

METHODS FOR THE ASSESSMENT OF AQUEOUS
ORGANIC MATERIALS

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ABSTRACT

Methods for the Assessment of Aqueous Organic Materials

XAD resins have been evaluated with a range of known organic compounds for possible use in a fractionation method intended to comprehensively analyze the organic contaminants present in water. Among the parameters investigated are the effects on the extraction efficiency of solute polarity, flow rate, pH, elution solvent, and the container in which the extraction and elution are carried out. These studies provide a basis for a suggested procedure using XAD resins that can be rapid and efficient for isolating a wide range of non-volatile contaminants from water.

Using this method, high recoveries allow isolation and recovery of organics initially present in sub part per billion concentrations. Furthermore, water samples can be extracted in the field. Extraction of water and elution of the resin can take place in a single vessel, which eliminates many handling and concentration problems attendant with carbon adsorption methods. The batch desorption characteristic allows for greater recoveries, and spiking of the desorption solvent can provide an internal standard which aids accurate and reproducible quantitation, two significant improvements over other suggested resin methods. This method provides a solution of non-volatile organics in concentrations necessary for GLC or GC/MS identification and quantitation.



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SUMMARY AND CONCLUSIONS

The following conclusions have been drawn from the investigation and regard the five questions delineated in section two.

1. The Carolina Method is an improvement over carbon adsorption and other resin techniques due to in situ desorption, reduction of resin handling, and internal standardization which allows for reproducible quantitation.

2. With respect to previously published methods, the Carolina Method appears to be more comprehensive and quantitative.

3. Using the Schnare Tube, and XAD-2 resin, the Carolina Method will extract from water high proportions of experimentally dissolved organic compounds of widely differing polarities and configurations at part per billion concentrations with a 10 ml/min flow rate and under favorable pH conditions.

4. The batch desorption technique which differentiates the Carolina Method from other existing resin procedures increases recovery efficiencies. Flow rates of approximately 10 ml/min allow very strong binding of some neutral solutes, especially aliphatic compounds, which may be partially mitigated by solvent selection.

5. Losses due to ultra-cold drying techniques and concentration by solvent evaporation can be accounted for through use of an internal standard.

6. All organic solutes appear to be adsorbed to some extent, but flow rate of loading, eluting solvent and method of elution are important considerations in determining the amount that is ultimately recovered.

7. To do quantitative work it is necessary to know resin capacity

and recovery efficiency for each specific compound or class of compounds you are attempting to identify.

8. The technique can be very useful when the objective is to quantify known compounds, where recovery experiments can be done, and flow and elution parameters optimize so that recoveries are known. For compounds where this information is not available, the concentration found represents a minimum environmental level, but the actual amount by which this underestimates the real concentration is not known. Experimental data suggest that the underestimates would be no more than by a factor of 2-5.

RECOMMENDATIONS

Future research on the isolation and identification of organics in natural waters should stress several analytical needs.

1. The need for comprehensive information on the occurrence of organic pollutants in natural waters is even more critical than at the start of this project. Legislative mandates and future regulations will require the monitoring of a large number of organic pollutants.
2. The combination of resin adsorption techniques with a gas stripping technique for volatiles could add appreciably to our overall knowledge of the range of organics present.
3. The material adsorbed and subsequently eluted from XAD resins may need further fractionation before a sample suitable for analysis by GC or GC/MS can be obtained. High performance liquid chromatography appears to offer promise in this type application.
4. Future research on XAD resin applications to pollutant monitoring would be facilitated by research concerning:
 - a. Investigation of optimum solvent combinations for best elution of the broadest range of solutes.
 - b. Experiments with known compounds added to natural water samples to determine interferences due to turbidity, color, and suspended organics.
 - c. Integration of XAD resin technology into an overall scheme for the total organic load of natural waters, including procedures to isolate and identify the non-volatile fraction and ionic organic species.



INTRODUCTION

Christman and Hrutfiord (1973) are representative of the many investigators that have commented on the basic purpose of research into the possible health and environmental risks that may exist in natural waters. They state: "The ability of professional panels to recommend water quality criteria for public water supplies is severely limited by a lack of sufficiently comprehensive information on potentially dangerous or otherwise undesirable constituents."

One of the principal objectives of the research presented here was to provide methods that can be used to assess the types of potentially harmful organic constituents that might be present in water supplies and waste water. The purpose of this work was to begin evaluation of a method designed to provide some knowledge about the entire range of organic compounds present in water, and in what amounts. No single method for this purpose currently has been accepted. Several workers have referred to the need for a method of this type. Middleton (1973): "Techniques for identifying individual compounds at low concentrations are becoming sophisticated, but no simple and inexpensive method is yet available for routine use." Tardiff and Deinzer (1973): "There is relatively little information about the identity of organic compounds in the environment, particularly in drinking water. In those cases where identities of some agents are known, their concentrations are not." Ongerth et al. (1973): "In an effort to gain some insight into the nature of these stable organic residues, a detailed review was made of the literature. These efforts produce the disquieting information that

very little work has been done to identify these organic constituents in treated sewage or in water supply sources and even less has been done to determine the related health effects. ...[T]he literature indicated only six references in which major efforts were made to isolate and identify the constituents in specific organic fractions in water supply sources."

Robeck (in: Christman and Hrutfiord, 1973): "Of course, knowing the occurrence of a chemical in water implies there is an analytical method for quantifying the substance. In reality, however, especially with organics, there is no quick, reasonable way to measure certain compounds." Andelman (in: Christman and Hrutfiord, 1973): "The state of knowledge about the incidence... of organic matter in drinking water can generally be characterized as most unsatisfactory, if not alarming."

To construct and test an analytical procedure requires knowledge of existing technologies. The first section of this report will review what has been done. Section two will describe the procedure selected, and section three will discuss the results. The underlying goal of this work is to construct and evaluate a method designed to extract, fractionate and concentrate organic contaminants of water using known compounds representative of those expected to be present in the environment.

Section I

Discussion of Current Analytical Practices

The nature of organic material in water ranges from very simple hydrocarbons to very complex synthetic and natural polymers. Analytical procedures designed to identify these compounds began appearing in the scientific literature very early in the technological era (Saville, 1917).

The basis of the analytical procedures discussed in this section lies in the capability to detect organic molecules. The sensitivity of the detection methods create requirements for extraction, concentration, and in some cases fractionation of the organic compounds initially present in water. A review of the available detection methods will provide a framework for discussion of the extraction, concentration and fractionation procedures available.

Detection Technologies

Detection of a chemical compound is always a measurement of some characteristic of the compound. If the characteristic is highly specific to the compound, detection will provide information of high qualitative value and in some cases permit positive identification of the compound. Requirements imposed by detector sensitivity and specificity determine what preparative technologies must be used. Many detection technologies are available to the investigator interested in organic contaminants of water. Their current uses and limitations are described below.

CCE - CAE - OCA : The weight of the carbon compounds adsorbed and ether or alcohol extracted is determined gravimetrically and reported to

the nearest tenth of a gram for carbon chloroform extract (CCE), carbon alcohol extract (CAE), and organics-carbon adsorbable (O-CA). This method provides very little information about the nature of the organics extracted since it is intended as an indication of total organics. EPA is continuing an investigation on the value of these methods, and their most recent findings were published in May 1975. For the current method (O-CA) see Buelow et. al., 1973.

Total Organic Carbon: This method differentiates organic carbon from inorganic carbon. Malcom et. al., (1971) have developed a standardized method for routine sampling using commercially available equipment. Sensitivity is 0.1 mg per liter without prior concentration. Cohen has developed an online, instream apparatus for industrial use. Many investigators have used similar methods for monitoring of effluents (Bunch et al., 1961; Murtaugh and Bunch, 1965; Paluter, 1973) or for determining breakthrough of carbon or resin beds (Tilsworth, 1974). Arin (1974) gives an excellent review of these methods for routine monitoring.

Titration/Indicator Methods: These procedures involve a specific chemical phenomenon such as oxygen use, proton transfer, or decoloration of an indicator upon reduction of the organic material to another chemical form. The five day BOD test is in this category. Tsuchida and Matsura (1974) suggest observation of the loss of $KMnO_4$ color of a low pH solution for use as a simple method. Keiser (1928) measured the chlorine demand assumed to be from the organic content of the water.

The titration method measures residual chlorine content. Skopintsev and

Krylova (1955) describes the standard dichromate method, one that reduces organic carbon. Color of the resultant solution is measured. Each of these tests may be diminished in accuracy and value due to interfering materials. These methods may have value for specific applications and routine monitoring, but reveal little or nothing about the nature of the organic constituents measured.

Voltammetry: Voltammetry can be used to detect organic contamination. Afghan *et. al.* (1975) report that in a twin cell potential sweep apparatus he was able to detect nanogram quantities of carbonyl compounds. No pre-concentration or separation was required. The value of this work, like other gross parameter methods, is limited by its inability to comprehensively identify organic contaminants. It has some value as a monitoring technique.

Energy absorption and emission: As early as 1910, Dienert (1910) used emission spectrometry to investigate the nature of fluorescent substances in surface water. Ochi and Okaichi (1973) used a similar procedure to characterize sea water. In 1974, Gaevaya and Khesina (1974) were able to differentiate fifteen polycyclic aromatic hydrocarbons in octane at 0.1 ppm levels. However, Gaevaya's methods are relatively insensitive, due to compound interference, the basic weakness of all spectrometric methods. To ensure exactness in identification, the compounds under investigation must be isolated prior to the spectrometry. For fluorescent compounds this is typically done by thin-layer chromatography (TLC) (Segura and Gotto, 1974). An analog of emission spectrometry is absorption spectrometry. The adsorp-

tion spectrum of colored waters was used by Skopintsev and Krylova (1955) to investigate humic acids. Datsko (1944) attempted to develop the method for quantitative work in 1940. Both reported less than satisfactory results due to the many different and interfering compounds that will absorb in the visible band.

Mrkva (1969) abandoned the visible spectrum for the Ultraviolet (UV) in an attempt to find a more discriminating phenomenon. Analyzing at three specific wavelengths, he unsuccessfully attempted to distinguish various humic acids. Huhn (1974) used similar methods while investigating lipophilic substances in the recharge of groundwater. UV spectrometry, like the visible methods, is a nonspecific method. Balch et al. (1975) has used this technique for general monitoring. Operating qualitatively when only one compound is present, UV is the detector of choice for high pressure liquid chromatography. In such a system both qualitative and quantitative data can be recorded (Knox, 1975). There are, however, organic compounds that do not absorb well in the UV or visible spectrum. Turbidity measurements should be included in this subsection because they are often conducted on the same instrument upon which absorbance is measured. Lee and Walden (1970) used turbidity to characterize kerosene in effluents after lengthy preparative work. They reported sensitivities of 10 to 100 ppm.

Mallevalle (1974) moved to the infrared energy band (IR) when investigating the carbon tetrachloride extracts of surface water at the three wavelengths that are characteristic of alkanes, thereby attempting to develop a method for the measurement of hydrocarbons. Simard et al. (1951) also working in carbon tetrachloride, investigated phenols by concentrating their

attention at the appropriate wavelength for C-OH absorption. Frisch and Kunin (1960) and Ungar (1962) both used the full IR band to attempt to characterize the organics that were fouling the anion exchange resins in water treatment systems. Jelts and Dem Tonkelaar (1972) compared gas chromatography and infrared spectrometry for the determination of mineral oil in water. They favored IR because it identified exactly the presence of mineral oil, and because of the relative non-volatility of mineral oil. Obremski (1974) analysed specific compounds such as dieldrin and aldrin at ug levels by IR. He did not describe how he separated one from the other. If both were present, there would be extensive interference.

Quantitation by IR spectrometric detection is subject to interference just as is visible and UV spectrometric methods. The solution to this problem is similar to the solution for UV work, pretreatment by chromatographic procedure. For IR, gas chromatography lends itself well. The interfering solvent and solutes are well separated, and IR work is easily adapted to the gas phase. In 1971 Brown et al. (1971) reported success with both support coated open tubular (SCOT) and packed column methods. In 1975 Katlafsky and Dietrich (1975) constructed and evaluated an online GC/IR that required 200 ug of compound to produce a spectrum sufficient to identify the compound. With 20 ug functional groups could be identified. This is a sizable amount of material and concentration of 20 to 200 times is required for identification of materials present at ppb levels in waters.

GLC Detectors: The most sensitive detection technology is that used with GLC. Three basic detectors are in use, and are described in detail in the scientific literature (McNair and Bonelli, 1969). Most sensitive,

electron capture detectors are able to detect 0.1 picogram quantities of electron trapping compounds such as halogens, carbonyls and oxidized nitrogen compounds. Flame ionization detectors can detect 20 picograms of aliphatic compounds. Thermal conductivity detectors can detect 10 micrograms of most compounds. The detectors cannot differentiate between similar compounds so are useful only after gas chromatography has been used to separate the constituents to be identified.

Mass Spectroscopy: Mass spectroscopy (MS) is perhaps the best current detection technique. The spectrum of the unknown compound can be printed, televised, or transmitted to a computer for comparison with spectra of known compounds. It has been suggested that research on and practical application of such methods are primary and paramount (Christman and Hrutfiord 1973; Middleton, 1973). Hites and Biemann (1972) and Arpino et al. (1974) also suggest HPLC/MS, but the major impetus has been in the GC/MS area. These expensive methods have been used primarily for research, although use for routine analysis has become more common in recent years.

Early work on organics in water by MS was published by Melpolder et al. in 1953. Using hydrogen stripping techniques, they examined the volatile fraction of organic contaminants in surface waters. In 1973, Burnham et al. reported on two Iowa water supplies contaminated by taste producing material. Evan's (1973) study of Clear Lake pollution by organics did make use of a computer reference file. Manka et al. (1974) characterized organics in secondary effluents by GC/MS/Computer, and Hellar et al. (1975) reports on the future of routine monitoring with these methods. They suggest that a file of about 50,000 compounds will be available in the near future.

Table 1-1 provides a summary of the discussion above. As the data indicate, any compound that is present in water in concentrations of less than 25 ppb will require some form of concentration prior to detection. If specific identification of the compound is essential, then extraction from water is also required, thereby necessitating analyses by UV, IR, Visual and Mass spectrophotometry, usually preceded by liquid, thin layer or gas chromatography.

Extraction Schemes

With several detection methods available, attention should be turned to concentration schemes which have been developed to provide the masses of organic solutes needed to be within the detection limits of the available instruments. Typically, solubility characteristics are exploited, but some concentration procedures are based on other physical properties of organic solutes.

Gas-stripping: Gas-stripping has been used effectively to concentrate low weight organic compounds of the C_1 to C_9 range. Perras (1973) developed a portable technique that extracted alkanes from C_3 to C_6 . The EPA recognized the volatiles method as developed by Bellar and Lichtenberg (1974), who reported recoveries of 90 to 95% for C_5 to C_9 compounds. This method was able to extract compounds up to the C_{15} range at 27% recovery. Bellar suggests the method for those compounds less than two percent soluble in water and with boiling points less than 150°C . High extraction efficiencies for such compounds are common. Using such stripping methods, Webber and Burks (1972) extracted 95% of the methane and 97% of the butadiene present

Table 1-1

APPROXIMATE SOLUTE/SOLVENT REQUIREMENTS
FOR VARIOUS METHODS OF ANALYSIS

Method	Maximum Sensitivity	Sample Size	Min. Detectable Conc.	Solvent	Ref.
GRAVIMETRIC CCE/CAE	1 mg	-	100%	N*	32,33
TITRATION					
KMnO ₄	2 ug	20 ml	0.1 ppm	water	196
Dichromate	2 ug	20 ml	0.1 ppm	water	189
ELECTRODYNAMIC					
Voltammetry	25 ng	10 ml	25 ppb	water	1
Electrophoresis	-	6 ml	50 ppm	water	120
OXYGEN DEMAND					
BOD	100 ug	100 ml	100 ppm	water	165
ABSORBANCE					
TOC	15 ng	10 u1	1.5 ppm	water	57
IR	20 ug	1 u1	20 ppth	N,NI*	97
UV/VIS	20 ug	2 ml	10 ppm	NI	98
CHROMATOGRAPHY					
GLC - EC	10 pg	1 u1	10 ppb	volatile	134
GLC - FID	1 ng	1 u1	1 ppm	volatile	134
TLC	100 ng	0.5 ml	0.2 ppm	volatile	28
MASS/ION RATIO					
Mass Spec.	50 ng	1 u1	50 ppm	N,NI	35,36

*N = none, NI = non-interfering

at 20-30 ppm levels. Mieure (1973) extracted up to 93% of the chloroform present in prepared waters.

Commonly, this method is used prior to gas-chromatography. In 1953, Melpolder et al. (1953) used gas-stripping techniques in conjunction with GC and mass spectrometry to identify volatiles present in concentrations of 0.01 ppm. In 1960, Frisch and Kunim (1960) found 0.72 ppm volatiles by infrared spectrophotometry used in line with gas stripping. Ploder (1974) used air-stripping and a SCOT column to find compounds present at 0.1 ppm levels. Air-stripping is a valuable adjunct to gas chromatography. Grob (1973) was able to identify 63 compounds at concentrations as low as 2 ppb. However, many investigators feel that identification of compounds present at such levels is not quantitative. Desbaumes and Imhoff (1972) attempted to mitigate that complaint by running calibration curves with each series of extractions. However, when they reported 0.01 ppb concentrations of hydrocarbons in field samples, they specifically withdrew their statement of confidence in the accuracy of their quantitation methods.

The attempt to counteract the solubility of volatiles with stripping techniques appears to be successful, as Morita et al. (1974) were able to identify 25 compounds using this procedure. However, comparison with approaches that take advantage of solubility verify that the stripping method has its limits. Hewes, Smith and Davison (1974) found that extraction can compete with stripping at low relative volatilities.

Liquid - Liquid Extraction: Liquid extraction is the oldest and perhaps the most widely used extractive tool at the investigators disposal. Two basic parameters determine the efficiency of these methods, the choice

of solvent and the extraction apparatus.

Choice of solvent effectively limits the extraction, no matter what apparatus is used. For example, Goldberg et al. (1973) were able to get only 4.80% of the solute, 2-pentanol, from water using benzene. They reported the ability to get 110.35% of it out using trichlorotrifluoroethone. Their apparatus was a counter-current continuous four stage extractor. Cooper and Wheatstone (1973) were equally successful by selecting methyl isobutyl ketone (MIK) for removal of phenol from water. They reported 100% recoveries and suggested this work for standard use.

The attributes of a universal solvent, useful in all circumstances, include: immiscibility with water, polarity sufficient for extraction of acids, as well as relatively nonpolar aliphatics and aromatics, and the ability not to mask solute compounds during detection. Although no simple compound has been found that is best in all cases, some standard solvents are in use which approximate these requirements. For example, hexane has been used for all types of work from identification of pesticides and PCB's, to diesel and outboard motor oil, hydrocarbons, lignosulfonics and lipophilics. Ether is often used for pesticides, PCB's, and many other compounds. Chloroform is the solvent for the CCE method, and has been used for other work as well. Table 1-2 is a short list of investigations with data on solvents, solutes, recoveries and sample sizes. This list is also a quick entry into the literature on liquid-liquid extraction.

There are two basic approaches to extraction with liquid solvents, batch extraction and continuous extraction. The purpose of both methods is to mix the solvent with the sample water optimizing transfer of organic

Table 1-2

REPORTED LIQUID - LIQUID EXTRACTION METHODS

Reference	Date	Solvent	Volumes Smp1/Slvnt	Conc. Factor	Recovery %	Solute	Method
Kawahara	1967	hexane hexane-benzene	2 l/ 50 ml	40	64-100 66-83	dieldrin, endrin	batch
Goldberg	1971	hexane, benzene CCl ₄ C ₂ Cl ₃ F ₃	37.81/50ml	Var. 75.6	72-118	10ppm toluene, 2-pentanol	multistage continuous
Kahn	1964	ether	1351/500 ml	Var.	83-97	1ppb aldrin	continuous
Headington	1953	benzene	-----	----	75-127	10ppm oil	batch
Hoak	1962	MIK	500ml/20ml	25	88-99	100ppm phenol	continuous
Luessem	1972	liq. butane	-----	----	>hexane	--	batch
Borneff	1969	benzene	500l/18 l	2717	---	10ppt PAH	batch
Cooper	1973	MIK	50ml/50ml	1	100	100ppb phenol	batch
Eichelberger	1971	ether, hexane	1 l/60ml	16.6	90-100	10ppb pest.	batch
EPA	1974	tetralin	1 l/2ml	500	---	various	batch
Harvey	1973	acetonitrile	80 l/300 ml	260	---	1ppt PCB's	batch
Hughes	1972	hexane	1.51/50ml	30	74-85	toxaphene	batch
Jelts	1969	CCl ₄	100ml/5ml	20	---	1ppm oil	batch

Table 1-2 Continued

Reference	Date	Solvent	Volume Smpl/Slvnt	Conc. Factor	Recovery %	Solute	Method
Mallevalle	1974	CCl ₄	51./10 ml	500	95-100	50ppb hydrobn	multistage batch
Murtaugh	1967	hexane	21./100ml	20	---	100ppt sterols	batch
Hites	1972	methylene chloride	3.5 1/200ml	17.5	---	50ppt pyrene	batch
Stoeber	1969	trioctylamine CCl ₄	--	--	---	lignosulfonics	---
Veith	1971	hexane	1.6 1/400ml	4	---	10ppt PCB's	multistage batch
Huhn	1974	HCCl ₃	--	--	49	lipophilous	---

solutes into the solvent according to solubility principles. The advantage of a continuous extraction device is that far more water can be extracted with the same amount of solvent used in most batch methods. The basic disadvantage is that contact time between solvent and sample can be much less than batch methods. With appropriate flow rates, this disadvantage can be overcome. However, large volumes of sample water are difficult to transport, and the glassware and auxiliary heating or cooling equipment required generally prohibit field extraction.

Solvent extraction is useful for two reasons, it removes water from the characterization process, and concentrates the organic solutes, an essential for many detection techniques. The solvent volume is usually further reduced from that volume necessary for extraction by evaporation procedures which will be dealt with in full in a subsequent section. Considering only the extraction process, concentration nearly always takes place. One agency that has placed great confidence in liquid extraction is the EPA. One liter of New Orleans drinking water was extracted with two ml of tetralin. However, the recoveries were not as high as obtained using the carbon adsorption method (CAM), so there are no reported efficiencies (US-EPA, 1974). Another ambitious method was reported by Borneff and Kunte (1969). They extracted 500 liters of water with 18 liters of benzene, reproducibly extracting 10 ppt of the polynuclear aromatic hydrocarbons (PAH) present. Veith and Lee (1974) were able to extract PCB's at similar concentrations with 400 ml hexane and 1.6 liters of sample water.

Two basic conclusions can be made regarding liquid-liquid extractions: (1) proper solvent selection strongly influences extraction efficiency; and (2) recovery of a particular solute can only be roughly estimated unless

recovery efficiency is determined by investigations with that solute.

Adsorption: By 1916 water specialists had already recognized and published conclusions about the absorptive qualities of various adsorbents, in particular with respect to color materials of organic origin (Saville, 1917). In 1940, Lemaire (1940) published a review of synthetic adsorbents. That review disclosed the primary research interests as removal of organics from water. Such work has continued (Luh and Baker, 1971; Dufort and Rud, 1972; Orhme and Martinola, 1973; Ohtani, 1974; Shevchenko et al., 1974; Love et al., 1975).

Removal of organics from water by adsorption onto various resins and polymers does not of necessity presume an ability to desorb them from the adsorbent. This presumption, if valid, would allow methods to be designed to recover the extracted materials for the purpose of analysis.

In August of 1951, Brause, Middleton and Walton (1951) described a method for the extraction and recovery of organic materials using carbon adsorption and ether extraction. It was this work that has evolved into the standard method for extraction of organics by adsorption. The current method (organics-carbon adsorbable, O-CA) is used by EPA, and is fully described by Buelow, et al. (1973).

Carbon adsorption is not without technical weaknesses. In 1962, Hoak demonstrated that desorption was less than quantitative, and that compounds may change chemically while adsorbed. In 1965, Booth, English and McDermott (1965) "confirmed that activated-carbon columns, even with the greatest practical contact times, do not adsorb all organic matter present." More recently, Pahl, Allen, Mayhan and Bertrand (1973) published a series of

articles which show that there is no reasonable method that quantitatively desorbs all organics from carbon. The data on chemical reactivity of activated carbon and poor desorption capability when using it instigated serious research into other adsorbents.

The logical replacement for carbon would be an organic solid that is not reactive, that would adsorb as well, and would desorb better. Ion exchange resins do not meet these criteria, but historically were the next adsorbent to undergo intense investigation. The investigation was of short duration as it was found that the neutral compounds do not adsorb quantitatively (Frisch and Kunin, 1960) and the polar ones do not desorb quantitatively (Petrariv et al., 1969), even with appropriate pH correction. It is assumed that those forces which encourage solution are not strong enough to compete with the ionic forces of dissociated acids and bases.

The proliferation of solid materials from a growing chemical and plastics industry have begun to provide candidates for a better adsorbent. Three groups have investigated polyurethane foam (Bedford, 1974; Gesser et al., 1971; Musty and Nickless, 1974). They reported recoveries of 95-100% for pesticides and PCB's with appropriate pH corrections. There has not been extensive field testing, however, and Bedford (1974) indicated that the foams fail rapidly in relatively turbid waters.

Tenax, a recently described adsorbent is characteristic of the national concern for removal and identification of organics in water. It was developed specifically for that purpose. Leoni et al. (1975), published recoveries of 90% and better for pesticides and PAH using this registered product. It is the second in a growing generation of commercially produced

adsorbents designed to replace carbon. The first, and the one used in the research undertaken by the author, is an Amberlite product called XAD resin. There are various types of this macroreticular resin, and the character of the one used is discussed immediately following Table 1-3. Recoveries using XAD are continually reported as near 100% (Bastos et al., 1973; Burnham et al., 1972, 1973; Kelsey and Mosgatelli, 1973; Musty and Nickless, 1974; Riley and Taylor, 1969).

An example of a new direction in adsorbent development is the work Ahling and Jensen (1970) have done with what has heretofore been used as gas-chromatographic solid and liquid phases. They used 10% carbowax and 30% undecane on Chromasorb W and reported up to 100% recoveries for pesticides and PCB's. Table 1-3 describes some of the literature on adsorbents.

XAD-2 Macroreticular Resin: The solid adsorbant used throughout this investigation is the macroreticular resin XAD-2, an Amberlite product of Rohm and Hass Company, Philadelphia, Pennsylvania. The resin is a polystyrene-divinylbenzene (DVB) co-polymer.

In 1965 research with this resin indicated an increase in entropy for the adsorption of organic solutes to the copolymer (Schneider, et al., 1965). Schneider described 'icebergs' of fatty acids in water being broken up and adsorbed by the resin. The best source for information about XAD-2, and other similar resins, remains an article by Gustafson and Paleos (1971). They suggest Van der Waal's forces as the important chemical phenomenon explaining adsorption. It remains unclear if physical size of organics solutes affects adsorption significantly.

The copolymer is formed into spheroids of varying mesh size. Each

Table 1-3

RECOVERY DATA FOR ADSORBENTS

Ref.	Date	Adsorbent	Sample Source	Volume Smp1/Slvnt	Solvent	Conc. Factor	Recovery %	Solute
Brause	1951	carbon	surface	45420L/300m1	ether	151,400	--	3ppb var.
Carswell	1973	carbon	drnk wtr	60 L/250m1	CHCl ₃	200	---	CCE
Eichelberger	1971	carbon	drnk wtr	1500L/3 L	CHCl ₃	500	5-88	pest. aldrin
Greenberg	1965	carbon	surface	1500L/ 3L	CHCl ₃	500	67	CCE
Hoak	1962	carbon	surface	-	CHCl ₃	-	21-44	pheno1
Lee	1970	carbon	effluents	1L/ 15m1	acetone	66.6	90-97	10-100ppm org.
Rosen	1959	carbon	surface	8L / -	CHCl ₃	-	75	5ppm chlordan
Shevchenko	1974	carbon	drink wtr	-	-	-	70	1indane
EPA	1975	carbon	drnk wtr	60L	CHCl ₂	-	-	CCE, CAE
Gesser	1971	U. foam	pure wtr	-	acetone	-	91-98	2ppb PCB's
Musty	1974	U. foam	pure wtr	1L/ 150m1	ether	6.6	100,44-99	pest, PCB's
Laqua	1973	vinylacetate	drnk wtr	-	ether	-	>carbon	var.
Ahling	1970	chromasorb		200L/ 10m1	ether	20000	100	10ppb pest
Murtaugh	1965	ion exch	river	60L/30m1	ether	200	-	-

Table 1-3 Continued

Ref.	Date	Adsorbent	Sample Source	Volume Smp1/Slvnt	Solvent	Conc. Factor	% Recovery	Solute
Leoni	1975	Tenax	drnk wtr	20L/20ml	ether	1000	85-100	1ppb pest, PAH
Burnham	1972	XAD2/7	river	50L/50ml	methanol	1000	97	.37ppb neutrals
	1973	XAD2	grnd wtr	1000L/100ml	ether	10000	90	1ppb var.
Harvey	1972	XAD2	ocean	5L/40ml	acetonitrile	125	100	10ppt chlororg.
Kamikubo	1970	XAD1/2			methanol		100	neutrals .5ppm
Musty	1974	XAD 4	pure wtr	1L/100ml	hex/ether	10	100	1ppb PCB
		XAD 2	"	"	"	"	45-71	"
		XAD 8	"	"	"	"	28	"
Richard	1974	XAD 2	river	4L/200ml	acetonitrile	20	=to liq. extn	1ppb pest.
Ripley	1969	XAD 1	ocean	1L/100 ml	methanol	10	100	pest.
Bastos	1973	XAD 2	Urine	100ml/10ml	ether	10	81-100	acids/bases
KeIsey	1973	XAD 2	Urine	500ml/30ml	methanol	16.6	-	chlorpromazine
Junk	1975	XAD 2	pure wtr	1L/25ml	ether	40	100	var. org.
EPA	1975	XAD2,4,7,8	pure wtr	1L/20ml	chloroform	50	40-90	var. org.

sphere is 'open latticed' which provides for very high surface area, compared to traditional crystalline resins.

Differentiation by Size and Weight

One approach to the analysis of organics in water will not fit appropriately into the proscribed sections on extraction, concentration, fractionation and detection because it involves all of these processes. That approach involves centrifugation and filtration. The terms centrifugation and filtration each indicate a class of methods. Centrifugation can be batch or continuous flow; it can be varied to separate by weight and/or size down to, but not usually including, colloidal sizes. It can be used alone or in a train including preceding filtration devices. Filtration typically removes materials of 0.45 micron diameter or greater. Below 0.45 microns, the term ultra-filtration is usually applied. As greater selectivity is desired, the investigator begins to encounter reverse osmosis (RO) techniques and gel permeation; and at some point, only gases pass through the media (pervaporation).

The utility of these methods depends to a large degree upon the intent of the researchers. Investigation of secondary and primary effluents have put major emphasis on differentiation by size or weight (Groves, 1974; Rickert and Hunter, 1967; EPA, 1971). Characterization of organics in effluents has been conducted by centrifugation (Rebhun and Manka, 1971), reverse osmosis (Gurtz, 1967; Reuter, 1973), and gel permeation (Chudoba et al., 1973; Manka et al., 1974). Tardiff and Deizner (1973) used RO and pervaporation to concentrate organics found in drinking water. Hall and Lee (1976), Varshal et al., (1974) and Migalati and Pushkarev (1973) in-

investigated organics in natural waters using RO and gel permeation.

There is little data on the efficiency of these methods. Varshal et al., (1974) reported that during fractionation by permeation techniques less than forty percent of the organics were lost. Reuter (1973) indicated that 150 mg/l total carbon permeated a RO apparatus designed to remove organics from primary effluent waters. This is an inordinately large concentration in a supposedly clean effluent and belies the inefficiency of one RO apparatus.

At best, these methods provide fractions that must be subjected to further fractionation or extraction before being amenable to identification of organic constituents. Reports have not been published on a comprehensive system of methods designed to get all components of the organic fraction in waters. These methods do not specify much more than size of the components unless the methods are followed by more sensitive detectors.

Concentration Methods

Concentration usually takes place at every step of a search for organics in water. However, some steps are designed to do only the task of concentration. This is necessary because most organics are present in natural waters in low concentrations relative to the amounts needed by the detection methods.

Concentration generally exploits the characteristic solubility and volatility of substances in solution. Plumb and Lee (1973) concentrated organics by vacuum distillation of raw waters. The assumption is that the solubility of the organics is so great that at low temperatures and pressures, the loss of mass from the distillation flask is predominately water.

Some organic loss may occur through formation of azeotropes, however the success of vacuum distillation has been shown by Kuninobu and Morikawa (1974). They distilled 300 ml water treated with 0.115 eq. $\text{Ca}(\text{OH})_2$ to 50 ml and recovered 99.995% of the formaldehyde that was placed in solution.

For water samples containing less soluble organics, such recoveries should not be expected. In non-quantitative work Rebhun and Manka (1971) and Katz et al. (1972) used this method to concentrate effluent contaminants. In both cases, precipitates formed and were redissolved in an organic solvent. Other work of this nature is indicated in Table 1-4.

Similar methods of concentration are used when organic compounds have been concentrated in organic solvents. In this case, an additional property aids the process. Generally, organic solvents have lower boiling points than the solutes being investigated so lower temperatures are required. This allows simple distillation, leaving the solutes in the original flask in a concentrated form. Many methods and apparatus have been developed to effect such distillation. The method of choice, as described in the published O-CA method (Buelow et al., 1973) and other work (Junk et al., 1974) is use of the Kuderna-Danish (KD) evaporator. Developed in a Denver lab in 1951, it has been used extensively, and its efficiency has been investigated at length (Gurtz, 1967). Gunther et al., (1951) were able to concentrate pesticides in solution by reducing volumes from 200 ml to three ml with recoveries of 80-84%. Goldberg et al., (1973) found that such recoveries are not routine, and that depending upon evaporation rate and final volume, recoveries are from 26-72%. They suggested solvent volume reduction to only 50ml from 500. Junk et al. (1974) found that evapora-

Table 1-4
REPORTED CONCENTRATION TECHNIQUES

Ref.	Date	Solvent	Solutes	Method	Conc. Factor	% Recovered
Plumb	1973	nat wtr	various	vac dist	-	-
Katz	1972	effluent	various	vac dist	-	-
Rebhun	1971	effluent	various	vac dist	-	-
Kuninobu	1974	pure wtr	formaldehyde	distil.	6x	99.995
Mueller	1958	pure wtr	org acids	evap	-	91-100
Bunch	1961	effluent	various	vac evap	20x	-
Black	1963	nat wtr nat wtr	fulvics fulvics	evap freeze	151x 75x	- -
Baker	1967	pure wtr	various	freeze	var.	48-99
Gunther	1951	org. sol.	org. sulfite	KD*	66x	80-84
Goldberg	1973	org. sol.	various	KD	10x	26-72
Junk	1975	org. sol.	various	KD	41x	93-105

* KD = Kuderna-Danish

tion rate has no effect provided it is maintained within the range of 0.5 to 2 ml/min. They did suggest that the shape of the concentration vessel is critical, and, using a special flask constructed from a 50 ml round bottom flask and a tapered centrifuge tube, obtained recoveries of no less than 93% while concentrating from 25 ml to 0.6 ml.

A second concentration technique is crystallization. In current work, the solvent is frozen out, leaving the solutes in the remaining water and in high concentration. Black and Christman used this method in 1963, freezing out water in a large drum. Water volume was reduced from 40 gallons (151 L.) to one liter. Recovery efficiencies were not reported.

The American with the greatest experience in freeze concentration is Robert Baker. He published a series of four papers entitled "Trace Organic Contaminant Concentration by Freezing" (Baker, 1967a; 1967b; 1969; 1970). Using a rotating flask and cascade or multistage techniques, many liters of water can be concentrated to a final volume of no less than 30 ml with recoveries of up to 100%. Factors that interfere with the process involve the presence of inorganic salts in solution. No good solution to that problem was identified.

Fractionation Schemes

Fractionation is useful as it facilitates the detection process by permitting better separation of the components present and removal of interferences. For example, 66 separate organic compounds were discovered in the New Orleans water supply in a search conducted by EPA (1974). Most of these compounds were identified by gas chromatography. No one column can adequately separate all materials present. However, if, for example,

only acids were present, a column can be used so that excellent separation of acids will occur. A distinct separation is important if detection is further refined by mass spectrometry, infrared spectrometry, or UV spectrometry.

Acid Fractionation: The character of organic compounds may be described by functional groups such as amines, carboxylic acids, esters and so on. They may also be described by structural characteristics, for example alkanes, alkenes, alkynes, aromatics and so on. In acid fractionation procedures organics are divided into strong acids, weak acids and phenolics, neutrals, weak bases, strong bases, and amphoteric. This is accomplished by pH adjustment and extraction. The classic work on this method is that of Shriner and Fuson (in: Malcolm et al., 1971). The method relies on the partitioning of organic species between an acid or alkali water phase and an organic solvent phase. As pH is varied the non-polar (unionized) species dissolved in the organic solvent while the polar (ionized) species remain in aqueous solution. Neutrals migrate into the organic solvent with very wide ranges of pH.

The appeal of this method lies in its wide applicability. A pH adjustment can be made prior to the extraction of water, thereby causing selective extraction (Bark et al., 1972; Bunch et al., 1961; Rebhun and Marka, 1971). The adjustment can be done prior to use of an adsorbent (Junk et al., 1974). A pH adjustment can facilitate selective desorption of adsorbents (Bastos et al., 1973; Burnham et al., 1972, 1973; Christman and Hrutfiord, 1973; Hoak, 1962; Laqua, 1973; Tardiff and Deizner, 1973). Or as Shriner and Fuson described, the fractionation can be done after extraction of waters or ad-

sorbents (Kawahara et al., 1967; Malcolm et al., 1971).

An important classification system that was developed prior to common use of gas chromatography and mass spectrometers involves the acid fraction of the above method. Investigations on the nature of color in water resulted in the determination of the percentage of organic matter in each of three subgroups within the acid fraction. These are known as the generic groups fulvic acids, humic acids and humic acids. Table 1-5 is a short listing of research that has used the acid fractionation method.

Chromatographic Fractionation: Another method used to separate organic solutes into groups or individual components is chromatography. Four types of chromatography are in wide use, gas, liquid, high pressure-liquid, and thin-layer. Each of the methods exploit compound specific partition coefficients between a carrier solvent or gas and a solid support coated with a liquid phase. Partitioning may be on the basis of solubility, adsorption, molecular configuration and/or molecular weight.

Liquid chromatography (LC), and its successor, high pressure liquid chromatography (HPLC), are valuable fractionation methods. However the detection techniques typically used in conjunction with LC/HPLC are not specific. To improve specificity, Knox (1975) depicts the role of HPLC as a preparative method for mass spectral analysis. He reports that such methods can separate 0.1 to 1.0 mg solute per gram of packing, and is useful for separation of compounds of greater than 1000 molecular weight. Both Knox and Saika (1970) have reported that certain organics adsorb strongly onto some column packing materials reducing the utility of the method.

Because the carrier phase is liquid, pumps are routinely employed.

Table 1-5
 INVESTIGATIONS USING ACID FRACTIONATION

Ref.	Date	Sample	Fractions	Method
Bastos	1973	Urine	acid-neutral, base-neutral	selective desorp'n of XAD w/HCl/ether then borax/HCCl ₃
Laqua	1973	drnk wtr	all	SF* frac. of ether extract of various adsorbents
Tardiff	1973	drnk wtr	all	selective desorp'n of XAD
Hoak	1962	drnk wtr	all	SF frac. of ether extract of carbon
Christman	1973	drnk wtr	all	suggests selective desorp'n of XAD
Burnham	1972	drnk wtr	neutrals	selective desorp'n of XAD 2/acid +base discarded
Junk	1975	drnk wtr	all	pH adjustment prior to XAD adsorption
Brause	1951	surf wtr	all	SF frac. of ether extract of carbon
Kawahara	1967	surf wtr	all	SF frac. of ether extract of carbon
Bark	1972	effluent	bases	extract'n of pH adj. water
Rebhun	1971	effluents	all	SF frac. of ether extract of vac. evap'd concentrate
Bunch	1961	effluents	all	SF frac. of ether extract of vac. evap'd concentrate
Black	1963	colored wtr	acids	fulvic/hymatomeLANIC/humic

*SF = Shriner and Fuson

The pressure established introduces further complications upon injector design. If used with a detector as a characterization apparatus, HPLC tends to have high background noise to pumps and injectors (Berry and Kargen, 1973), although recent developments in injector and detector design have eliminated many of these difficulties. HPLC offers extremely high theoretical separating capability which has led to increased application of this technique. Ohtani routinely separated xylene isomers, a task possible at high efficiency only by LC or GLC. Lee and Chang (1975) devised a scheme of repeated chromatography with a combination of various absorbents, stationary phases and elutents. It is noteworthy that they feel their methods are too tedious and long for general work. Table 1-6 lists some of the recent work in LC and HPLC on organics in water.

Table 1-6

LIQUID CHROMATOGRAPHY INVESTIGATIONS OF NATURAL WATERS

Ref.	Date	Method	Support	Solute
Chu	1973	HPLC	XAD 2	Steroids, Phenols
Lee	1975	HPLC	various	Flavor Compounds
Jolly	1973	HPLC	-	Trace org. in nat waters
Hites	1972	LC	-	Org. compounds in Charles River
Koehl	1974	LC	-	39 amino acids
Plumb	1973	LC	sephadex	Org. compounds in nat waters
Zaika	1970	LC	polystyrene	Org. compounds in nat waters
Hall	1974	LC	-	Org. matter in Lake water
Ohtani	1974	LC	zeolites	xylene in effluents waters

Gas-liquid chromatography (GLC or GC) provides markedly better separation capability than standard, non pressurized, LC, and comparable to HPLC. Sample sizes are reduced to microliter levels because detectors used with GLC are capable of responding to nanogram and picogram quantities of solute mass. GLC is most often limited by the volatility of the sample compounds. Sophistication of column design continues to increase the capability of the technique. Urov et al. (1974) reported the use of a column which separated anthracene and phenanthrene, two representatives of the polynuclear aromatic hydrocarbon (PAH) family that are normally considered high boilers and unlikely to volatilize. In other cases where volatility is low, derivatives can be formed which allow use of GLC methods. Table 1-7 is a short compilation of reports on organics in water separated and detected using the gas chromatograph. Note that two basic extraction procedures are used prior to gas chromatography, purging and solvent extraction.

Thin-layer chromatography provides an alternative to GLC when high boilers are under investigation. For example, Borneff and Kunte (1969) developed a method for identification of over fifteen PAH. Thin-layer also provides a technique for repetitive testing requirements. Thideman (1974) has reported on coated foils for the detection of insecticides and pesticides. Atanus (1974) reported that the Chicago Metropolitan Sanitary District used a TLC method for daily testing of waters containing hexane solubles. Aly (1968) suggests TLC for routine identification of phenols. Although separation is excellent for some compounds, the detection of those compounds following TLC is not as sensitive as those used with HPLC or GLC,

Table 1-7

GAS CHROMATOGRAPHIC SEPARATION AND DETECTION
OF ORGANIC MATERIAL IN WATER

Ref.	Date	Source	Solute	Concentration Method
Ploder	1974	surf wtr	CHCl ₃	Headspace purge
Perras	1973	ocean	hydrocarbons	purge
Mieure	1973	surf wtr	HCCl ₃ , phenol	purge
Desbaumes	1972	effluent	hydrocarbons	purge
Bellar	1974	surf wtr	volatiles	purge
Cooper	1973	effluent	phenols	MBK extr'n
Goma	1971	nat wtr	hydrocarbons	surfacant emulsion
Jelts	1972	nat wtr	mineral oil	nitrobenzene extr'n
Kawahara	1971	surf wtr	phenols, acids	CAM extr'n
Lamar	1963	surf wtr	acids	butane extr'n
Mueller	1958	surf wtr	acids	ether extr'n
Nurtaugh	1967	effluent	sterols	hexane extr'n
Smith	1971	-	aliphatic ciamines	-
Van Hyssteen	1970	pure wtr	fatty acids	none
Urov	1974	-	anthracene	-

and quantitation is very difficult without removing the solutes from the thin layers and subjecting them to additional analytical techniques.

Summary

This review points out that not enough is known about, nor are appropriate methods available for, the identification of high molecular weight organic compounds that may be in water - compounds that are assumed to cause color and filter clogging. However, for many compounds, especially those being manufactured and deposited in water resources, a legitimate train of processes may be constructed which allows accurate identification and quantitation.

Section II

Experimental Design

The underlying goal of this work was to develop and evaluate a method designed to extract, fractionate and concentrate organic contaminants of water using known compounds representative of those expected to be present in the environment. Under investigation is an XAD resin procedure consisting of five steps. Figure 2-1 indicates the flow of the organic solutes through this procedure.

Five questions required investigation: (1) What is the potential of this procedure for lab and field applicability, for reduction in handling of liquids and solids, and when there are large numbers of analyses? (2) What is the experimental assessment of previously published methods that approximate this new XAD procedure? (3) What is the ability of this procedure to extract organic solutes, especially with respect to the varying nature of the solutes and the range of possible flow rates through the resin? (4) What is the ability of a solvent or solvent mixture to remove adsorbed organic solutes? (5) What is the effect of ultra-cold drying techniques and concentration by solvent evaporation, and can losses during these steps be accounted for in a systematic way?

The description of materials and equipment follows, with the description of the experimental procedures concluding the section.

Equipment and Materials

Macroreticular Resin: XAD-2 resin, described in section one, is shipped in plastic gallon bottles, and is saturated with water. New resin

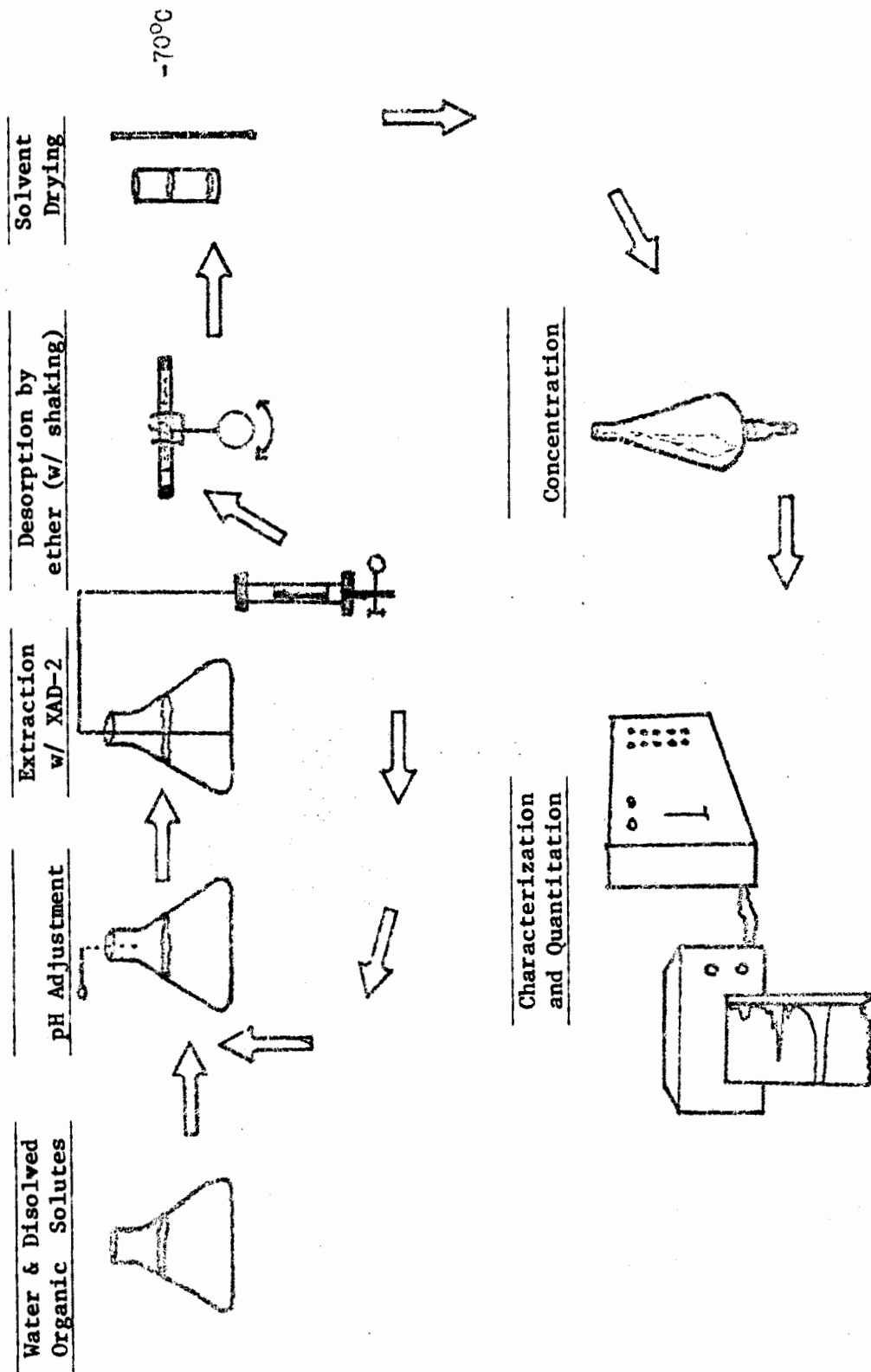


Figure 2-1
 FLOW OF ORGANIC SOLUTES THROUGH
 THE ANALYTICAL PROCEDURE

and used resin, kept separate, are stored under water. As received the resin is contaminated and must be cleaned before use. Both new and used resins are cleaned by a method consisting of acid and base washing, followed by a series of extractions (Soxhlet apparatus), using methanol, acetone or acetonitrile, and ether, in that order, and each for eight hours. The resin is then washed with methanol under which it is stored in ground glass stoppered flasks, and refrigerated. Electron capture-GC has detected some contaminants that remain on used resin in spite of the cleaning procedure, and that were extracted from the resin with the ether used in the experiments. It is unclear whether these contaminants were on the resin or in the solvents. FID-GC did not detect any contaminants remaining on the resin after cleaning using the above procedure. It is suggested that any contaminants remaining on the resin will not interfere with FID-GC characterization, but that they can potentially affect the quality of GC/MS analysis. Since the contaminants only appear on used resins, new resins may be a requirement for routine uses. Additional work may be required to produce a cleaning procedure capable of removing all contaminants from used resin, although the procedure given above produces a resin adequate for most applications. Only new resin, appropriately cleaned, was used in the work described by this report.

Prior to use, the methanol, under which the resins are stored, must be replaced by water. It was discovered that some ether also remains on the resin, and adding water quickly results in the formation of a very small ether fraction. The methanol and ether are removed by washing 200 ml of water through the resin in the experimental extraction column with

gravity. The ether fraction that collects at the top of the column is flushed off by gently over filling the column with water. Experimental extraction columns, once filled with resin and washed with water, can be stored in a sealed condition for reasonable periods of time, (up to a week) and may be carried into the field for on-sight extraction. Columns to be stored for more than a day should be refrigerated to reduce the possibility of contamination by microbial action. Appendix A provides a comprehensive topical bibliography of the literature on XAD resins.

Solvents: Three solvents are used in the procedures described below; water, diethyl ether and acetone. Water, used to dissolve the organic solutes, is Chapel Hill tap water treated by activated carbon filtration followed by cationic and anionic exchange columns. The treatment is a commercial product called Ultrapure Water Systems, maintained by Hydro Service & Supplies, Inc., Durham, N.C. There are no discernable halogenated organic compounds present in the waters as determined by EC-GC. Sensitivity of that detection system is 10 ppb for chloroform and a 1 ul water injection. Solvent extraction of one liter of water with 200 ml ether, reduced to 1 ml by KD, indicated the presence of no compounds. Detection was by FID-GC, sensitive to 10 ng of 3,4-dimethoxy acetophenone with a 1 ul injection. This suggests that no discernable organic compounds were present at concentrations above 10 ppb. The pH of the water, determined by Fisher, ACCumet Model 420 Digital pH/ion meter averaged 6.91 with a standard deviation of 0.12 over a 10 month period.

Diethyl ether, $(C_2H_5)_2O$, was used as a desorption solvent. It is relatively insoluble in water, dissolves organic compounds with a wide range

of polarities, is readily volatilized, and does not freeze at -70°C . Absolute diethyl ether (anhydrous) was purchased from either Matheson Coleman and Bell Manufacturing Chemists or Mallinckrodt, Inc. The solvent was redistilled in a glass apparatus at a slow rate, and stored in extracted tinned cans with teflon cap liners. The distillate that came over from 34.6 - 35.2°C was retained. Purity was determined by FID-GC. At 80°C , with an OV 101 column, only one peak is recorded (74 sec.). At 225°C with a porapak QS column, four peaks are recorded at 10, 19, 39 and 56 seconds. The major peak is at 39 seconds and contained over ninety-nine percent of the total peak area.

Pesticide quality acetone, $(\text{CH}_3\text{COCH}_3)$ was used to dissolve and dilute organic compounds prior to dissolution of them in purified water, and is used with ether for desorption. The solvent was purchased from Matheson in dark glass one gallon bottles with teflon lined caps. Purity was determined by FID-GC. At 100°C , with an OV 101 column, one peak is recorded at fifty seconds.

Organic Solutes: Eleven organic compounds were used to evaluate the extraction scheme. Two other organic compounds were used as internal standards to determine efficiency of the freezing and concentrating step.

(1) Anthracene, $\text{C}_{14}\text{H}_{10}$, M.W. 178.23, a solid at room temperature, was purchased from Eastman Chemicals. Flat white crystals typically 2-15 mm in diameter, the chemical was dissolved in ether and analyzed for purity by FID-GC. On OV 101 at 210°C one sharp peak was detected at 345 seconds.

(2) 3,4-Dimethoxy-acetophenone, $\text{C}_{10}\text{H}_{12}\text{O}_3$, M.W. 180.20, a solid at room temperature, was purchased from Aldrich Chemical Co. Transparent

prisms of varying sizes, the crystals tended to aggregate into opaque chunks. Purity was determined by FID-GC. At 180°C with OV 101 one sharp peak was detected at 352 seconds.

(3) Benthiazole, C_7H_5NS , M.W. 135.19, a liquid at room temperature, was purchased from Aldrich. The purity of the clear liquid, having a faint almond odor, was determined by FID-GC. At 150°C with an OV 101 column, one very sharp peak was detected at 230 seconds.

(4) m-Xylene, C_8H_{10} , M.W. 106.17, a liquid at room temperature, was purchased from Aldrich. The slightly amber liquid was distilled, and then stored in a glass bottle. The fraction from 136.5 - 137°C was clear and produced a light mothball odor. Purity was determined by FID-GC. Programming at 4°/min from 45°C to 110°C with an OV 101 column, three peaks were observed at 403, 688 and 724 seconds. The second peak accounted for nearly all of the peak area. Chromatography of 300 ng of the distillate, in ether, with a porapack QS column at 225°C, produced a single peak at 358 seconds.

(5) o-Xylene, C_8H_{10} , M.W. 106.17, a liquid at room temperature, was purchased from Eastman Chemicals. The clear liquid, stored in a brown glass bottle, produced a single peak by FID-GC with a porapack QS column at 225°C. Retention time was 272 seconds.

(6) p-Xylene, C_8H_{10} , M.W. 106.17 a liquid at room temperature, was purchased from Eastman Chemicals. The clear liquid, stored in a brown glass bottle, produced a single peak by FID-GC with a porapack QS column at 225°C. Retention time was 241 seconds.

(7) Toluene, C_7H_8 , M.S. 92.13, a liquid at room temperature, was pur-

chased from Allied Chemicals. The clear liquid, stored in a brown bottle, produced a single sharp peak by FID-GC with a Porapak Q column at 215°C. Retention time was 86 seconds.

(8) Ethyl Benzene, C_8H_{10} , M.W. 106.17, a liquid at room temperature, was purchased from Aldrich. The clear liquid, stored in a brown glass bottle, produced a single sharp peak by FID-GC with a Porapak Q column at 215°C. Retention time was 160 seconds.

(9) Cumene, [isopropyl benzene] C_9H_{12} , M.W. 120.20, was purchased from Aldrich. The clear liquid, stored in a brown glass bottle, produced a single sharp peak by FID-GC with a Porapak Q column at 215°C. Retention time was 284 seconds. Cumene was used as an internal standard with the xylene isomers.

(10) 3-Methyl Butanoic Acid, [iso-valeric acid] $C_5H_{10}O_2$, M.W. 102.13, a liquid having a pungent stench was purchased from Eastman. Purity was determined by FID-GC. At 125°C with a Porapak Q column, one sharp peak was observed at 400 seconds.

(11) n-Nonane C_9H_{20} , M.W. 128.26, a liquid at room temperature, was obtained from Aldrich. Used as an internal standard with isovaleric acid, toluene, ethyl benzene and cumene, the clear liquid was not redistilled. At 215°C, with a porapak Q column, a sharp peak was observed at 501 seconds. No interfering peaks were observed at the retention times for the experimental compounds.

(12) n-Hexadecane, $C_{16}H_{34}$, M.W. 226.45, a liquid at room temperature, was obtained from Aldrich. Used as a solute and an internal standard with anthracene, 3,4-dimethoxy-acetophenone, and Benzothiazole, the clear liquid

was not redistilled. At each of the following temperatures, only one peak was observed, and no interference peaks were observed at the elutions times of the compounds under investigation: 150°C-603 sec., 180°C-451 sec., 210°C-207 sec.

(13) n-Octadecane, $C_{18}H_{38}$, M.W. 254.5, a solid at room temperature, was obtained from Aldrich. Used as an internal standard with hexadecane, the opaque solid was not purified. At 210°C with a OV 101 column, a single peak was observed at 620 seconds.

Gas Chromatography: Determinations of concentrations of organic solutes in both water and ether were determined by flame ionization gas chromatography (FID-GC). A Perkin Elmer Model 900 gas chromatograph coupled to an Infotronics electronic digital integrator Model 208 and a Westronics strip chart recorder was used to detect organics present at part per million concentrations with one microliter injections. Table 2-1 indicates typical GC parameters and columns used throughout the experimentation.

Sensitivity of GC was determined for each solute by analysis of an ether dilution series of authentic standard compounds. Accuracy was determined for each solute at the same time by repeated injections of known amounts. Peak height and integrator printouts were used for quantitation by comparison with the peak heights and printouts of standard dilutions analysed at the same time. This method, although more time consuming, was more reliable than if a calibration curve was used. This is justified because no one compound received enough attention to build an exceptionally stable calibration curve, at best, an even more time consuming procedure.

Table 2-1

GAS CHROMATOGRAPHIC PARAMETERS

Gas Chromatograph	Perkin Elmer Model 900
Column Temperature	Operated isothermally at temperatures from 150° to 225°C
Injector Temperature	Ten degrees greater than column
Manifold Temperature	Twenty degrees greater than column
Detector	Flame ionization
Carrier Gas	Nitrogen (Zero Grade Gas)
Carrier Flow Rate	45 ml/min
Hydrogen Pressure	22 PSIG
Air Pressure	30 PSIG
Operation Mode	Single Column (uncompensated)
Columns	
I	
Solid Support	Chromasorb W, 60-80 mesh
Stationary Phase	10% OV-101
Column Material	Stainless Steel
Column Plugs	Silanized Glass Wool
Length	1.8 m
Outside Diameter	3.17 mm
Inside Diameter	2.0 mm
Theoretical Plates (N)	
Benzothiazole	1617
dimethoxyacetophenone	1129
Anthracene	3481
II	
Solid Support	Porapak Q, 50-80 mesh
Stationary Phase	None
Column Material	Stainless Steel
Column Plugs	Silanized Glass Wool
Length	1.8 m
Outside Diameter	3.17 mm
Inside Diameter	2.0 mm
Theoretical Plates (N)	
iso-valeric acid	785
III	
Solid Support	Porapak QS, 50-80 mesh
Stationary Phase	None
Column Material	Stainless Steel
Column Plugs	Silanized Glass Wool
Length	1.8 m
Outside Diameter	3.17 mm
Inside Diameter	2.0 mm
Theoretical Plates (N)	
m-Xylene	455

Although retention time, in seconds, were derived from the integrator print-out, quantitation was done by peak height measurements. The peak heights were selected over the integrator on the basis of deviation of quantitation. Using reference solution of xylene, standard deviation of peak heights was determined to be approximately five percent of a half scale deflection. The variance increased for smaller deflections, so attenuation was adjusted to provide large scale deflections.

Standard deviation of the integrator printout was greater than ten percent for the maximum sensitivity required by the experimentation.

Retention times and detector response varied slightly from day to day, but was mitigated by the quantitation technique that depended upon standard dilution series injections integrated with experimental injections. Sensitivity of the GC did not appear to change over the period of experimentation with the exception of when the gas train was open for a period of approximately a month. The detector was cleaned, and sensitivity returned,

The glass injector liners were acid cleaned when they appeared dirty upon visual inspection. Leaks and contamination of the column did not appear to occur, and were controlled by careful assembly of the gas train and adequate baking out of the columns before use. Columns that remained in the GC for long periods of time were kept at temperatures above that at which they were operated, but below their maximum recommended levels. Septums were replaced frequently, usually upon gross loss of sensitivity. With the exception of when the detectors were cleaned, this took care of any losses in sensitivity. Septums were extracted with acetone prior to use, a practice that began immediately after gross interference was caused

by an apparently clean and new septum. No problems were noticed after this practice began. Injection of pure ether or water was used to indicate lack of column or septa contamination prior to quantitation of experimental aliquots.

Approximately 1.0 microliter of each sample, measured and recorded accurately to 0.05 ul was injected onto the column. To insure accuracy, each sample was injected at least twice. Typically, injections of the standard dilution that would most nearly approximate the peak heights of the samples were made after every three or four sample injections.

Equipment: The cold sink required for drying of the solvent prior to concentration is an upright Kelvanator Series 100 Ultracold Freezer. The temperature of the freezer is maintained at -70°C . The freezer is opened two to six times a day. Such frequent use allows ice formation on the shelves and doors. All flasks or containers placed into the cold sink were covered with aluminum foil to prevent contamination.

A steam bath is used to evaporate the solvent during the concentration step. A Fisher Thermix hot plate provided heat and a support for an eighteen cm. diameter by 12 cm. deep copper steambath, with concentric ring cover. Heat to the evaporator was controlled by use of the concentric ring cover. The hot plate was placed on maximum temperature and non re-adjusted.

Desorption of the solute occurs while the resin is shaken with ether within the extraction glass column. The column, described below, is shaken by a Burrel Wrist-Action Shaker. This apparatus can be adjusted to shake twelve tubes through all degrees from verticle to horizontal. It was used in the horizontal position only.

Glassware: Various pieces of standard laboratory glassware were used. These vessels are indicated in the experimental methods section. One item was designed and manufactured specifically for the resin work. The resin column has been designated the Schnare Tube, and was designed in our laboratory. This tube is glass and stainless steel mesh as indicated in figure 2-2. Of particular significance are the two capping arrangements. As indicated in the figure, the tube can be capped with perforated connectors consisting of teflon washers and a perforated cap which seals the washer onto the tube and around the connecting tubing. The tube can also be closed completely with solid caps and teflon liners. The test tubes and capping apparatus are French products from Sovirel. The stainless steel screen is approximately 100 mesh. The Schnare tubes were constructed by University Glassware, Carrboro, North Carolina.

While this device provides a convenient method for doing the adsorption and elution of organics from XAD resins, many other column arrangements are possible that should yield comparable results. The most significant consideration is to provide adequate mixing of the resin with the eluting solvent to achieve maximum removal of adsorbed organics from the resin.

All glassware used was scrubbed with hot water and Alconox detergent, rinsed with tap water, acetone, then carbon filtered deionized water. After draining, the glassware is left for at least eight hours in an oven maintained at 200°C. After drying, vessels and tubes are capped with aluminum foil until used.

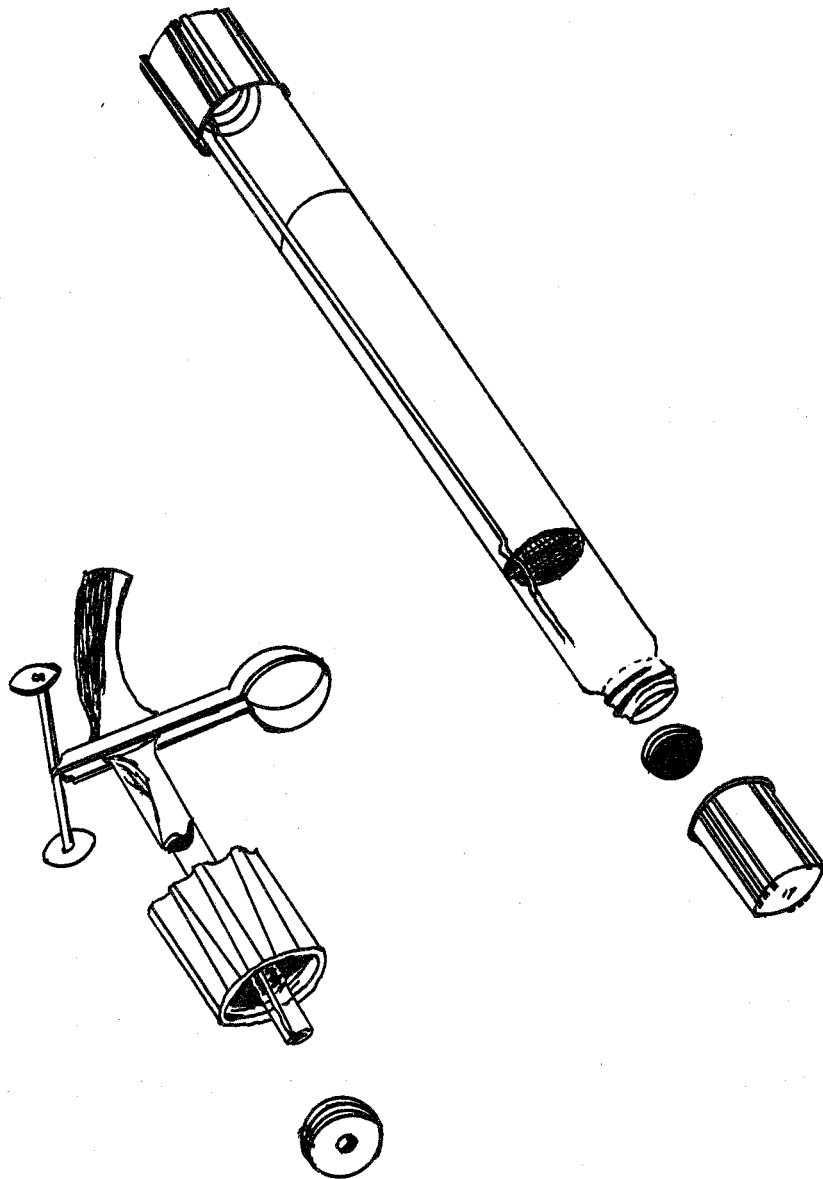


Figure 2-2
THE SCHNARE TUBE

Experimental Procedures

Six groups of experiments were conducted in line with the five questions previously described: (1) testing of the XAD adsorption method as reported by Junk et al. (1974), (2) testing of the Carolina method as developed by the authors, (3) determination of the loading capacities of the resin, (4) determination of the influence of polarity on recovery efficiency, (5) determination of the influence of molecular configuration on recovery efficiency, and (6) determination of the influence of solvent selection and contact time on desorption efficiency.

Iowa Method: The Iowa method was used as reported by Junk et al. (1974) with one modification. An internal standard was used to determine efficiency of the freezing and concentration steps. Essentially, the method follows the flow diagram in Figure 2-1 with the exception that desorption is not aided by shaking of the resin. Figure 2-3 is a scale drawing of the Junk apparatus. It was constructed in our laboratory according to literature specifications.

The referenced analytical procedure lacks some important comments about anomalies of the method. To insure that there is no confusion about what was done while using the Iowa method, the following notes provide clarification on the nature of the anomalies, and the steps taken to overcome them.

Column preparation: During column preparation, a methanol saturated column of resin is doused with water. The heat of solution of methanol in water is sufficiently high to cause gas bubble formation in and around the beads of the resin. These evacuated portions of the column remain free

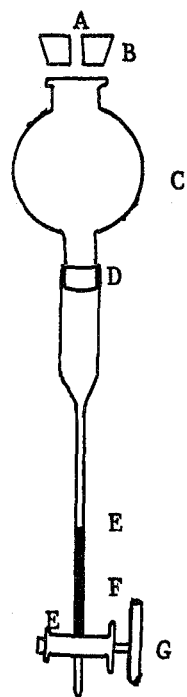


Figure 2-3

Scale drawing of Junk apparatus (94). A - pure inert gas pressure source; B - cap; C - 2 liter reservoir; D - 24/40; E - silanized glass plugs; F - 0.6 cm I.D. x 10 cm column of XAD-2 20-60 mesh; G - PTFE stopcock.

of water no matter what amount is flushed downward through the column. This is an undesirable condition since not all the resin is being used, and therefore the capacity of the resin bed is lowered. Further, there may be channelization of the flow of liquid through the column which might quickly mitigate the utility of the column as the adsorptive surface area of the channel may be rapidly filled. Two procedures can be used to insure a saturated column free of gas filled voids. The column may be tapped with a rubber tipped stirring rod. This will jar gas bubbles free from their position as the resin beads rearrange themselves. This is time consuming. A second method is quicker, but requires more elaborate preparation. A back flushing or upward flow of water through the column quickly frees trapped bubbles. The rapid reverse flow tends to send the entire column of resin out the top of the glassware, so a pumping motion imparting pulses of reversed flow water is suggested, although a very gentle reverse flow for a longer time works as well. This takes about one and one half minutes. After the column is completely saturated with water, three 20 ml portions of pure water are applied. A very uniform column, with large beads on the bottom is the result of this change in procedure.

Sample preparation: The Iowa method suggests adding organic solutes diluted with ether or methanol. Adding ether to a reservoir of water tends to transfer the organic solutes in the water into the ether layer that is floating around on the top of the water. When attempted, it was found that the ether fraction never did reach the column, but was held up at the constrictions of the glassware. When the reservoir was washed with water, the ether fraction re-floated and again settled on the walls of the

glassware. Acetone was used to aid dilution of the organic solutes in water.

With simple injection of the solute into a calm reservoir, mixing takes place very slowly. When anthracene was injected into the reservoir, it immediately came out of solution and gradually fell out onto the reservoir walls. Such an experimental procedure does not simulate natural waters containing dissolved organic compounds. Because of the construction of the apparatus, mixing of the reservoir could not be done.

Column Extraction: Extraction of the water was not different from that described by Junk. However, washing the walls of the reservoir with 20 ml of pure water three times can only be done effectively if the reservoir is removed from the column and the water agitated within the vessel. Removal of the reservoir allows some of the organic material that collected on the constrictions around the joint to drip off or evaporate. When the reservoir is left in place, not even three washings will adequately wash the entire reservoir surface area.

Elution: Washing of the reservoir walls with two ten ml portions of ether was found to be inadequate. Large crystals of anthracene were left on the walls of the reservoir after this step. The assumption that ether poured into a drained, but water saturated, column of XAD-2 resin will mix well is also invalid. At no point did the ether flow past the first glass wool plug. Furthermore, no more than two or three drops of the ether ever passed through the column in less than ten minutes with the stopcock fully open. A nitrogen head had to be applied to push the ether through the column. Rarely did more than 10 ml of ether ever get collected, with or without a nitrogen head.

Carolina Method

Column Preparation: The apparatus used for removing trace organics from water is shown in figure 2-1 and 2-2. With the siphon and top tubing adaptor detached, the lower tubing adaptor in place and closed off, purified water sufficient to cover the mesh is allowed into the column. If the water does not move through the mesh, ten to fifteen pumping squeezes on the lower tubing will force trapped air out of the lower portion of the reservoir. Purified XAD resin in a methanol slurry is added until an 80 mm column bed is formed. An etched ring on the column indicated the proper height. Addition of the resin was facilitated by use of a 10 ml pipet with tip removed. Methanol is allowed to drain from the tube until the liquid reached the top of the resin bed. The reservoir siphon (Figure 2-1) is attached loosely and purified water from the reservoir is allowed to fill the tube. The reservoir siphon is then firmly attached and approximately 200 ml of water is allowed to flow through the column. At this point two phenomena occur: (1) gas bubbles form in the column, and (2) an ether bubble forms at the top of the tube. The reservoir siphon is disconnected. Water is allowed to gently enter the tube from the bottom thereby causing a backflushing, carrying away the ether and a few floating beads. With the cap still disconnected, the resin bed is gently disturbed by a swirling motion of a stiff stainless steel wire. The motion is continued until the gas bubbles trapped in the resin column are removed and the resin bed appears uniform. Sufficient water is introduced into the tube so as to fill it. The siphon is reconnected and an additional fifty ml water is allowed to flow through the column. At this point the

column may be stored for a day or two with both ends sealed by rubber tubing clamps. This preparative operation requires approximately five minutes per tube.

Sample preparation: The reservoir is filled with sufficient purified water to allow one liter of water per extraction tube to be used, plus an extra 500 ml of water to insure good siphoning. Acetone is used to dilute the organic solute into the water. A calibrated volume of the dissolved organic solute is injected into the reservoir. A magnetic stirrer is used and adjusted throughout the extraction procedure to insure good mixing in the reservoir. The reservoir is allowed to mix for approximately five minutes to insure proper dissolution. In this study, the amounts of organic compounds added varied from 50 to 300 ug/liter (ppb). Additional pretreatment of the water such as pH adjustment, or addition of salt, is done immediately after injection of the organic solute. In the case of the organic acid tested during this work, approximately 10 ml of concentrated HCl was added to bring the pH to about two as determined by paper pH tape.

Column Extraction: Both pinch clamps are removed to allow gravity flow of the prepared water through the column and into a graduated flask or beaker. Flow rates vary slightly as the level of the reservoir decreases, and average one hundred ml per minute. Slower flow rates can be maintained with the use of adjustable clamps at the lower tubing adapter. After one liter of the water is allowed to flow through the column, the flow is stopped and the column is allowed to drain.

Elution and Internal Standardization: The tube is removed from the siphon equipment, and both caps are removed while insuring that the tube

is kept upright. Excess water is allowed to flow into the measuring beaker if a second extraction is to be done. The resin remains wetted. A solid cap and liner is placed on the bottom of the tube. A known amount of an internal standard, dissolved in a known amount of ether, is added as the initial aliquot of solvent begins to saturate the resin. The resin bed will contain many air pockets, some of which are removed by gentle swirling with a stainless steel wire. The top cap and liner is tightened down and the tube is inverted. The bottom cap (now on top) is removed and additional ether sufficient to fill the tube is added. The cap is replaced and the tube is shaken with sufficient force to dislodge the resin bed, so as to facilitate good mixing. The tube is attached horizontally to a wrist action shaker and allowed to shake for various chosen elution times. After shaking, the tube is removed from the shaker and tapped gently to reform the resin bed. The tube is inverted and the bottom cap removed. The tube is righted and the solvent is poured into a small flask of twenty to fifty ml. capacity. The top cap is removed and the remaining solvent flows into the small flask. An additional ten ml of clean ether is poured into the tube and allowed to drain through the column into the collection flask. If a second elution is to be done, the tube is refilled with solvent and eluted again as described above.

Drying: The flask is covered with aluminum foil and placed into an ultra-cold freezer (-70°C) for fifteen minutes. An aliquot of purified ether is also placed into the freezer. Upon removal, the dried elutant is quickly poured into a Kudurna-Danish evaporator through a silanized glass wool plug placed in a glass funnel. The ice left behind is washed with a two to three ml aliquot of the equally chilled ether. This is re-

frozen, then is added to the initial elutant. Typically, two to five ml of water is removed by this procedure.

Concentration: The dried ether is transferred to a Kuderna-Danish evaporator and is then reduced in volume to one ml by gentle heating over a steam bath. Evaporation rates are not critical because of the internal standard, but the slower the evaporation rate, the greater the efficiency of the concentration step. Typically, the boiling of the ether is aided by a porcelain boiling chip, but even that aid does not eliminate relatively rapid bubbling when volumes are below three ml. The end point of the concentration is not easily observed due to this phenomenon. The evaporator is removed from the heat source when there is definitely less than one ml left in the KD thimble. Rapid cooling of the evaporator occurs upon removal of the heat source and condensing ether washes the walls of the KD. The thimble is quickly removed from the evaporator when it is filled to one ml. A ground glass stopper is used to cap the thimble until measurement of the solute by GLC. Chromatographic analysis is usually done no later than one day after concentration. Final one ml aliquots are refrigerated if an interval of more than a few minutes is expected to elapse before characterization by GLC.

Determination of loading capacity of XAD resin: Preparation of the column and solutes is done exactly as described in the Carolina Method above. Rather than determine the amount of mass adsorbed by the column, the amount of solute not adsorbed by the column was measured. A one ml sample was drawn at five ml intervals. From that column effluent sample, a one ul aliquot was injected into the GLC and the resultant peak reflected the concentration of solute in the column effluent. Minimum concentra-

tions quantifiable were five percent of the initial concentration of the prepared solute (prior to extraction by the resin column).

Anthracene was not tested since it is so insoluble in water that a saturated solution is marginally quantifiable without further concentration. Otherwise, typical concentrations of the prepared waters were 100 mg per liter (ppm).

Section Three

Results and Discussion

As the protocol in Section two indicates, six evaluation actions will describe the merits and weaknesses of the experimental work conducted. Some of these evaluations such as ability to adsorb, or ability to desorb, can be dealt with in distinct sections. Other evaluations must be carried through each part of this section. For that reason, the results of the work undertaken by the authors will be compared with that of Junk et al. (1974), Webb (1975), Musty and Nickless (1974), and Goldberg et al. (1973).

Of primary importance are three experimental phases of the work with the Carolina Method: (1) extraction of solutes from water, (2) desorption of solutes from the resin, and (3) concentration of the solutes by solvent evaporation.

(1) Extraction of solutes from water: The ability of the XAD-2 macro-reticular resin to extract non-volatile organic solutes from water has been reported to range from 100% to less than 4% for widely differing compounds (Junk et al., 1974; Webb, 1975). Junk et al. (1974) has concluded: "These porous polymer resins are completely effective in extracting neutral organic solutes from water. Many dissociated solutes are also extracted provided the acidity of the water sample is adjusted prior to the extraction. No significant improvements or detrimental effects can be definitely attributed to salting-out, flowrate variations, pore diameter, bead size, resin bed volume, and mixtures vs. single component contaminations".

To the contrary, Harvey (1973) reports that there is an optimal bed

dimension, and that flow rates are significant. Webb (1975) also reports that flow rate significantly influences extraction efficiency; and further, that the resin adsorbs the polar and aromatic portions of fuel oil, but not the aliphatic hydrocarbons. Musty and Nickless (1974) also report that flow rate exerts a significant influence on extraction efficiency.

The significance of the bed dimension was not tested by this research. The recommendation of Harvey (1973) for a column depth seven times the diameter of the column was followed throughout. For the Schnare Tube, the resin column is 1.15 cm x 8.0 cm.

The capacity of the XAD-2 resin to adsorb four non-volatile organic solutes is indicated in Table 3-1. A 95% adsorption level (5% leakage) occurs at loading rates well in excess of that concentration normally found in natural or polluted water. In all cases, it was possible to put at least three milligrams of solute onto one gram of resin with no more than 5% leakage. These capacities compare favorably with other reported data. Rohm and Haas loaded phenol at 73 mg/g resin with a very low leak rate, and Musty and Nickless (1974) loaded lindane at 20 mg/g resin with an apparent six percent leak rate. Figure 3-1 indicates the nature of leakage through a column as loading increases for compounds of varying polarity. At similar flow rates, the resin adsorbs greater amounts of non-polar solutes than polar or dissociated solutes, even when pH is adjusted to favorable conditions.

The effect of two flow rates on adsorptive capacity was determined with iso-valeric acid. Figure 3-1 indicates that a flow rate of 10 ml/min

Table 3-1

CAPACITY OF THE XAD-2 RESIN TO RETAIN ORGANIC
SOLUTES ON AN 80 X 11.5 mm BED

Compound	mg solute adsorbed per gram resin, with column leakage of:				Column Flow Rate
	5%	10%	20%	40%	
m-Xylene	42.	79.	-	-	100 ml/min
Benzothiazole	29.5	36.6	43.3	59.8	100
3,4-Dimethoxy acetophenone	6.6	7.5	10.	-	100
Isovaleric Acid*	2.9	3.4	4.7	-	100
	8.4	12.	15.	-	10

* pH of water was adjusted to approximately pH = 2 prior to column extraction

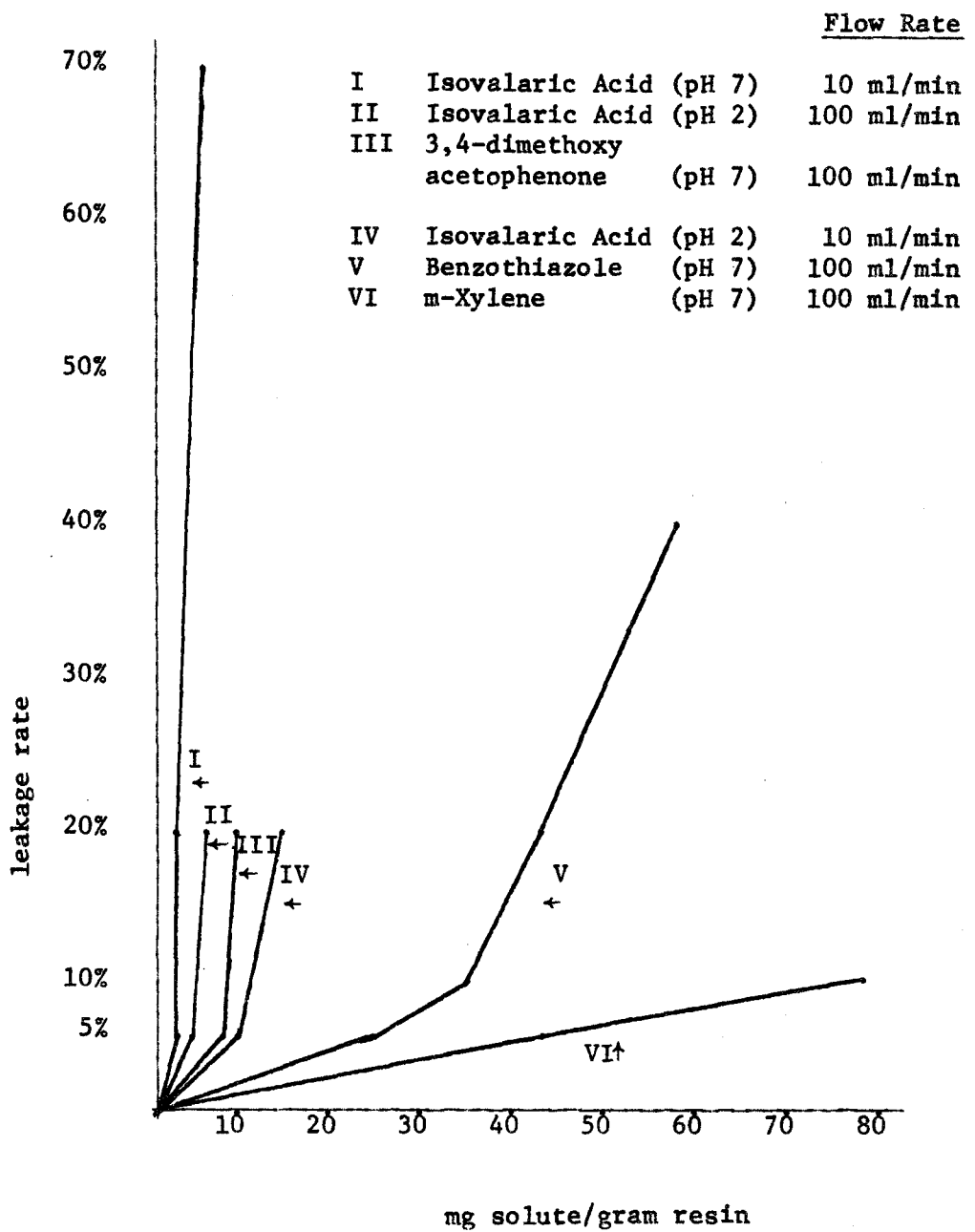


Figure 3-1

LEAKAGE VS. LOADING FOR AN 80 x 11.5 mm XAD-2 RESIN COLUMN

through the resin bed resulted in an adsorption of nearly three times as much isovaleric acid as at a 100 ml/min flow rate. The determination of the flow rate giving maximal adsorption would require extensive investigation. Flow rates much below 10ml/min would not be particularly useful for environmental applications where large volumes of water must be filtered to trap enough solute to permit analytical quantitation and compound identification.

It is not immediately obvious from total recovery data that a moderate flow rate of about 10-20 ml/min increases extraction efficiency compared to a 100 ml/min flow rate. Table 3-2 appears to indicate that for the neutral compounds the slower the flow rate, the less the extraction efficiency; and for the more polar and ionic compounds the slower the flow rate, the greater the extraction efficiency. It is suggested that the apparent anomaly is a function of desorption efficiency of solutes from the resin rather than extraction efficiency. The nonpolar solutes appear to adsorb so tightly at low flow rates that they are not effectively desorbed. This is supported by the finding that less than 2% of the n-hexadecane dissolved in water was found in the column effluent water, although only 12% of the solute was recovered. This problem will be discussed more fully in the discussion on desorption.

With respect to extractive capability, it is appropriate to conclude that the Carolina Method can be used to extract organic solutes from natural waters at a variety of flow rates. The capacity appears to be sufficient to allow use of relatively small columns (50 gm of resin) and still have efficient trapping of solutes. In choosing resin bed size for environmental

Table 3-2

THE EFFECT OF FLOW RATE ON RECOVERY EFFICIENCY

Compound	% Recovered @ 10 ml/min	% Recovered @ 100 ml/min	
<u>Neutral Compounds</u>			
m-Xylene	19.4	40.8	increase
o-Xylene	26.3	27.8	
p-Xylene	27.4	39.8	increase
Toluene	56.5	81.9	increase
Ethyl Benzene	63.8	84.6	increase
Cumene	59.9	85.3	increase
n-Hexadecane	12.0	11.7	

<u>Polar Compounds</u>			
Benzothiazole	87.5	95.1	increase
3,4-Dimethoxy acetophenone	85.3	62.6	decrease
Isovaleric Acid	79.0	42.3	decrease

applications it is critical that a large enough resin bed be used so column capacity is not exceeded.

(2) Desorption of solutes from the resin: Since most compounds appear to be adsorbed, and an internal standard has been included that accounts for losses of solute mass during the concentration step, the recoveries that are observed can be presumed to be directly reflective of desorption efficiency, when all other conditions are favorable. Four factors were investigated to determine the degree to which they affected desorption efficiency, solvent selection, polarity of the solutes, aliphatic and aromatic nature of the solutes, and batch or column desorption technique.

There is some question as to the utility of flow through column desorption, versus batch desorption, in light of the wetting characteristics of XAD resins. Once a column is water saturated, ether will not quickly permeate the top of the column. In the procedure developed by Junk et al. (1974) a plug of glass wool covers the column. In our use of his method, ether would not quickly saturate the plug, and was less able to enter the resin column. The ten minute period during which ether was to elute the adsorbed organics is in actuality only about one minute, the period of time it takes to force the ether through the column. A further problem in column desorption is the characteristic air pocketing that occurs when immiscible, or miscible solvents are replaced by one another as column elution is attempted. Such pocketing indicates that there are numerous areas of resin surface that are not brought into contact with the eluting solvent. Finally, glass wool plugs apparently adsorb some of the solutes. Webb (1975) reports up to 15% of the organic compounds extracted by solvent methods adhere to a glass wool plug used as a drying agent. Musty and

Nickless (1974) report up to 32% of insecticides studied adhere to glass and glass wool before they had an opportunity to reach an XAD column. For that reason, glass wool was abandoned in the Carolina Method. Further, wrist action shaking of the column while covered by eluting solvent breaks up the column and allows wetting of the entire resin surface. Table 3-3 indicates an improvement in recoveries with the batch-type elution when compared to the column type elution. For m-xylene this accounted for an increase in recovery from 34.8% recovered by the Junk method to 46.4% recovered by the Carolina Method. An increase was also noted with benzothiazole, but was not marked, as initial recoveries were very high.

A second important condition for significant desorption of organic solutes is solvent selection. This is most significant for those solutes that partition on to XAD-2 from an organic solvent. Such solutes appear to be straight chain hydrocarbons and small neutral aromatic compounds. Table 3-4 indicates that normal straight-chain compounds adsorb very well to XAD-2 resins, and do not desorb well at all. Similarly, the di-substituted benzenes, meta-,ortho- and para-xylene, appear to desorb poorly from the resin. This does not seem to be a function of polarity as ethyl benzene, with a dipole moment very similar to o-xylene, is recovered in much larger amounts. The affinity of the resin is further described as strong for small neutral aromatic compounds and neutral aliphatic compounds as indicated in Table 3-2. These factors make the amount of any specific solute that will be recovered by XAD-2 difficult to predict on the basis of known chemical characteristics. To be able to quantitate organic pollutants it is necessary to have recovery information for each specific pollutant that must be quantified.

Table 3-3

RECOVERY EFFICIENCY WITH RESPECT TO
ELUTION TIME AND MODE OF CONTACT

Compound	Contact Time	Mode of Contact	Method	% Recovered
m-Xylene	10 min	quiescent	Junk*	34.8
	60	shaken	Carolina	46.4
	60	mag stir	batch	86.8
Benzothiazole	10	quiescent	Junk	90.1
	60	shaken	Carolina	91.9
	90	shaken	Carolina	95.1

* Junk refers to the Junk *et al.* (1974) method as used by the authors, and does not refer to recovery efficiency reported by Junk

Table 3-4

RECOVERY EFFICIENCY WITH RESPECT TO
AROMATIC VERSUS ALIPHATIC SOLUTES

Compound	% Recovered @ 10 ml/min	Dipole Moment	Configuration
n-Hexadecane	12.0*	-	normal straight-chain
m-Xylene	19.4	-	di-substituted (meta)
o-Xylene	26.3	0.62	di-substituted (ortho)
p-Xylene	27.4	0.0	di-substituted (para)
Toluene	56.5	0.36	mono-substituted (CH ₃)
Ethyl Benzene	63.8	0.59	mono-substituted (C ₂ H ₅)
Cumene	60.3	-	mono-substituted (isopropyl)

* Less than 2% of the n-Hexadecane initially present in the sample water was found in the column effluent

Proper choice of solvent may mitigate this very strong attraction. Table 3-5 shows the effect of varying the eluting solvent. Recovery of m-xylene improved from 46.4% to 72.3% by eluting with 50% acetone/ 50% ether rather than pure ether. It was noted that wetting of the resin occurs more quickly with the mixed solvents. However, when applied to the Junk et al. (1974) procedure, air pockets remained. A further complication with solvents that are miscible in water, such as methanol, is that they are difficult to dry, a prerequisite for solvent evaporation.

When considering the entire range of compounds that could be present in water, the use of XAD-2 resin appears useful for recovering a high percentage of solutes present. Table 3-6 indicates that with ether, and at slow flow rates that encourage high adsorption for most compounds, the polar compounds are recovered at relatively high levels. If ether is replaced by a solvent mixture (acetone/ether), recoveries of about 75% can be expected for most classes of compounds, and polarity need not appreciably affect recovery. The effective use of these resins requires attention to all the variables discussed about, including flow rate, desorption solvent, and method of solvent/resin contact during desorption. The most critical factor for achieving high recoveries appears to be the use of a solvent system that permits maximum contact between the solvent and the surface of the resin bead.

(3) Concentration of solutes by solvent evaporation: In order to use detection methods such as GLC/MS, the concentration of a compound must be on the order of 50 ug/ml. Elution of solutes adsorbed on the resin results in an eluate concentration of about 2 ug/ml, compared to an initial water

Table 3-5

RECOVERY EFFICIENCY FOR m-XYLENE
WITH RESPECT TO SOLVENTS

Solvent	Contact time	% Recovered
ether	60 min	40.8
	180	46.4
10% acetone/ 90% ether	60	60.4
	180	56.9
50% acetone/ 50% ether	180	72.3

Table 3-6

RECOVERY EFFICIENCY OF ETHER DESORPTION
WITH RESPECT TO POLARITY AND SOLUBILITY

Compound	% Recovered @ 100 ml/min	% Recovered @ 10 ml/min	Dipole Moment	Solubility
Anthracene	71.8	-	0	i
p-Xylene	39.8	27.4	0	i
n-Hexadecane	11.7	12.0	-	i
Toluene	81.9	56.5	0.36	i
Ethyl Benzene	84.6	63.8	0.59	i
o-Xylene	27.8	26.3	0.62	i
Benzothiazole	95.1	87.5	-	ss
Acetophenone, 3,4-dimethoxy	62.6	85.3	-	s ^h
Isovaleric Acid	42.3	79.0	-	s

concentration in the part per billion range. Concentration of the solutes using the Kudurna-Danish (KD) technique is sufficient to increase solute concentration to required levels. There is, however, some question as to the reproducibility and efficiency of this concentration technique.

Goldberg et al. (1973) recovered 66% of the toluene in a chloroform solution but recovered only 30% of the toluene in a carbon tetrachloride solution using KD techniques. Junk et al. (1974) designed a special concentration thimble for use with the KD apparatus so as to eliminate variation in recovery efficiency for different compounds in the same solvent.

The problems that arise from using the KD technique can be nearly mitigated by using an internal standard similar to the solutes under investigation. Prior to desorption of the resin, an organic compound not found in waters, or not expected to be found in waters, can be introduced into the elution solvent in known amounts. Quantitation of this compound will indicate efficiency of the concentration procedure as well as account for losses during shaking of the extraction apparatus, transfer of elution solvent, and drying of the solvent by freezing. Table 3-7 indicates the reproducibility of the Carolina Method. The standard deviation of recovery efficiencies was typically less than three percent.

Table 3-7

RECOVERY EFFICIENCY OF
THREE XAD RESIN METHODS

Compound	Sol. Dipole		Carolina Method			Junk Method 30ml/min		EPA Method 20ml/min
			100ml/min % \pm SD	10ml/min % solvent		This report	Junk ^a (1974)	Webb ^b (1975)
Anthracene	i	0	71.8 \pm 4.8	-	ether	40.	83.	
m-Xylene	i	-	40.8 \pm 4.7	46.4 58.6 72.3	ether 10%acetone 50%acetone	34.8		
o-Xylene	i	.62	27.8 \pm 1.1	26.3	ether			
p-Xylene	i	0	39.8 \pm 0.4	27.4	ether			
Toluene	i	.36	81.9 \pm 1.6	56.5	ether			
Ethyl Benzene	i	.59	84.6 \pm 2.9	63.8	ether		81.	
Cumene	i	-	85.3 \pm 3.1	59.9	ether		93.	
Benzothiazole	ss	-	95.1 \pm 5.1	87.5	ether	90.1	100.	74.
3,4-Dimethoxy acetophenone	s ^h	-	62.6 \pm 2.6	85.3	ether			
Iso-valeric Acid	s	-	42.3 \pm 1.4	79.0	ether			
n-Hexadecane	i	-	11.7 \pm 2.2	12.0	50%acetone			3.

^a Reported in Junk et al. (1974)

^b Reported in Webb (1975)



APPENDIX A

A Topical Bibliography

Chemical and Theoretical Properties of XAD Resins

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