

ACCUMULATION OF ORGANIC POLLUTANTS
BY
SOLID ADSORBENTS



FINAL REPORT
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OFFICE OF TOXIC SUBSTANCES
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D. C. 20460

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INTRODUCTION

With the passage of the Federal water and air pollution control acts and the increasing concern over degradation of the environment, there has been a growing demand for the development of techniques for measuring trace amounts of chemical contaminants in the environment. Efforts to improve the ability to detect trace substances have proceeded on two fronts; new instrumentation has been developed, and older methods have been improved to detect ever-smaller quantities of material. In conjunction with these efforts, methods have been developed to quantitatively accumulate trace chemicals from environmental media, thus concentrating the sample prior to analysis.

A review of the literature on the available preconcentration techniques for all types of environmental contaminants was prepared as the first phase of this project and has been published as "A Review of Concentration Techniques for Trace Chemicals in the Environment" (EPA-560/2-75-003). An evaluation of this material indicated that the area in which there is the most need for an improvement in preconcentration techniques is that of the analysis of trace organics.

Recently there has been an increasing concern with the contamination of the nation's water by organic chemicals. It has, therefore, become important to develop techniques for the analysis of organic compounds in the very low concentrations (parts per trillion to parts per billion) in which they occur in the environment. While current techniques for the analysis of volatile organics (gas chromatography and gas chromatography/mass spectrometry) (GC/MS) can detect minute quantities of a given compound (from 10^{-11} to 10^{-13} grams), the severe limitation in the sample volume which can be injected into a gas chromatograph limits the over-all sensitivity of these analyses. The most promising approach to increasing the sensitivity of the analysis of trace organics is the design of a system to accumulate the organic material from very large sample volumes. The standard preconcentration technique is solvent extraction, but this can become very cumbersome when applied to the large volumes of water which are required for the analysis of very low levels of contamination.

A more convenient technique for sampling large volumes of water is the use of a solid to adsorb the organic contaminants. Activated carbon, which is well known for its ability to bind organic molecules, has often been used for this purpose. This is the basis for the Environmental Protection

Agency (EPA) standard method for the determination of gross organic contamination of water.¹ Carbon, however, has disadvantages as an adsorbent. Its efficiency is highly variable depending upon its source, the activation procedures, and the moisture content of the carbon during extraction. Its high activity can also lead to irreversible adsorption of some species and decomposition of others. Grob has designed a sampling system which uses carbon as the adsorbent medium.² This system shows a very high degree of retention of organic compounds, but great care must be taken to avoid contamination once it has been activated.

Recently, a number of polymeric resins have been studied as replacements for carbon in adsorption columns. Junk and coworkers at Iowa have examined XAD resins, and in particular XAD-2, for their retention of organics from standard solutions and from natural waters.³ Dr. Ronald Webb of the EPA Southeastern Environmental Research Laboratory has investigated these same resins for their ability to adsorb organics from sewage treatment and industrial discharges.⁴ Laboratory experiments indicate that XAD resins will adsorb a wide variety of lipophilic organic compounds from dilute solution. They are much less effective for the accumulation of alkanes than for aromatic compounds, however. Among other polymers

¹R.W. Buelow, J.K. Carswell, and J.M. Symons, "An Improved Method for Determining Organics by Activated Carbon Adsorption and Solvent Extraction - Part I;" Journal of the American Water Works Association 65 (1973): 57; and R.W. Buelow, J.K. Carswell and J.M. Symons, "An Improved Method for Determining Organics by Activated Adsorption and Solvent Extraction - Part II" (Test Method), JAWWA 65 (1973): 195.

²Kurt Grob, "Organic Substances in Potable Water and in Its Precursor, Part I. Methods for Their Determination by Gas-Liquid Chromatography," Journal of Chromatography 84 (1973): 255-273.

³G.A. Junk et al., "Use of Macroreticular Resins in the Analysis of Water for Trace Organic Contaminants," Journal of Chromatography 99 (1974): 745-762; and A.K. Burnham et al., "Identification and Estimation of Neutral Organic Contaminants in Potable Water," Analytical Chemistry 44 (1972): 139-142.

⁴Ronald G. Webb, Isolating Organic Water Pollutants: XAD Resins, Urethane Foams, Solvent Extraction, for the U.S. Environmental Protection Agency, EPA-660/4-75-003, June 1975.

which have been evaluated for this purpose, polyurethane and coated polyurethanes have been used in sampling for pesticides⁵ and Tenax GC will efficiently adsorb many pesticides and high molecular-weight aromatics from dilute solution.⁶ This resin is also used as a trapping material for volatile organic components which are removed from aqueous solution using a gas sparging technique⁷ such as the EPA Volatile Organics Analysis.⁸

The relative adsorption efficiencies of a number of commercially available solids were obtained in a laboratory study using standard mixtures containing a range of environmentally interesting compounds. Section One describes these experiments. The major differences which were observed in the retention efficiencies of polymeric resins occurred for moderately polar volatile organics such as benzene and chloroform.

The few materials (Tenax GC, Chromosorb 101, and activated carbon) which showed the most promise as accumulators of volatile organics from solution were then examined for their utility when heat-desorption was used to release adsorbed compounds directly onto a gas chromatographic column for analysis. Section Two describes the experiments which led to the choice of Tenax GC as a good general adsorbent, and to the design of a technique for the analysis of purgeable organics using direct adsorption from water.

⁵J.F. Uthe, J. Reinke and H. Gesser, "Extraction of Organochlorine Pesticides from Water by Porous Polyurethane Coated with Selective Adsorbent," Environmental Letters 3 (1972): 117.

⁶V. Leoni, G. Puccetti and A. Grella, "Preliminary Results on the Use of Tenax for the Extraction of Pesticides and Polynuclear Aromatic Hydrocarbons from Surface and Drinking Waters for Analytical Purposes," Journal of Chromatography 106 (1975): 119.

⁷Thomas G. Bellar and J.J. Lichtenberg, "Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography," for the U.S. Environmental Protection Agency, EPA-670/4-74-009, November 1974, in Journal of the American Water Works Association 66 (1974): 739-744.

⁸A. Zlatkis, H.A. Lichtenstein and A. Tishbee, "Concentration and Analysis of Trace Volatile Organics in Gases and Biological Fluids with a New Solid Adsorbent," Chromatographia 6 (1973): 67.

Once it had been shown that Tenax could effectively be used to concentrate volatile organics from aqueous solution, its utility as an adsorbent for the less volatile materials which are found in the environment was investigated, as described in Section Three. Drinking water and surface water samples were passed through Tenax columns; the volatile components were heat-desorbed and the remaining organic compounds were extracted with ethyl ether. The GC/MS identification of the compounds which were obtained by this method indicate the range of materials which this resin will accumulate. Compounds which have been identified include both aliphatic and aromatic materials.

Using Tenax resin as the adsorbent, a complete sampling and analytical procedure for both volatile and less-volatile gas chromatographic organic analysis has been designed. This procedure is described in Appendix A. A simple field sampling system for use with adsorbent columns has also been constructed and tested.

This standard sampling procedure can now be used to compare a number of resins in terms of their utility as adsorbents in sampling a variety of environmental water samples. Such a comparison would be of value in finding methods to extend the range of compounds which can be accumulated by an adsorbent column. A thorough evaluation of the ability of Tenax and other resins to retain alkanes would be particularly useful. An efficient accumulation system for these compounds is very desirable at the moment for use in baseline oil contamination studies. Further efforts which could be made in this area are described in Section Four.

SECTION ONE

COMPARISON OF SOLID ADSORBENTS USING STANDARD MIXTURES

1.1 Summary

A laboratory study has been conducted to determine the retention of a number of selected organic compounds on polymeric resins, activated carbon, polyurethane foam, and uncoated glass beads when eluted with water. Of the adsorbents tested, carbon was the only one which gave close to quantitative retention of volatile compounds (CHCl_3 , benzene, CH_3CCl_3) while Chromosorb 101 and Porapak Q gave moderate recoveries (65 to 70 percent) of benzene and methylchloroform. Higher molecular weight compounds were retained well by all of the solids, including significant retention by the glass beads. These compounds could not be eluted efficiently from the activated carbon, however, and this appears to be a result of irreversible adsorption under the experimental conditions.

1.2 Introduction

In order to identify and determine the concentration of organic pollutants in the environment it is necessary to isolate them from the environmental matrix (air, water, or soil) and to concentrate the sample by several orders of magnitude. Liquid/liquid extraction of aqueous samples becomes very cumbersome for large volumes and the need for an effective adsorbent to replace carbon for the accumulation of organic compounds has been widely recognized. Therefore the retention efficiencies of a variety of lipophilic solids for selected groups of organic compounds have been examined. Most of these solids are porous polymers which have been produced for liquid or gas chromatography. The physical and chemical characteristics of these solids are listed in Table 1-1.

Although the basic structures of most of these polymers are very similar, and therefore their retention of organics should be similar, a comparison is useful in order to ascertain the effect of differences in polarity, surface area, and functional groups.

TABLE 1-1

CHARACTERISTICS OF SOLID ADSORBENTS

ABSORBENT	MATERIAL	MESH SIZE	SURFACE AREA (M ² /g)	PORE SIZE (μ)	TEMP. MAX. (°C)	POLARITY
CARBON	Coconut Charcoal	60/80			>700	Nonpolar
POLYURETHANE					~87	Moderately Polar
XAD-2	Polystyrene	20/50	330	.009	250	Nonpolar Dipole = .3
XAD-7	Cross-linked Acrylic Ester	20/50	450	.008	150	Moderately Polar Dipole = 1.8
TENAX GC	Poly 2,6-diphenyl p-phenyleneoxide	60/80			320	
CHROMOSORB 101	STY-DVB	60/80	<50	.3-.4	275	Nonpolar
CHROMOSORB 103	Polystyrene	60/80	15-25	.3-.4	275	Strongly Polar Absorbs Acids
CHROMOSORB 104	ACN-DVB	60/80	100-200	.06-.08	250	Highly Polar
PORAPAK Q	EVB-DVB	50/80	50-600		250	Nonpolar
ABBREVIATIONS: STY = Styrene ACN = Acrylonitrile DVB = Di-vinyl Benzene EVB = Ethylvinylbenzene						

The compounds were selected for inclusion in the standard mixtures on the basis of the variety of chemical structures which they represented and because of current interest in them as environmental pollutants. They are listed in Table 1-2.

1.3 Experimental

1.3.1 Materials

The solid adsorbents and the sodium sulfate for drying were cleaned by exhaustive Soxhlet extraction with ethyl ether and with methanol. An ether eluate of the materials after this procedure showed no significant organic contamination.

Identical glass columns (20 ml burets) were packed with approximately 1 gram (g) or 5 cubic centimeters (cm³) of an adsorbent, with plugs of silanized glass wool above and below the packing material. The packed columns were rinsed with ether, methanol, and organic-free water.

All chemicals were reagent grade, used without further purification.

1.3.2 Organic Mixture No. 1 - Volatile Organics

This mixture consisted of benzene (2.2 g), chloroform (22.48 g), methylene chloride (13.36 g) acrylonitrile (3.96 g), and methyl chloroform (23.19 g).

In these experiments, a 50 microliter (μl) quantity of the standard solution was placed directly on each column by means of an Eppendorf pipet. One liter of tap water was then run through the column.

After elution with water, the columns were extracted with methanol (first run) or N,N-dimethyl formamide (DMF) (second and third runs). The first 5.0 milliliters (ml) of extract were collected. Concentration by evaporation was omitted due to the volatility of these organic accumulants.

Gas chromatographic separation was accomplished on a Chromosorb 101 column, 6 feet in length, using a flame-ionization detector. The temperature program was an initial 140° C increasing at the rate of 8°/minute to a final temperature of 220° C.

TABLE 1-2

CHARACTERISTICS OF TEST COMPOUNDS

TEST COMPOUNDS	M.W. (a.u.)	m.p. (°C)	b.p. (°C)	v.p. (25°) (mm Hg)	H ₂ O solubility	dipole
CH ₂ Cl ₂	85	-97	41	400	1:50	1.57
CHCl ₃	119	-63	61	250	1:200	1.02
CH ₃ CCl ₃	133	-33	74	150	<i>i</i>	1.79
CCl ₃ CCl ₃	237	187	sub.	<1	<i>i</i>	
ACRYLONITRILE	53	-82	78	125	1:14	3.83
BENZENE	78	6	80	100	1:1,430	0
ETHYLENE GLYCOL	62	-13	198	<1	∞	2.20
1-NAPHYTHYL AMINE	193	50	301 sub.	<<1	1:590	
PYRENE	202	156	404			
TRI- ρ CRESYL PHOSPHATE	368	-28	410		<1:500	
3,3' DICHLORO- BENZIDINE	253	132			<i>v.s.s.</i>	

ABBREVIATIONS: *i* = insoluble*v.s.s.* = very slightly soluble

1.3.3 Organic Mixture No. 2 - Higher Molecular Weight Organics

This mixture consisted of a solution of: pyrene (0.64 g), hexachloroethane (5.00 g), 1-naphthylamine (0.64 g), 3,3' dichlorobenzidine (2.00 g), and tri-*p*-tolyl phosphate (1.60 g) in 100 ml of methylene chloride.

A 0.1 ml aliquot of this mixture was pipetted directly onto each column. The passage of 1.0 liter of tap water followed immediately.

The columns were then eluted with ethyl ether, a total of 5 bed-volumes, about 25 ml. The ether extract was dried with anhydrous, previously cleaned, sodium sulfate and concentrated in a Kuderna-Danish evaporator to a standard sample volume of 0.5 ml.

A 3 percent OV-1 column was used to separate these compounds with a program of 70° C for 4 minutes rising to 250° C for 4 minutes at a rate of 32°/minute.

1.3.4 Polychlorinated Biphenyls (PCB's)

An aliquot of 0.1 ml of an Aroclor 1242 solution (1 µg/µl in iso-octane) was placed on each wet column. One liter of tap water was then passed through the column and, following elution with water, the columns were extracted with 25 ml of ethyl ether, 1 bed-volume followed by 4 bed-volumes. The ether extract was filtered through anhydrous sodium sulfate and concentrated in a Kuderna-Danish evaporator to 0.5 ml.

The analysis was performed with a Ni⁶³ electron capture detector using a 5-foot, 1/8 inch stainless steel column packed with 3 percent OV-1. A temperature program of 4 minutes at 172° C increasing by 4°/minute to 192° C and remaining there for 8 minutes was used.

1.3.5 Ethylene Glycol

A 1 cm³ sample of a solution of ethylene glycol in water (1 cm³/l) was added to the top of each column. This was followed by elution with 1 liter of tap water.

The columns were extracted with 4 bed volumes of methanol and the solution was concentrated to a volume of 0.5 cm³.

Analysis was performed on a Carbowax 20M column with a flame ionization detector and a constant temperature of 155° C.

1.4 Results and Discussion

The method used in determining retention efficiencies for the solutions described above was that of direct application of the material of interest to the top of a column followed by elution with water. This does not mimic the situation which occurs in environmental monitoring, in which the solute is adsorbed from a very dilute solution in water. An adsorbent column used in this manner, however, is also a chromatographic column and the same theoretical considerations apply. The volume of solvent which is required to elute a given solute from a column of a given size is constant regardless of the amount of solute which is adsorbed as long as this amount does not load a significant portion of the column. Therefore, if a material is eluted from a column with a liter of water, the same material, dissolved in the water, would also have been eluted from the column. If elution does not occur, the adsorbent has a much higher affinity for the solute than water does, and retention from a dilute solution would be quantitative as long as there is sufficient contact with the adsorbent for proper adsorption.

This technique was used to avoid low yields due to adsorption of standard solutions onto container and glass column walls. Methylene chloride extractions of duplicate standard solutions in water gave recoveries which varied with the time elapsed prior to extraction, leading to uncertainty about the quantity which was actually applied to the adsorbent. In similar experiments standard solutions have been made directly in the chromatographic column in order to avoid this problem.⁹ The subsequent extraction of the column, however, would also elute any material which had adsorbed to the glass walls of the apparatus, a factor that was desirable to avoid. A column packed with unsilanized glass beads was included in the experiment to indicate the amount of adsorption which could be attributed to glassware.

⁹A.K. Burnham et al., Analytical Chemistry 44 (1972): 193-142; G.A. Junk, Journal of Chromatography 99 (1974): 745-762.

The retention efficiencies which were obtained in these studies are listed in Table 1-3. A precision of ± 6 percent was obtained for two replicate experiments unless otherwise indicated.

Since all of the porous polymers are lipophilic in character, it was expected that there would be no major differences in their accumulation of lipophilic organic compounds. Differences in polarity and surface area, however, were expected to lead to differences in the accumulation of the more volatile or water-soluble test chemicals.

The results are consistent with these expectations. None of the adsorbents accumulated the very water-soluble ethylene glycol, or the polar acrylonitrile, while the other low molecular weight compounds (CHCl_3 , CH_2Cl_2 , and benzene) were only partially retained by the polymers.

Activated carbon gave by far the highest retention of volatile compounds. Recovery of the higher molecular-weight compounds from activated carbon, however, was dependent on the past history of the material. Recoveries were very low when fresh carbon was used, but they improved substantially when the same column was reused without activation, other than thorough elution with an organic solvent. This is indicated by the second run recoveries of pyrene, tricresyl phosphate, and dichlorobenzidine shown in Table 1-3. These results are apparently due to the irreversible adsorption of these materials by carbon under the experimental conditions. The most active sites were already occupied (deactivated) when the second standard solution was added, permitting a larger percentage of this standard to be eluted. A simple change of solvent from ether to methylene chloride or chloroform did not improve the recoveries. Carbon, therefore, appears to be a more efficient adsorbent of a wide variety of organic compounds, but it requires much more stringent conditions for activation and desorption than the polymeric materials.

The polymers, Tenax GC, Porapak Q, and Chromosorb 103 are excellent accumulators of benzene and chloroform in the vapor phase.¹⁰ Porapak Q and Chromosorbs 101 and 103 also retain these compounds efficiently from an aqueous system while XAD-2 shows moderate efficiency; the low recoveries from Tenax are surprising, however. Further extraction of

¹⁰T.G. Bellar and J.J. Lichtenberg, JAWWA 66 (1974): 739-744.

TABLE 1-3

RETENTION OF ORGANIC COMPOUNDS

		CH ₂ Cl ₂	CHCl ₃	CH ₃ CCl ₃	BENZENE	C ₂ Cl ₆	3,3'-DICHLORO- BENZIDINE	1-NAPHTHYL- AMINE	PYRENE	TRI- <i>p</i> -CRESYL PHOSPHATE	AROCLOR 1242
		(P E R C E N T)									
CARBON ^a	FIRST	50	99	94	83	38	10	4	17	37	87
	SECOND					48	30	4	61	85	
PORAPAK Q		1	15	69 ^b	67 ^b	49	76	4	76	80	70
TENAX GC		<2	7	29	31	48 ^b	78	45 ^b	72	84	98
CHROMOSORB 101		<1	27	70	68	46	72	32 ^b	71	79	71
CHROMOSORB 103		3	13	63	59	50	74 ^b	38 ^b	76	80	80
CHROMOSORB 104		--	5	50	44	52	60	31	71	76	91
XAD-2		5	25	53	48	59	81	51 ^b	80	83 ^b	74
XAD-7		--	<10	29	38	52 ^b	78	44	84	86	72
POLYURETHANE		--	5	<2	0	49	76	4	88	92	98
GLASS BEADS		0	<2	<3	<2	43	70	<2	93 ^b	98 ^b	40-90

^aTwo samples run in succession on the same column.^bDeviation of results is 5 to 12 percent.

the Tenax column did not result in the elution of significant amounts of these materials, indicating that complete elution had been achieved. While these low recoveries were consistently reproducible under the experimental conditions used in this study, further work using heat-desorption of volatile organics (see Section Two) has shown that Tenax is highly effective in concentrating volatile organics from dilute aqueous solution. This discrepancy has not been explained.

Most of the larger aromatic compounds were well retained by all of the materials. A variety of aromatic compounds, including phenols and cresols, have previously been efficiently accumulated using XAD-2,¹¹ Chromosorb 102,¹² and activated charcoal,¹³ while pyrene has been collected using Tenax GC¹⁴ as the adsorbent, and polyurethane¹⁵ has been used for PCB recovery. The low recovery of 1-naphthylamine (40 to 60 percent) in all cases was due, at least in part, to partial decomposition of this compound during the experimental procedure.

The very high retention of pyrene, tricresyl phosphate, PCB's and dichlorobenzidine by the glass beads was unexpected. Unsilanized glass is not free of adsorptive properties, as was clearly indicated by the decrease in concentration of standards made up in glass containers. Low surface-area

¹¹A.K. Burnham et al., Analytical Chemistry 44 (1972): 139-142; G.A. Junk, Journal of Chromatography 99 (1974): 745-762.

¹²J.P. Mieure and M.W. Dietrich, "Determination of Trace Organics in Air and Water," Journal of Chromatographic Science 11 (1973): 559-570.

¹³James W. Eichelberger, Ronald C. Dressman, and James E. Longbottom, "Separation of Phenolic Compounds from Carbon Chloroform Extract for Individual Chromatographic Identification and Measurement," Environmental Science and Technology 4 (1974): 576-578.

¹⁴V. Leoni, G. Puccetti and A. Grella, Journal of Chromatography 106 (1975): 119.

¹⁵James W. Bedford, "The Use of Polyurethane Foam Plugs for Extraction of Polychlorinated Biphenyls (PCB's) from Natural Waters," Bulletin of Environmental Contamination and Toxicology 12 (1974): 5.

glass beads, however, were not expected to show the observed high retention of these aromatic hydrocarbons. Passage of a dilute solution of tricresyl phosphate through a bed of glass beads resulted in greater than 90 percent retention by the beads, a result comparable to that obtained by direct addition of a concentrated solution to the column. The values obtained for pyrene on all of the adsorbents, however, are more closely related to the ease of extraction through the material than to adsorption effects since, with its very low water solubility, it precipitated immediately upon contact with the wet column and did not totally dissolve in the volume of elution water.

1.5 Conclusions

A comparison of the abilities of a number of polymeric solids to retain organic chemicals when eluted with water has shown that there is little variation in their retention of highly water-insoluble compounds. The nonpolar polystyrene resins are the most effective polymers for the accumulation of the volatile organics from water, complementing their adsorption properties for vapor-phase organics. While activated carbon is a more powerful adsorbent, particularly for the volatile organic substances, irreversible adsorption may lead to a loss of some components unless stringent extraction procedures are used.

The information gained from this study has been used to choose the solid adsorbents for investigation in the development of a technique for sampling and analyzing the organic contaminants of drinking and surface waters using an adsorbent-packed column.

SECTION TWO

ANALYSIS OF VOLATILE ORGANICS BY DIRECT ADSORPTION ONTO TENAX RESIN

2.1 Summary

After a preliminary study of a number of adsorbents, Tenax GC was chosen for the development of a technique for analyzing the most volatile components of drinking water by direct adsorption from water followed by heat-desorption onto a GC analytical column. This method gives results which are comparable to the EPA Volatile Organics Analysis (VOA)¹⁶ gas-sparging technique for the most common volatile organics.

2.2 Introduction

The VOA gas-sparging method is a very sensitive technique for measuring the concentrations of low molecular weight organic contaminants in drinking waters. Because the entire organic content of the sample is analyzed at one time, relatively small sample volumes are required in order to obtain measurements at the part per billion (ppb) level. For less volatile compounds which are generally isolated by extraction, however, only a portion of the extract can be analyzed at one time. Very large sample volumes are then necessary to isolate the quantities of material which are needed for qualitative and quantitative analyses. The use of a solid adsorbent to accumulate the trace organic constituents of a water sample is generally regarded as the most efficient sampling method for these large volumes. It would be advantageous, therefore, to collect the most volatile constituents of a sample in the same manner, thus eliminating the need to ship bottles of water from the sampling site to the analytical laboratory with the consequent danger of loss of components. A sampling cartridge which collects the entire volatile range of lipophilic organics (the range which can be analyzed by gas chromatography) would be ideal.

¹⁶T.A. Bellar and J.J. Lichtenberg, JAWWA 66 (1974): 739.

An adsorbent should meet four requirements if it is to be used as an accumulator of the total range of volatile organic contaminants from drinking and surface waters: (1) it must retain volatile organics strongly, (2) it must be heat-stable to allow for heat-desorption of these volatile components, (3) it should reversibly adsorb less volatile organics, and (4) it should be easily purified.

Previous experiments (Section One) have indicated that activated carbon is an excellent adsorbent for low molecular weight organics, and that a number of polystyrene resins are also moderately efficient in retaining such compounds when eluted with water. Initially, consideration was given to activated carbon, Chromosorb 101, and Tenax GC as possible "universal" adsorbents. XAD-2, which shows some promise for retaining the volatile compounds, was not investigated because of its low heat stability. Of these, Tenax GC was chosen as the material to be used in designing and testing a general procedure for sampling and analysis of trace organics.

2.3 Experimental

The following procedure was used for most of the experiments discussed in this chapter.

1. Each sampling column consisted of a 1/2-inch by 6-inch stainless steel tube packed with approximately 1 gram of pre-extracted adsorbent, held in place with silanized glass wool.
2. Prior to its use for sampling, each column was thoroughly washed with methanol and ether, and heated to above 150° C in a stream of nitrogen. Heat desorption into the GC was then used to verify that no volatile impurities remained on the column.
3. Standard solutions were passed through the adsorbent columns under gravity or drinking water samples were collected by attaching the column to a tap with pipe fittings and running the water through it as a rate of 30 cm³/min. Standard solution A contained 250 µ/l each of methylene chloride, chloroform, trichloroethylene and ethylenedibromide in water. Standard solution B contained 50 µ/l each of methylene chloride, chloroform, trichloroethylene, dibromoethane, and *o*-chlorobenzene in water.

4. The column was then attached to a stream of pre-purified nitrogen or argon and the free water was blown from the column with a rapid stream of gas. The gas flow was then reduced to 30 cm³/min and continued for 2 hours to further dry the packing material.
5. The column was connected into the carrier-gas line of a Perkin-Elmer 3920 gas chromatograph as indicated in Figure 2-1. The gas passed through a trap packed with precleaned sodium sulfate to remove most of the water vapor which resulted from heating the column. Heat-desorption was carried out at 100° C or lower onto a Chromosorb 101 analytical column which was held at 50° C during this period. The carrier gas was then set to bypass the sampling column while the analysis was performed.
6. For later samples on which gas chromatography/mass spectrometric analysis was performed, the columns were heat-desorbed in a gas stream which was then run through a condenser to remove the water vapor and through two smaller Tenax traps. These traps were placed directly in the injection port of the gas chromatograph, heat-desorbed at 250° C, and analyzed (see Appendix A). A Hewlett-Packard 5981A GC/MS was used for the identification of drinking water contaminants.

2.4 Results and Discussion

2.4.1 Preliminary Studies

A standard solution of methylene chloride, chloroform, trichloroethylene, and dibromoethane (250 µg/l) was used to examine the feasibility of direct adsorption from water followed by heat-desorption as a method for analyzing volatile water contaminants. All of these compounds could be effectively desorbed from the three solids which were tested -- carbon, Chromosorb 101, and Tenax GC -- but the water which remained in the column after adsorption interfered with the subsequent gas chromatographic analysis. This problem could be eliminated by using a stream of prepurified nitrogen to elute most of the water from the column prior to the desorption step. When nitrogen was passed through the columns at a low flow rate of 30 cm³/min for 2 hours, only the methylene chloride and a fraction of the chloroform were eluted from the resins, and no material was removed from the carbon.

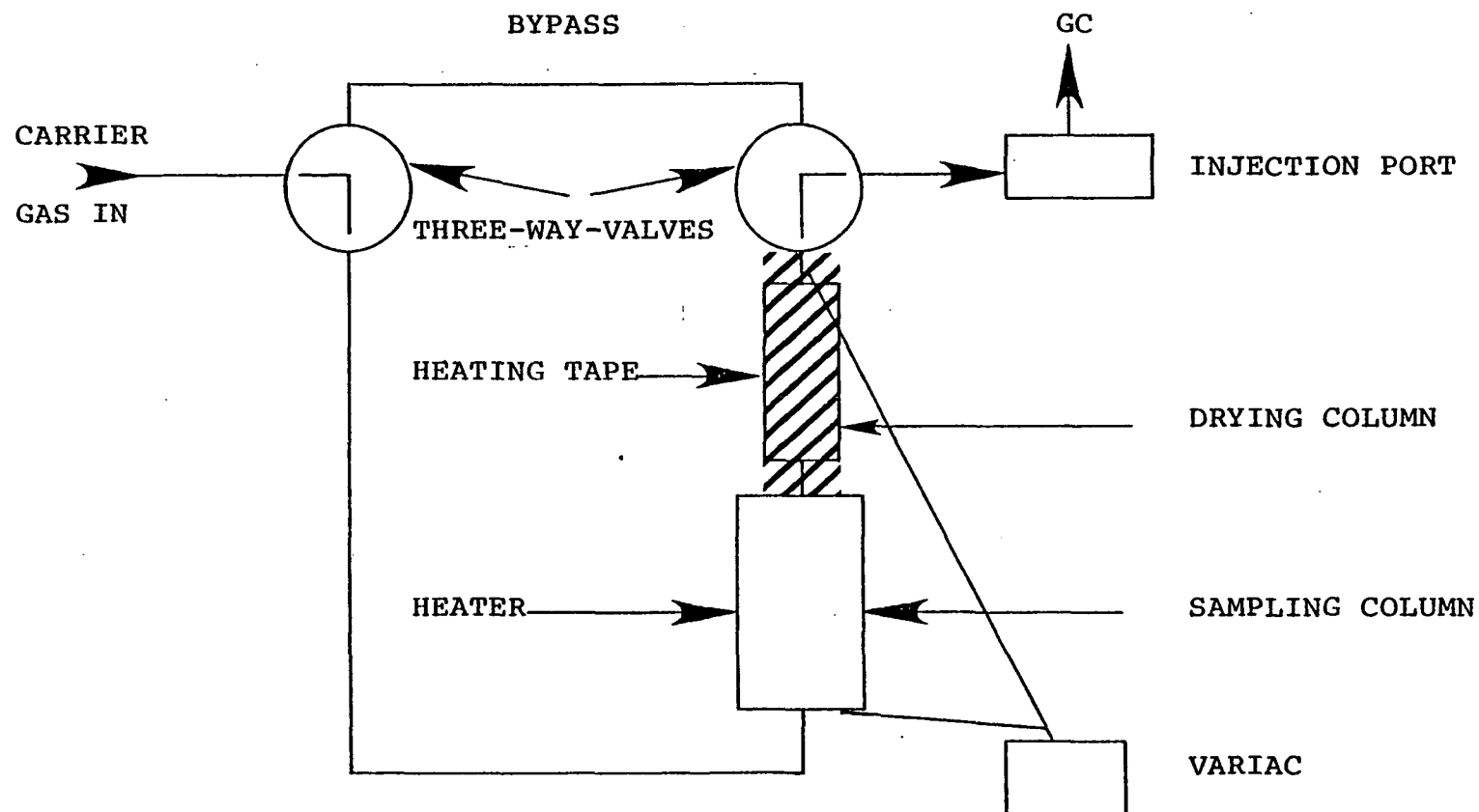


Figure 2-1. Heat-desorption apparatus, direct to GC.

A drying tube packed with prewashed sodium sulfate, placed in-line to the GC after the sampling column, was used to remove the remaining water from the carrier gas stream. Using these procedures, any water which did get onto the analytical column was eluted at least 5 minutes before the chloroform peak, and therefore did not interfere with the analysis in any way.

Only one adsorbent was needed for the further development of an analytical technique for organic water contaminants. After initial consideration of Chromosorb 101, Tenax GC, and activated carbon, the carbon was rejected because of extreme difficulty in purifying it and in avoiding contamination prior to analysis. Chromosorb and Tenax both retain volatile organics quite well, even after a nitrogen drying step. These two materials were compared for their retention and desorption properties using 100 cm³ of standard solution A. Each column was heat-desorbed at 80° C onto a Chromosorb 101 analytical column and analyzed. After a total of 48 minutes of heat-desorption over 90 percent of all the materials had been removed from the Tenax column, while the Chromosorb column still retained from 20 to 40 percent of the standards and carbon retained more than 20 percent of the dibromoethane.

Tenax GC was therefore chosen as the material to be used in the development of a standard procedure of organic sampling and analysis. Tenax GC is stable to high temperatures (375° C), is easily purified, requires mild conditions for the desorption of volatile organics, and shows a high retention of these materials.

2.4.2 Comparison With Volatile Organics Analysis

Most of the analyses which have been performed for the identification of volatile organic contamination in water systems have used the VOA gas-sparging technique. This is, therefore, the technique against which any new method for the analysis of volatile organics must be compared. This comparison has been made using both a spiked water solution and using duplicate drinking water samples.

One hundred milliliters of standard solution B were analyzed by the VOA method and by direct adsorption onto a Tenax column. In this experiment the column was heat-desorbed into the heat-desorption apparatus described in Appendix A and shown in Figure 2-2. The same small Tenax traps were used for both types of analysis. Table 2-1 gives the total recovery from each method as compared with the calculated concentration of the standard. The low values

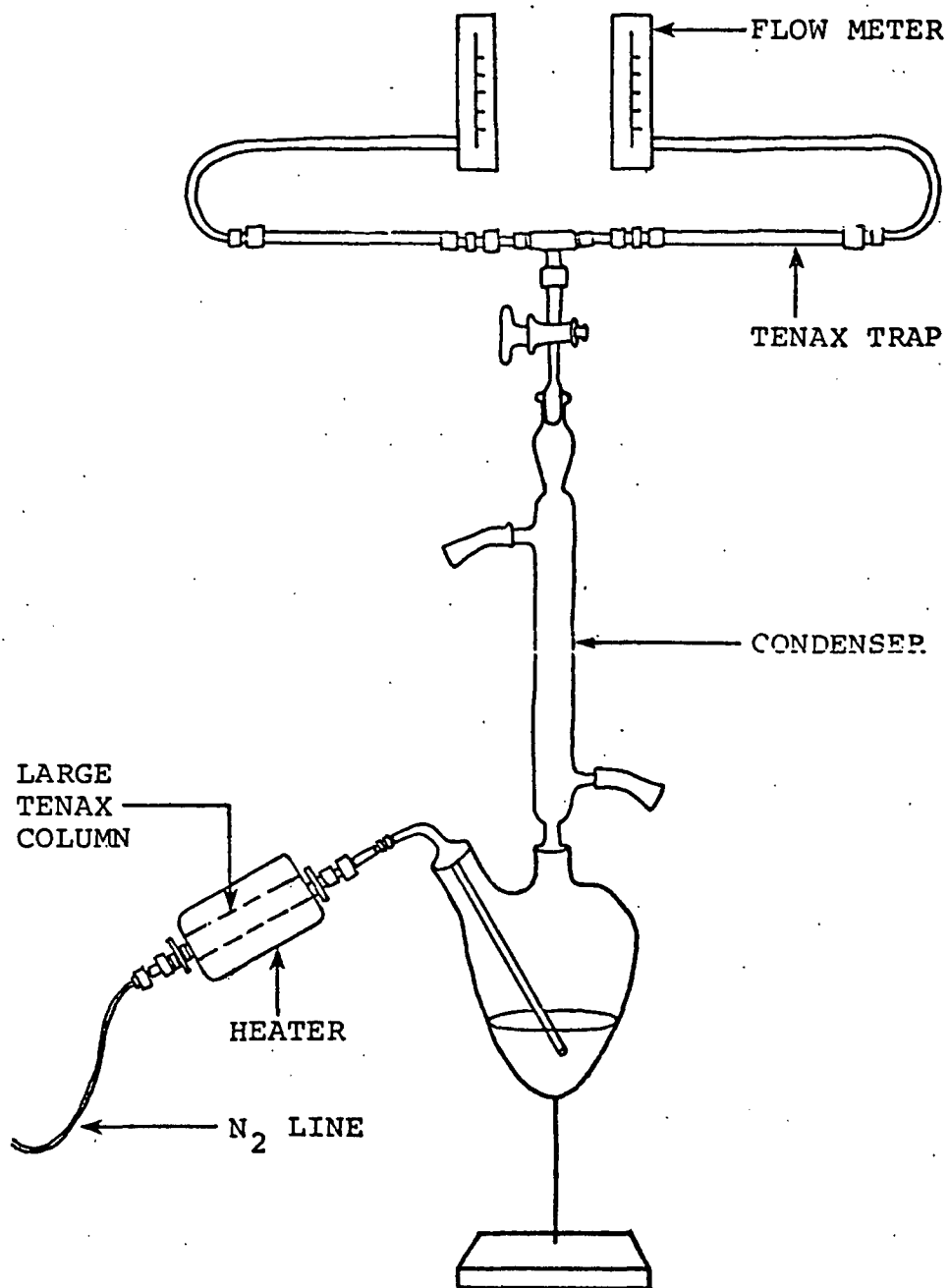


Figure 2-2. Heat-desorption apparatus.

for the recovery of some of these components may be due either to adsorption onto glassware or evaporation of the standard during its preparation and use.

TABLE 2-1

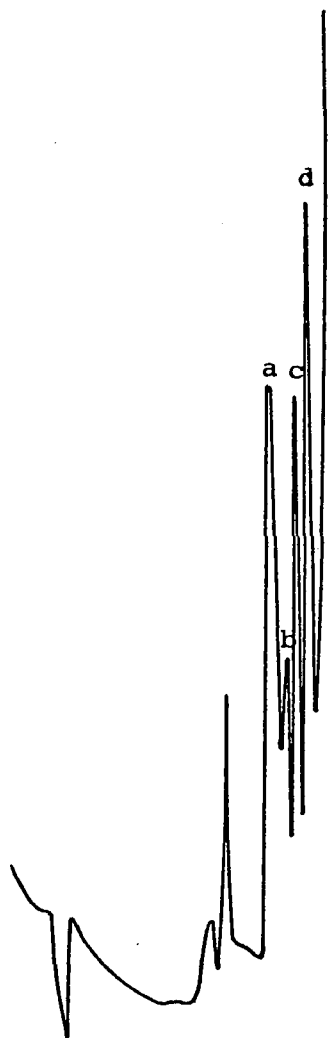
TOTAL RECOVERY COMPARED TO CALCULATED CONCENTRATION

	VOA	TENAX GC
chloroform	92	87
trichloroethylene	66	63
dibromoethane	75	64
σ -dichlorobenzene	96	74

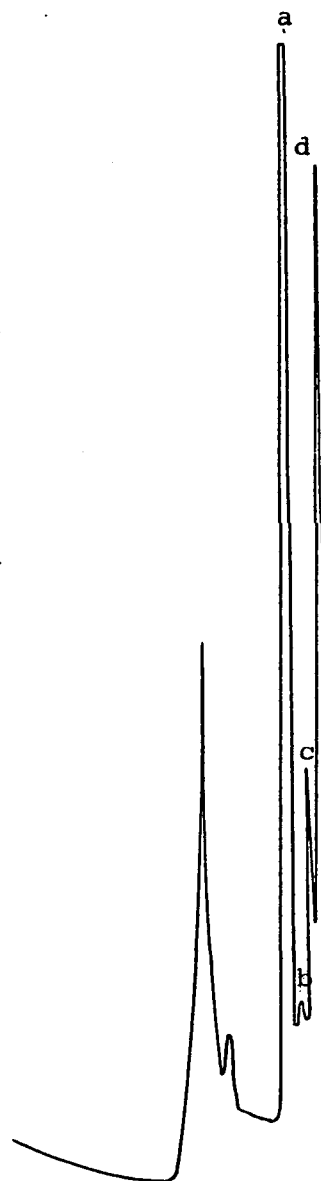
Gas chromatographic analysis using an electron-capture detector (ECD) gave a recovery of greater than 100 percent for methylene chloride for both methods because of the interference of a small amount of water vapor in the ECD scan.

These data show that the Tenax recoveries, while slightly lower than those from the VOA analysis are comparable for highly volatile organics. The much lower recovery of dichlorobenzene from the Tenax column is probably due to condensation in the unheated heat-desorption apparatus.

The concentrations (50 ppb) of the standard solution were rather high in order to avoid interferences from true organic contaminants in the water which was used to make the standards. The same method was therefore used to analyze Cambridge tap water samples (100 cm³) taken on the same day. Four major ECD detectable substances were observed by each method as shown in Figure 2-3. The quantities observed were very similar, although not identical. The three largest peaks were identified by GC/MS analysis as chloroform (peak a), trichloroethylene (peak c) and bromodichloromethane (peak d).



Tenax adsorption analysis
100 cm³ tap water



VOA analysis -
100 cm³ tap water

Figure 2-3. GC on Chromosorb 101 (50° C to 250° C at
8°/minute ECD Detector.

2.4.3 Sampling and Analysis of Large Volumes of Drinking Water

The potential advantage of using a direct adsorption technique instead of gas sparging for the analysis of volatile water components is the ease with which large volumes (i.e., gallons) can be sampled and analyzed at one time. In order to obtain quantitative recoveries of compounds, breakthrough of components must be prevented. In other words, the volume of water required to elute an adsorbate must be larger than the volume that is to be sampled. Because the low-molecular weight organics are more easily eluted than larger lipophilic molecules, the retention of these materials with a Tenax column was investigated.

Progressively larger samples of Cambridge tap water were analyzed and the retention of the three largest components, chloroform, trichloroethylene, and bromodichloromethane were computed. Table 2-2 lists the concentrations of these three contaminants which were observed when 4-, 8-, and 30-liter samples of tap water were analyzed. Since the Tenax columns were attached directly to the taps for sampling, and the samples were taken sequentially, there is no basis for estimating the variability to be expected between samples. The values for the two 4-liter samples may, however, give some indication of the variability which may be expected. Only the chloroform shows a decrease in apparent concentration which is large enough and consistent enough to be attributed to losses due to elution during the sampling period. The sampling column used in this work contained approximately 1 gram of Tenax GC. The use of a larger column could improve the recovery of chloroform, but this technique cannot be considered quantitative for compounds with chloroform's high volatility.

TABLE 2-2

CONCENTRATIONS OF CHLORINATED HYDROCARBONS
IN CAMBRIDGE TAP WATER ($\mu\text{g/l}$)

COMPOUND	<u>VOLUME OF WATER SAMPLES (l)</u>			
	4	4	8	30
CHCl_3	6.2	4.8	2.3	1.1
C_2HCl_3	0.2	0.3	0.4	0.4
CHCl_2Br	6.4	5.3	6.5	3.8

2.4.4 Reproducibility of Direct Adsorption

The reproducibility of Tenax adsorption of trace organics from drinking water was investigated by splitting a stream of tap water through two sets of sampling columns (Figure 2-4). After 30 liters of water had passed through each column, heat-desorption and GC/MS analysis led to the identification of the nine major organic contaminants listed below.

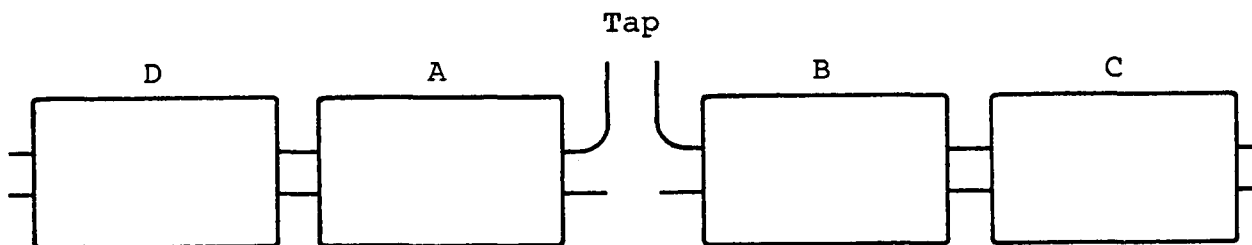


Figure 2-4. Sampling arrangement.

a.	chloroform	CHCl_3
b.	trichloroethylene	C_2HCl_3
c.	dichlorobromomethane	CHCl_2Br
d.	mesityl oxide	$(\text{CH}_3)\text{C}=\text{CHCOCH}_3$
e.	toluene	$\text{C}_6\text{H}_5\text{CH}_3$
e'.	tetrachloroethylene	C_2Cl_4
f.	chlorodibromomethane	CHClBr_2
g.	ethyl benzene	$\text{C}_6\text{H}_5\text{C}_2\text{H}_5$
h.	tetrachloroethane	$\text{C}_2\text{H}_2\text{Cl}_4$

Figure 2-5 shows the chromatogram obtained from Column A with the identified peaks labelled. Table 2-3 gives a comparison of the GC peak heights and the calculated concentration of components which were obtained from the two duplicate columns. The values obtained from Column A are consistently higher than for Column B, probably an indication of unequal splitting of the stream due to inaccurate flow control. Except for the most volatile species, however, the results show that the technique gives essentially reproducible results.

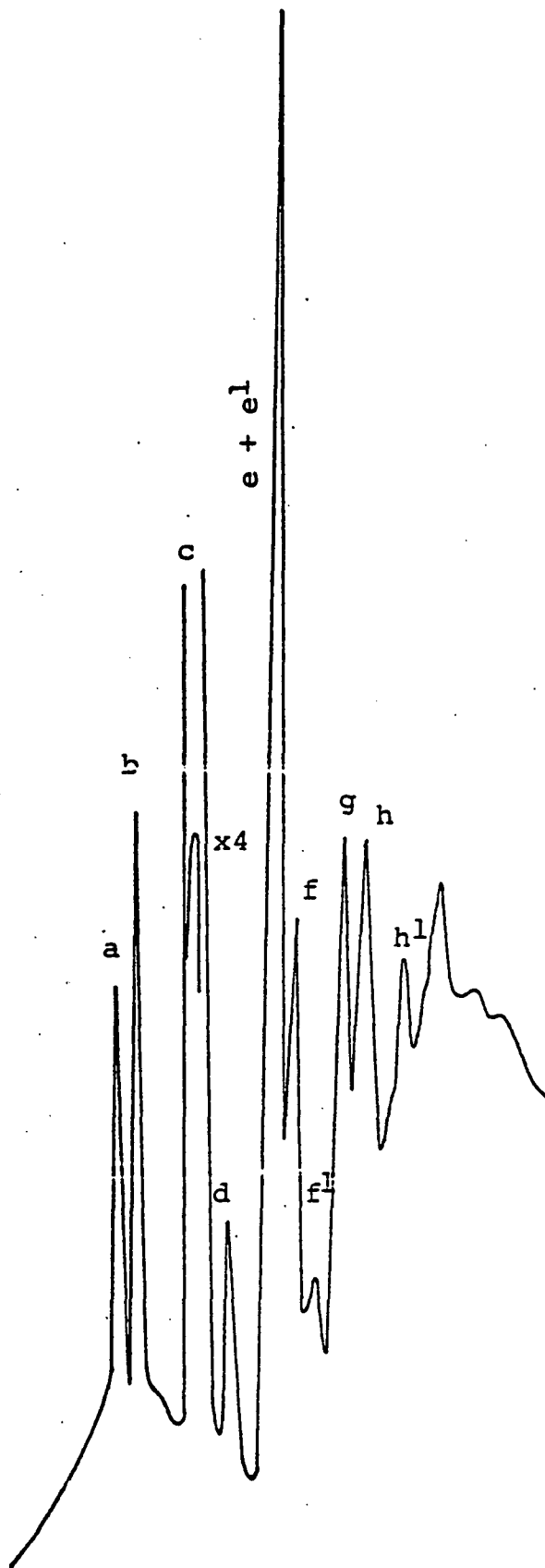


Figure 2-5. Volatile components of drinking water (30 liters).

TABLE 2-3
VOLATILE ORGANICS FROM TAP WATER

COMPOUND	<u>COLUMN A</u>		<u>COLUMN B</u>	
	PEAK HEIGHT	CONC. $\mu\text{g/l}$	PEAK HEIGHT	CONC. $\mu\text{g/l}$
a. CHCl_3	46	0.8	23	0.4
b. C_2HCl_3	62	0.4	29	0.2
c. CHCl_2Br	297	13.0	182	8.0
d. Mesityl oxide	25	0.1	22	0.1
e. C_2Cl_4 + toluene	138	0.3 (toluene)	100	0.2 (toluene)
f. CHClBr_2	47	2.1	38	1.7
f' - ?	10	-	9	-
g. Ethyl benzene	45	0.07	44	0.07
h. $\text{C}_2\text{H}_2\text{Cl}_4$	36	0.2	29	0.2
h' - ?	15	-	13	-

Columns C and D were also analyzed to give an indication of the degree to which components were eluted from the first sampling columns into the second ones. The gas chromatograms of the heat-desorbed organic components from these columns show less than 10 percent of the material found on the first column for most of the identified compounds. Toluene is an exception, with a recovery of 20 percent on the second column.

2.5 Conclusions

These studies show that a direct adsorption of volatile organic contaminants of drinking waters can be accomplished using Tenax GC as an absorbent. This method is comparable

to the VOA analysis for compounds with volatilities above that of chloroform, and it simplifies the sampling of very large volumes of water (and therefore the detection of very minor contaminants). Heat-desorption may also be followed by extraction of the column to obtain less volatile components as described in Section Three.

SECTION THREE

ACCUMULATION OF ORGANICS FROM NATURAL WATERS ONTO TENAX RESIN

3.1 Summary

The general utility of Tenax GC as an adsorbent for trace water contaminants was examined. Surface and drinking water samples were passed through a trapping column which was subsequently heat-desorbed to remove volatile components. Extraction with ether was used to remove less volatile contaminants which were then analyzed by gas chromatography/mass spectrometry. Among the compounds which were accumulated were alkanes, PCB's, and phthalates.

3.2 Introduction

An adsorbent column packed with Tenax GC has been used to accumulate trace volatile organic contaminants of drinking water by direct adsorption (see Section Two). Since there is a need for a system which will collect a wide range of organic contaminants, the ability of this material to retain less volatile materials which can be removed subsequent to heat-desorption of the volatiles was examined. Laboratory studies¹⁷ have already shown high retentions of non-polar materials by Tenax. To derive more information on its utility for field sampling, the compounds which were accumulated by Tenax from drinking and surface water samples were examined.

3.3 Experimental

Surface water samples were pumped through a stainless steel line and Tenax-packed glass sampling columns (described in Appendix A) at a rate of 5 liters per hour. Drinking water samples were collected by attaching stainless steel sampling columns directly to the tap and running the water at a flow rate of approximately 50 cm³/minute until 20 liters had been sampled.

¹⁷V. Leoni, G. Puccetti and A. Grella, Journal of Chromatography 106 (1975): 119.

Both sets of columns were heat-desorbed (see Section Two), cooled, and extracted with anhydrous ethyl ether. The larger glass columns were extracted with 250 cm³, while 50 cm³ were used for the smaller stainless steel columns. The ether was then evaporated to less than 0.5 cm³ on a Kudern-Danish evaporator, transferred to a graduated vial and further reduced under a stream of nitrogen to 0.1 cm³.

Preliminary GC analyses were run on a Perkin-Elmer 3920 GC using a 12-foot SP2100 (Supelco) column and both FID and ECD detectors on a split effluent line.

GC/MS analyses were carried out on a Hewlett-Packard 5981A system using either an SP2100 or an OV-1 GC column.

3.4 Results and Discussion

The two surface water samples were taken from the Acushnet River, at New Bedford, Massachusetts, and the south branch of the Pawtuxet River, in southeastern Rhode Island. The Acushnet at the sampling point is tidal, and quite polluted from the manufacturing plants which line its banks. Near the sampling point (which was just offshore) were a machine shop, capacitor manufacturer, and leather goods factory. Sewage pollution was also obvious. The Pawtuxet River is a small, swift-flowing stream which passes by a number of small industrial plants. The sampling location was about one mile downstream from a large chemical plant.

The major classes of contaminants which were accumulated from a 5-gallon sample from the Acushnet River by the Tenax were alkanes, PCB's and phthalates. The mass chromatogram of the extracted components is shown in Figure 3-1. Those compounds which could be identified are listed below next to their assigned peak number.

2	C ₁₄ alkane
3	C ₁₅ alkane
5	dichlorobiphenyl
6	C ₁₆ alkane
7	a phthalate
8	C ₁₇ alkane
9	C ₁₈ alkane
10-14	trichlorobiphenyls
15-16	tetrachlorobiphenyls

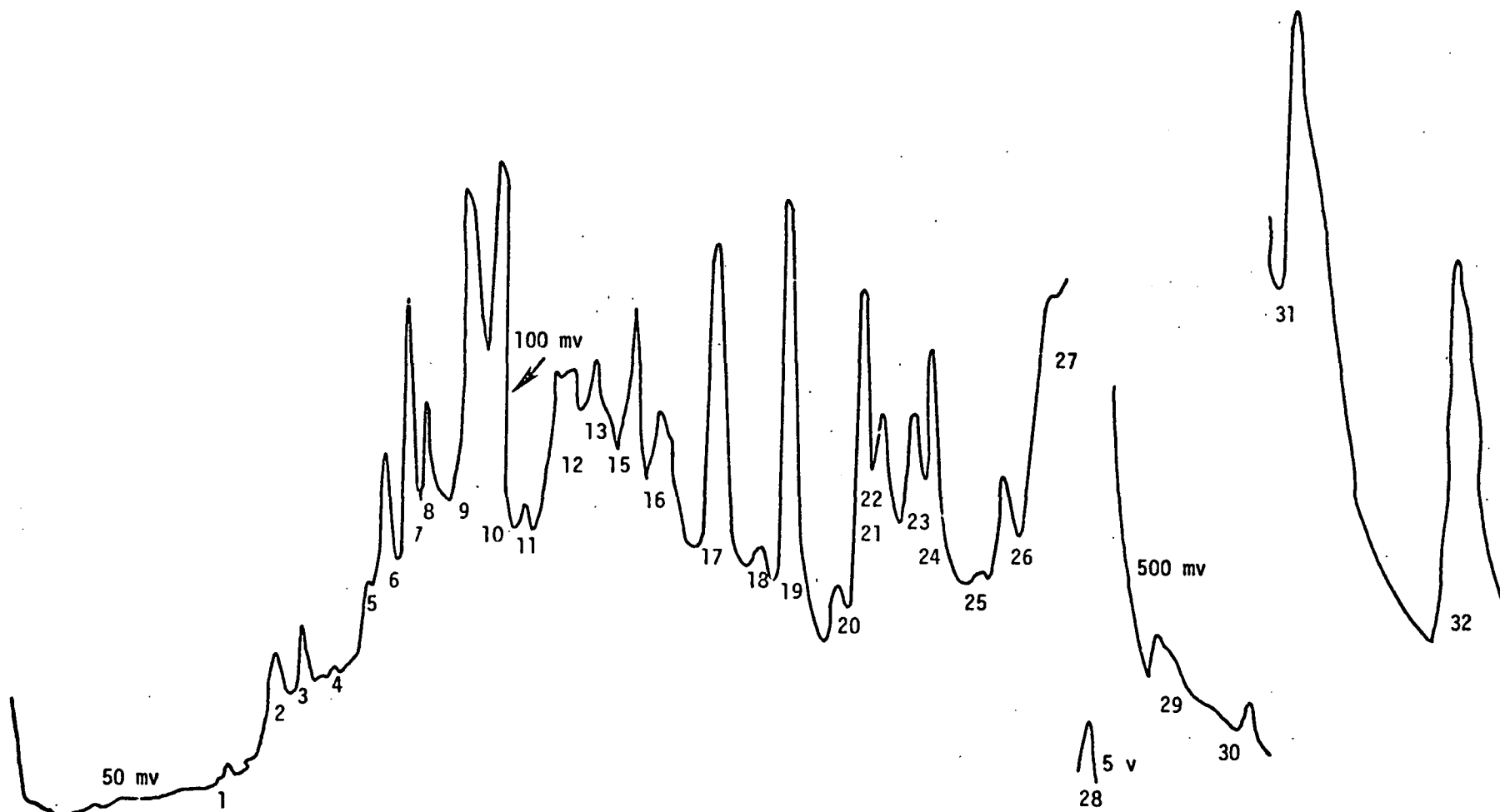


Figure 3-1. Extracted components from Acushnet River, mass chromatogram -- 3 percent OV-1.

17-18	pentachlorobiphenyls + C ₁₉ alkane
19	C ₂₀ alkane
20	diphenyl phenol or biphenyl phenyl ether
21	C ₂₁ alkane
22	trihydroxyxanthone
23	dibutyl phthalate
26	C ₂₅ alkane
27-28	dioctyl phthalate

The concentration of PCB's in this water was 0.07 µg/l based upon a comparison with a standard Arochlor mixture. The alkanes were recovered in the following amounts:

C ₁₄	0.3 µg	C ₂₀	1.1 µg
C ₁₅	1.0 µg	C ₂₁	1.9 µg
C ₁₇	3.2 µg	C ₂₅	0.5 µg

Other alkanes were undoubtedly present, since alkane peaks were present in the background of many of the mass spectra in which other compounds were also identified. The GC conditions could not be improved to the point where a separation of these components could be obtained.

A similar analysis of a 6-liter sample of water collected at the same time and place led to the recovery of the same range of hydrocarbons and PCB's, and in addition, diphenyl amine and diphenyl quinone were also observed in this sample. Quantitative comparisons of the recoveries were beyond the scope of this work which was carried out using packed columns which could not give the necessary resolution of the hydrocarbon background and other organics.

The Pawtuxet River sample (5 gal) also contained a large hydrocarbon background in the C₁₆ to C₂₅ region. Above this background the series of compounds listed below were observed.

bromochloroaniline (2 isomers)
tribromoaniline
chlorodibromoaniline (3 isomers)
N-ethyl carbazole
dichlorobiphenyl
dibromodichloroaniline
dioctyl phthalate

The Tenax traps used for both of these surface water samples were heat-desorbed for volatiles prior to extraction with ether. Only trace quantities of volatile compounds were observed.

The less volatile components of a 20-liter drinking water sample have been obtained and analyzed in the same manner as the surface waters. Below are listed the compounds which have been identified from Cambridge tap water. In this case the major classes of substances which were observed using this analytical procedure were halogenated compounds or simple aromatic molecules.

- mesityl oxide
- toluene
- chlorodibromomethane
- bromoform
- tetrachloroethylene
- ethyl benzene
- xylenes
- benzaldehyde
- ethyl toluene
- C₄ - benzenes
- naphthalene
- methyl naphthalenes
- coumarin

Two adsorbent columns were used in series for the analysis of the drinking water and Pawtuxet samples. The extracts from the second columns had much lower levels of organic material, although some hydrocarbons and phthalates did pass through from the first columns. Since XAD resins, which are often used for organic accumulation, do not retain alkanes well, the efficiency of Tenax for the recovery of these materials should be investigated in more detail.

These analyses have shown that Tenax GC is an effective adsorbent of organic contaminants from clean, polluted, fresh, and brackish waters. In general the types of compounds which it will accumulate are consistent with its lipophilic chemical structure and with the results of previous laboratory tests with standard solutions. Water-insoluble lipophilic compounds such as alkanes, aromatics and PCB's are retained by the resin. In addition to these classes of compounds the

more polar substituted anilines and halogenated methanes are adsorbed by Tenax. As expected, however, no water-soluble compounds were observed in the GC/MS analyses.

Specific recovery studies must be carried out if Tenax GC is to be used in quantitative studies of individual pollutants. It seems to meet the need for a general adsorbent of organics, however, because of its high retention of a wide range of common organic pollutants. This property makes it particularly appropriate for use in drinking water analyses.

SECTION FOUR

RESULTS AND FURTHER LINES OF INQUIRY

The results of this work have shown that a system can be devised, using a polymeric adsorbent, for the analysis of a wide range of organic water pollutants from the volatile halogenated methanes and ethanes to higher molecular weight substituted aromatics and alkanes. A number of additional experiments would be useful first in determining the full range of utility of the present technique, and secondly in developing possible modifications to broaden its application.

One possible method of extending this technique would be to use a different (or additional) adsorbent from Tenax GC. Tenax was used as the adsorbent in the development of an analytical technique because of its high retention of the small halogenated drinking water contaminants and of the ease of heat-desorbing materials from this resin. Other resins, notably the Chromosorb or Porapak series, are also efficient accumulators of volatile organics. Desorption from these materials is slower, and they retain a larger amount of water, but with the recent improvements which have been made in the heat-desorption procedure they may prove to be at least as effective as Tenax. There are two major advantages to finding an alternative to Tenax as an adsorbent: a reduction in the cost of the resin, and the ability to use chlorinated extraction solvents in which Tenax dissolves.

A number of resins are unsuitable for heat-desorption because of their low heat-stability. The use of other materials in addition to Tenax, however, could extend the range of accumulated materials for extraction. Polar resins, support-bonded liquids or ion-exchange resins may be effective in adsorbing those polar compounds which pass through Tenax and other lipophilic resins. A support-bonded long-chain alkane may prove to be the most effective adsorbent for the analysis of trace hydrocarbon contamination.

New materials can be compared to Tenax as general adsorbents of organic water contaminants by using the standard analytical procedure which has been developed with Tenax. A direct comparison can be made of the compounds which are obtained from drinking and surface waters using a number of different adsorbents. This should highlight differences in organic retention under field-sampling conditions. Materials

which look promising can then be studied for their retention of particular compounds of interest.

The Tenax system itself should be further tested for its ability to retain hydrocarbons and, in particular, alkanes. Analyses on river water samples have shown that Tenax will accumulate these compounds, but the retention efficiency and recovery for a range of alkanes should be examined further using dilute standard solutions. A good adsorbent for aliphatic and aromatic hydrocarbons would be an immense aid in analyses for trace oil contamination or baseline hydrocarbon levels.

The sampling and analysis technique using a resin adsorbent can be further developed by the design of an automated sampler which incorporates all of the necessary control apparatus in a neat package. Part of this development would involve a more thorough investigation of the optimum sampling rates and column sizes as related to the sample size. In the experiments run to date the amount of packing and flow-rates used have been very conservative to assure that contact time with the resin is sufficient for complete adsorption.

In addition to the studies suggested above, more analyses conducted using the present system on a wide range of samples will lead to a greater understanding of its utility and its limitations.

APPENDIX A

DESCRIPTION OF METHOD FOR
SAMPLING AND ANALYSIS OF ORGANIC WATER POLLUTANTS

APPENDIX A

DESCRIPTION OF METHOD FOR SAMPLING AND ANALYSIS OF ORGANIC WATER POLLUTANTS

A procedure has been developed whereby the organic components of a drinking or surface water are adsorbed onto a Tenax-packed column. The very volatile organics and the less volatile compounds are then removed sequentially by heat desorption and extraction. An outline of the procedure is given in Figure A-1.

A.1 Experimental Details

A.1.1 Preparation

Commercial Tenax GC is exhaustively extracted in a Soxhlet for 8 hours with methanol followed by a similar extraction with ether. Five grams of resin are packed into a 1-inch by 4-inch glass tube and held in place with glass beads and silanized glass wool. This sampling column is then washed with methanol and ether to remove any extractable impurities.

Volatile contaminants are removed by passing a stream of prepurified nitrogen through the column while it is heated to 200° C for one hour. The results of this purification step may be checked by heat-desorption into the GC and analysis of the vapor. The column is then capped until it is used.

A.1.2 Sample Collection

Water is sampled by passing it (20 liters or more for a part per billion analysis) through the column at a flow rate of from 50 to 100 cm³ per minute. The water touches only stainless steel and glass before entering the column to avoid any organic contamination. A small, battery-operated centrifugal pump (Teel) was used to pull surface water samples through the resin bed. A diagram of the sampling system is shown in Figure A-2.

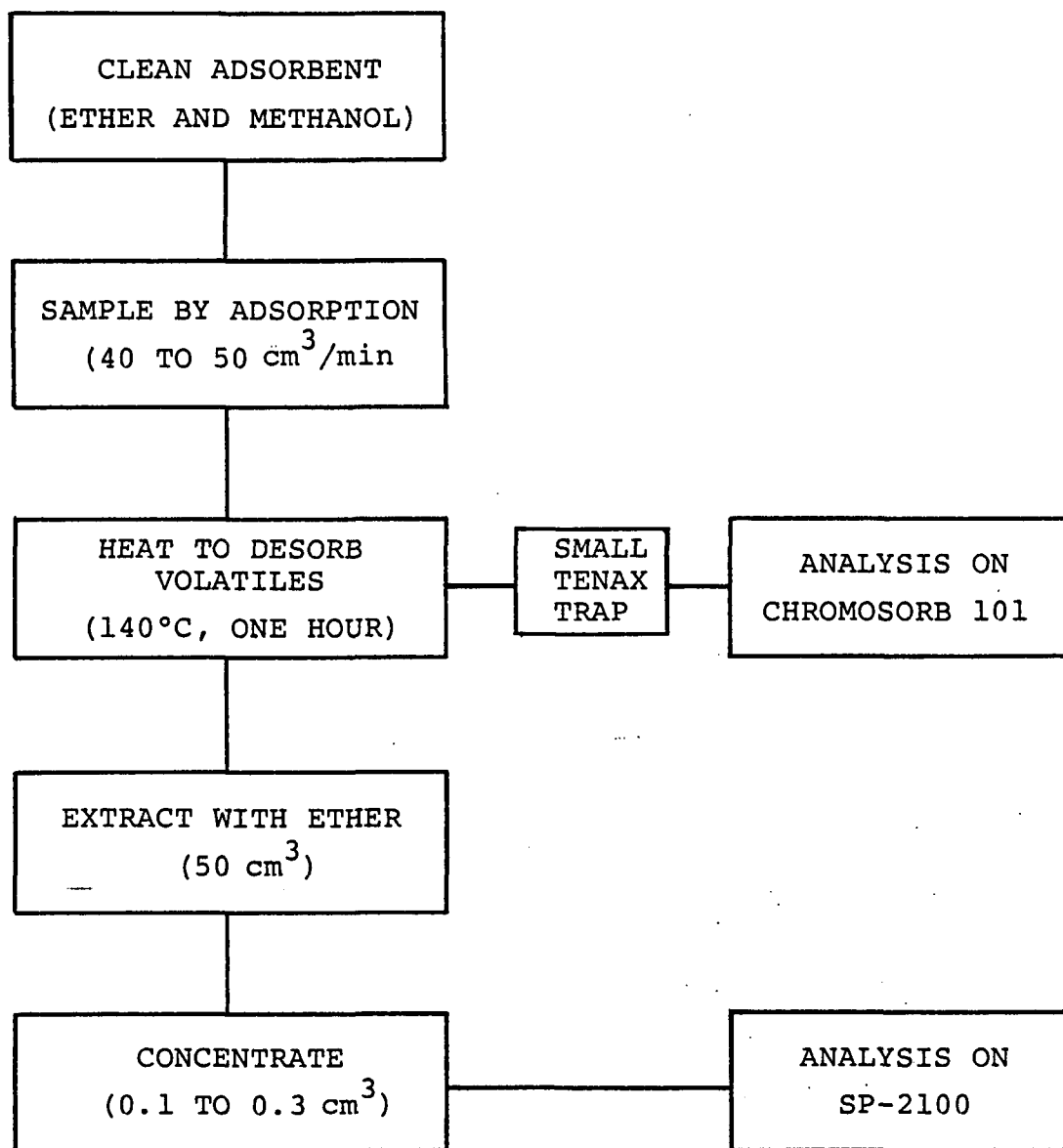


Figure A-1. Procedure for analysis of organic water pollutants.

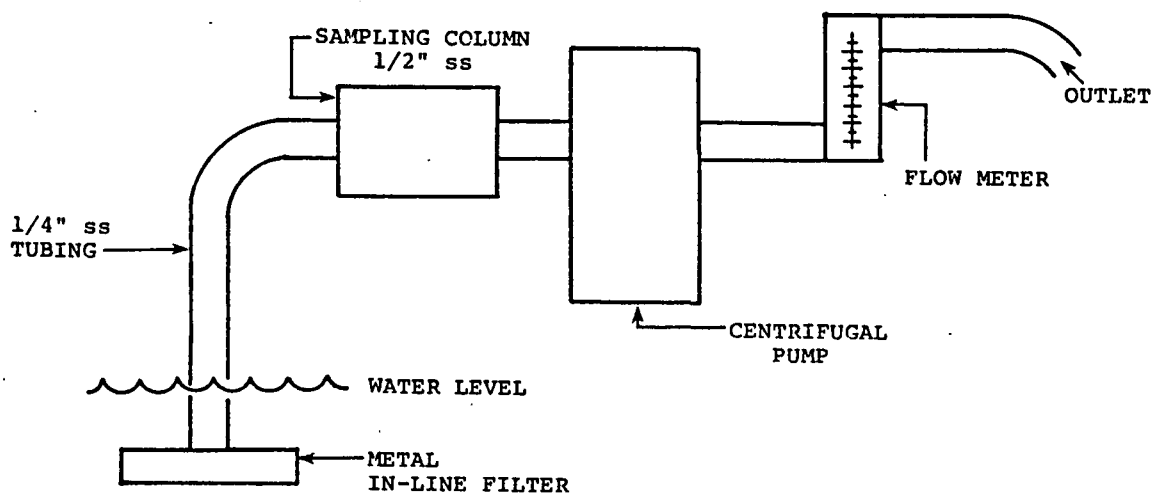


Figure A-2. Sampling System.

A.1.3 Heat-Desorption

The sample column is then attached to a prepurified nitrogen or argon line and the heat-desorption apparatus shown in Figure A-3.

The heat-desorption apparatus consists of a heating unit which fits tightly over the sampling column, a flask for collecting condensed water vapor, a condenser to remove water vapor from the gas stream, and two small Tenax traps which readsorb the organics from the gas stream. Flow meters are used to control the flow rate through each of these traps. The gas stream is directed through the water to prevent any loss of purgeable organics by absorption. The smaller Tenax traps have been designed to fit directly

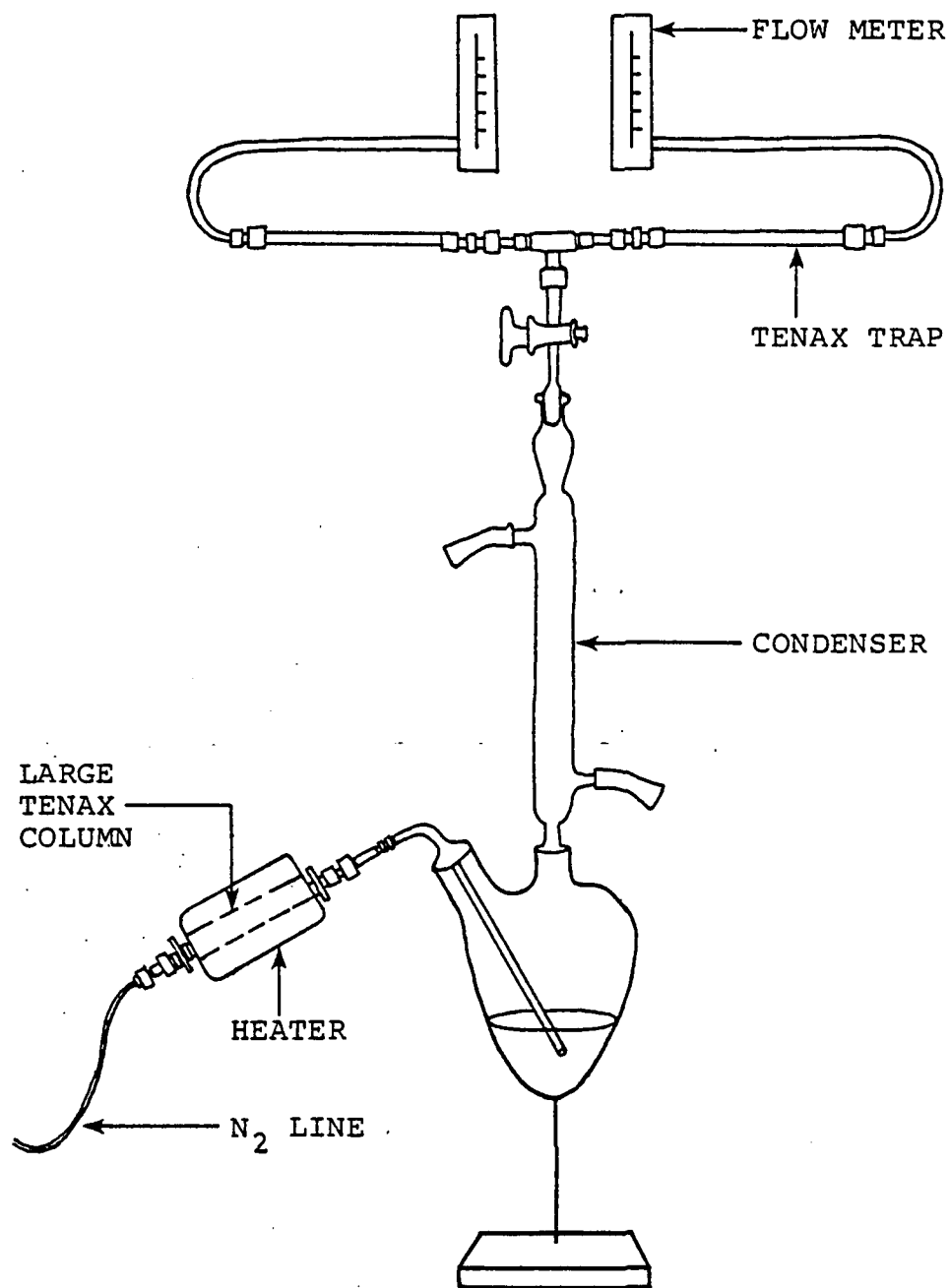


Figure A-3. Heat-desorption apparatus.

into the injection port of a Perkin-Elmer 3920 gas chromatograph. The use of two or more of these columns allows for duplicate analyses of the same sample.

Ten minutes after the gas flow is started, when the air and major portion of free water has been removed from the sampling column, the heating coil is turned on. Heat-desorption is continued for one hour at 140° C.

A.1.4 Analysis of Volatile Organics

The small Tenax traps are inserted directly into a GC injection port and heat-desorbed for 4 minutes at 250° C onto a 6-foot Chromosorb 101 analytical column. The temperature is then programmed from 50° C to 250° C at 8°/minute for the analysis of a water sample.

A.1.5 Analysis of Extractable Organics

After cooling to room temperature, the resin column is removed from the heat-desorption apparatus and extracted with 250 cm³ of ethyl ether. This ether solution is concentrated to 0.2 cm³ on a Kuderna-Danish evaporator followed by a mini Snyder column, washed into a vial, and further evaporated to from 0.1 to 0.3 cm³ under a stream of prepurified nitrogen.

The GC or GC/MS analysis is carried out using 2 µl to 5 µl of solution injected onto a 12-foot glass SP2100 column. A standard temperature program is from 100° C (for 4 minutes) to 280° C at 4° C per minute.

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
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4. TITLE AND SUBTITLE Accumulation of Organic Pollutants by Solid Adsorbents		5. REPORT DATE 1/75 - 6/76
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7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Energy Resources Co. Inc. 185 Alewife Brook Parkway Cambridge, MA 02138		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-01-2925
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15. SUPPLEMENTARY NOTES		
16. ABSTRACT A number of solid adsorbents have been examined as accumulators or organic compounds from aqueous systems. Using Tenax GC, a method was developed to sample and analyze both volatile and less volatile organics by direct adsorption from water followed by heat desorption for the volatiles and extraction for the remaining non-volatile organic. This system has been used for the analysis of tap water and several surface water samples.		
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