAH in water. For this study they used 5-ℓ samples of water spiked with eight PAH

Downloaded At: 16:07 17 January 2011

and employed the methylene chloride/Ultra-Turrax® extraction method of Acheson et al.[4] They added 300 m*l* of distilled methylene chloride and emulsified the samples for 5 min in the Ultra-Turrax® apparatus. After standing in the dark overnight, the methylene chloride layer was separated, concentrated, and analyzed by gc. Using octacosane as an internal standard, recovery efficiencies for the eight PAH ranged from 64 to 68%. Harrison et al.[47] studied the effect of a time delay on the extraction efficiency of the PAH from water. A standing time of 45 min did not affect the recovery efficiency of benzo(*a*)pyrene and perylene, decreased the recovery of pyrene, fluoranthene, benz(*a*)anthracene and benzo(k)fluoranthene by 10%, and decreased the recovery of indeno(1,2,3-cd) pyrene and benzo(ghi)perylene by 20%. The concentration of free chlorine, the temperature, and pH of the water also affected the recovery of PAH.

Particulate matter was found to affect significantly the PAH level of the water. When larger particles settled out, only a small reduction of the PAH level in the water was observed, but a 50% reduction in PAH occurred when the smaller particles were removed by filtration. These observations of Harrison et al.[47] are in accordance with the estimate of Reichert et al.[48] that 60% of the PAH in river waters exist adsorbed on particulate matter. Borneff and Fischer[49] have noted that the backwash mud from sand filters contains high levels of PAH. Paralleling these observations, Harrison et al.[50] have previously reported that filtration of water through beds of activated carbon removed up to 99% of the PAH.

Continuous liquid extraction overcomes two limiting factors in solvent extraction: (1) the saturation capacity of the solvent is eliminated by continuously providing fresh solvent, and (2) the volume of liquid available for extraction is not limited as in batch extraction. Continuous liquid extractors designed to use either heavier- or lighter-than-water solvents have been described by Goldberg et al.[51] The extractors consist of a two-cycle system: a water cycle and a solvent cycle. The extractor that uses lighter-than-water solvent is shown in Figure 13. Water enters at A and exits at B, passing through the chamber C which is half-filled with solvent. The solvent cycles exclusively in the extractor. The bulb C contains the solvent. When the bulb is gently heated, the solvent vaporizes, rises through the apparatus, is condensed at H, and drops into the funnel J.The hydraulic head in the funnel stem forces the solvent through the fritted disc K. The frit homogenizes the solvent which results in fine beadlike particles which form an emulsion as they rise through the water in chamber C, extracting organic solutes. The emulsion separates at L and the solvent-solute mixture spills over into the flask E.

The heavier-than-water solvent extractor is shown in Figure 14. Water enters at M and exits at N. While in the lower section of the extractor P, the water flows through the solvent. The solvent cycle is as follows: the solvent is vaporized in Q, condenses at S, and drops into the funnel U. In the funnel, a hydraulic head is created and this forces the solvent through the frit V and it drops into the upper part of the extractor W. Extraction of the organic solutes takes place at the interface between the emulsified solvent and the water. A stirring bar X stirs the solvent-water mix. The solvent separates in the lower section of the extractor and flows through the tube Y into the bulb Q. The extracted organic solutes are concentrated in flask Q.

The extractors were tested by setting up three solvent heavier-than-water extractors in one series and four solvent lighter-than-water extractors in a second series. Each extractor was charged with 500 m*l* of solvent, and a continuous feed of test water was passed through the extractors. Data were presented for a number of solute-solvent combinations.

Since a large volume of solvent is involved in this system, the extraction is followed by a volume reduction step with a Kuderna-Danish apparatus. This step involves the risk of concentrating impurities in the solvents as well as losing some of the lighter

Downloaded At: 16:07 17 January 2011

Downloaded At: 16:07 17 January 2011

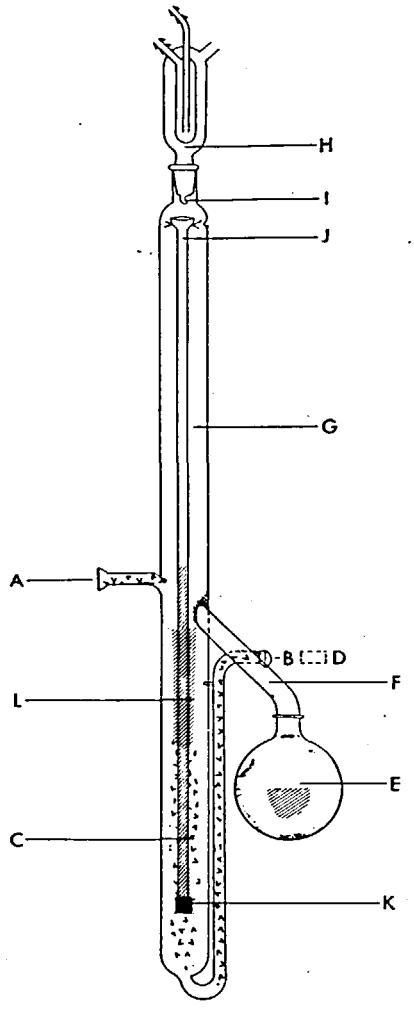


FIGURE 13. Extractor design for lighter-than-water solvents. The designated parts are described in the text.

solutes. However, concentration factors up to 10^5 can be achieved with the system. The dipole moment difference between the solvent and solute was shown to be an index of extraction efficiency for liquid-liquid extraction. Kahn and Wayman[52] have also described a continuous extractor using lighter-than-water organic solvents.

Another continuous liquid-liquid extraction apparatus has been described by Ahnoff and Josefsson.[53] The apparatus is in principle a mixer-settler in which the mixing and settling chambers are not completely separated but combined in one cylinder. The efficiency of this extractor was tested by analyzing standard solutions in three extractors connected in series. In these tests cyclohexane was used as the solvent, and standard solutions of pesticides prepared in triple-distilled water were pumped through the three extractors at pump rates of 1.1, 2, and 5 *l*/hr. At a pumping rate of 1.1 or 2 *l*/hr, the extraction efficiency averaged between 89 and 96% and dropped to between 83 and 86% when the pump rate was increased to 5 *l*/hr.

The apparatus was field tested with water volumes of 175 to 305 *l*, using series and

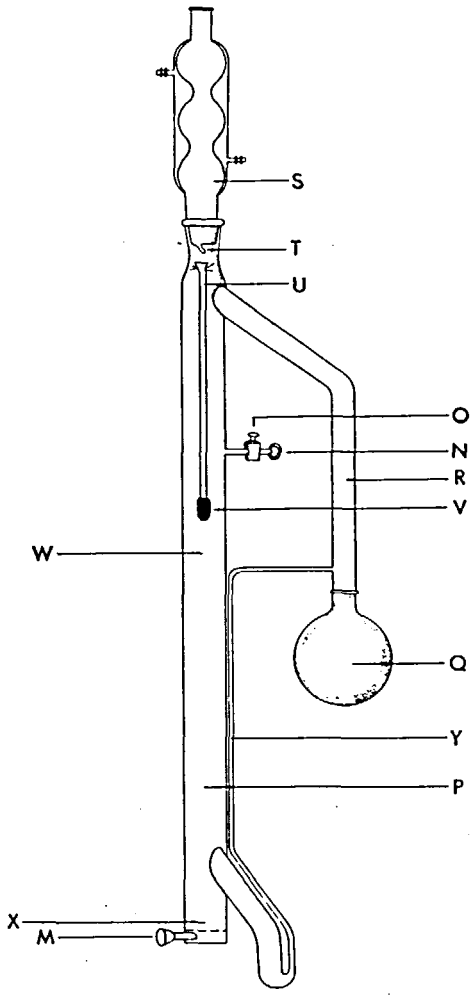


FIGURE 14. Extractor design for solvents heavier than water. The designated parts are described in the text.

parallel arrangements at flow rates between 3 and 5 ℓ/hr. The extracted solvent was cleaned and concentrated and analyzed with an ECD gas chromatograph; PCB concentrations in the range 0.1 to 1.0 ng/ℓ were reported.

More recently Ahnoff and Josefsson[54] have published the description of an integrated sampler which combines two extractors of the type described above placed in series. Data is given for the extraction and analysis of PCB in estuarine water at a dredging sludge disposal area.

V. COUPLED-COLUMN LIQUID CHROMATOGRAPHY

The principle of coupled-column/high pressure liquid chromatography has been used by a number of investigators to concentrate and analyze PAH from water systems. In this method the PAH are enriched on an adsorption column, directly eluted from this adsorption column onto an analytical column, and separated by reversed phase high pressure liquid chromatography. The advantages of this method are first

Downloaded At: 16:07 17 January 2011

that the volume of the sample is minimized, since all the PAH in the water sample that are extracted are transferred to the analytical column and determined, and second that sample handling for extraction and concentration is eliminated.

A system of this type has been described by Eisenbeiss et al.[55] A block diagram of the enrichment and analytical system is shown in Figure 15. The water sample is initially pumped through the enrichment column. At the end of the sampling period, the four-port valve is rotated and a second pump forces the mobile phase through the enrichment column. The PAH are eluted and transferred to the analytical column where they are separated.

The packing of the enrichment precolumn must adsorb the PAH from the water sample and readily desorb the PAH when the mobile phase used in the analytical column is passed through it. Eisenbeiss et al.[55] found that no commercially available packing would fulfill both these requirements. They developed a special packing for the precolumn which is identified only as a "Special Merck packing". To achieve enrichment on this collection column, it was necessary that the water sample contain 17.5 to 20% isopropanol. This configuration was tested with a 500-mℓ test solution containing 17.5% isopropanol, 100 ng fluoranthene, 20 ng B(b)F, 20 ng B(k)F, 20 ng B(*a*)P, 20 ng benzo(ghi)perylene, and 20 ng IP, and the recovery factors are listed in Table 4.

Ogan et al.[56] have reported a similar analytical approach to the determination of PAH in water. In their procedure, they use a precolumn 10.0 × 0.26 cm packed with 40 μm C_{18}-bonded phase pellicular material, ODS-Sil-X-11, for the extraction of the PAH. About 800 mℓ of a model solution containing 20% methanol, and the five PAH, 7H-benz(de)anthracene-7-one (BA-one), fluoranthene, perylene, benzo(*a*)pyrene, and benzo(ghi)perylene were used to measure recovery factors and the sensitivity of the method.

The extraction and analytical apparatus used by Ogan et al.[56] is shown in Figure 16. In operation, the injection valve is turned to the INJECT position and 400 mℓ of the sample are pumped through the sample pump to equilibrate the pump and lines with the sample. The sample pump is turned off, the valve is turned to the FILL position, and 100 mℓ of sample are pumped through the extraction column and out to waste. After 100 mℓ have been pumped through the extraction column, the sample pump is stopped, the valve is turned to the INJECT position again, the LC pump is started and the extraction column is backflushed with the mobile phase and the PAH are transferred onto the analytical column. Since only 500 mℓ of the water sample have been used up to this point, a second 100-mℓ sample is pumped through the extraction column, while the first sample is eluting from the analytical column. With this procedure a duplicate can be run as soon as the first sample has eluted. The percentage recovery of the individual PAH, as measured by the ratio of chromatographic peak areas of diluted samples to the areas obtained when the sample was directly injected into the chromatograph, is uniformly high and significantly better than the recoveries obtained by most other methods (Table 5). The method of Ogan et al., when used with a 400-mℓ sample, allows detection of PAH in water samples at levels as low as 0.2 ng/ℓ and is linear up to the microgram per liter range of heavily polluted waters.

In all the procedures for sampling, concentration, and analysis reported and used, the adsorption of PAH on glass and metal parts can seriously affect the recovery efficiency. Ogan et al. found that the flushing of all the components with the sample to saturate the adsorption sites and silanization of the glass significantly improved recoveries.

Other investigators[57,58] have also reported on the use of an hplc sampling and analytical procedure for the analysis of PAH in water. These other procedures do not include the addition of alcohol to the water sample before it is pumped through the

Downloaded At: 16:07 17 January 2011

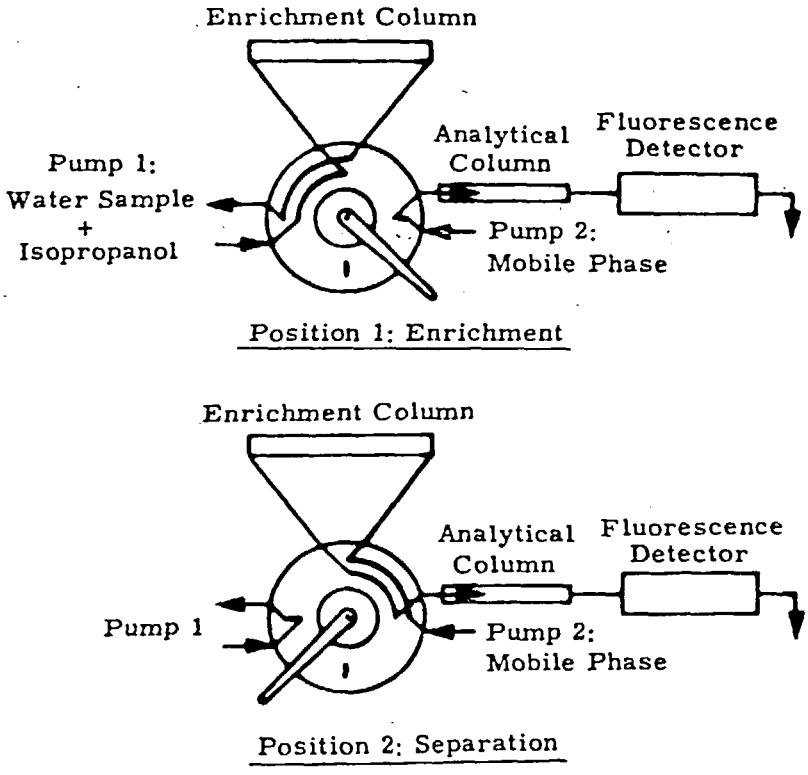


FIGURE 15. Configuration of components for the two positions of the injection valve for the separation and determination of PAH by hplc.

Downloaded At: 16:07 17 January 2011

precolumn. Eisenbeiss et al.[55] reported that without the addition of isopropanol, there was poor wettability of the precolumn packing and no enrichment of PAH. Ogan et al.[56] reported that the addition of methanol greatly reduces adsorption on glass and metal surfaces and recovery is improved. They state that "...methanol undoubtedly improves the solubility of the PAH in the aqueous solution." Also it may enhance the interaction of the PAH with the extraction column packing ("wetting" the surface), or it may directly modify the packing surface.[56]

May et al.[57,58] used coupled-column chromatography to analyze the water for PAH remaining after headspace analysis. They used a 6.5 × 0.6 cm O.D. stainless steel precolumn packed with Bondapak C_{18}, a 37- to 50-μm pellicular support with a bonded C_{18} stationary phase. The water sample was pumped through this column at the rate of 10 mℓ/min. After the sample was passed through the precolumn, the precolumn was attached to a 30 × 0.6 cm analytical column that was packed with μBondapak C_{18}, a 10-μm microparticulate support with a bonded C_{18} stationary phase, and the sample was eluted with a mobile phase that was programmed from 30:70 methanol/water to 100% methanol. The recovery factors for five PAH by this procedure are shown in Table 6. It can be seen that the recoveries are not as high as those reported by Eisenbeiss et al.[55] and Ogan et al.[56] where an alcohol was added to the water sample before it was pumped through the preconcentration column.

Oyler et al.[59] have also used coupled-column hplc in a study to determine the aqueous chlorination reaction products of PAH, and they also did not add alcohol to

Table 4
RECOVERY FOR THE PRECOLUMN ENRICHMENT RELATIVE TO DIRECT INJECTION[a] OF THE STANDARD SAMPLE

PAH compounds	Recovery rates (%)
Fluoranthene	100
Benzo(b)fluoranthene	85
Benzo(k)fluoranthene	75
Benzo(a)pyrene	76
Benzo(ghi)perylene	86
Indeno(1,2,3-cd)pyrene	85

[a] Determined as the ratio of chromatographic peak heights obtained from a 10-μl PAH standard solution in 500 ml of water and concentrated on the precolumn before analysis to the peak heights obtained by the direct injection of a 10-μl standard sample onto the analytical column.

Downloaded At: 16:07 17 January 2011

the water. Their reported recovery factors range from 36 to 115%. In this study, however, pyrene (MW206) was the highest molecular weight PAH used in the model solutions.

Euston and Baker[60] have reported several procedures in which the automatic features of the Hewlett-Packard model 10848 liquid chromatograph can be used to include a concentration step as part of the analytical cycle. One option is to replace the water, which is normally used as the "weaker" component of the mobile phase in reversed-phase chromatography, by the water sample and to concentrate the impurities on the column in this manner. The column is first cleaned by pumping 100% acetonitrile through it for 5 min. At the end of this period, the mobile phase is changed to the environmental or spiked water sample which is pumped through the column for 50 min at 2 ml/min. In this manner, the nonpolar impurities from the 100-ml water sample are concentrated at the inlet of the column. At the end of the sampling period the composition of the mobile phase is adjusted to elute the PAH. The sharp peaks in the resulting chromatogram indicate that there was only negligible migration of PAH on the column during the 50-min loading period.

A second option described by Euston et al. is an automated version of the procedure used by Eisenbeiss et al.[55] and Ogan et al.[56] An automatically controlled six-port valve first switched the water sample to a 5 cm × 2.1 mm I.D. precolumn packed with Perisorb® RP (a superficially porous reversed-phase material) and out to waste. After the desired volume of water had been sampled, the six-port valve was automatically switched, so that the mobile phase backflushed the solutes that are adsorbed on the precolumn onto the analytical column. No data for recovery factors were given. The apparatus has a sensitivity for PAH in the range of 70 pg to 1 ng, depending on the molar absorptivity of the individual PAH.

Huber and Becker[61] also used a high pressure liquid chromatograph to enrich water samples by displacement chromatography. The water sample was pumped through the enrichment column and the trace components were adsorbed on the stationary phase.

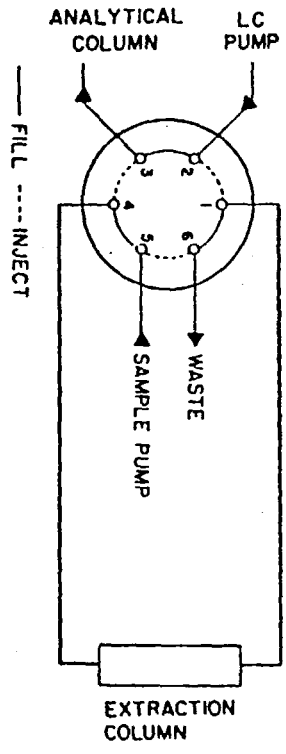


FIGURE 16. Connection of the extraction column to the loop injection valve for the separation and determination of PAH by hplc. The solvent path is indicated for the valve in the FILL position (—) and the INJECT position (---).

Table 5
RECOVERY EFFICIENCY OF PAH BY THE INTEGRATED HPLC TECHNIQUE OF OGAN[56]

Compound	Recovery (%)
7H-Benz(de)anthracene-7-one	97
Fluoranthene	101
Perylene	98
Benzo(a)pyrene	94
Benzo(ghi)perylene	96

The trace components were subsequently shifted to the end of the column by the displacer fluid and measured either in-line or collected for off-line measurement. The enrichment of dibenz(a,h)anthracene is described. LiChrosorb® RP-18 (5 μm) was used as the column packing and dioxane was used as the displacer. A 250-mℓ sample

Downloaded At: 16:07 17 January 2011

Table 6
RECOVERY FROM WATER (2 l) OF INTERNAL STANDARD COMPOUNDS USING COUPLED-COLUMN LIQUID CHROMATOGRAPHY

Compound	Concentration (μg/kg)	Recovery (%)
Naphthalene	28	19 ± 2
Phenanthrene	1.5	92 ± 12
Pyrene	2	78 ± 17
Benzo(*a*)pyrene	1.5	58 ± 12
Dibenzanthracene	3	14 ± 8

of an aqueous saturated solution of dibenz(a,h)anthracene was extracted and concentrated to 0.2 m*l*, corresponding to an enrichment factor of 1250. The applicability to field sampling was investigated by loading samples on the columns and storing them for 3 days before displacement. Only slight tailing of the enriched sample was observed.

VI. HEADSPACE ANALYSIS

In headspace analysis, nitrogen or another inert gas is bubbled through or over the water sample and the inert gas, water vapor, and organic solutes are passed through a resin or cryogenic trap. When a hydrophobic resin trap such as Amberlite® XAD-2 or Tenax-GC® is used, the organic compounds are adsorbed on the resin and the inert gas and water vapor pass on through the trap. The advantages of headspace analysis are as follows:[44]

1. Many handling problems such as the filtering of particulates are avoided.
2. The technique can be readily automated for continuous monitoring.
3. No solvent extraction is involved, so that low molecular weight, volatile compounds are not masked by the gc solvent peak and left undetected.

On the other hand, there is the disadvantage that nonvolatile, very insoluble pollutants, such as the heavier PAH, or pollutants that are adsorbed on particulates will not be completely removed from the water sample, giving rise to low results, whereas a pollutant concentrated in a surface film will give high results.

Zlatkis et al.[62,63] used a small tube filled with Tenax-GC® to analyze trace volatile metabolites in serum and plasma. The organic substances collected on the Tenax-GC® were thermally desorbed, collected in a cold trap, and determined by gas chromatography.

Mieure and Dietrich[44] have used headspace analysis to determine the organic pollutants present in water. The method was used for substances that had boiling points less than 250°C and concentrations in the parts per million range. The apparatus consisted of a 125-m*l* filter flask in which a 10-m*l* water sample was placed. Tenax-GC® or another solid adsorbent was used in the collection column. Laboratory air purified by passage through a charcoal trap was used to sweep the organics onto the collection column. Good reproducibility was achieved when the temperature of the flask was held constant at 25 ± 1°C. Because detection limits in this method are a function of

Downloaded At: 16:07 17 January 2011

the volatility of the solute, in a 10-g water sample they range between 1 ppm for relatively nonvolatile solutes to 1 ppb for volatile solutes. Sensitivity of the method can be increased or the analysis time shortened by heating the sample. Mieure and Dietrich point out that a 25°C increase in water temperature results in a 20-fold increase in the concentration of the volatile organics over the water. The analysis time can also be reduced if the inert gas is bubbled through the water rather than passed over it.

May et al.[57,58,64-66] have developed a procedure for the determination of hydrocarbons in marine sediments and seawater. The procedure uses headspace analysis for the light hydrocarbons and low molecular weight PAH, and coupled-column liquid chromatography for the nonvolatile compounds, which include the high molecular weight PAH. Water samples are collected in the field, an internal standard consisting of a solution of aromatic hydrocarbons is added, and the sample is stored in a freezer at −10°C. Prior to analysis the samples are thawed overnight in a laminar flow hood in a room maintained at 4°C. After thawing, approximately 750 mℓ of water or 100 g of sediment are transferred to the headspace sampling flask. In the case of the sediment samples, approximately 600 mℓ of hydrocarbon-free water (distilled from potassium permanganate and passed through an XAD-2 column) and the internal standard are added to the 100 g of sediment in the headspace analysis apparatus. The headspace analysis is carried out with scrubbed nitrogen in the apparatus shown in Figure 17. Sampling is carried out for 2 hr at room temperature, then the flask is heated to 70°C and sampling is continued for a further 2 hr. The Tenax-GC® trap is cooled with a stream of air passed through a copper coil immersed in an ice bath. At the lower temperatures there is less likelihood of losses of adsorbed material from the Tenax-GC. At the end of the sampling period, the Tenax-GC® collection column is disconnected from the apparatus, cooled, and dried for 2 hr by a stream of nitrogen gas at a flow rate of 150 mℓ/min. No data were given for losses of adsorbed material during this step.

The dried Tenax-GC® traps are capped and stored at 4°C. The materials adsorbed on the trap are determined by installing the trap as a precolumn between the injection port and a coiled glass SE-30-coated SCOT column (shown in Figure 18) and the sample is transferred to the gc column by flash heating. After the volatiles have been extracted from the water or sediment sample by headspace analysis, the water remaining in the flask is pumped through a liquid chromatography precolumn which is subsequently attached to a liquid chromatograph capable of providing gradient elution.

The efficiency of the headspace analysis method can be assessed from the internal standard data listed in Tables 7 and 8 which show the recovery factors obtained from the headspace/gas chromatography analysis. The improvement in recovery factors when the sampling time is increased is shown in Table 8.

The Stepan and Smith method[7] is similar to that of May et al. The water sample is placed in the three-neck flask of the headspace apparatus, the flask is placed in a water bath thermostated at 95 ± 0.3°C, and nitrogen is bubbled through the sample at 10 mℓ/min. The trace organics are collected on a resin adsorption column that contains 2 g of XAD-2. The extraction time is 1 hr. Stepan and Smith were able to increase the extraction efficiency from 68 to 78% by placing the 2 g of XAD-2 in a 75 × 0.4 cm I.D. coil rather than a 8 × 1.2 cm cartridge. They were able to increase the recovery of ethyl benzene to 89% when the temperature of the coil containing the XAD-2 was reduced from 20 to 3°C. A similar improvement in recovery by cooling the polymeric adsorbent was also noted by Chesler et al. and May et al.[57,58]

The resin was extracted in the standard manner with one 20-mℓ portion and one 10-mℓ portion of diethyl ether. The eluates were combined, dried over magnesium sulfate, and analyzed by gc.

Downloaded At: 16:07 17 January 2011

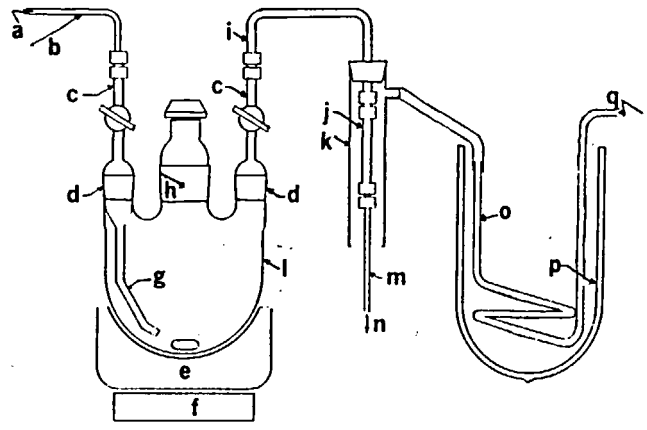


FIGURE 17. Headspace sampling vessel. (a) N_2 Gas inlet; (b) copper tubing, 1/8 in.; (c) glass tubing, ¼ in.; (d) tapered joint 24/40; (e) heating mantle; (f) magnetic stirrer; (g) dispersion tube with coarse frit; (h) tapered joint 45/50; (i) glass transfer line, ¼ in.; (j) Tenax® trap; (k) glass cooling jacket maintained at 15°C with air; (l) 2-ℓ round bottom flask; (m) Teflon® tubing, 1/8 in.; (n) to rotameter (o) copper coil; (p) ice bath; and (q) compressed air inlet.

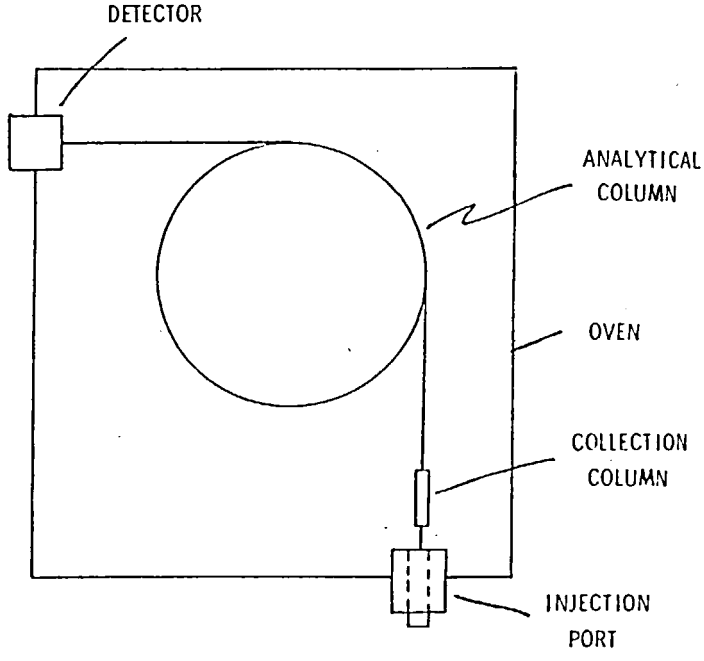


FIGURE 18. Collection column connected to an analytical column in gc oven.

Grob[43] has carefully examined the problem of the extraction of organic pollutants from water. He has developed a highly sensitive and sophisticated headspace analysis procedure that, in conjunction with glass capillary gas chromatography, has made pos-

Downloaded At: 16:07 17 January 2011

Table 7
RECOVERY FROM WATER (600 ml) OF INTERNAL STANDARD COMPOUNDS USING HEADSPACE SAMPLING AND GAS CHROMATOGRAPHY

Compound	Concentration (μg/kg)	Recovery (%)
Mesitylene	2.7	8 ± 5
Naphthalene	3.5	38 ± 7
n-Propylnaphthalene	3.3	51 ± 10
Phenanthrene	3.3	19 ± 12

Table 8
PERCENT RECOVERY OF AROMATIC AND ALIPHATIC HYDROCARBONS FROM WATER BY HEADSPACE SAMPLING AND GAS CHROMATOGRAPHY

Compound	4-Hr sampling	18-Hr sampling
Mesitylene	8 ± 2[a] (6)[b]	6 ± 1 (3)
Naphthalene	29 ± 4 (6)	52 ± 9 (3)
2,3,6-Trimethyl naphthalene	—	95 ± 5 (3)
Phenanthrene	12 ± 4 (6)	92 ± 4 (3)
Pyrene	—	82 ± 4 (4)
5-Methyltetradecane	62 ± 4 (6)	84 ± 3 (3)
2-Methyloctadecane	57 ± 8 (6)	94 ± 3 (3)

[a] Data reported as the SD of a set of replicate values from the mean of the replicate values.
[b] Denotes number of samples.

sible the identification of more than 100 pollutants from drinking water. These contaminants include compounds up to C_{24} at concentrations down to the parts per trillion (pg/g) level.

Grob rejected solvent extraction for pollutants at the parts per trillion level. The extraction can be made very efficient by using a countercurrent system; however, large volumes of solvent are involved which must subsequently be concentrated. The concentration step introduces losses of extracted sample and increases the mole fractions of the impurities that are present in the solvent. The drawback to headspace analysis is the large volume of helium or nitrogen at high flow rate that is required to extract the heavier, low vapor pressure pollutants. Grob concluded that it was not possible to purify these gases sufficiently or to effect 100% collection of the extracted material in either a cold trap or on a solid adsorbent.

Grob has overcome these drawbacks in headspace analysis with a closed circuit stripping system which includes a 1.5- to 5-mg carbon disc as the adsorbent to collect the organic materials. The inert gas-stripping system operated at 20 to 30°C and illustrated in Figure 19 is used to recover organic solutes up to about C_{14}, and a water-vapor stripping system is used for the recovery of higher molecular weight hydrocarbons.

Downloaded At: 16:07 17 January 2011

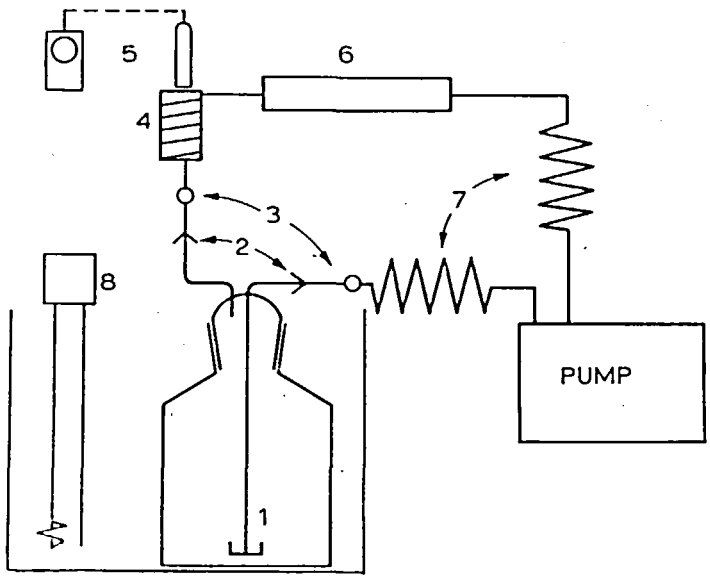


FIGURE 19. Closed circuit apparatus for stripping with inert gas. (1) Glass frit with porosity 0; (2) Rotulex® bowl joints with PTFE seal (Sovirel®); (3) fused-glass/metal connections; (4) aluminum heating cylinder; (5) soldering iron (15 W) with time relay; (6) filter holder; (7) stainless steel tubing, 1 m × 3.2 mm O.D., 2.0 mm I.D.; (8) thermostatic water bath.

Downloaded At: 16:07 17 January 2011

The feature of the system that is especially interesting is the use of the 1.5- to 5-mg charcoal adsorbent disc to collect the organic materials. Charcoal has not been widely used as an adsorbent in pollution studies because of many reported difficulties with irreversible adsorption of some materials and the structural modification of others.[44] Grob has shown that the first problem arises only if the amount of adsorbed material is too low in comparison to the active adsorbent surface. Since the specific surface area of carbon is extremely high, an adsorbing filter with a small amount of carbon should be used. Structural modification of the adsorbates have been avoided by the use of ultrapure carbon, free from organic salts that can catalyze structural changes,[67] and by the use of a solvent instead of heating to desorb the organics.[68] A further advantage achieved by the use of a small amount of adsorbent is that the organics can be extracted from the filter with a small volume of purified solvent.[69] For the 1.5-mg filter, 5 to 15 μl of carbon disulfide purified by the method of Obach[70] are used and for the 5-mg filter, 10 to 100 μl of methylene chloride are used. No further concentration of the extracts is required for gc analysis.

The filters are prepared by drawing a weighed amount of carbon into a constricted glass tube and fitting the tube with stainless steel screens to retain the carbon. The filter is washed with dilute nitric acid, water, methanol, and chloroform and stored in carbon disulfide overnight. After this treatment, the filter can be used without further activation. Between uses, the filters are stored in an organic solvent and appear to have an unlimited lifetime.

The sensitivity of the method is so great that a number of special precautions must be taken. Materials leached out of PTFE have been identified in the chromatogram, and the use of this material is avoided in the apparatus. In addition, the filter tube must be held in place by stainless steel or glass sleeves. The apparatus must be absolutely gas tight to prevent the introduction of ambient air. It is noted that the introduc-

tion of 1 to 2 *l* of ambient air into the apparatus would introduce as many pollutants as are present in 5 *l* of drinking water. Air leakage is avoided by immersing the apparatus in fresh tap water. The method is so sensitive that care must be taken to avoid turbulence when introducing the water sample into the apparatus to avoid dissolution of contaminants from the laboratory atmosphere. The gas used in the stripping circuit must be purified with an auxiliary filter before the analytical filter is installed.

In drinking water where the concentration of major pollutants is about 5 ppt, stripping with air at room temperature can be used to extract the alkanes up to C_{20} with losses of less than 20%. In lightly polluted water, the limit is C_{22}. For oxygenated, nitrogenated, and aromatic compounds, the recovery factors of the individual compounds should be checked. Stripping with water vapor increases the recovery efficiency for high molecular weight substances and polar materials, but low molecular weight substances are lost. Recovery factors increase with higher concentration of pollutants.

To appreciate more fully the advantages of this extraction procedure, it is valuable to examine the material balance aspects of the system. In a 5-*l* sample of pure drinking water, 20 ng of an organic pollutant corresponds to a pollution level of 4 ppt. This will represent 1 of perhaps 50 similar organic compounds in the sample. If the extraction efficiency from water is 50%, the extraction efficiency from charcoal is 100%, and the adsorbates are eluted with 10 μl of carbon disulfide, the final sample contains 1 ng of pollutant in 1 μl of solvent. This method therefore has the same attraction as thermal desorption (*vide infra*) in that almost the total extract is used in the analysis. In the case of extremely pure water samples, the 10 μl extract can be further concentrated.

VII. THERMAL DESORPTION

In thermal desorption, all of the organic pollutants from a water sample that have been adsorbed on a resin column are transferred onto a gc column. This is contrasted to an extraction procedure in which the volume of the extracted sample is reduced to 0.2 to 1.0 m*l*, and a 2- to 10-μl aliquot (or about 1/500) is used for the gc analysis. Thus, by using thermal desorption, a gain of a factor of 500 in sensitivity is achieved. The analyst has the option of either utilizing this gain in sensitivity or reducing the volume of the water sample from 1 *l* to 20 to 25 m*l*. A second advantage of thermal desorption is that volatile compounds are not lost in the extraction and preconcentration steps.

In 1973, Mieure and Dietrich[44] investigated thermal desorption to determine organic pollutants in air and water. They suggested that the samples be collected in an adsorption tube which can also serve as a precolumn for the gc. When the adsorption tube and the analytical column can be heated simultaneously, the configuration in Figure 18 is used. When the adsorption tube and the analytical column must be heated independently the configuration in Figure 20 is used. For the latter configuration, the collection column is constructed as an insert to fit into the heated injection port of the chromatograph so that the sample can be flash heated onto the analytical column with the injection port heater.

Mieure and Dietrich used ¼ or 3/8 × 4 in. adsorption tubes filled with 0.2 to 0.5 g of 60- to 80-mesh packing materials that were cleaned and preconditioned by conventional techniques. For the collection of pollutants from air, a number of packings were investigated for the adsorption and desorption of specific classes of pollutants. Chromosorb® 101 was useful for acidic and neutral compounds, Chromosorb® 105 was useful for low boiling species, and Tenax-GC® was efficient for the collection of basic, neutral, and high boiling substances. For the collection of pollutants from water samples Chromosorb 102® was used.

Downloaded At: 16:07 17 January 2011

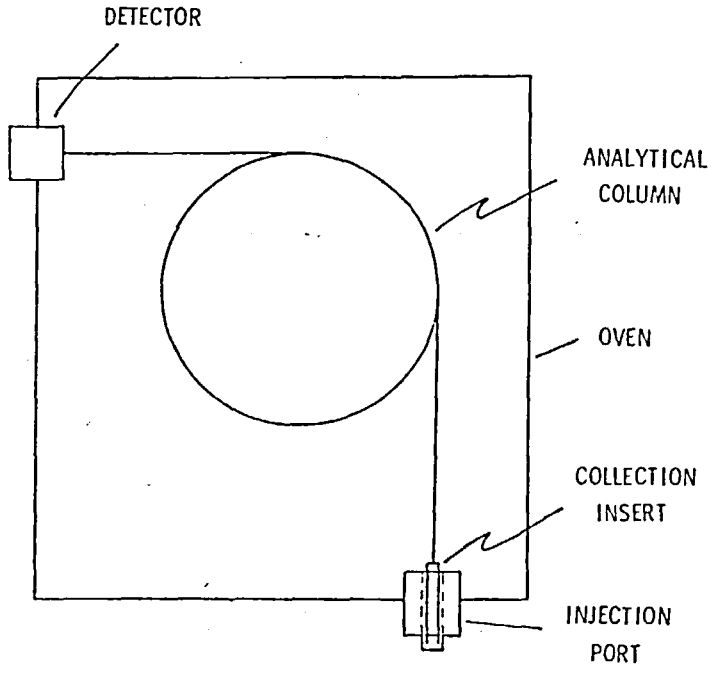


FIGURE 20. Collection column connected into a gc as an injection port insert.

Downloaded At: 16:07 17 January 2011

A major difficulty in the analysis of water samples by thermal desorption methods that does not occur in the analysis of air samples is that more than 10 $\mu\ell$ of water remains in the interstitial volume of the collection column packing, and this is flashed onto the analytical column with the sample. The presence of this water in the effluent from the gas chromatographic column may necessitate operating at a greater hydrogen flow to avoid blowing out the flame in the detector and the water peak may mask some of the pollutant peaks in the chromatogram.

Versino et al.[71] used Tenax-GC® as the packing in their adsorption tubes. For air sampling, a 15 × 1 cm glass column filled with 2.5 g of Tenax-GC® was preconditioned at 350°C for 3 hr and then overnight at 200°C with a flow of high-purity helium. Then 2 to 40 ℓ of air were sampled by aspirating the air through the adsorption tube at the rate of 0.5 ℓ/min. For water sampling, the collecting tube contained 4 g of Tenax-GC® mixed with 20% 60- to 80-mesh glass beads. The combination of the packing with glass beads facilitates the flow of water through the column. They sampled 0.5 to 1.5 ℓ of water, depending on the level of contamination. After sampling, the excess water was removed from the column by placing the adsorption tube in a desiccator over phosphorus pentoxide at 10 torr. This drying procedure minimized the losses of compounds that had been collected on the Tenax-GC® and appears to be a much safer way to remove water than drying with a stream of helium (see Section VI).

In the Versino procedure, the adsorbed materials were thermally desorbed from the Tenax-GC® at 250 to 270°C with helium flowing at 15 mℓ/min and collected in a glass-lined U-tube. The condensed materials were flash heated from the U-tube at 300°C into two parallel glass capillary columns with different stationary phases.

Chang and Fritz[72] and Ryan and Fritz[73] have investigated the thermal desorption technique using collection columns packed with XAD resins. The sampling column

was an 8 cm × 2 mm I.D. Pyrex® tube that was packed with 120- to 140-mesh XAD-2 or XAD-4 resin. A 2.5-cm resin bed was centered in the tube with silanized glass wool. Connections were made with Swagelok® fittings using PTFE ferrules. The XAD adsorption tube was cleaned prior to use by passing 5 mℓ of distilled water through the tube and then placing the tube in a desorption chamber at 200°C. Helium was passed through the tube at the rate of 20 mℓ/min. The tube was held at 200°C for 4 min and then raised to 240°C for 10 to 15 min. After repeating this procedure four or five times, the tube was capped and ready for use. The water sample was pumped through the collection tube at the rate of 4 to 5 mℓ/min by either a 20-mℓ syringe or a 50-mℓ syringe pump. After sampling, 20-mℓ of air were passed through the tube to remove excess water, then the tube was thermally desorbed immediately or capped and stored. In the procedure of Ryan and Fritz,[73] the thermal desorption is accomplished by connecting the minicolumn adsorption tube to the thermal desorption apparatus shown in Figure 21. In this apparatus the organics are thermally desorbed from the XAD resin at 180 to 200°C and transferred to a Tenax-GC® precolumn by a stream of helium flowing at 5 mℓ/min. During the transfer the Tenax-GC® precolumn is held at 45°C; at this temperature the Tenax-GC® does not adsorb water. After the sample has been transferred, the Tenax-GC® precolumn is isolated by means of the four-port valve shown in Figure 21, and it is heated to 275 to 300°C. When this temperature is reached, the four-port valve is opened so that the carrier gas can backflush the hot Tenax-GC precolumn and transfer the desorbed material onto the gas chromatographic analytical column. Although this does not accomplish a plug sample injection, sharp, well-resolved chromatographic peaks are obtained if the gc column is kept cool during this transfer and temperature programming is used.

Ryan and Fritz[73] have tested this thermal desorption procedure with a mixture of model compounds and obtained good recovery factors with water samples spiked with organic solutes in the 1- to 10-ppb range. A 96% recovery was obtained for 1-methylnaphthalene when the sampling tube was desorbed for 10 min.

May et al.[58] compared Tenax-GC® and XAD-2 under thermal desorption conditions. Their results are shown in Figure 22. It can be seen that the Tenax-GC® blank gives an acceptable background at 400°C, and even the small peaks shown in the figure do not appear at 375°C. The XAD-2 blank is unsatisfactory at 275°C.

VIII. STEAM DISTILLATION

Minsley[74] has reported on the use of steam distillation for the analysis of gasoline, fuel oils, kerosene, and motor oils in water systems. Recently, Veith and Kiwus[75] have developed a modified Nielsen-Kryger steam distillation apparatus (Ace Glass Co., Vineland, N.J.) (Figure 23) for the extraction of pesticides and industrial chemicals from water, sediments, and tissue. The apparatus provides for the simultaneous distillation and extraction of organic solutes from water by a small volume of organic solvent.

A water sample of 1 to 2.5 ℓ or a sediment or tissue sample with added water is placed in a 2- to 3-ℓ round-bottom flask. This flask is attached to the apparatus shown in Figure 23 and the water is boiled vigorously for 1 to 7 hr, depending on the type of sample. As the water boils, the steam distillate rises through the inner tube and condenses on the cooling jacket shown in the figure. The condensate passes through and collects under a layer of solvent whose density is less than that of water and the organic pollutants are extracted into the solvent in this step. Isooctane and toluene are recommended as solvents. The water returns to the distilling flask through the overflow tube which also serves as the solvent trap. At the end of the distillation, the solvent is re-

Downloaded At: 16:07 17 January 2011

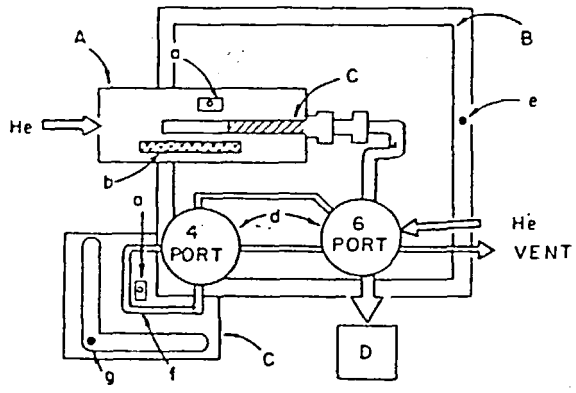


FIGURE 21. Thermal desorption apparatus. (A) Sliding aluminum block, (a) thermocouple, (b) 200-W cartridge heater controlled by a Variac®, (c) XAD-4 minicolumn; (B) heated zone insulated with temp-mat glass insulation (Pittsburgh Corning, Pittsburgh, Penna.), (d) one four-port and one six-port zero-volume high-temperature valve, (e) 200-W high-temperature heating cord controlled by a Variac® (Gears-Col Apparatus Co., Terre Haute, Ind.); (C) removable insulated sheet-metal heating zone (as B) containing the Tenax® precolumn, (f) Tenax® precolumn (stainless steel 1/8 in. × 18 cm Tenax-GC®, 80 to 100 mesh), (g) high-temperature heating cord (as e) controlled by a Variac® (Ames Lab, Instrument group); (D) gas chromatograph.

Downloaded At: 16:07 17 January 2011

moved through the stopcock and is either analyzed directly or concentrated prior to analysis.

The recovery of PCBs and related chemicals from 2.5 *l* of spiked water was evaluated for a 45- to 60-min boiling time. Recovery efficiencies for concentrations in the range of 20 ng/*l* were between 90 and 100%.

IX. ANALYSIS OF HEAVILY CONTAMINATED ENVIRONMENTAL SAMPLES

The papers reviewed up to this point have dealt primarily with the separation and concentration of PAH from model samples, tap water, and raw water. In many environmental samples, especially heavily polluted waters and sludges, the PAH content makes up only a small fraction of the DOC. In addition to the PAH. the sample contains other hydrocarbons and compounds with oxygen, nitrogen, sufur, and phosphorus functional groups. In this section, a number of studies for isolating the PAH from heavily contaminated water samples will be discussed. Many of these methods incorporate some of the sampling and concentration techniques discussed in the earlier sections.

Pancirov et al.[45] have developed a procedure to separate water pollutants into several classes as outlined in Figure 24. The special feature of the method is the addition of ^{14}C-labeled B(*a*)P and B(*a*)A to the water sample as an internal standard to correct for losses and incomplete and variable recoveries. The radioactive internal standards are added to a 20-*l* water sample before any separations or concentrations are carried out. The PAH are identified and quantified by injecting an aliquot into a gas chromato-

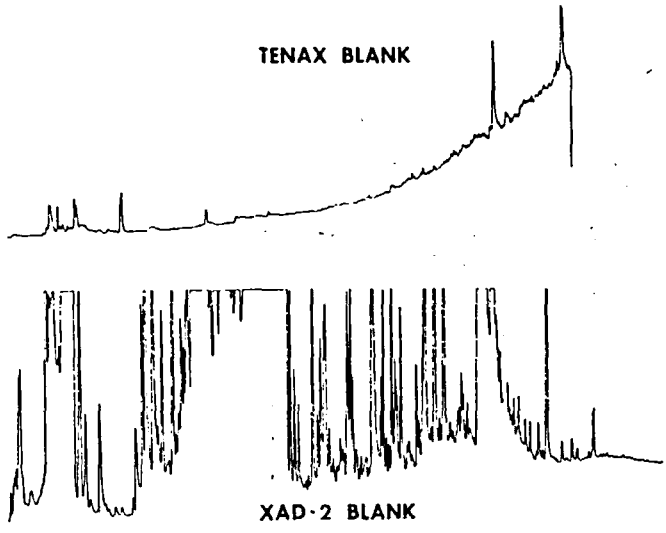


FIGURE 22. Gas chromatograms obtained by flash heating XAD-2 to 275°C and Tenax-GC® to 400°C.

Downloaded At: 16:07 17 January 2011

graph, trapping each gc peak, and measuring its UV spectrum. The measured values are corrected on the basis of the observed recovery of the ^{14}C B(*a*)P and ^{14}C B(*a*)A. The recovery factor of ^{14}C B(*a*)A is used to determine the original concentrations of B(*a*)A, chrysene, and triphenylene, and the recovery factor of ^{14}C B(*a*)P is used to determine the original concentrations of B(*a*)P and B(e)P.

Lysyj and Russel[76] have examined the extraction of oils from waste water using the nonpolar solvent Freon 113® (1,1,2-trichloro-1,2,2-trifluoroethane), as is recommended in Methods 502A and 502B of the *Standard Methods for the Examination of Water and Wastewater.*[42] They found that the Freon 113® extraction method gave an average recovery of about 56% when used on five different water samples contaminated with crude oil. For this reason, the Freon 113® extraction was supplemented with procedures that would extract the polar and water soluble components of the crude oil.

Lysyj and Russel[76] have reported a method that utilized a 1- and 2-*l* sample of wastewater. The 1-*l* sample is used for overall chemical characterization; 30 to 100 μl are used to determine the total organic carbon with a Beckman® or Dohrmann® TOC analyzer. The remainder of the 1-*l* sample is extracted with Freon 113® and the characteristic hydrocarbon peaks in the 3200 to 2700 cm^{-1} spectral region are examined.

The 2-*l* sample is used for specific chemical characterization. The volatile solutes are analyzed by headspace analysis, using nitrogen gas and collecting the desorbed solutes on activated carbon. The adsorbed materials are eluted from the activated carbon with carbon disulfide and determined by gas chromatography. The suspended organic matter is removed from the water with a 0.45-μm filter, and the dissolved organics are extracted from solution in two ways: (1) with three 50-m*l* volumes of chloroform and (2) by adsorption on XAD-7 resin. The concentrated extracts were analyzed by gc/ms and hplc. It was found that the chloroform extract contained up to 70% of the dissolved organics present in untreated bilge water. This complex mixture that contained phenols and cresols, nitrogen-containing heterocyclics, alkyl ben-

Downloaded At: 16:07 17 January 2011

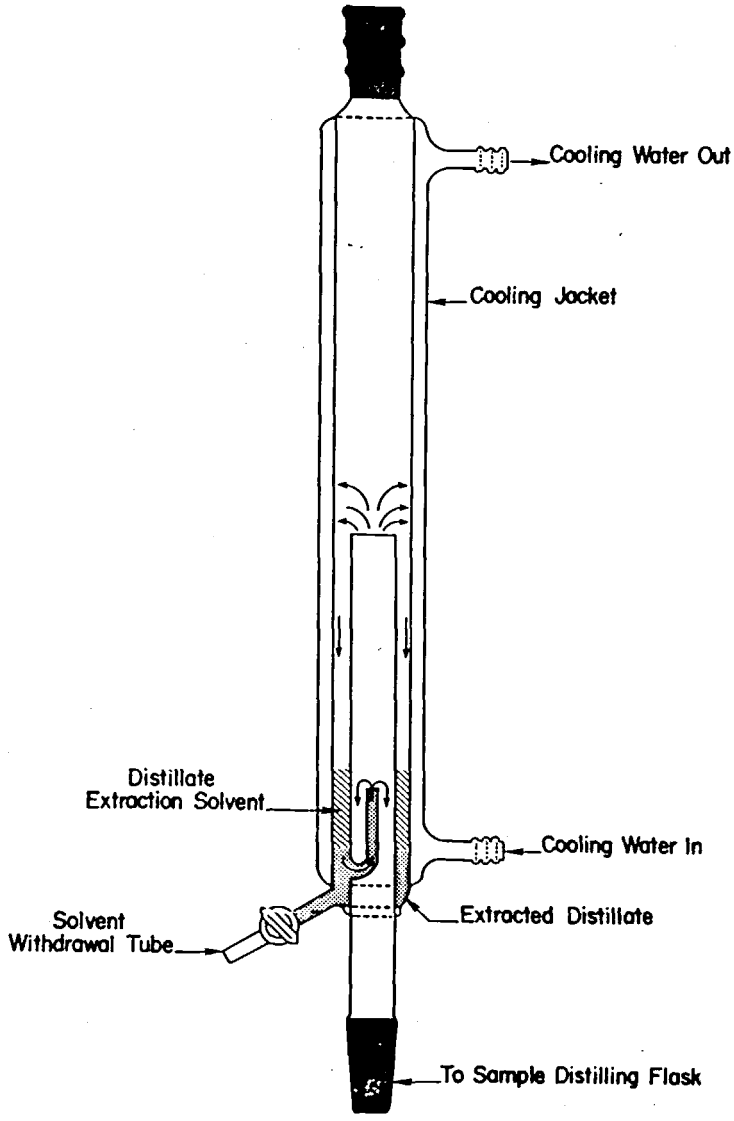


FIGURE 23. Exhaustive steam-distillation and solvent-extraction apparatus.

zenes, and PAH was separated with hplc using a reversed-phase column of the ODS type.

Grimmer et al.[77] reported on a separation procedure (Figure 25) to extract the PAH from sludge samples. It can be seen from the left-hand column of this figure that the PAH with four or more rings make up only 0.01% of the sample and that without a separation procedure, the PAH would be swamped by the other pollutants in the gas chromatogram.

The solid samples are freeze dried, 1,2,7,8-dibenzphenanthrene (10 μg/g) is added as an internal standard, the sample is extracted three times with 50 mℓ of acetone, and the extract is concentrated with a rotary evaporator. The water samples are spiked with the same concentration of internal standard, and 100 mℓ of methanolic potassium hydroxide is added. The sample is refluxed for 2 hr and extracted with three 100-mℓ

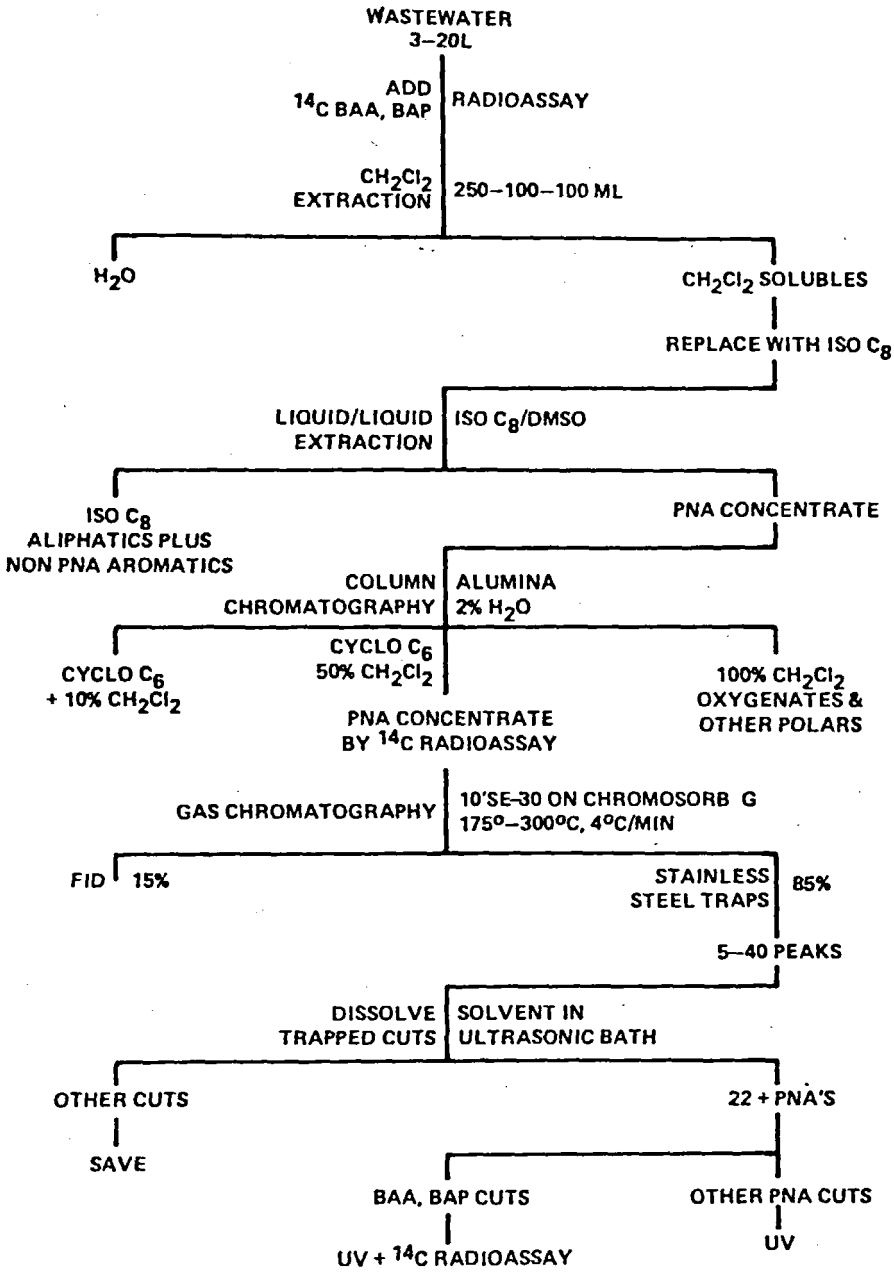


FIGURE 24. GC/UV method for determining PAH in wastewaters illustrating the extraction steps involved.

portions of Freon 113®. After the phases separate, the methanol-water phase is discarded.

The acetone extract from the solid sludge sample or the Freon 113® extract from the water sample (approximately 350 mg) is dissolved in 25 m*l* of cyclohexane and shaken with a solution of 45 m*l* of dimethylformamide (DMF) and 5 m*l* of water. The DMF-water phase is retained and this fraction is diluted to 100 m*l* with water and

Downloaded At: 16:07 17 January 2011

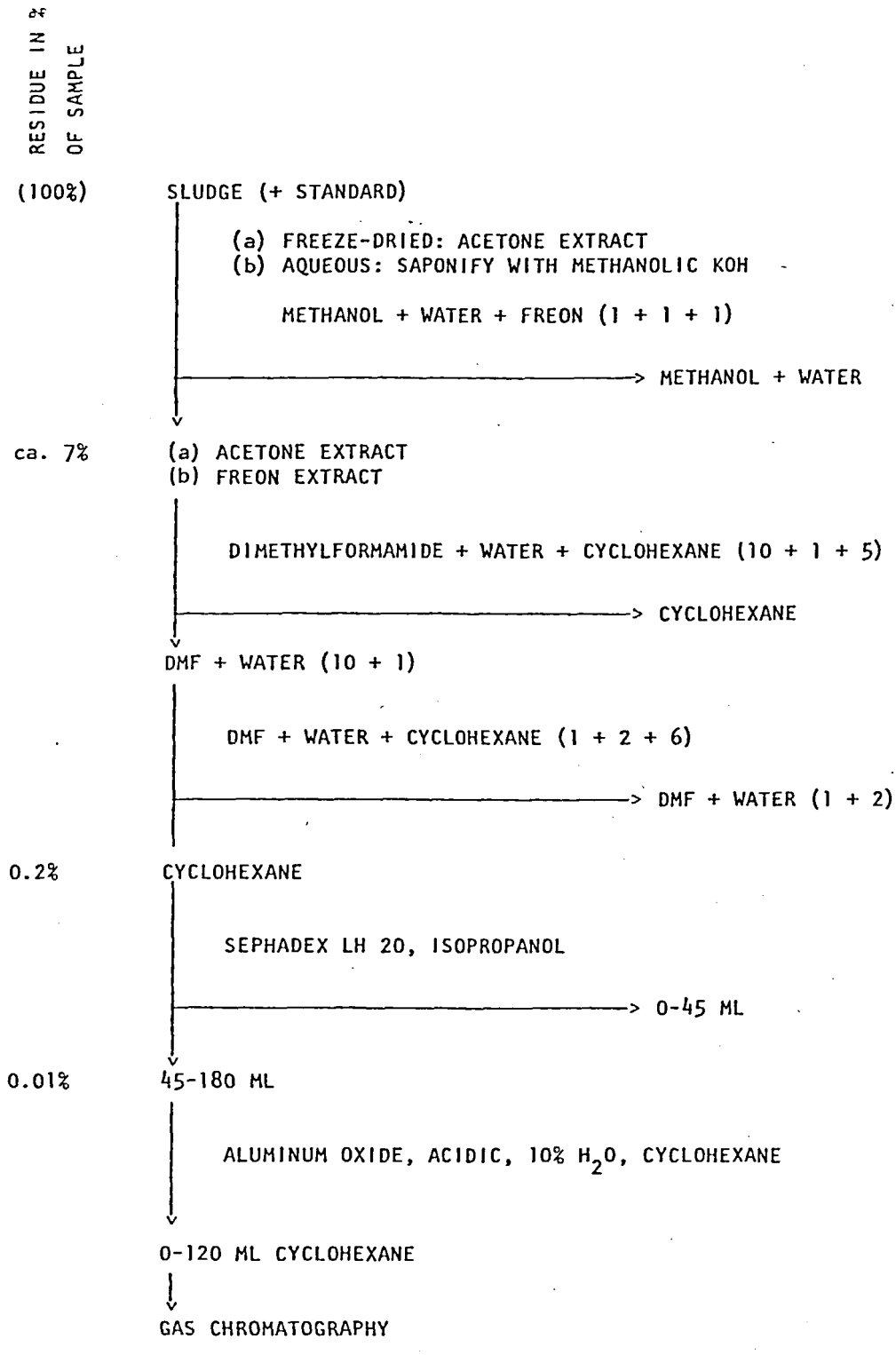


FIGURE 25. Cleanup and extraction procedure for isolating PAH from sewage sludge samples.

Downloaded At: 16:07 17 January 2011

a further 300 mℓ of cyclohexane to make the liquid composition DMF/water/cyclohexane = 1:2:6. The cyclohexane phase is retained and dried in a rotary evaporator. The residue in the rotary evaporator is dissolved in three sequential 1-mℓ portions of isopropanol, and the sample is placed on a Sephadex® LH-20 column and eluted with isopropanol. The first 45 mℓ of eluate contained the two- and three-ring PAH and are discarded in the Grimmer et al. procedure. The next 135 mℓ of eluate are concentrated and transferred to an alumina column that has been acid treated and contains 10% water. The sample is eluted from the alumina with 120 mℓ of hexane, and this eluate contains PAH with four to seven rings. The sample is again concentrated for analysis by gas chromatography. About 20 PAH were identified in a sludge sample using this procedure. The SD of the individual components for five replicate analyses ranged from 1.6 to 11.3%.

Natusch and Tomkins[78] have used a cleanup method in which dimethyl sulfoxide (DMSO) is used to separate the PAH from hydrocarbons and oxygenates in both air and water samples. The method permits the isolation of (1) aliphatic hydrocarbons, (2) alcohols, phenols, and low molecular weight aliphatic and aromatic acids and (3), PAH, phthalates, aromatic bases and high molecular weight aliphatic acids.

A pentane extract of the organic solutes is partitioned three times with fresh DMSO. The DMSO layers are separated, combined, and two volumes of water are added. The original pentane solution contains the hydrocarbon fraction and the DMSO-water solution contains the PAH and oxygenates. The DMSO-water solution is then partitioned three times with equal volumes of pentane. The PAH are concentrated in the pentane layer in this step. Chromatograms obtained by this method were presented to demonstrate the separations for model systems and extracts of airborne particulates.

Acheson et al.[4] have also used DMSO in an extraction procedure to separate the organic solutes in environmental samples obtained from rivers and sewers adjacent to highways. Nonfluorescing compounds do not seriously interfere with PAH analysis by TLC and fluorescence, whereas they do make analysis by gc very complex. Acheson et al.[4] examined the cleanup procedures of Hoffman and Wynder[79] and Haenni et al.[80] In the Hoffman and Wynder procedure, the pollutants are dried to constant weight and dissolved in 40 mℓ of 4:1 methanol-water. This solution is extracted three times with 40 mℓ of cyclohexane and the cyclohexane extract is extracted five times with nitromethane. The nitromethane phase contains the PAH. In the Haenni et al. partition method, DMSO replaced the nitromethane. The methanol-water solution was extracted with cyclohexane and the cyclohexane was extracted three times with 15-mℓ portions of DMSO. The DMSO phases were combined and diluted with water and back-extracted with two 25-mℓ portions of cyclohexane. Acheson et al. compared the recovery efficiencies of the two methods for nine PAH for weights of two sets of samples ranging from about 1 μg and 20 μg. In all cases, the DMSO partition method gave better recovery, and in some cases the recovery was improved by a factor of four. Basu and Saxena[3] have also found the DMSO partition method superior to the nitromethane method for the cleanup of environmental samples collected on open-pore polyurethane foam columns (see Section III.C and Table 2).

On the other hand, Sorrell et al.[81] found the DMSO clean-up unsatisfactory for the separation of PAH from other pollutants in their study of the leaching of coatings from water distribution pipes. The DMSO introduced impurities that interfered with the subsequent hplc analysis of the PAH,[81a] and they selected a clean-up procedure on an alumina column (see below).

Giger and Blumer[82] have described an isolation procedure for PAH from environmental samples that utilizes gel filtration, adsorption chromatography, and charge transfer complexations. They have applied the procedure to the analysis of complex

Downloaded At: 16:07 17 January 2011

mixtures of aromatic hydrocarbons from marine sediments. A 100- to 150-g sample of sediment is Soxhlet extracted with 275 mℓ of methanol for 24 hr, then 75 mℓ of benzene are added and the extraction is continued for a further 24 hr. The hydrocarbons are partitioned from the benzene-methanol mixture with three 75-mℓ portions of pentane, the pentane extract is dried with anhydrous sodium sulfate, and its volume is reduced to 1 mℓ in a rotary evaporator. Elemental sulfur, which would chromatograph with the PAH fraction, is removed by eluting the extract through a copper column with a 1:1 benzene-pentane mixture. The eluate from the copper column is evaporated to dryness, redissolved in a minimum volume of 1:1 benzene-methanol, and put on a Sephadex® LH-20 gel permeation column. This column was prepared by placing 20 g of Sephadex® in 1:1 benzene-methanol in a 1.6-cm I.D. tube, giving a packing length of 38 cm. The sample is eluted from the Sephadex® column with benzene-methanol at a flow rate of 6 mℓ/min under slight pressure. The first 50 mℓ of eluate are discarded; the next 50 mℓ contain the PAH and are evaporated to dryness in a rotary evaporator. The aromatic fraction from the Sephadex® is dissolved in 1 mℓ of n-pentane, transferred to a column of alumina over silica gel (both 4 mℓ and deactivated with 3% water), and eluted with n-pentane. The first 20 mℓ of eluate from the column contain the saturated hydrocarbons and most of the olefins and are discarded. The flask which had contained the concentrate from the Sephadex® separation is washed with a 2- and a 13-mℓ portion of methylene chloride, and these washes are used to elute the PAH from the alumina-silica column. A 20-mg sample of 2,4,7-trinitro-9-fluorenone (TNF) is added to the methylene chloride eluate from the alumina-silica gel column to form adducts with the PAH. This solution is evaporated to dryness and the uncomplexed material dissolved in pentane and discarded. The excess TNF and the adducts are dissolved in methylene chloride and passed through silica gel to split the adduct. The PAH are eluted with 75 mℓ of methylene chloride and this volume is reduced to near dryness in a rotary evaporator.

Giger and Blumer point out that for the best separation of TNF and PAH, critical attention must be paid to column dimensions, elution volumes, and full activation of the silica gel. In their work they obtained a 97% recovery of a 10-μg sample of coronene that was separated from 20 mg of TNF. They also note that the chromatography on the alumina-silica column is an important step. In this separation the lipids remaining in the PAH fraction are removed. Their presence would solubilize the TNF adduct or completely prevent its precipitation. The PAH can now be analyzed by gc/ms or glass capillary gc/ms. Or, in the procedure of Giger and Blumer, this fraction was further separated into seven cuts according to ring-type on an alumina column for UV analysis. Subsequently, Giger and Schaffner[82a] have used glass capillary chromatography rather than UV analysis to identify the PAH, and they note that with this analytical procedure, the TNF clean-up of the PAH fraction was not necessary.

Sorrell et al.[81] used solvent extraction with cyclohexane followed by a clean-up with an alumina column to isolate the PAH leached from water pipes in preparation for analysis by hplc. The extract was separated into five fractions on an alumina column with (1) pentane, (2) 25% methylene chloride in pentane, (3) 50% methylene chloride in pentane, (4) 50% methylene chloride then 75% methylene chloride in pentane, and (5) methylene chloride.

Recently Keith and Telliard[83] reported on the present status of the Environmental Protection Agency (EPA) list of Priority Pollutants and the analytical methods used to monitor them in environmental samples. The list at present contains 129 compounds, 16 of which are PAH. These 16 PAH include the six PAH listed by the World Health Organization (WHO). The compilation is based on the Toxic Pollutant List and on an EPA report which tabulates all known pollutants in water identified worldwide up to June 1976.[84]

Downloaded At: 16:07 17 January 2011

The analytical scheme reported by Keith and Telliard uses three water samples. The first sample is collected in a 40-mℓ vial with a PTFE lined septum, care being taken to exclude air bubbles. Then 5 mℓ of this sample, spiked with bromochloromethane and 1,4-dichlorobutane as internal standards, is used to extract the purgeable compounds by headspace analysis. The purging is carried out with helium in a sparging tube with a fritted glass bottom. The volatile organic compounds stripped from the water are adsorbed in a stainless steel trap packed with Tenax-GC® and silica gel. After the purging, the adsorption trap is backflushed with helium at 180°C and the organics are thermally desorbed to the inlet of a gas chromatography column held at room temperature. A total of 29 of the Priority Pollutants have been identified in this way.

A second 2-ℓ water sample is used for liquid-liquid extraction. The sample is made strongly alkaline and extracted with methylene chloride. The methylene chloride exract is concentrated in two stages, first with a Kuderna-Danish apparatus and then to 1.0 mℓ with a micro-Snyder distillation column. Then d_{10}-anthracene is added to the 1.0 mℓ concentrate as an internal standard. This fraction contains the Base-Neutral Priority Pollutants, and 46 of these have been identified by this method. The same water sample is acidified and re-extracted with methylene chloride. The methylene chloride phase is reduced to 1.0 mℓ, and d_{10}-anthracene is added as an internal standard. This fraction contains the acid Priority Pollutants, and 11 phenols have been identified by this technique.

The third 1-ℓ sample was used to extract the 26 pesticides with a hexane-methylene chloride mixture. The volume of the extract was reduced to 10 mℓ, and the components were separated on a Florisil® column. All the determinations were carried out with a gc/ms system.

In the EPA procedure outlined above, the lighter PAH are separated in the headspace step and the higher molecular weight PAH in the neutral/basic fraction of the methylene chloride extraction. We suggest that the use of the procedures outlined may lead to difficulty in determining PAH losses in the concentration step since the internal standard is not added until after the volume has been reduced.

Keith and Telliard also list a number of tentative monitoring methods and prime contractors who are studying 12 classes of Priority Pollutants. The analysis of 16 PAH is being investigated at Battelle Memorial Institute. The PAH are extracted from water with methylene chloride and the solvent exchanged with cyclohexane. The extract is fractionated on silica gel and analyzed by hplc using gradient elution with a Perkin Elmer HC-ODS reversed-phase column. Fluorescence at two different excitation and emission wavelengths is used for identification.

X. SUMMARY AND OUTLOOK

The fundamental problem faced by the analyst is the collection of a representative sample and the identification and quantitation of its components. The additional complications imposed by working with trace amounts are the problems of losses of some sample components and contamination. These constraints favor procedures that involve a minimum of sample handling. On this basis, one should examine critically any preconcentration procedure that involves volume reductions by a large factor. Procedures of this type lead to the loss of volatile components and the concentration of impurities in the solvent. Solid adsorbents are convenient for the sampling of large volumes of water in the field, although this procedure leads to the losses of volatile components. Volatile components are best analyzed in the laboratory by headspace analysis where the sample is collected on a solid adsorbent and transferred to a gas chromatograph by thermal desorption. The analysis of the nonvolatile components can best be carried out by a liquid-liquid extraction method with a minimal volume of

Downloaded At: 16:07 17 January 2011

solvent that will not require further volume reduction. In all of these procedures, losses should be monitored by the use of appropriately selected internal standards which should be added at the beginning of the analytical procedure. The availability of highly efficient glass capillary gas chromatography/mass spectrometer/data systems and their very large dynamic range should minimize the need for extensive separations that were described in many of the procedures cited in this review. The use of hplc has made it possible to identify and quantify isomeric PAH.

A problem that appears unresolved at present are the PAH that are adsorbed on particulate matter. In a number of procedures, the particulate matter is filtered prior to the analysis of the water sample. It is the authors' opinion that when filtration is used, the sorption of PAH on the filter and on the particulates should be monitored, since in the case of drinking water the particulates are ingested.

It is hoped that rapid advancement of the state of the art will make it possible to establish uniform analytical procedures for the analysis of PAH and other pollutants. The intense effort by the EPA and the many workers in this field should achieve this end in the near future.

ACKNOWLEDGMENTS

The work upon which this publication is based was supported in part by funds provided by the Office of Water Research and Technology (Project No. A-084-CT), U.S. Department of the Interior, Washington D.C., as authorized by the Water Research and Development Act of 1978 (P.L. 95-467). The devotion of Ms. Lori Krol and Ms. Bonnie McNabb Crowe in preparing the manuscript is gratefully acknowledged.

Downloaded At: 16:07 17 January 2011

REFERENCES

1. Hertz, H. S., May, W. E., Wise, S. A., and Chesler, S. N., *Anal. Chem.*, 50, 429A (1978).
2. Strup, P. E., Wilkinson, J. E., and Jones, P. W., *Polynuclear Aromatic Hydrocarbons*, Vol. 3, Jones, P. W. and Freudenthal, R. I., Eds., Raven Press, New York, 1978.
3. Basu, D. K. and Saxena, J., *Environ. Sci. Technol.*, 12, 791, (1978).
4. Acheson, M. A., Harrison, R. M., Perry, R., and Wellings, R. A., *Water Res.*, 10, 207, (1976).
5. Jones, P. W., Giammar, R. D., Strup, P. E., and Stanford, T. B., *Environ. Sci. Technol.*, 8, 806, (1976).
6. Leoni, V., Puccetti, G., and Grella, A., *J. Chromatogr.*, 106, 119 (1975).
7. Stepan, S. F. and Smith, J. F., *Water Res.*, 11, 339 (1977).
8. Gustafson, R. L. and Paleos, J., *Water and Water Pollution Handbook*, Vol. 1, Ciaccio, L. L., Ed., Marcel Dekker, New York, 1971, chap. 10.
9. Fritz, J. S., *Acc. Chem. Res.*, 10, 67 (1977).
10. Junk, G. A., Richard, J. J., Grieser, M. D., Witiak, D., Witiak, J. L., Arguello, M. D., Vick, R., Svec, H. J., Fritz, J. S., and Calder, G. V., *J. Chromatogr.*, 99, 745 (1974).
11. Junk, G. A., Richard, J. J., Fritz, J. S., and Svec, H. J., Identification and Analysis of Organic Pollutants in Water, Keith, L. H., Ed., Ann Arbor Science, Ann Arbor, Mich., 1976.
12. Junk, G. A., Richard, J. J., Svec, H. J., and Fritz, J. S., *J. Am. Water Works Assoc.*, 68, 218 (1976).
13. Junk, G. A., Chriswell, C. D., Chang, R. C., Kissinger, L. D., Richard, J. J., Fritz, J. S., and Svec, H. J., *Fresenius Z. Anal. Chem.*, 282, 331 (1976).
14. Tateda, A. and Fritz, J. S., *J. Chromatogr.*, 152, 329 (1978).
15. Van Rossum, P. and Webb, R. G., *J. Chromatogr.*, 150, 381 (1978).

16. Musty, P. R. and Nickless, G., *J. Chromatogr.*, 89, 185 (1974).
17. Thurman, E. M., Malcolm, R. L., and Aiken, G. R., *Anal. Chem.*, 50, 775 (1978).
18. Smith, S. R., Cordes, H. F., and Johnson, J. H., NWC TM 3279, Naval Weapons Center, China Lake, Calif., 1978.
19. Shinohara, R., Koga, M., Shinohara, F., and Hori, T., *Bunseki Kagaku*, 28, 856 (1977).
20. Thurman, E. M., Aiken, G. R., and Malcolm, R. L., Proc. 4th Joint Conf. Sensing of Environmental Pollutants, 1978, 166.
21. Malcolm, R. L., Thurman, E. M., and Aiken, G. R., *Trace Subst. Environ. Health*, 11, 307 (1977).
22. Gustafson, R. L., Albright, R. L., Heisler, J., Lirio, J. A., and Reid, O. T., Jr., *2nd Eng. Chem. Prod. Res. Develop.*, 7, 107 (1968).
23. Leenheer, J. A. and Huffman, E. W. D., Jr., *J. Res. U.S. Geol. Surv.*, 4, 737 (1976).
23a. Leenheer, J. A. and Huffman, E. W. D., Jr., *Water Resources Investigations*, 79(4), January 1979.
23b. Stuber, H. A. and Leenheer, J. W., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 23, 105, (1978).
24. May, W. E., Wasik, S. P., and Freeman, D. H., *Anal. Chem.*, 50, 997 (1978).
25. Burnham, A. K., Calder, G. V., Fritz, J. S., Junk, G. A., Svec, H. J., and Vick, R., *J. Am. Water Works Assoc.*, 65, 722 (1973).
26. Burnham, A. K., Calder, G. V., Fritz, J. S., Junk, G. A., Svec, H. J., and Willis, R., *Anal. Chem.*, 44, 139 (1972).
27. Stepan, S. F., Smith, J. F., Flego, U., and Reukers, J., *Water Res.*, 12, 447 (1978).
28. Brown, J. J. M., *J. Chem. Soc. A*, 1062 (1970).
29. Gesser, H. D., Chow, A., Davis, F. C., Uthe, J. F., and Reincke, J., *Anal. Lett.*, 4, 883 (1971).
30. Uthe, J. F., Reincke, J., and Gesser, H., *Environ. Lett.*, 3, 117 (1972).
31. Gough, K. M. and Gesser, H. D., *J. Chromatogr.*, 115, 383 (1975).
32. Navratil, J. D. and Sievers, R. E., *Am. Lab.*, 9, 38 (1977).
33. Navratil, J. D., Sievers, R. E., and Walton, H. F., *Anal. Chem.*, 49, 2260 (1977).
34. Saxena, J., Kozuchowski, J., and Basu, D. K., *Environ. Sci. Technol.*, 11, 682 (1977).
35. WHO *International Standards for Drinking Water*, 3rd ed., World Health Organization, Geneva, 1971.
36. Basu, D. K. and Saxena, J., *Environ. Sci. Technol.*, 12, 795 (1978).
37. Braus, H., Middleton, F. M., and Walton, G., *Anal. Chem.*, 23, 1160 (1951).
38. Rosen, A. A. and Middleton, F. M., *Anal. Chem.*, 31, 1729 (1959).
39. Hoak, R. D., *Int. J. Air Water Pollut.*, 6, 521 (1962).
40. Eichelberger, J. W. and Lichtenberg, J. J., *J. Am. Water Works Assoc.*, 62, 25 (1970).
41. Booth, R. L., Report from Sub-Committee on Applicability of Carbon Adsorption Technique to the Mission of the National Water Quality Network, January 1963.
42. *Standard Methods for the Examination of Water and Wastewater*, 13th ed., American Public Health, Washington, D.C., 1971, 259.
43. Grob, K., *J. Chromatogr.*, 84, 255 (1973).
44. Mieure, J. P. and Dietrich, M. W., *J. Chromatogr. Sci.*, 11, 559 (1973).
45. Pancirov, R. J., Searl, T. D., and Brown, R. A., Methods of Analysis for Polynuclear Aromatic Hydrocarbons in Environmental Samples Symp. Analytical Chemistry of Petroleum Hydrocarbons in Marine/Aquatic Environment, American Chemical Society Meeting, Miami Beach, 1978, 855.
46. Grob, K., Grob, K., Jr., and Grob, G., *J. Chromatogr.*, 106, 299 (1975).
46a. Murray, D. A. J., *J. Chromatogr.*, 177, 135 (1979).
47. Harrison, R. M., Perry, R., and Wellings, R. A., *Environ. Sci. Technol.*, 12, 1151 (1976).
48. Reichert, J. K., Kunte, H., Engelhardt, K., and Borneff, J., *Arch. Hyg. Bakteriol.*, 155, 18 (1971).
49. Borneff, J. and Fischer, R., *Arch. Hyg. Bakteriol.*, 146, 183 (1962).
50. Harrison, R. M., Perry, R., and Wellings, R. A., *Water Res.*, 9, 331 (1975).
51. Goldberg, M. C., DeLong, L., and Sinclair, M., *Anal. Chem.*, 45, 89 (1973).
52. Kahn, L. and Wayman, C. H., *Anal. Chem.*, 36, 1340 (1964).
53. Ahnoff, M. and Josefsson, B., *Anal. Chem.*, 46, 658 (1974).
54. Ahnoff, M. and Josefsson, G., *Anal. Chem.*, 48, 1268 (1976).
55. Eisenbeiss, F., Hein, H., Joester, R., and Naundorf, G., *Chromatogr. Newsl.*, 6, 8 (1978).
56. Ogan, K., Katz, E., and Slavin, W., *J. Chromatogr. Sci.*, 16, 517 (1978).
57. Chesler, S. N., Gump, G. H., Hertz, H. S., May, W. E., and Wise, S. A., NBS Special Publication 464, November 1977.
58. May, W. E., Chesler, S. N., Cram, S. P., Gump, G. H., Hertz, H. S., Enagonio, D. P., and Dyszel, S. M., *J. Chromatogr. Sci.*, 13, 535 (1975).
59. Oyler, A. R., Bodenner, D. L., Welch, K. J., Liukkonen, R. J., Carlson, R. M., Kopperman, H. L., and Caple, R., *Anal. Chem.*, 50, 837 (1978).
60. Euston, C. B. and Baker, D. R., *Am. Lab.*, 9, 91 (1977).

Downloaded At: 16:07 17 January 2011

61. Huber, J. F. K. and Becker, R. R., *J. Chromatogr.*, 142, 765 (1977).
62. Zlatkis, A. and Thiskie, H. A., *Chromatographia*, 6, 67 (1973).
63. Zlatkis, A. Bertsch, B., Bafus, D., and Lukich, H. M., *J. Chromatogr.*, 91, 379 (1974).
64. Wise, S. A., Chesler, S. N., Hertz, H. S., Hilpert, L. R., and May, W. E., Polynuclear Aromatic Hydrocarbons, Vol. 3, Jones, P. W. and Freudenthal, R. I., Eds., Raven Press, 1978.
65. Chesler, S. N., Gump, B. H., Hertz, H. S., May, W. E., and Wise, S. A., *Anal. Chem.*, 50, 805 (1978).
66. Hertz, H. S., May, W. E., Chesler, S. N., and Gump, B. H., *Environ. Sci. Technol.*, 10, 900 (1976).
67. Barileul, G., *Aktive Kohle*, Verlag F. Enke, Stuttgart, 1962.
68. Palamand, S. R., Markl, K. S., and Hardwick, W. A., *Am. Soc. Brew. Chem. Proc.*, 75, 1968.
69. Grob, K. and Zurcher, F., *J. Chromatogr.*, 117, 285 (1976).
70. Obach, E., in *Organic Solvents*, Riddik, J. A., and Bunger, W. B., Ed., Interscience, New York, 1970.
71. Versino, B., Knoppel, H., De Groot, M., Peil, A., Poelman, J., Schauenburg, H., Vissers, H., and Geiss, F., *J. Chromatogr.*, 122, 373 (1976).
72. Chang, R. C. and Fritz, J. S., *Talanta*, 25, 659 (1978).
73. Ryan, J. P. and Fritz, J. S., *J. Chromatogr. Sci.*, 16, 488 (1978).
74. Minsley, G., Detection and Identification of Trace Levels of Petroleum Products in Aquatic Environments, M.S. thesis, University of Wisconsin, Madison, 1973.
75. Veith, G. D. and Kiwus, L. M., *Bull. Environ. Contam. Toxicol.*, 17, 631 (1977).
76. Lysyj, I. and Russell, E. C., Determination of Aromatic and PAH Content of Oily Wastewaters, Symp. Analytical Chemistry of Petroleum Hydrocarbons in Marine/Aquatic Environment, American Chemical Society Meeting, Miami Beach, 1978, 910.
77. Grimmer, G., Bohnke, H., and Borwitzky, H., *Fresenius Z. Anal. Chem.*, 289, 91 (1978).
78. Natusch, D. F. S. and Tomkins, B. A., *Anal. Chem.*, 50, 1429 (1978).
79. Hoffmann, D. and Wynder, E. L., *Anal. Chem.*, 32, 295 (1960).
80. Haenni, E. D., Howard, J. W., and Loe, F. L., Jr., *J. Assoc. Off. Anal. Chem.*, 45, 68 (1962).
81. Sorrell, R. K., Dressman, R. C., and McFarren, E. F., High Pressure Liquid Chromatography for the Measurement of Polynuclear Aromatic Hydrocarbons in Water, paper presented at the Water Quality Control Conf., Kansas City, Missouri, December 5 and 6, 1977.
81a. Sorrell, R. K., private communication, February 1980.
82. Giger, W. and Blumer, M., *Anal. Chem.*, 46, 1663 (1974).
82a. Giger, W. and Schaffner, C., *Anal. Chem.*, 50, 243 (1978).
83. Keith, L. H. and Telliard, W. A., *Environ. Sci. Technol.*, 13, 416 (1979).
84. Shackelford, J. and Keith, L. H., Frequency of Organic Compounds Identified in Water, EPA-600/476-062.

Downloaded At: 16:07 17 January 2011