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The analysis of organic compounds in water by direct adsorption and thermal desorption

by

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INTRODUCTION

Review of Water Analysis Problem

Research over the past decade devoted to the detection of toxic chemicals in the environment has engendered concern about the quality of drinking water in this country. The Safe Drinking Water Act, United States Public Law 93-523, was enacted December 16, 1974. Applicable to drinking water systems serving 25 persons or more, it states that all systems must be monitored by certified analysis laboratories by October 1980. These laboratories are to be certified in the areas of Microbiology, Chemistry and Radiochemistry.

In 1975, the United States Environmental Protection Agency published a report on their National Organics Monitoring Survey (NORS) (1) which delineates the extent of drinking water contamination by compounds which had been previously established as suspected carcinogens. It was noted that 83% of the organic compounds identified in the survey were anthropogenic chemicals of industrial origin. Following NORS, the National Organics Monitoring Survey (NOMS) was conducted to establish the extent and sources of surface water contamination in the United States. Effluent streams from a wide variety of industrial sources were characterized and more than 200 surface waters were analyzed (2). The results of these surveys indicate the importance

of regularly monitoring our drinking and surface waters for potentially hazardous organic contaminants.

Two general approaches describe the analysis of water. These have been designated the Broad Spectrum and the Target Compound approaches (3). In the Broad Spectrum approach, virtually everything in a given water source is identified and measured to the extent of the laboratory's analytical capability. The Target Compound approach only seeks to identify and quantitate compounds designated prior to the analysis.

At present, the Broad Spectrum approach to the analysis of water is an expensive and painstaking proposition requiring many hours of analysis time and extremely high-powered equipment. Many surface waters are almost impossible to analyze because of their enormous complexity (4). Even the least complex of these samples virtually requires Gas Chromatography-Mass Spectrometry for the identification of the many individual components (5,6). Simple economics precludes the Broad Spectrum analysis of more than a few water sources on anything like a routine basis at this time.

The United States Environmental Protection Agency established a Target Compound approach in 1976 when it furnished a list of "priority pollutants", 106 organic compounds known to be carcinogenic or toxic (3). The Environmental Protection Agency is in the process of placing limits

on the acceptable concentrations of these compounds in industrial effluent streams and is recommending the technology for achieving them. Solvent extraction is currently the recommended method for isolating these compounds from effluent stream samples prior to their analysis by gas chromatography.

One of the major causes for concern has been the possibility that chronic exposure to some of the organic pollutants in drinking water may cause people to develop cancer (7). Exposure to potentially hazardous chemicals can also occur, but at much higher levels, where people eat fish taken from contaminated surface waters. The concentration of lipophilic compounds from anthropogenic sources is often 10,000 times greater in fish than in the surrounding water (8).

The development of the Ames Test for mutagenicity has been a large step forward in the effort to assess the environment qualitatively. With this test most of the qualitative information gained by live animal tests for carcinogenicity can be acquired at a much lower cost per compound, in much less time and with a great deal more sensitivity (9,10,11). This has made it feasible to evaluate individual compounds in terms of their hazzard potential in order to choose the most important "Targets" for analysis.

The complexity of water samples is such that the separation of the individual components from each other prior to identification and measurement is not a trivial problem. Gas

chromatography is currently the method of choice and is likely to remain so for these substances to which it is applicable. Tsuda and Novotny (12,13) have demonstrated that the best liquid chromatographic separation capability lies with liquid chromatographic capillary columns, but due to the slow kinetics of mass transfer in liquids the time required to achieve separations is prohibitively long. It requires many hours to achieve peak resolution even approaching that of short glass capillary gas chromatographic columns. For the purpose of this thesis then, liquid chromatography will be considered a useful and necessary compliment to gas chromatography, but will not be discussed further.

The fundamental problem in water analysis by gas chromatography is to transfer the sample components from the water to the front of the analytical column (14,15,16) in a convenient, efficient, and reproducible manner. Attempts at the solution are many and varied, each having its advantages and disadvantages.

Review of Related Research

Direct injection

The most basic solution to the problem is also the most obvious. By simply injecting a water sample into the gas chromatograph one can achieve the transfer of a measured, albeit small, amount of sample to the analytical column.

Unfortunately, water tends to destroy analytical columns and degrade the performance of the commonly used detectors.

Various attempts have been made at circumventing this problem. Precolumns containing Ascarite, Drierite or some other hygroscopic material have been used to remove the injected water as the carrier gas sweeps the sample through to the analytical column (17). However, such precolumns need frequent replacement, and more importantly, tend to react with many of the sample components making it impossible to chromatograph them (18).

Hydrophobic polymeric resins have been used as stationary phases in analytical columns (19-21). Tenax GC, a linear polymer of 2,6-diphenyl-p-phenyleneoxide (see Table 1), gives symmetrical peaks for water and can tolerate a virtually unlimited number of injections (22). The polystyrene-divinylbenzene resins, while less stable thermally, behave almost equally well toward water. Unfortunately, these materials have not proven to be suitable chromatographic substrates for anything but the most volatile and polar compounds. Their high porosity tends to increase the apparent multipath causing nonideal chromatographic behavior. The retention times of even moderately volatile compounds on these resins tend to be excessively long.

Another major deficiency of direct injection is lack of sensitivity. Since there is no concentration of the sample

Table 1. Absorption substrates

Resin and Chemical Description	Source	Surface Area (m^2/g)	Pore Diameter (Angstroms)	Comments
Spherocarb/ Carbonaceous	Analabs	1200	30	Irreversible adsorption, poor thermal desorption
Tenax GC/ 2,6-diphenyl-p-phenylene	Alltech Associates	18.6	720	Poor adsorptive capacity, excellent thermal stability
XAD-2/ polystyrene-divinylbenzene	Rohm and Haas	300	90	Poor thermal stability, excellent adsorbent
XAD-4/ divinylbenzene	Rohm and Haas	784	50	Moderate thermal stability, excellent adsorbent
XE-340/ Carbonaceous	Rohm and Haas	---	---	High blank, irreversible adsorption, poor thermal desorption

and the more sensitive detectors tend to abhor water, direct aqueous injection is not generally applicable to the analysis of components present at concentrations below parts per million (ppm) (18).

As a consequence of these limitations, of the 106 Target Compounds previously mentioned, only two, acrolein and acetonitrile, are usually analyzed by direct aqueous injection (3). Acrolein and acetonitrile are simply too water soluble to be conveniently isolated prior to injection.

Solvent extraction

The methods of water analysis which are based on solvent extraction are probably the most widely practiced. In these procedures a solvent is chosen which has a minimal solubility in water. The dipole moment of the solvent must be compatible with that of the compound(s) to be extracted (23). The solvent is shaken with the water sample for an appropriate length of time, separated from the aqueous fraction, and dried over an anhydrous salt. This procedure is sometimes repeated to enhance recovery and the solvent fraction may be concentrated to enhance sensitivity. Some portion of this extract is then injected into the gas chromatograph.

Solvent extraction procedures are somewhat more sensitive than direct injection methods. A few are capable of analyzing organic impurities at the parts per billion level. Austern et al. (24) used Freon as the extracting solvent and were able

to detect many compounds at the parts per billion level by concentrating the extract. Goldberg et al. (24) used a special device to continuously extract an aqueous stream in order to attain part per billion sensitivity but observed a decided selectivity in the efficiency of extraction. This selectivity appeared to be related to the dipole moment similarities between the solvents used and the compounds extracted. Grob and his co-workers (25) have taken the solvent extraction procedure to its limit. Samples on the order of 1-2 liters in volume were extracted with 200 microliters of pentane. The extract was then concentrated, often to the point where the entire sample could be injected into the gas chromatograph. While the "theoretical" detection limits, which Grob calculated to be on the order of parts per trillion based on 100% extraction efficiency, are quite impressive, the method has limited utility. Pentane is a highly selective solvent which makes it unsuitable for the extraction of most compounds. The method itself has significant disadvantages, not the least of which being the impossible degree of skilled manipulation required to reproduce any part of the sequence accurately.

It should be mentioned in passing that solvent extraction with smaller and smaller volumes reaches the point of diminishing returns rather rapidly. The effective concentration enhancement resulting from a simple solvent extraction

must always be numerically less than the distribution coefficient, D_c. Therefore, although smaller volumes result in relatively more concentrated extracts, considerations of extraction efficiency and sample manipulation have led most workers to choose water-to-solvent volume ratios of 1000 or less.

Certain limitations of solvent extraction seem to be fundamental and inescapable. A sensitive gas chromatographic analysis of water which uses solvent extraction as the technique for isolating the analyte from the aqueous matrix requires that the solvent be concentrated after the extraction procedure. The solvent must therefore be much more volatile than any component of interest in the sample and exceedingly clean since solvent impurities are concentrated as well as the sample components.

There are many compounds which are not extracted well by solvents amenable to chromatography. As previously stated, the efficiency of extraction is highly dependent on the compatability of the analyte to the extracting solvent. This property is used to some advantage in determining specific compounds or groups of compounds (3) but extraction by a single solvent is not recommended for the analysis of a broad spectrum of compounds.

Even those compounds which are well extracted generally cannot be determined at part per billion concentrations

without a significant amount of sample manipulation. However, the use of specific detectors such as the Hall electroconductivity detector and the electron capture detector make it possible to determine selected compounds at much lower levels after solvent extraction. Concentrations on the order of 100 parts per trillion of some halogenated compounds can be measured this way (26,27).

Gas purging

Methods of water analysis based on gas purging have become extremely popular in the last few years. Early work by Swinnerton and Linnenbom (28), and McAuliffe (29) indicated that, within limits, gases could be used to remove organic compounds from water. McAuliffe simply shook up a syringe filled with either nitrogen or helium and an aliquot of the water to be analyzed. After a certain equilibration time, the inert gas was injected into a gas chromatograph. A portion of the more volatile compounds would be thereby transferred from the aqueous phase to the gas chromatograph. Swinnerton and Linnenbom (30) and Swinnerton and Lomontagne (31) used a continuous stream of inert gas and passed it through a water sample to a cryogenic trap containing alumina. Ascarite was used to prevent water vapor from interfering with the analysis and a carbon trap followed the alumina in the cryogenic trap to adsorb methane. The samples were thermally desorbed from the traps into the gas

chromatograph. Simple hydrocarbons up to butane were analyzed in ocean water by this method at concentration levels as low as 0.1 parts per trillion.

Bellar and Lichtenberg (32) popularized the method somewhat by publishing a rather thorough study of the limitations and advantages of a gas purging method using Tenax in the cold trap. Tenax is an extremely stable porous polymer of 2,6-diphenyl-p-phenyleneoxide (see Table 1). It is hydrophobic and inert, and retains most compounds extremely well, even at ambient temperature. Possibly the most important advantage of using Tenax is the fact that trapped compounds can be thermally desorbed from it cleanly and efficiently.

Zlatkis and a number of his co-workers have used gas purging procedures extensively in clinical applications (33-37) and have refined the use of the Tenax trap with high resolution systems. Bertsch et al. (38) applied these techniques to water analysis by Gas Chromatography-Mass Spectrometry but found they were unable to purge compounds less volatile than naphthalene or octadecane. All of the above methods employ thermal desorption to transfer compounds from the Tenax trap to the analytical column.

Porous polymers, especially Tenax, are usually used in purge traps in preference to alumina, activated carbon and other materials. They tend to adsorb organics as well as or better than the alternative materials without trapping as

much water, and generally do not demonstrate the irreversible adsorption behavior that is observed with activated carbon, alumina, and other materials of similarly high surface energy. This has helped to make thermal desorption the most attractive means of transferring organics from the purge trap to the gas chromatograph.

Grob and his wife (39,40) have elected to use activated carbon as the adsorbent in purge traps and they have developed a method of purging in a closed system to expand the volatility range of the compounds that can be purged. The most significant disadvantage of the method involves the necessity for using solvents to elute analytes from the carbon trap. This makes it impossible to transfer an appreciable fraction of the sample to the gas chromatograph without a great deal of sample manipulation. By comparison, with thermal desorption methodology the entire collected sample can be introduced into the gas chromatograph, simply, quickly, efficiently and reproducibly.

A number of workers have designed systems for thermal desorption from Tenax traps (41-44). The most recent of these are simply heated insertion probes containing the Tenax trap from a gas purge sampling device (45-46). Dowty, Green and Laseter (47) automated the whole gas purging and thermal desorption process following the sampling step. A computer was used to record the retention times of the sample

components and control automated sequences. In summation, gas purging is a very powerful tool for the analysis of water. The use of thermal desorption makes it possible to recover virtually all of the purgable organics from a water sample. For ideally suitable compounds it is theoretically possible to analyze water volumes of 10 ml at the 100 parts per trillion level. There are relatively few matrix effects, and samples that would be considered too "dirty" for other methods can be analyzed successfully. The only real difficulties with the method appear to lie in the sample volatility requirements, sampling problems and the total elimination of water.

The volatility requirements noted by Bertsch et al. (30) and others are basically determined by the sample vapor pressure at the purge temperature limit. Even when the temperature of the water is raised to 70°C, it is impossible to quantitatively purge compounds that have boiling points above that of naphthalene within a reasonable amount of time. It has also been observed that compounds which are significantly soluble in water are purged rather poorly.

Two of the most important sampling problems are sample degradation (36,48) and losses through sample adsorption on container walls (42,49). In many instances great care must be taken to prevent almost quantitative losses.

Cryogenic trapping on a precolumn or on the front of a capillary column is widely employed in high resolution thermal

desorption systems to achieve a narrow injection band for gas chromatography (38,50,51). While this has been the best method of attaining high chromatographic resolution, it is susceptible to icing problems. Even very small amounts of water can form ice plugs and cut off desorption flow completely. Of course, water is also prohibited in systems using electron capture, Hall electrolytic conductivity, or mass spectrometry.

In practice, the problem of water vapor entrainment has effectively reduced the range of gas purging methods. Increasing the water temperature during purging enhances the efficiency of the method for less volatile compounds, but so much water vapor is trapped that the usual transfer procedures are impaired (38). The current methods of eliminating water vapor from trapping columns are simply not adequate.

Direct adsorption

Solid sorbants have long been used to isolate organic compounds from water. The earliest procedures used activated carbon (52,53,54). Large amounts of water were passed through a bed of activated carbon which retained most of the organic material. The carbon bed was then treated with several bed volumes of a solvent, usually $CHCl_3$, to recover the organics. The solvent could then be treated in various ways. By evaporating it to dryness, a measure of the total organic carbon

(TOC) in the water was attained. Injection of the $CHCl_3$ extract into a gas chromatograph yielded somewhat more qualitative data. Although the huge sample sizes resulted in tremendously concentrated water extracts, it was observed that the recovery of many compounds was quite poor. The highly energetic surface of the activated carbon either retained a compound poorly or held on so strongly that the adsorption was essentially irreversible. Activated carbon was not a suitable sorbant for exacting analytical work.

The resin sorption procedures are essentially the same as those using activated carbon. A known volume of the water to be analyzed is passed through a bed of resin, and the organic compounds are recovered by solvent elution. Methods based on the use of polystyrene-divinylbenzene copolymers in the form of macroreticular resins (55-59) have proven to be among the most sensitive yet developed for water analysis. Most of this work has been done with two resins developed by Rohm and Haas Corporation of Philadelphia, Pennsylvania, for the treatment of industrial effluents. They are designated XAD-2 and XAD-4, and their physical properties are listed in Table 1. Both resins have been found to be superior to activated carbon for the purposes of water analysis (60,61). Adsorption efficiency is excellent for a broad cross-section of organic compounds and irreversible adsorption is not observed. In applications involving the Ames Test, it was found that these resins,

particularly XAD-4, were clearly superior for the concentration of mutagenic chemicals (62,63,64).

In the standard method, Junk et al. (58) used 1.5-2.0 grams of 20-60 mesh XAD-2 resin in tubes 10 cm in length x 6 mm i.d. They were able to routinely concentrate 1000 ml of water by a factor of 1000. The elution was performed with a total of 25 ml diethyl ether, which was subsequently concentrated to 1.0 ml, or less, in a special concentrator vessel. The same basic procedure was successfully applied to much larger volumes of water by using larger resin beds and slightly more eluting solvent (59). On-site sampling was accomplished by connecting resin beds directly to a pressurized water source, such as a water faucet. The detection limit of the method was on the order of parts per trillion for most compounds.

It was observed (58,59) that using resin columns to sample directly from the faucet has some important advantages. Aside from being the only practical way to take very large water samples, it eliminates adsorption losses to the walls of the transporting containers used in other sampling procedures. This is extremely important in the analysis of sparingly soluble compounds.

The direct adsorption-solvent elution procedures generally require large sample volumes for the attainment of their extreme sensitivity. Typically, only about 2

microliters of the final extract can be injected into the gas chromatograph. In the standard procedure (58), this represents only 1/500th of the total sample. A significantly greater amount of solvent removal in the concentration step would result in the partial or complete loss of the more volatile sample components and poor reproducibility.

Tatada and Fritz (65) avoided both large sample volumes and the eluent concentration step. A much smaller resin bed (1.2-1.8 mm x 25 mm XAD-4, 150-200 mesh) was used and the smallest possible solvent volumes were used to elute the components of interest. The method was sensitive to about 2 ppb with about 2% of the total sample being injected into the gas chromatograph.

Bertsch et al. (38) summed up direct resin sorption methods as follows:

> "Recoveries were excellent at ultratrace levels. As opposed to batchwise solvent extraction methods, the coefficient of adsorption does not necessarily have to be large in order to ensure complete retention on the column since frontal development takes place. Adsorbent capacity, however, might be quite small for the more volatile components which are generally less well retained than higher-molecular-weight substances. The simplicity and economy of the approach are obvious, but the use of a solvent makes the method less attractive."

Direct adsorption-thermal desorption

In the course of working with gas purging methods, Versino et al. (50) also thermally desorbed organic components that had been sorbed directly from water. The adsorbent was Tenax GC. The removal of entrained water was effected by overnight vacuum desiccation. Some loss of volatile components was reported to have occurred in the drying process. One-liter volumes of water were spiked with diesel oil and gasoline at the 10 ppb level and analyzed by this method.

Murray (51) used the proprietary "polyaromatic" resin Chromosorb 105 to directly adsorb volatiles from brandy. The entrained water was removed by purging with dry nitrogen (40 ml/min) for 2 hours at 25 C. Breakthrough of volatiles was noted, but no quantitative results were given. The compounds which were retained were thermally desorbed to a cold trap at the front of the chromatographic column.

Chang and Fritz (66) proposed a novel approach for removing water from the resin bed. Water was sampled directly by passing it through a small tube, called a minicolumn, containing about 80 mg of XAD-2 resin. After passing a sufficiently large water sample through the minicolumn, 20 ml of air were used to blow most of the residual water through. The minicolumn was then placed in a modified injection port which was maintained at 220 C. Another minicolumn containing Tenax GC was connected so that helium flowing through the

injection port passed through it. This second minicolumn was maintained at about 45 C, and helium flow was approximately 50 ml/min. The organic compounds that had been trapped on the XAD-2 column were thermally desorbed and carried by the helium flow to the Tenax GC minicolumn, along with any water that remained on the XAD-2. The organics were retained by the Tenax but the water vapor passed through completely.

Both minicolumns were disconnected after a ten-minute initial desorption period. The Tenax GC minicolumn was then placed into the modified injection port and an analytical column was connected in the usual configuration. The organic compounds evaporated and were transported by the helium carrier gas to the analytical column where chromatographic separation took place.

Standards were injected through the heated injection port to a Tenax minicolumn and subsequently desorbed, giving a measure of the combined efficiencies of recovery from water and desorption from XAD-2. The reported values agreed well with previous methods using XAD-2 and solvent elution. Volatile breakthrough and recovery from Tenax GC were not measured but appeared to be quite favorable.

Although the background from resin decomposition was rather high, the method was inherently sensitive. Most of the organics in a water sample could be concentrated and injected into a gas chromatograph, and the elimination of

water was accomplished with a minimum of volatile sample loss.

The least volatile compound analyzed by this procedure was 2-methylnaphthalene (67). Acetone was reportedly recovered with 56% efficiency from water, but losses through the Tenax trap were not measured.

In implementing the method, it was found that the process of connection and disconnection of the minicolumns was extremely tedious and was liable to cause volatility losses, as observed by others working with modified injection ports (45,46). Also, the modified injection port did not force all carrier gas flow through the Tenax GC minicolumn during the second thermal desorption. Desorption efficiency may have suffered as a result. Significant peak broadening was, in fact, observable in the chromatograms of the less volatile compounds.

The most serious difficulty with the method was the high background resulting from resin decomposition. Even after several blank desorption runs, the background was often found to be unacceptably high.

Object of Research

The object of this research was to develop a method of analyzing water based on the direct adsorption of organic compounds from water and their subsequent thermal desorption

into a gas chromatograph. It was felt that this approach was potentially applicable to a range of compounds that was not encompassed by either gas purging or resin extraction methods. Furthermore, it was felt that such a method might have significant advantages in terms of sensitivity, sampling ease, and the prevention of analyte losses due to adsorption or evaporation.

Organization of Dissertation

The experimental portion of this dissertation is divided into two main sections which roughly parallel the evolution of the method. The first section describes a new device for transferring organic material from a wet resin substrate to a gas chromatographic analytical column. Experimental work is described, and the advantages and disadvantages of the system are discussed.

The second section is devoted to the improvement of the resolution of the system. The conversion of the gas chromatograph for use with glass capillary columns is described along with the means of coupling the device to the modified chromatographic system. Desorption parameters are discussed further, and chromatograms of real and spiked water samples are presented.

The final two sections of this dissertation are devoted to the design and future application of a totally automated

and somewhat more powerful thermal desorption instrument. Final modifications of the gas chromatograph which enhance its power as an analytical tool are also discussed.

THERMAL DESORPTION

Basic Thermal Desorption Method

Schematic

Since the object of this research was to develop a method of water analysis based on direct adsorption-thermal desorption, the initial work was done with the method of Chang and Fritz (66) and Chang (67). After following their procedure, it seemed that a useful instrument could be designed based on their idea of using a preliminary desorption to a second resin substrate to eliminate water. The instrument would be used to perform two sequential thermal desorptions in transferring organic compounds from a wet resin adsorption substrate to a gas chromatographic analytical column. The block diagram of the desired sequence is shown in Figure 1.

Fundamental requirements

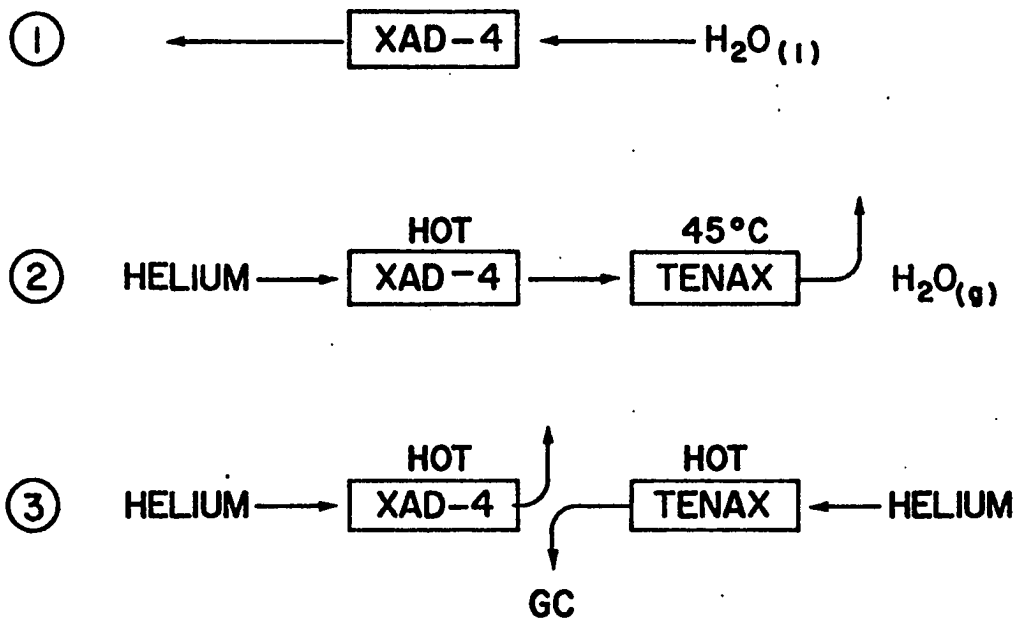
In order to solve the major problems of the previous methods, there had to be a number of requirements for the desorption instrument. These were and are as follows:

1) The desorptions must be performed in a closed system. There can be no connection or disconnection steps after the initiation of the desorption procedure. This also applies to the analytical column, which should be maintained without interruption of carrier gas flow and particularly

Figure 1. Flow diagram and schematic of the thermal desorption instrument

The three steps of an analysis run are illustrated:

1) The water sample is passed through a glass minicolumn which contains about 70-80 mg of XAD-4.
2) The XAD-4 minicolumn is connected to the thermal desorption device, it is heated, and a stream of helium sweeps the organic compounds out of the minicolumn into the Tenax precolumn. Any residual water vapor passes through the Tenax precolumn to vent.
3) After the Xad-4 desorption is completed, a valve is switched which causes the helium stream from the XAD-4 minicolumn to bypass the rest of the system. The Tenax precolumn is simultaneously isolated and heated. When the Tenax precolumn has reached a sufficiently high temperature, another switch of a valve causes a helium stream to sweep the organics off of the hot Tenax into the gas chromatograph.


①
XAD-4
$H_2O_{(l)}$
②
HELIUM
HOT
XAD-4
45°C
TENAX
$H_2O_{(g)}$
③
HELIUM
HOT
XAD-4
HOT
TENAX
HELIUM
GC

without the introduction of oxygen. In this way, problems of contamination, volatility loss, analyte decomposition (in the presence of oxygen) and column degradation can be minimized.

2) Gas flows must be directed through the system without any possible alternate pathways. This is especially important with the resin traps, because flow rate through them is an extremely important parameter.

3) Condensation cannot be allowed to take place in transfer lines or anywhere along the flow path, other than in the traps. Therefore, the instrument would have to be operable at high temperatures, and any dead volume would have to be kept to a minimum.

4) The traps must be insulated from each other and have separate temperature controls. The second trap must be maintainable at 45 C or lower. Temperatures and flow rates must be carefully controlled.

5) The second thermal desorption must be accomplished in a minimal volume in order to approximate the ideal "plug" injection into the gas chromatograph. The alternative is cryogenic trapping, which can

be awkwardly inconvenient, time-consuming, and expensive.

6) The time of analysis should be as short as possible.

Experimental Materials and Equipment

Apparatus and reagents

Adsorption tubes The tube was made from standard Pyrex glass tubing, 6 mm o.d. x 2 mm i.d. x 8 cm in length. The resin bed was 2.5 cm in length and positioned 1 cm from the closest end. The resin was held in place with plugs of silanized glass wool. Connections were made with 1/4" Swagelok nuts and PTFE reducing ferrules. A pair of each were dedicated to an adsorption tube. The complete adsorption tube assembly will be referred to as a minicolumn.

Resins A number of materials were used in the minicolumns (see Development of procedures section and Table 1) but the only material found to be satisfactory for this work was XAD-4. This resin is a polymer of divinylbenzene made by Rohm and Haas, Philadelphia, Pennsylvania. A modified XAD-4 was also used and found to be the equivalent of the standard resin, except that its thermal stability was somewhat improved.

Standard XAD-4 was ground in a Model 4-E Quaker City mill and sieved to collect the 120-140 mesh fraction. The

collected resin was washed repeatedly with methanol and then acetone to remove the fine resin particles produced in the grinding process. The resin was then stored under a mixture of methanol and acetone in an Ehrlenmeyer flask with a ground glass stopper.

The modified XAD-4 resin was received pre-sized, 120-140 mesh. The fines were removed and the resin was stored in the same manner as the standard resin.

Adsorption tubes (minicolumns) were packed by simply placing a glass wool plug approximately 1 cm from one end of the Pyrex tube and drawing the resin slurry up to the plug with a 20-ml syringe. The syringe was attached to the minicolumn with a special Kel-F fitting designed by Chang (67) and described in Figure 2.

Tenax GC was used in the second resin bed, which will be described under the heading "Thermal desorption instrument". Tenax GC, 60-80 mesh, was purchased from Alltech Associates, Arlington Heights, Illinois. It was used exactly as received and was packed dry.

Resin conditioning The following procedure for purification of the XAD-4 resin was found to be superior to the earlier procedures for cleanup of XAD-2: first, 5 ml of distilled water was passed through the newly slurry-packed XAD-4 adsorption tube, and the tube was placed in a specially constructed heating block. The temperature was held at 200°C

Figure 2. The coupling system used to connect minicolumns tc the sampling syringe

A) Glass syringe (20-ml, 30-ml, or 50-ml)

B) Water sample

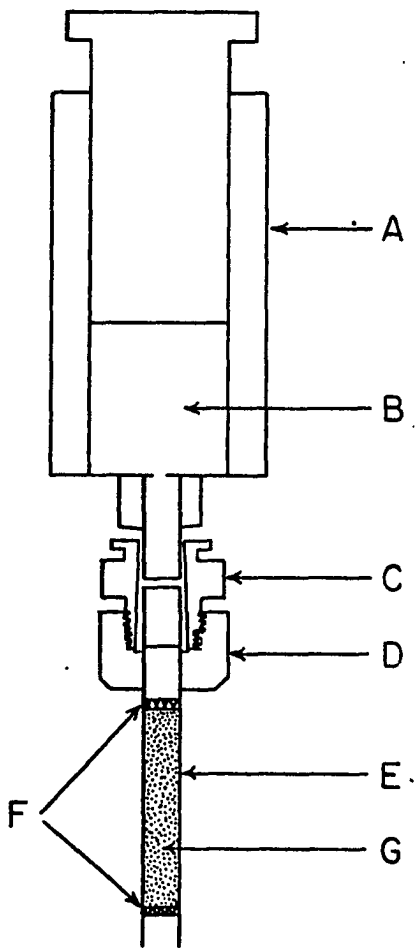
C) Special Kel-F coupler

D) 1/4" Swagelok nut and 1/4" Teflon ferrule

E) 1/4" o.d. x 2 mm i.d. Pyrex glass minicolumn

F) Silanized glass wool plugs

G) XAD-4 resin bed (120-140 mesh)


A
B
C
D
E
F
G

and helium passed through the adsorption tube at about 20 ml/min. After about 4 min, the temperature was raised to 240°C for 15 min. The tube was removed, allowed to cool on a metal plate, and then the wetting-heating-cooling cycle was repeated three more times. Four adsorption tubes were conditioned at the same time in the heating block. This procedure resulted in tolerably low blank levels when the tubes were tested in blank desorption runs.

Tenax GC was conditioned after placement in the desorption instrument by heating it to 300°C with helium flow of about 40 ml/min for 30 min.

Reagents All solvents and chemicals used were reagent grade. Water was doubly-distilled, the second distillation being performed over alkaline potassium permanganate.

The distillation procedure was as follows: a 5-liter round-bottomed flask was cleaned by sequential washings with methylene chloride, acetone, and methanol, and dried in an oven. It was then placed in a heating mantle and connected to a Snyder distillation column, a condenser, and a receiving vessel that had been cleaned in a similar fashion. Four liters of distilled water were then added to the flask with 1.6 g sodium hydroxide and 6.32 g potassium permanganate.

The mixture was slowly distilled with a stream of pure nitrogen bubbling through the system.

Although this procedure effectively removed organic compounds from the distilled water, it was found that a third distillation was required to remove all of the permanganate color from the water. Presumably, the observed discoloration represented some oxidative capacity but it did not appear to adversely affect the resin.

Except for resin blank studies, distilled water was used directly from the tap, as the few organic compounds present did not interfere with the analyses being performed.

Gas chromatography

A Tracor 560 gas chromatograph was used for all work with the thermal desorption instrument. Detection was by flame ionization and the recorder was a Hewlett-Packard Model 7128A strip chart recorder.

Helium, Matheson Zero Gas quality (certified total hydrocarbons as methane less than 0.5 ppm) was used for thermal desorption and chromatography.

Separations were done on glass columns 6 ft x 2 mm i.d.; 10% Carbowax 20 M on Chromosorb W 80-100 mesh, 5% FFAP on Chromosorb W 80-100 mesh, and 5% OV-1 on Chromosorb W 8-100 stationary phases were used.

Temperature programs were routinely run at 10°C/min with the initial ranging from 50-75 C. Final temperature was usually 190 C. Attenuation was generally about 4 x 10.

Thermal desorption instrument

The instrument is shown in Figure 3 and consists of the following components:

A. An aluminum block that can be moved in and out of a hole in the main body. The block is cylindrical in shape and rests freely on its mounting bracket. A 1/4" hole has been drilled through the block, and 1/4" pipe threads were cut at each end. (a) Thermocouple connected to an external pyrometer. (b) One 200-watt cartridge heater, controlled by a variable transformer. (c) XAD-4 minicolumn (adsorption tube). A standard 1/4" swagelok-to-pipe union was drilled out to 1/4" i.d. and screwed into the pipe thread at the end of the heating block. The minicolumn is connected to the aluminum block with a 1/4" stainless steel nut and a Vespel ferrule. It is connected to the 6-port valve via 1/8" stainless steel tubing and a 1/4"-to-1/8" reducing union.

B. Heated valve box insulated with Temp-mat Glass Insulation acquired courtesy of Pittsburgh Corning, Pittsburgh, Pennsylvania. (d) Two zero-volume, high-temperature valves, one 4-port and one 6-port, as shown. These were the very best valves available for high-temperature gas chromatographic work and were tested for helium cross-port

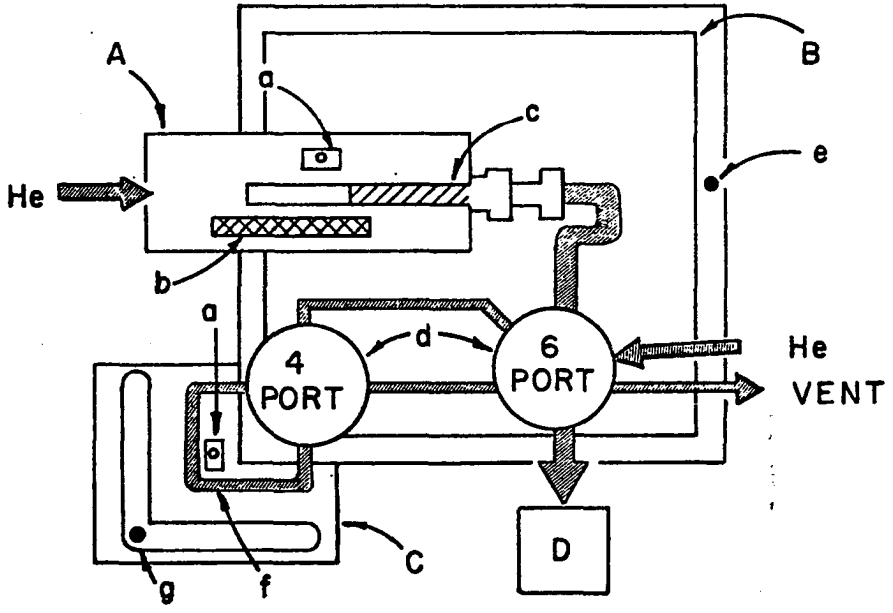


Figure 3. Diagram of the thermal desorption instrument. The letter code is described in the text

and out-port leakage to better than 3.5×10^{-6} torr-liters/sec at 300°C. They were purchased from Valco Instruments Co., Inc., Houston, Texas. (e) High-temperature heating cord, 200 watt, quartz-insulated, with an upper temperature limit of 600°C. This cord heated the valve box and was controlled by a variable transfermer. The heating cord is commercially available from Glas-Col Apparatus Co., Terre Haute, Indiana.

C. A removable, insulated (as B) sheet metal enclosure, containing the Tenax desorption heating zone. The enclosure is placed as shown when the Tenax trap is being heated and is removed at other times to keep the Tenax trap at the desired lower temperature. (f) Tenax trap, standard stainless steel tubing 1/8" x 18 cm, packed with Tenax GC 60-80 mesh. The total internal volume of the trap was calculated to be slightly less than 1 ml. The trap contained 90 mg of resin. (g) High-temperature heating cord (as e) controlled by a temperature controller which was built by the Instrumentation and Electronics Group, Ames Laboratory.

D. Gas chromatograph. The connection to the gas chromatograph was made with a special fitting that was essentially a septum nut with a 1/8" male swagelok fitting silver-soldered to the front of it. The regular septum nut was replaced with the modified fitting. A lead washer was used to make the connection gas-tight, rather than a septum, to avoid the possibility of interaction with the sample and

the septum material, and because a conventional septum tends to flow under pressure and thermal stress. The 6-port valve was connected to the modified septum nut with 1/8" stainless steel tubing. The resulting flow path to the column was both smooth and straight.

Development of Procedures

Resin selection

A number of materials were used in the adsorption tubes on an experimental basis. These are tabulated in Table 1.

Initial experiments, performed with XAD-2, proved that direct adsorption-thermal desorption could be a practical means of transferring organics from water to a gas chromatograph. XAD-2 was found to be an excellent adsorption substrate for a broad range of compounds. Unfortunately, it has rather limited thermal stability. Even after extensive conditioning, it was impossible to achieve a reproducible blank that was low enough to permit analysis at the ppb level.

Experiments with the carbonaceous materials, Spherocarb and XE-340, have shown them to be efficient adsorbents. However, it was not possible to recover adsorbed compounds from these materials by thermal desorption. The observed blank was also rather high, even though thermogravimetric analyses indicate that the materials do not actually decompose, at even extremely high temperatures. It is possible

that the irreversibly adsorptive behavior of these substrates is mechanistically related to decomposition of organic compounds trapped on the resin surfaces. This would logically explain the observance of high blank and background, as well as the loss of sample material.

Tenax GC is a clean adsorbent that shows no tendency to adsorb irreversibly. Of the volatile components that have been investigated, only phenols have been observed to react with Tenax to any great extent (68). The chromatographic characteristics of Tenax were thoroughly investigated by Sakodynskii et al. (69) who observed somewhat anomalous behavior with respect to the retention of unsaturated materials by Tenax. Alkenes were observed to be preferentially retained, as were aromatic compounds. Tanaka (70) found that Tenax has a greater affinity for chloroform than for the heavier compounds carbon tetrachloride and 1,1,1-trichloroethane, but these observations only related to retention and relative capacity. Tenax is generally an excellent substrate to thermally desorb from.

The specific surface area of Tenax is quite low relative to many other adsorptive materials. It is, therefore, not surprising that Tenax is a poor substrate for adsorbing material from water. Experiments at this laboratory have shown it to be quite inferior to the polystyrene-divinylbenzene polymers which have been used for the same purpose.

Aside from having relatively low specific surface area, Tenax is extremely hydrophobic. It is probable that its performance as a sorbant is related to the high contact angle of water on the surface of this resin. A large portion of the measured surface area may be excluded from contact with the compounds being sorbed from water because the surface tension of water stands in the way. The combination of these properties make Tenax an extremely suitable substrate for the purposes of the second thermal desorption trap, but except for possible special applications, quite unusable as an absorbent for direct sampling from water.

There are a number of factors which favor the use of XAD-4 as the adsorption substrate. It has a high specific surface area (see Table 1). It has been proven to be an excellent substrate for the purpose of direct adsorption (57, 63), and it would seem that the higher degree of cross-linking might lend added stability to the structure. Also, since XAD-4 is virtually all divinyl benzene, it follows that it would be more pure than a resin made with additional material. Furthermore, XAD-4 has been found to be the most efficient adsorbent available for concentrating and collecting mutagenic materials from water (64,65).

Experiments were performed using the method of Chang and Fritz (66) which confirmed that XAD-4 was indeed a cleaner and more stable substrate for the purposes of thermal desorption.

Both resins were sized and soxhlet extracted with methanol, acetonitrile and diethyl ether. After being allowed to dry, they were packed into thin-walled glass tubes 2 mm i.d. x 10 cm in length. These minicolumns were then conditioned at 240°C for about 45 minutes.

The conditioning period was followed by conditioning runs consisting of wetting the resin with 5 ml of distilled water, and thermally desorbing from the resin by placing the minicolumn in a modified injection port, maintained at 220°C. Helium flowed through the minicolumn to a second minicolumn packed with Tenax at a rate of about 50 ml/min. After a 10-minute desorption period, the Tenax minicolumn was placed in the modified injection port and desorbed onto an analytical column. The resulting chromatograms were used to monitor the progress of column conditioning.

The results of these experiments indicated that XAD resins were not very stable in the presence of water at a temperature of 200°C. The comparison of XAD-2 and XAD-4 showed that nature of the blanks, as observed in the chromatographic profiles, were quite similar. However, XAD-4 appeared to be easier to condition and maintained a low blank level much more reproducibly than XAD-2.

Although XAD-4 seemed to be the best material available for use in the direct adsorbent trap, it still lacked thermal stability. Artifacts of the resin constituted an interference

in some sensitive analyses. Dr. R. L. Albright, of Rohm and Haas, felt that the resin could be made cleaner by using a different initiator in the polymerization process. The point of the change would be to reduce the amount of free monomer in the resin. The initiator itself may also have been a contributor to the observed background.

At Dr. Albright's suggestion, a batch of XAD-4 was made by Rohm and Haas using a special initiator. A cannister of it was donated to the author for thermal desorption research.

The modified XAD-4 was compared with the standard resin in experiments using the newly-developed thermal desorption instrument. The cleanliness and stability of the new resin far surpassed that of standard XAD-2 and compared favorably with standard XAD-4. The modified XAD-4 resin was observed to give a more reproducible blank at a level that was consistent with the best carefully-conditioned minicolumns filled with standard XAD-4. As expected, the structural stability of the resin was not changed by using a different initiator, but the amount of excess desorbable material had diminished. The reproducibility of the blank was improved with the modified XAD-4 resin, as was the detection limit of the analytical technique. Modified XAD-4 was therefore the material of choice for the minicolumn substrate.

Minicolumn preparation

In the course of evaluating the resin clean-up procedure it was observed that the modified XAD-4 resin could be cleaned without recourse to soxhlet extraction. After removing the fines with a methanol wash, the resin could be conditioned by simply wetting it with distilled water and then heating it to 240°C with helium passing through at a moderately high flow rate. A minicolumn filled with the modified resin was thoroughly conditioned by repeating this procedure three times. After the third desorption, the observed blank for the regular desorption procedure was quite acceptable.

Water sampling

Initial work was done with 10-50 ml of water in a sample. The XAD-4 minicolumn was attached to the special Kel-F coupler shown in Figure 2. The coupler could then be adapted to a syringe with either slip fittings or Luer-lok fittings. The actual sampling procedure consisted of filling the syringe with a measured volume of water and injecting it through the resin-filled minicolumn *via* the Kel-F coupling.

The 200-ml samples which were analyzed in the recovery studies were collected in a special pressure-flask. Approximately 15 psi of helium pressure were used to force the sample through an XAD-4 minicolumn, also *via* the special

Kel-F fitting. The design of such a sampling vessel is described by Chang (67).

Intermediate sample sizes were taken in a 50-ml syringe and injected through the minicolumn with the aid of a syringe pump. This method was also employed with many larger samples because the syringe was much easier to clean between samples than the pressure flask. A method using a syringe pump to sample volumes of water that exceed the capacity of the syringe is discussed by Murray (51). A simple three-way valve was used to make the process of filling and re-filling the syringe more convenient. This simple improvement could prove useful with some routine applications of the adsorption-thermal desorption method.

A virtually ideal method was used to take real finished-water samples. In such sensitive analyses, it is necessary to prevent adsorption on the walls of sampling containers and transfer lines. Volatility losses to any air-space above the sample, or in the collection and transfer of the sample, can also be very important in the analysis of highly volatile and insoluble compounds. The best way to eliminate these problems was found to be direct sampling.

A simple adaptor was made for connecting minicolumns to a water faucet. Once the minicolumn was connected, the water was turned on and the flow rate measured. By careful adjustment, the desired flow rate could be achieved. Sample

collection proceeded without the need for an intermediate collecting vessel. After collecting the organics from the desired water volume, the minicolumn was disconnected and sealed to await analysis.

The preferred method for sealing the minicolumns is to wrap the open ends with an inert material, such as Teflon tape. Parafilm, a moisture-resistant self-sealing thermoplastic, has been used successfully to seal minicolumns for as long as a week, but tests over a period of months indicate that Parafilm can contribute a significant amount of background to minicolumns that are sealed with it for long periods of time.

In real sample analysis, the samples are usually taken in triplicate or duplicate with some difference in the sampling volumes in order to assess the sampling efficiency. A blank consists of wetting a minicolumn with a minimal volume of the sample, and sealing it in the same way as the other samples. This is done in case the residual water from the samples has some effect on the trapping substrate, which could increase the background of the analysis. So far, there have been no deliterious effects observed, even upon long-term storage of finished water samples. It is anticipated that samples with some measure of biological activity may require analysis quite soon after sampling, to prevent bacteriological degradation of the adsorption substrate.

The sampling flow rate was generally 4-5 ml/min. This is somewhat faster than might be expected, based on a calculation of the ideal using only bed volume ratios. However, various factors override such a simplistic evaluation. For example, the cross-sectional area of the resin bed determines the linear flow velocity of the sample flowing past the resin, while the particle mesh size establishes the mean free path of turbulent flow through it. The resultant of these parameters was not assessed. Rather, an empirical evaluation of the optimal flow rate indicated that, at 4-5 ml/min, the recovery efficiency was comparable to other published values, even for compounds that are retained only moderately well. Much higher flow rates can be used where the components of interest have a very strong affinity for XAD-4.

If the minicolumn is to be stored prior to analysis, it is sealed with the resin bed filled with water. Prior to connecting it to the thermal desorption instrument, the bulk of the residual water is forced through the minicolumn with 2-3 ml of air. The still-wet minicolumn is then ready for thermal desorption.

Desorption from XAD-4

The thermal desorption procedure is divided into three steps.

A. The minicolumn is connected to the thermal desorption instrument by means of two Swagelok nut-PTFE ferrule combinations on the adsorption tube. The range of typical desorption conditions is: temperature, 180-220°C; time, 8-30 min; helium flow through the minicolumn, 5-60 ml/min.

The vapor passes through the two valves in the heated valve box to a Tenax precolumn (temperature, 45°C). Water vapor passes through the Tenax to vent while the organics are retained.

B. The Tenax precolumn is closed off by means of a 4-port valve (equipped with zero dead-volume fittings) and the sheet metal enclosure is placed over it. The enclosed chamber is then heated rapidly to about 280°C. The 6-port valve is also switched to direct the carrier through the 4-port valve before it passes to the chromatograph.

C. As the temperature of the chamber approaches maximum, the 4-port valve is opened. Carrier gas backflushes the hot Tenax precolumn. The low void volume of the Tenax precolumn assures a plug-like injection of the volatilized components into the chromatograph, while the less volatile compounds are trapped at the front of the analytical column as they elute.

The Tenax desorption chamber is reopened while the sample is being chromatographed. This allows it to cool down for the next injection, which can usually be made as soon as the chromatograph cycles back to the initial temperature. The

XAD-4 desorption temperature is generally raised to 230-240°C to regenerate the minicolumn. If the sample is excessively dirty, the minicolumn is simply discarded after the desorption step. However, if the minicolumn is to be reused, it should be cooled rapidly after regeneration to prevent oxygenation of the resin. This is usually accomplished by placing it on a metal plate which acts as a heat sink.

Results and Discussion

Recovery of model compounds

The thermal desorption method was initially tested in two ways. First, the recovery of model compounds from water was established. Then, the efficiency with which these could be transferred from the XAD-4 minicolumn to the chromatograph was investigated.

The percentage recovery from water for each model compound was estimated by the following procedure. A water sample was made up by spiking a measured volume of water with a standard acetone or methanol solution of the compound to be tested. The spiked water sample was then passed through an XAD-4 minicolumn and analyzed according to the thermal desorption procedure. The same amount of the acetone or methanol standard solution was then injected onto the front of the XAD-4 minicolumn, wetted with about 2 ml of distilled water, and analyzed in precisely the same manner. The

percentage recovery from water was calculated from the relative peak heights of the compound recorded for an analysis.

It was observed that 1-2 ml of distilled water should be passed through the minicolumn after injecting the standard directly onto it, to obtain a valid comparison with a sample concentrated from water. This is because the presence of water on the minicolumn has been found to increase the efficiency of desorption. Apparent recoveries of more than 100% were often obtained when samples taken from water were compared with standards desorbed from a dry minicolumn.

The recoveries of model compounds representing various functional groups are reported in Table 2. The values generally compare well with published recoveries obtained with direct adsorption-solvent elution techniques. The ability of XAD-4 to retain some of the more polar and water soluble compounds is limited. However, with the use of selective detection, a sample size of 20 ml is sufficient for determination of compounds such as chloroform and dibromomethane at the parts per trillion level.

It was found that this method of measuring recovery from water tended to yield low values for the less volatile compounds. This was because the standard was injected on the front of the minicolumn, and even the wetting procedure did not move it through the column to any great extent. However,

Table 2. The recovery of compounds from water by XAD-4[a]

Compound	Recovery, % 10 ppb 20 ml	Recovery, % 1 ppb 200 ml	Desorption Time (min)	Desorption Temp °C
Toluene	88	90	15	210
Ethylbenzene	79	79	15	210
Indene	96	102	10	180-200[b]
Naphthalene	90	81	15	210
1-Methylnaphthalene	95	97	10	180-200
Hexane	88	65	8	175[c]
Chloroform	93	56	4	175
Dibromomethane	88	57	4	175
Cyclohexanol	98	90	5	200
n-Heptyl Alcohol	100	98	6	200
Benzyl Alcohol	83	54	13	220
Methyl Isobutyl Ketone	100	98	8	200

[a]The recovery of compounds from water by XAD-4 is based on the comparison of spiked water sample determinations with standards injected directly onto an XAD-4 minicolumn using the "wet" column procedure. Standards were 1 x 10^{-7} g/µl in methanol or acetone. Spiked water samples contained 2 µl of the standard solution.

[b]The two numbers represent the initial and final temperatures of the desorption block. This crude temperature programming procedure seemed to minimize resin bleed while maintaining good desorption efficiency.

[c]Error was ∿±10%. Reproducibility as measured by (6) determinations of hexane was ±6.6% relative (range divided by two).

Table 2. (Continued)

Compound	Recovery, % 10 ppb 20 ml	Recovery, % 1 ppb 200 ml	Desorption Time (min)	Desorption Temp °C
Amyl Isopropyl Ketone	102	99	8	200
Methyl Nonyl Ketone	96	92	13	220
p-Methylacetophenone	99	104	13	220
Ethyl Heptanoate	96	68	10	200
Octyl Acetate	61	32	10	200
Bromobenzene	106	---	10	200
o-Dichlorobenzene	102	---	10	200

the water sampling procedure is likely to trap the component of interest further into the minicolumn. Thus, recoveries measured by comparing the results of the two procedures should be partially a function of desorption parameters. An example of the dependence of recovery on desorption temperature is provided in Table 3. Desorption time and flow rate were maintained at constant values that were insufficient for total desorption of the sample concentrated from water. This dependence is, of course, eliminated by choosing

parameters so that the sample collected from water is completely desorbed.

Table 3. The dependence of recovery on desorption temperature

Compound	Desorption Temperature (°C)	% Recovery
Methyl Nonyl Ketone	210°C (10 min)	63
	220	79
	225	96

Conversely, highly volatile compounds with low affinity for Tenax can be partially lost by passing through the second trap if the desorption time is too long or the carrier gas is too hot. Table 4 illustrates how this can occur with ketones.

Table 4. The dependence of the recovery of volatile ketones on desorption time and temperature

Compound	Desorption Temperature (°C)	% Recovery
Methyl Isobutyl Ketone	180 (8 min)	100
	225 (13 min)	75
Amyl Isopropyl Ketone	180 (8 min)	102
	225 (13 min)	60

As a consequence of these limitations, it is necessary to analyze two samples to optimize conditions for compounds of widely divergent volatility, especially where a quantitative analysis is desired. This problem is discussed at length under Thermal Desorption to Glass Capillary Columns.

After estimating the recovery of model compounds from water, the absolute efficiency of the system was investigated by comparing thermally desorbed standards to standards injected directly into the gas chromatograph.

The thermal desorption efficiency, as measured by comparison to direct injection, is definitely a function of the desorption parameters. This is clearly illustrated in Table 5. No attempt was made to optimize conditions for these. Rather, the effects of minicolumn condition (wet or dry), desorption temperature, and desorption time are presented here. The optimization of parameters for high-boiling compounds is discussed in pages 72-89.

The overall recovery of a compound by the direct adsorption-thermal desorption method is the product of the efficiency of desorption, from XAD-4 to the chromatograph (as in Table 5), and the recovery of the same compound from water (as in Table 2). This represents the fractional amount of the component of interest that is transferred from the water sample to the gas chromatographic detector. The overall recovery can also be measured by comparing the results of a

Table 5. Thermal desorption efficiency

Compound	Mini-column condition	Desorption time	Desorption temperature	Boiling Point	Fractional[a] Recovery
Cyclohexanol	Dry	10 min	180 - 200°C	161°C	0.94
Cyclohexanol	Wet[b]	10	180 - 200	161	1.02
Bromobenzene	Wet	8	200 - 215	156	0.97
Bromobenzene	Wet	10	180 - 200	156	0.97
Undecanone	Wet	10	210 - 225	232	0.66
Undecanone	Wet	10	180 - 200	232	0.50
Chloroform	Wet	10	180 - 185	62	0.93
Indene	Wet	10	180 - 200	183	0.99
1-Methylnaphthalene	Wet	13	200 - 235	245	0.96
1-Methylnaphthalene	Wet	10	180 - 200	245	0.86

[a]Fractional recovery is the ratio of peak height of injection onto the XAD-4 minicolumn to the peak height of direct injection into the gas chromatograph. Samples were 2×10^{-7} grams.

[b]Wet columns are wetted after the sample has been injected into them.

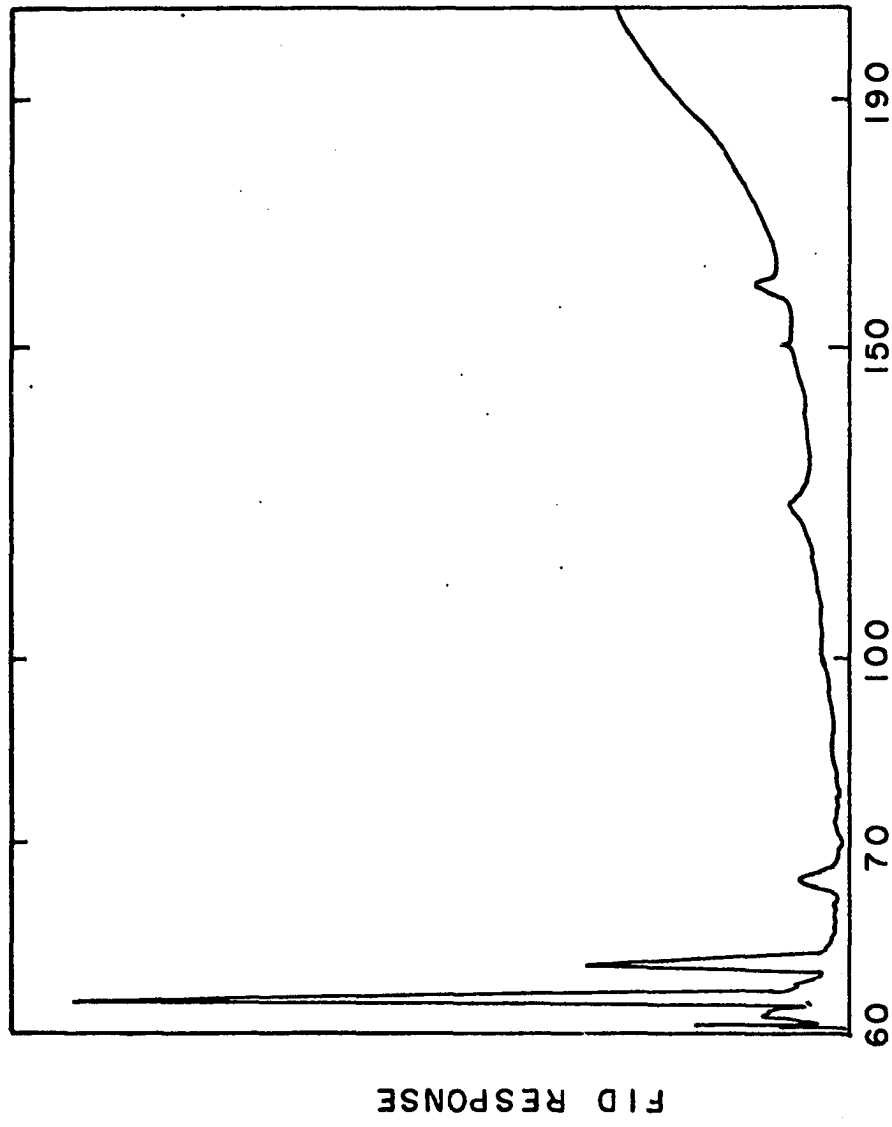
spiked water analysis with a standard injected directly into the gas chromatograph. The method first described was chosen for the sake of establishing the nature of any observed losses while investigating the absolute recovery of model compounds. It was observed that, for those compounds within the volatility range of the thermal desorption instrument, the overall recovery was approximately equal to the observed recovery from water as depicted in Table 2.

Real sample analysis

The direct adsorption-thermal desorption method was applied to real samples of drinking water and well water. A chromatogram of Slater, Iowa, water is shown in Figure 4, and one of Ames, Iowa, water is shown in Figure 5. The Ames water was sampled during the winter of 1977-78 following a severe drought, and the observed level of organic contamination was unusually high. The major peaks had been previously identified by gas chromatography-mass spectroscopy so the peaks were simply reidentified by retention time and internal standard injections.

A sample of water from Ames well number five was taken for comparison. This chromatogram is shown in Figure 6. Although Ames well number five is not normally used, a comparison of the two chromatograms indicated that it was being drawn from during the winter of 1977-78. A check with the City of Ames water department unofficially confirmed this.

Figure 4. A thermal desorption chromatogram of Slater, Iowa, tap water. A 200-ml sample was taken. The desorption time was 10 min, temperature 180-200°C. The chromatographic column was 6 ft x 2 mm i.d., Carbowax 20 M on Chromosorb W. The temperature was programmed from 60 to 190°C at 10°C/min. Attenuation was 4 x 10. The large peak represents approximately 70 ppb chloroform


FID RESPONSE
60
70
100
150
190

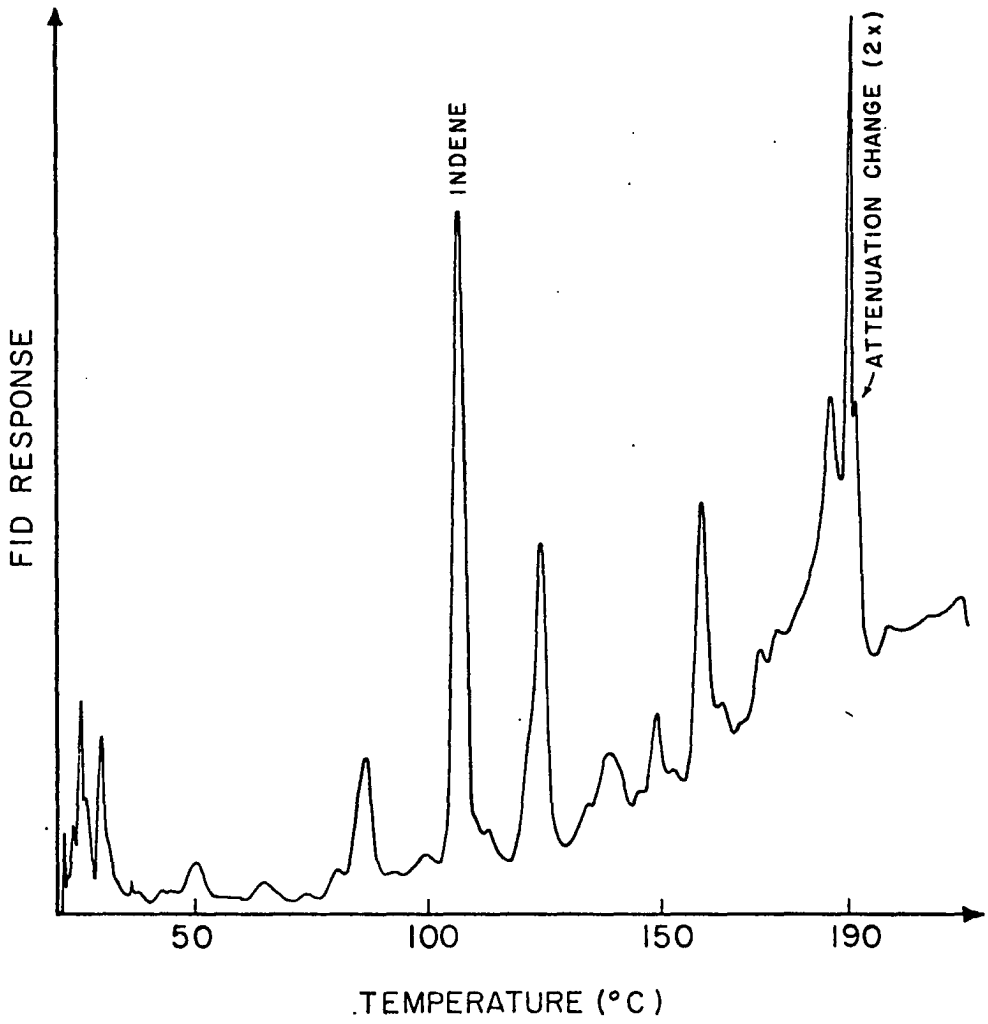
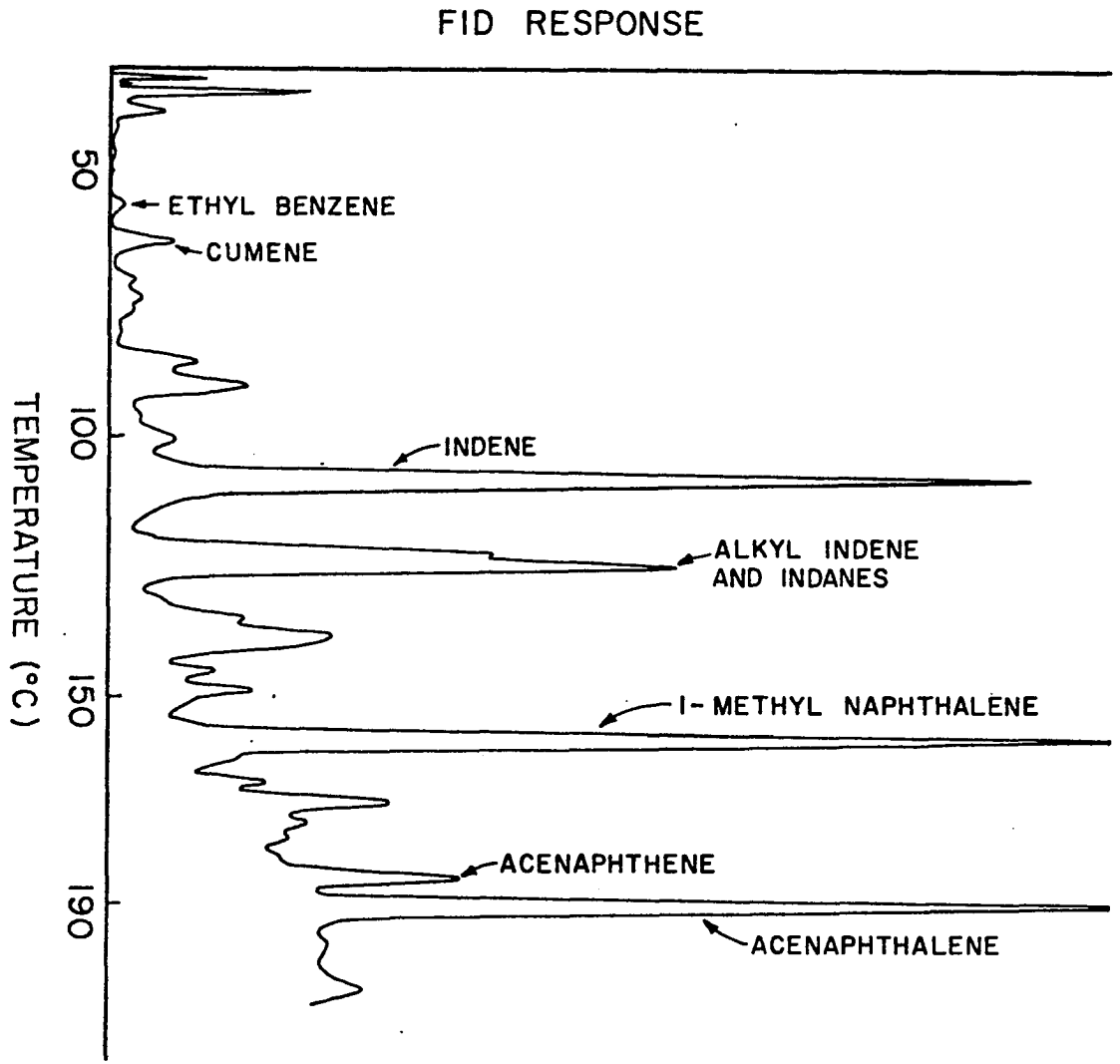


Figure 5. Ames tap water. A 200-ml sample was taken. The desorption time was 10 min, temperature 180-200°C. The initial temperature was 50°C, isothermal for 3 min. All other parameters are identical to Figure 4

Figure 6. A thermal desorption chromatogram of water taken from Ames well number five. A 20-ml sample was taken. The desorption time was 10 min, temperature 180-200°C. The analytical column was 6 ft x 2 mm i.d., 10% Carbowax 20 M on Chromosorb W. The temperature was isothermal at 50°C for 2 min and then programmed up to 190°C at 10°C/min. The attenuation was 16 x 10


FID RESPONSE
50
100
150
190
TEMPERATURE (°C)
ETHYL BENZENE
CUMENE
INDENE
ALKYL INDENE
AND INDANES
1-METHYL NAPHTHALENE
ACENAPHTHENE
ACENAPHTHALENE

The Slater water sample was passed through the XAD-4 minicolumn and stored without detrimental effects for 4 days, before completing the analysis. The tube was sealed, very simply, by wrapping a piece of Parafilm around each end. Tests showed that loss of chloroform from minicolumns so stored is about 15%; losses of less volatile compounds appear to be minimal.

Blanks were run by passing a small amount of water through an XAD-4 minicolumn. This was done in order to minimize any difference between the blank and the sample, with regard to the effects of storing the resin in the presence of the sample water; and it also negated the effects of water vapor on the thermal desorption procedure.

The chromatogram of a distilled water blank that was thermally desorbed after a four-day storage period is shown in Figure 7. The chromatogram of a distilled water blank that was desorbed immediately is shown above it for comparison. The distilled water tap was sampled for possible interferences in the model compound studies and was found to be sufficiently clean for most experimental purposes. The chromatogram of a 60-ml sample is seen in Figure 8.

Quantitation

In order to do quantitative work with this method by comparison to direct injection, it is necessary to know the

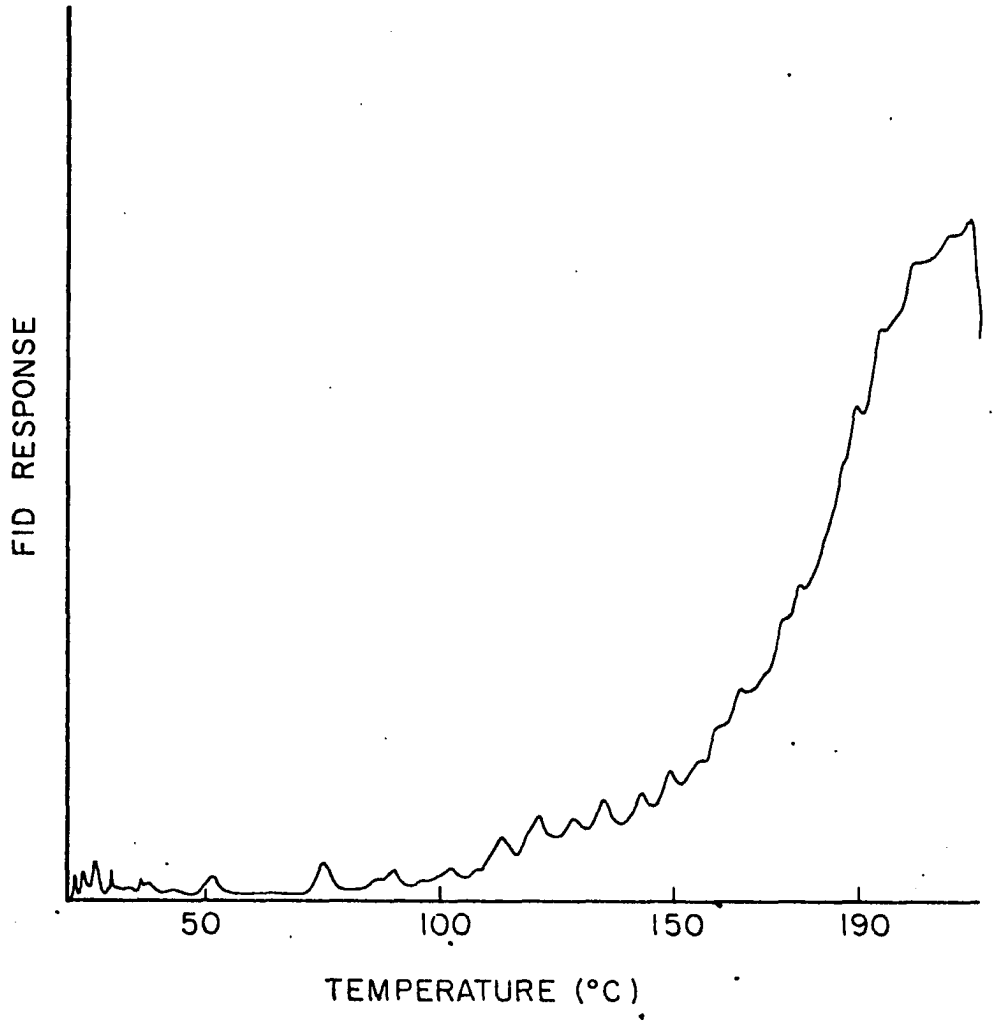


Figure 7. A 60-ml sample of water from the distilled water tap. All conditions were identical to those of Figure 5

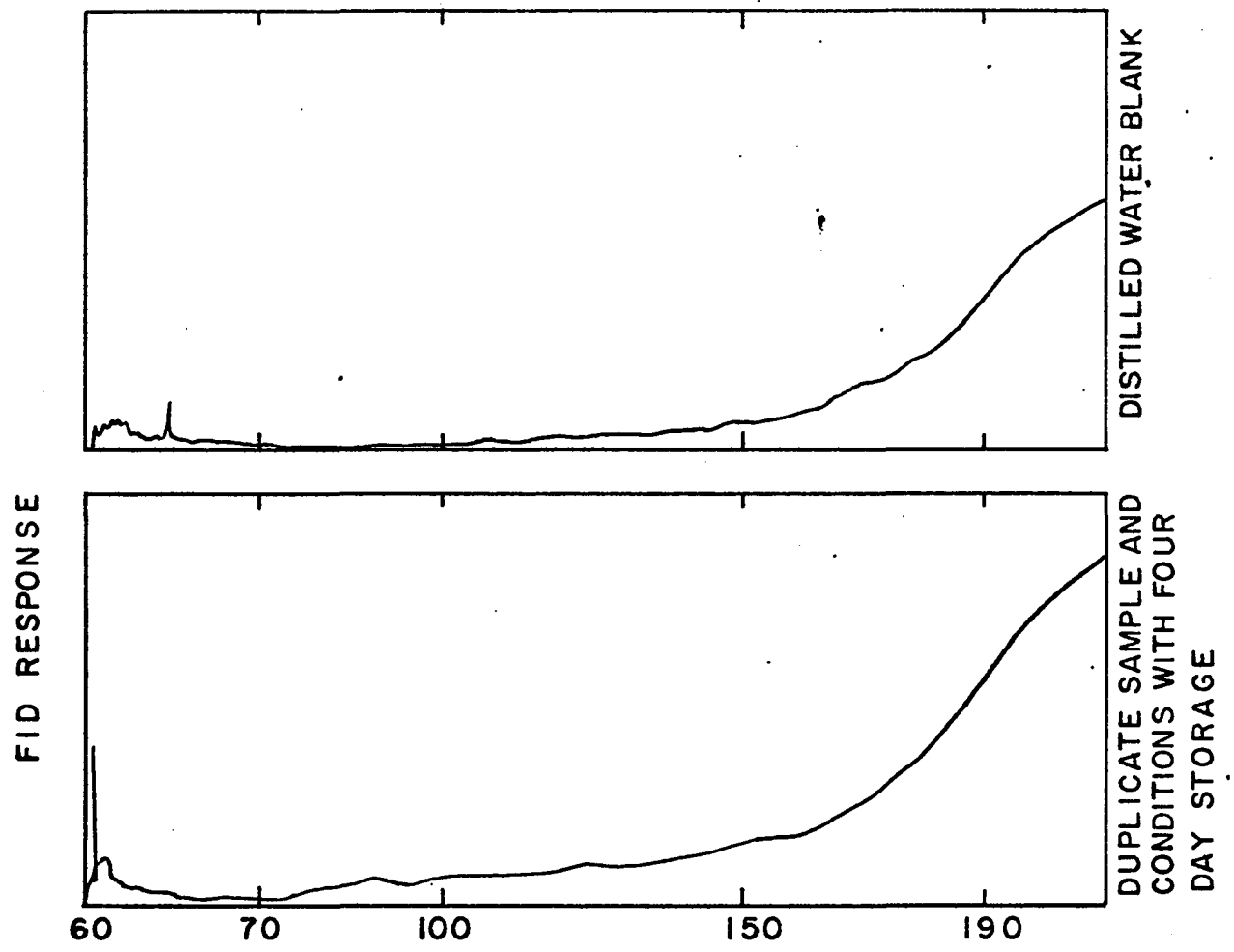


Figure 8. Distilled water blanks, 50-ml samples. All parameters were identical to those of Figure 4

overall recovery efficiency for each component of interest. In cases where recovery is highly dependent upon sample volume or desorption parameters, it is generally best to concentrate the standard from a small spiked water standard. This can be made up in a syringe and injected into the mini-column with a minimum of effort. Such standards are highly reproducible if conditions are maintained rigidly constant, but care must be taken to prevent adsorption losses to the walls of the syringe or through volatilization. Even for a highly volatile and insoluble compound like hexane, reproducibility was ±6.6% relative to this procedure.

The amount of indene in Ames finished water was measured by comparison to a standard injected directly into the chromatograph. This was done because the overall recovery efficiency for indene was determined to be virtually 100% for the sample sizes taken. In the winter of 1977-78, the amount of indene was estimated to be 0.90 ppb, using the thermal desorption method. By April, 1978, the level of indene concentration was estimated to have dropped to about 0.25 ppb. Ames tap water was analyzed again in January, 1979, and the indene concentration had risen to 0.70 ppb. The estimated accuracy of these figures is on the order of ±10%.

THERMAL DESORPTION TO GLASS CAPILLARY COLUMNS

Chromatographic Considerations

Resolution enhancement

Although the method described in the previous section is sensitive to concentration changes of some compounds well below the part per billion level, the gas chromatographic resolution was insufficient for the analysis of any but the major peaks in a complex sample. The limiting factor appeared to be the relatively poor resolving power of the packed stationary phase columns that were being used.

The obvious solution to the problem of resolution in this case was to modify the system for use with glass capillary columns. These columns are commercially available with ratings exceeding a quarter of a million theoretical plates. The execution of the transition from packed column chromatography to glass capillary column chromatography is discussed in this section as it applies to the thermal desorption system.

Range expansion

The range of the direct adsorption-thermal desorption method was also somewhat limited by the use of packed columns. Capillary columns have a much larger carrier gas linear flow velocity than do packed columns. As a result, compounds can

be eluted from capillary columns at relatively low temperatures. The advantage of this is that a much wider range of compounds can be chromatographed in a single run on a particular column.

For example, most of the low-boiling model compounds were best chromatographed on a Carbowax 20 M packed column, but the high bleed of this stationary phase precluded using it to analyze high-boiling compounds. However, a Carbowax 20 M capillary column can be used to chromatograph many high-boiling compounds that are not eluted satisfactorily from the packed column.

Interfacing

Glass capillary columns are well known to have extremely high resolving power, but they also have relatively low capacity. More importantly, the volume flow rate through capillary columns is very low (optimally about 0.7 ml/min). Thermal desorption from the second trap had been accomplished previously with helium flows that were optimal for a 2 mm i.d. packed column (about 50 ml/min). It would be impossible to reduce desorption flow to 0.7 ml/min and still attain efficient desorption.

Reducing the cross-sectional area of the Tenax pre-column (the second desorption trap) would make it possible to desorb efficiently with a reduced volumn flow rate. However, even if the internal diameter of the Tenax trap was reduced

to 0.5 mm, the volume flow rate through the system would still be five times the optimum for the glass capillary column, if the same desorption efficiency was desired. The cross-sectional area of the Tenax column could not be reduced much further without altering the packing efficiency to the point of significantly affecting performance.

It was decided that the thermal desorption instrument should be changed as little as possible for the initial investigation of the thermal desorption instrument-glass capillary chromatograph interface. This follows the general rule of minimizing experimental variables for the attainment of valid comparisons. With this end in mind, the interface was designed to be a variable splitting system. The effluent from the thermal desorption instrument would be split as much as necessary to achieve sufficient flow for the thermal desorption from Tenax.

Instrument Modification

Apparatus

The same Tracor model 560 gas chromatograph was used throughout this research; Tracor Instruments, Austin, Texas.

The glass capillary columns were made by J&W Scientific and were purchased from Supelco, Inc., Bellefonte, Pennsylvania. They were WCOT columns coated with either Carbowax 20 M or SE-30; typically 30 meters long and about 50,000 theoretical plates.

The gas switching valves were solenoid actuated, and were controlled by electronic microswitches; Skinner Electronic Valve Division, New Britain, Connecticut.

The restrictor valves used to regulate split and back-flush flows were needle valves, purchased from Omaha Valve & Fitting Co., Omaha, Nebraska.

The gauge used to regulate helium gas pressure at the capillary column was rated at 250 psi maximum inlet pressure and 30 psi maximum outlet pressure; Porter Instrument Co., Hatfield, Pennsylvania.

The split and exit tees were made by silver-soldering a 1/8" male Swagelok fitting into the side of a 1/4"-to-1/16" reducing union. The fittings were purchased from Omaha Valve & Fitting Co., Omaha, Nebraska. The tees were made in the metal shop at Ames Laboratory.

All gas transfer lines were of 1/16" o.d. stainless steel tubing. The split exit tubing was 1/8" o.d. stainless steel tubing in order to provide a buffer volume for the injection port.

Gas chromatographic inlet system

The inlet system of the Tracor 560 gas chromatograph was modified for the use of glass capillary columns. Kissinger (48) had previously converted a Tracor 550 gas chromatograph to a high-resolution capillary column instrument and

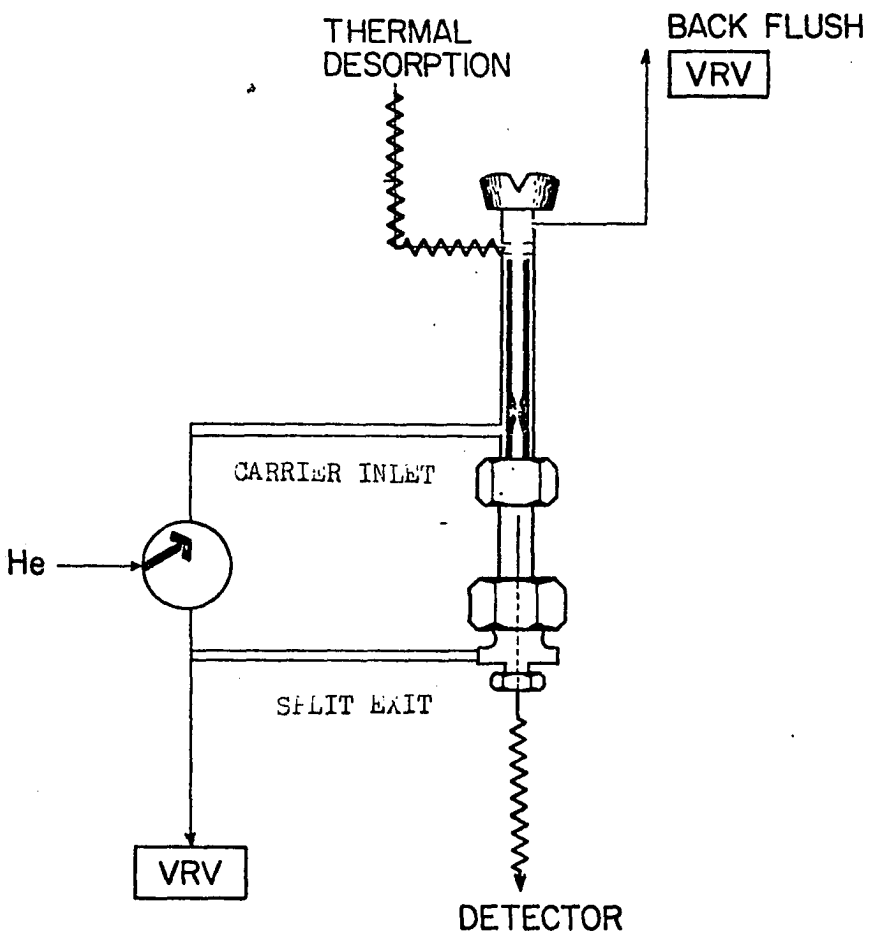
presented a thorough review of the related research literature. The basic flow patterns and the connection fittings for the column inlet and exit used in the modification process described here are patterned after this source.

Figure 9 is a diagram of the inlet system designed for the use of glass capillary columns in a Tracor 560 gas chromatograph. The interface with the thermal desorption instrument is also shown.

The modified gas chromatograph inlet system was designed to be used in three different modes of operation. These can be described as normal split, backflush, and splitless modes. The modes are interchangeable by simply throwing an electric microswitch.

In the normal split mode, the helium carrier gas enters through a 1/16" o.d. stainless steel tube silver-soldered into the side of the stainless steel injection port near the bottom. The carrier gas then passes upward along the outside of the Pyrex glass injection port sleeve. It enters the sleeve at the top, passes through a restriction, and chooses between entering the capillary column or passing through the split exit to vent. A sample injected into the glass sleeve is immediately vaporized, mixed with carrier gas at or near the sleeve restriction, and then carried into or past the column with the carrier gas flow.

Figure 9. Capillary column inlet and thermal desorption instrument interface. VRV stands for valve, restrictor and vent. The valve is a microswitch-controlled, solenoid-actuated, on-off valve. The restrictor is a needle valve and the vent is simply a port to open air to which a bubble flow meter can be connected. He represents helium carrier gas. The circle and arrow arrangement represent a microswitch-controlled, solenoid-actuated, three-way valve. The arrow in the diagram represents gas flowing in the normal split direction. The black hour-glass shape represents the glass injection port sleeve. The capillary column, represented by the straight and dotted line, extends up into the glass sleeve, almost to the hour-glass restriction


THERMAL
DESORPTION
BACK FLUSH
VRV
CARRIER INLET
He
SPLIT EXIT
VRV
DETECTOR

The split mode is a sampling step that is used to prevent overloading the column with the components of interest and excess solvent. The ratio of the carrier gas volume flow rate that bypasses the capillary column, to the carrier gas volume flow rate that passes through the column, is called the split ratio. In the system described here, the split ratio is continuously adjustable by opening or closing the needle valve that restricts carrier gas flow through the split vent.

In the backflush mode, the carrier gas enters through the split exit port (Helium 3-way valve pointing down). It passes upward inside the glass injection port sleeve and then either passes down into the column or goes with the majority of the flow, up, past the injection septum, to the backflush exit and vent. This orientation of the injection system is used to simply clean out the injection port while maintaining flow through the capillary column and constant inlet pressure. It serves to prevent sample tailing and background from septum degeneration.

In the splitless mode, both the split and the backflush exits are closed off. The carrier gas enters from the side of the injection port as in the normal split mode. However, there is only one flow path. Carrier gas flows at about 0.7 ml/min, through the injection port sleeve, through the capillary column, to the detector. In practice this mode is

only used in the splitless-backflush procedure known as Grob splitless injection (71).

The normal split mode was used for work involving the thermal desorption instrument. The split ratio was adjusted to accommodate the desorption flow rate required for efficient desorption from the Tenax desorption trap. Experimentation with complex standards indicated that split ratios greater than or equal to 10:1 were best for resolving samples with a broad range of component volatilities.

Sample injection

Injection of sample into the glass capillary column was done as follows. After thermal desorption from XAD-4 was complete, normal carrier gas flow to the gas chromatograph was switched off and the thermal desorption carrier gas flow was switched on. The backflush valve was closed and the instrument was placed in the normal split mode At this point the path of the carrier gas was through both valves in the thermal desorption instrument, into the injection port, down through the glass sleeve, and either into the capillary column or out through the split exit. The final injection step was to switch the 4-port valve of the thermal desorption instrument when the Tenax desorption trap reached 280°C, causing the carrier gas to sweep the organics out through the described flow path into the capillary column or to vent.

Desorption Efficiency

Model compounds

Aromatic hydrocarbons were used as model compounds in the following efficiency studies. The flame ionization detector responds well to hydrocarbons, and more importantly, aromatic hydrocarbons have an extremely strong affinity for XAD-4. Therefore, if they can be desorbed successfully, then more polar compounds of similar volatility should also be desorbed well, barring losses to metal surface adsorption and decomposition. The high-boiling aromatic hydrocarbons which were used are listed with some of their physical properties in Table 6.

The procedure followed in these studies was as follows. A standard, containing about 500 ng each of biphenyl, phenanthrene, anthracene, tritan and pyrene, and 1.0 micrograms of fluorene, was injected into one side of an XAD-4 minicolumn. Two ml of water were then passed through the minicolumn, followed by just enough air to displace most of the water from the tube. The minicolumn was then connected to the thermal desorption instrument.

Fluorene was chosen as the internal standard because it was desorbed well under almost all of the conditions chosen for the desorption efficiency investigations. In addition, fluorene is completely retained by the Tenax trap under all analysis conditions, and it is a large enough molecule to

Table 6. The physical properties of the high-boiling aromatic hydrocarbons used as model compounds in the thermal desorption studies (72)

Hydrocarbons				
Name	Formula Weight	Melting Point	Boiling Point	Density
Acenaphthene	154.21	96.2	279	1.225
Acenaphthylene	152.21	92-3	265-75	0.8988
Anthracene	178.24	216.2-.4	340	1.283
Bibenzyl	182.3	52	285	---
Biphenyl	154.2	71	256	---
Ditan (diphenylmethane)	168.23	25.35	264.3	1.0060
Fluorene	166.23	117	295	1.2
1-Methylnaphthalene	142.20	-22	244.64	1.0202
2-Methylnaphthalene	142.20	34.58	241.05	1.0058
Naphthalene	128.19	80.55	218	1.0253
Phenanthrene	178.24	101	340	0.98
Pyrene	202.26	156	393	1.271
Tritan (triphenylmethane)	244.34	94	359	1.014

closely approximate the splitting behavior of the heavier model compounds.

The dependence of desorption efficiency on temperature

The effect of temperature on desorption efficiency was noted previously. Rather high desorption temperatures are required for the efficient desorption of high-boiling compounds. Since this was already well understood, the next step was to study the scope of the method while maintaining the XAD-4 desorption temperature well within the range of thermal stability.

XAD-4 desorption temperatures were maintained either isothermally or "programmed" over a thirty degree temperature range, 180-210°C. The later approach was investigated for comparison, because the XAD-4 resin produced considerably less background with this treatment.

Whenever a desorption was performed with "programmed" temperature control, the median temperature was also the average temperature. This was accomplished by increasing the temperature in a linear fashion over the entire time interval. Comparison has shown that in such cases the data are approximately the same as for an isothermal desorption at the average temperature.

The dependence of desorption efficiency on flow rate

Flow rates The effect of helium flow rate on the efficiency of thermal desorption from XAD-4 was investigated for flows in the range of 7-80 ml/min under both isothermal and "programmed" temperature conditions. This represents a linear flow velocity range of about 4-44 cm/sec.

Isothermal investigation The results of the isothermal investigation of flow rate are recorded in Table 7. The peak heights produced with progressively higher flow rates are given from left to right. The numbers in parentheses are fractions which represent the ratio of the peak height of each compound to that of the internal standard, fluorene. Although the absolute peak heights jump around a bit, it is possible to evaluate the effects of increasing flow rate rather well by using this internal standard approach. No comparison with direct injection is required unless absolute recoveries are being determined.

Examination of the peak height ratio as it changes with increasing flow rate reveals that biphenyl is closely related to fluorene in terms of desorption efficiency, and is apparently desorbed somewhat better since the ratio decreases with increasing flow rate. The data for phenanthrene are rather scattered, but reasonably consistent values are obtained at the intermediate flow rates. The compounds that are significantly less volatile than fluorene

Table 7. The dependence of peak height on flow rate at a constant desorption temperature (200±1°C) and desorption time (15 minutes)

Compounds \ Flow rate (ml/min)	Peak Height (cm)				
	7.0	11.3	22.5	42.5	80.0
Biphenyl[a]	6.77 (.47)[b]	5.20 (.46)	5.90 (.44)	5.20 (.42)	6.12 (.38)
Fluorene	14.3	11.20	13.44	12.30	16.3
Phenanthrene	4.40 (.31)	4.50 (.40)	5.10 (.38)	4.40 (.36)	7.49 (.46)
Anthracene	4.15 (.29)	4.30 (.38)	5.40 (.40)	5.50 (.45)	8.2 (.50)
Tritan	1.98 (.14)	0.20[c] (.02)	2.30 (.17)	4.00 (.33)	9.46 (.58)
Pyrene	1.03 (.07)	0.29[c] (.03)	2.42 (.18)	3.50 (.28)	6.27 (.38)

Chromatography

Column: WCOT glass capillary, 30 meters x 0.25 mm i.d.; SE-30 stationary phase

Carrier gas: helium (zero grade), linear flow velocity 25 cm/sec

Split ratio: 25:1. Sample size, 500-1000 ng

Program: Initial temperature, 50°C; hold 2 min
Program rate; 4°C/min
Final temperature, 230°C; hold 15 min

[a]The compounds are listed in the order of elution from the SE-30 glass capillary column.

[b]Subscripts refer to the fraction of the internal standard (fluorene) peak height to which this corresponds.

[c]These values are anomolously low. No explanation of this could be found.

(i.e., anthracene, tritan and pyrene) were increasingly well desorbed as the flow rate was increased. The detector response (peak height ratio from Table 7) for these compounds is plotted as a function of flow rate in Figure 10.

The three compounds represented in Figure 10 appear to be fairly well desorbed at 80 ml/min. The slope of the curves for pyrene and anthracene are relatively low at that point. The tritan curve also seems to approach a maximum value, but this cannot be stated positively.

Nonisothermal investigation The dependence of peak height on the thermal desorption flow rate was also investigated under "programmed" temperature conditions. These data are presented with the data obtained from an isothermal desorption and a direct injection in Table 8. All splitter and chromatographic conditions were constant.

The desorption time was five minutes longer than in the isothermal investigation, but the results are comparable. The peak height ratios (numbers in parentheses) of the compounds that were more volatile than pyrene and tritan were independent of flow rate over the range studied, because of the longer desorption time. However, the peak height ratios of pyrene and tritan increased with flow rate as in the isothermal investigation.

A measure of the thermal desorption efficiency (fractional recovery) was obtained by comparing the peak height

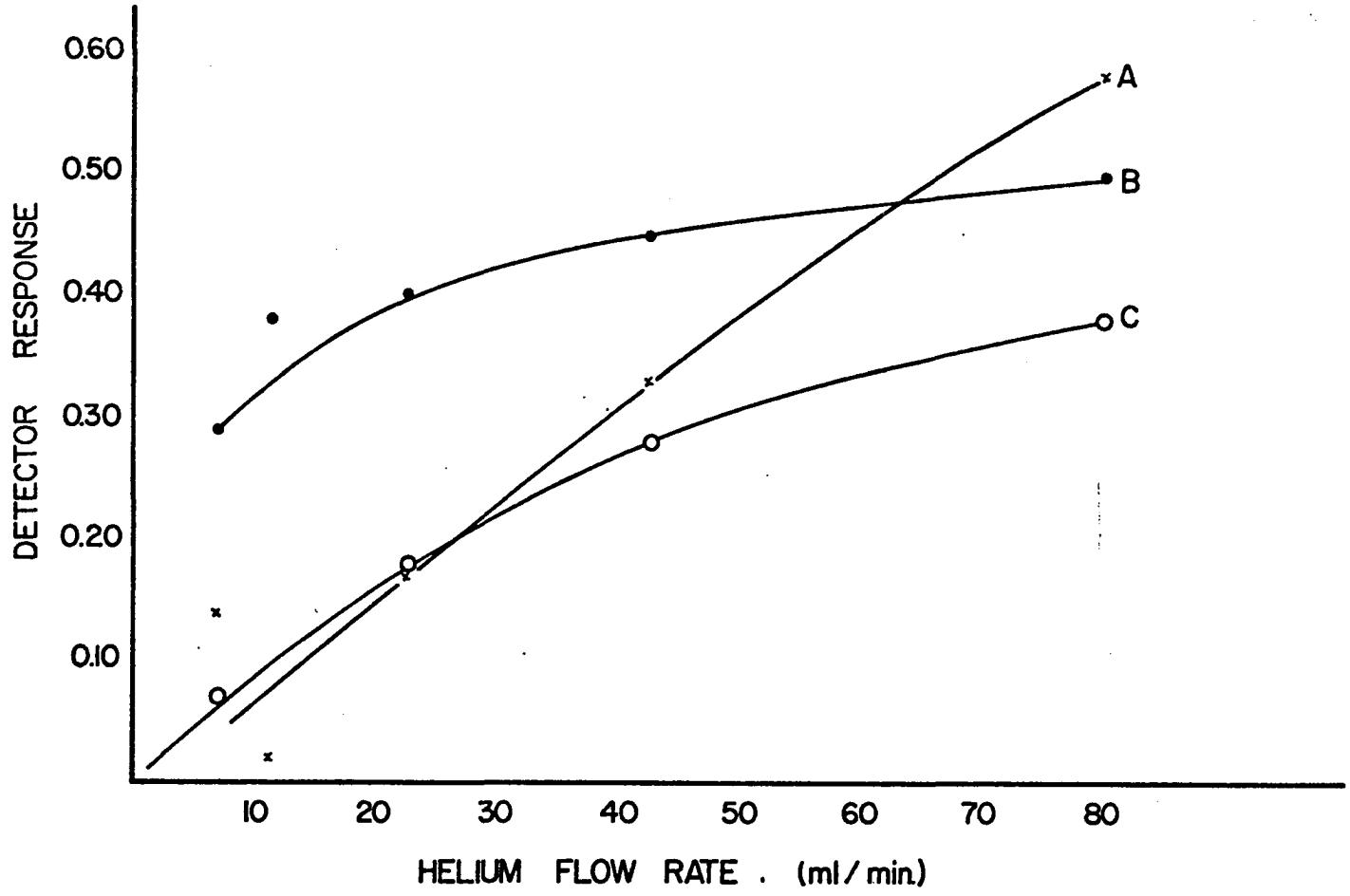


Figure 10. Isothermal desorption from XAD-4 as a function of helium flow rate. Tritan (A), anthracene (B) and pyrene (C) were desorbed over a 15-min desorption period at 200 ± 1°C. The ordinate represents the peak height of the compound divided by that of the internal standard, fluorene. The data are from Table 7

Table 8. Thermal desorption from XAD-4. The dependence of peak height on flow rate (programmed desorption temperature)

Compounds \ Flow rate (ml/min)	Peak Height (cm)					
	13.0	29.0	42.0	58.0	42.0[a]	Direct Injection
Biphenyl	7.90 (.42)[b]	7.85 (.43)	8.0 (.42)	7.96 (.42)	6.3 (.39)	7.3 (.44)
Fluorene	18.80	18.30	19.2	18.75	15.98	15.98
Phenanthrene	8.53 (.45)	8.80 (.48)	9.7 (.51)	8.7 (.46)	6.85 (.43)	6.79 (.42)
Anthracene	8.65 (.46)	8.40 (.46)	9.22 (.48)	9.1 (.49)	7.5 (.47)	7.08 (.44)
Tritan	1.40 (.07)	3.28 (.18)	5.33 (.28)	6.4 (.34)	7.94 (.49)	9.3 (.58)
Pyrene	2.20 (.12)	4.40 (.24)	5.4 (.28)	6.02 (.32)	7.4 (.46)	5.98 (.37)

Desorption

Average temperature: 195°C

Temperature range: 175-210°C

Desorption time: 20 min

Chromatography parameters are given in Table 7

[a]Temperature constant (203°C).

[b]Subscripts denote the peak height ratio of each compound compared to the internal standard, fluorene.

ratios of thermally desorbed standards to those of standards injected directly into the gas chromatograph. In doing so, it was assumed that the internal standard could be used to compensate for any differences in splitter characteristics between direct and thermal desorption injection. This assumption should become more accurate as the similarity of the internal standard and the component of interest increases.

The fractional recovery was obtained by first dividing the peak height of the component of interest by the peak height of the internal standard. This quotient represents the peak height ratio that is recorded in parentheses in Tables 7, 8, and 9. The peak height ratio for each thermally desorbed standard was then divided by the corresponding ratio obtained from the data of a direct injection of the same standard into the gas chromatograph. The fractional recoveries of pyrene and tritan were calculated in this manner from the data in Table 8, and were plotted as a function of flow rate in Figure 11.

Conclusions The initial slope of the detector response (peak height ratio) vs. flow rate curve in Figure 10 is relatively high. The slope decreases rapidly, however, as the flow rate increases. The same observation can be made of the nonisothermal desorptions on the basis of the data in Table 8. Fractional recovery, which is linearly related to the peak height ratio, is plotted for this data in Figure 11.

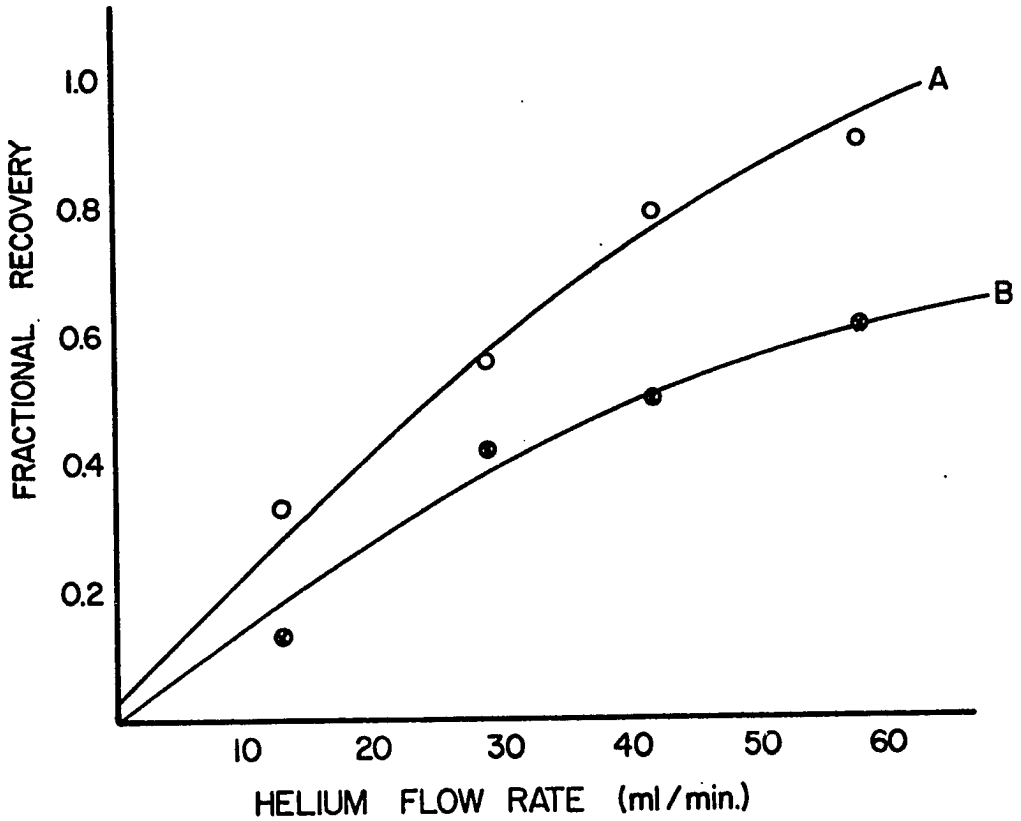


Figure 11. The fractional recovery of pyrene (A) and tritan (B) as a function of helium flow rate (data from Table 8). The fractional recovery was estimated by comparing the pyrene and tritan peak heights to the peak height of fluorene, which was the internal standard. This peak height ratio (the numbers in parentheses in Table 8) was divided by the ratio observed for these compounds when the same standard was injected into the gas chromatograph directly. The desorption time was 20 min, the temperature range was 180-210°C, and the average temperature was 195°C. Fluorene was virtually 100% recovered for all points along the curves

The curve shapes in Figures 10 and 11 are basically the same. The high initial slope of these figures indicates that the low thermal desorption flow rates are to be avoided. The gradual slope of both sets of curves at higher flow rates indicates a region of higher reproducibility.

Therefore, thermal desorption flow rates must be carefully chosen for high-boiling compounds. Conditions should be as near as possible to the working plateau, avoiding the region where small fluctuations in flow rate can have a pronounced effect on desorption efficiency. This tends to maximize sensitivity as well as reproducibility.

Intermediate flow rates are probably indicated for thermal desorption to a second trap (i.e., Tenax). Low flow rates were not effective, but high flow rates tend to reduce trapping efficiency for the more volatile compounds.

The comparison of isothermal and nonisothermal desorption was valuable in that no anomalous behavior was observed in the range of parameter testing. In fact, nonisothermal desorptions have not caused any difficulties except where poor reproducibility has been caused by inaccurate temperature control.

The dependence of desorption efficiency on desorption time

Although it is desirable to make an analysis as quickly as possible, it is often the case that the efficiency of a process is greatly dependent on time. This is true of the

process of thermal desorption. Therefore, desorption time is a parameter which must be chosen with care and a certain amount of compromise.

Table 9 shows the dependence of the peak height and the peak height ratio (compound/internal standard) of high-boiling model compounds on the time of desorption. The temperature and flow parameters were reproduced as rigidly as possible. The average temperature for each desorption was 195 C. The helium flow rate was maintained at 25-28 ml/min. The fractional recovery information extracted from this data are plotted in Figures 12-15. The amount of time required to desorb some high-boiling compounds under moderate desorption conditions can be estimated through the examination of these graphs.

The fractional recovery of biphenyl is plotted as a function of desorption time in Figure 12. It is obvious from this figure that biphenyl, which boils at 285 C, can be easily and reproducibly desorbed under the relatively mild conditions of Table 9.

The desorption of anthracene and phenanthrene, compounds which could not be resolved by the low resolution system, is plotted in Figure 13. It can be seen from this graph that the ratio of peak heights of these two compounds depends slightly on the desorption time It can also be observed that the efficiency of injection by thermal desorption is

Table 9. Thermal desorption from XAD-4. The effect of desorption time on the peak height of hydrocarbons

Compounds \ Time (minutes)	Peak Height (cm)					
	10.0	15.0	20.0	25.0	30.0	Direct Injection
Biphenyl[a]	5.62 (0.37)[b]	7.89 (0.44)	7.28 (0.43)	6.90 (0.44)	6.79 (0.44)	7.03 (0.44)
Fluorene	15.35	18.10	16.87	15.60	15.50	15.98
Phenanthrene	6.70 (0.44)	8.10 (0.45)	7.93 (0.47)	7.60 (0.49)	7.70 (0.50)	6.79 (0.42)
Anthracene	6.15 (0.40)	8.50 (0.47)	8.12 (0.48)	7.90 (0.51)	7.60 (0.49)	7.08 (0.44)
Tritan	0.39 (0.025)	0.95 (0.05)	3.09 (0.18)	6.64 (0.43)	7.58 (0.49)	9.30 (0.58)
Pyrene	0.51 (0.033)	1.40 (0.077)	3.28 (0.19)	5.70 (0.37)	5.75 (0.37)	5.98 (0.37)

Desorption

Average temperature: 195°C

Temperature range: 180-210°C

Flow rate: 25-28 ml/min

Chromatography parameters are given in Table 7

[a] In order of elution from SE-30 WCOT column.

[b] The numbers in parentheses represent ratio of peak height to that of the internal standard, fluorene.

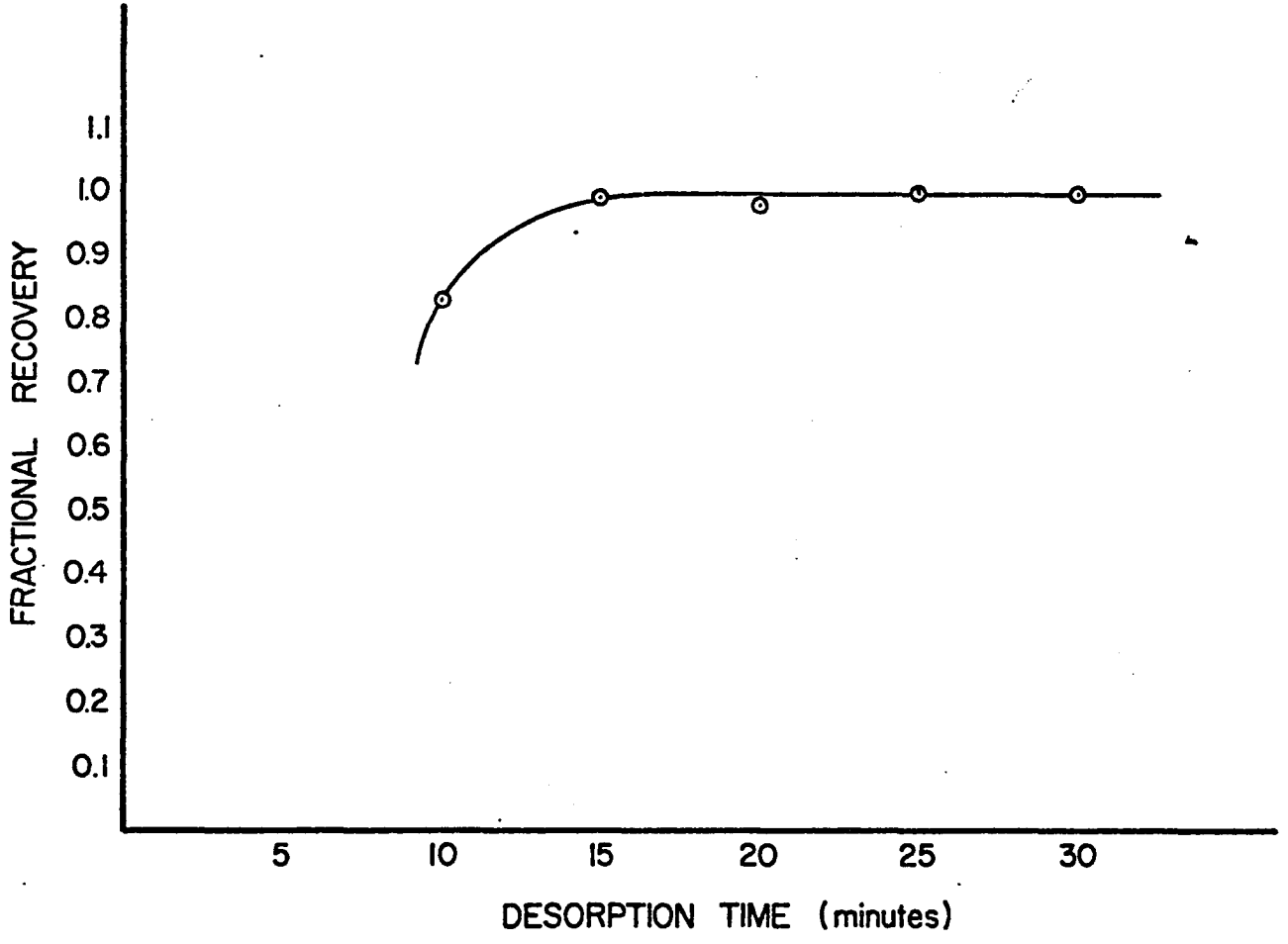


Figure 12. Fractional recovery of biphenyl as a function of desorption time. The data are from Table 9. Fractional recovery was estimated by the quotient of the compound-to-internal standard peak height ratios of thermal desorption and direct injection, as in Figure 11. The chromatographic parameters were as described in Table 8

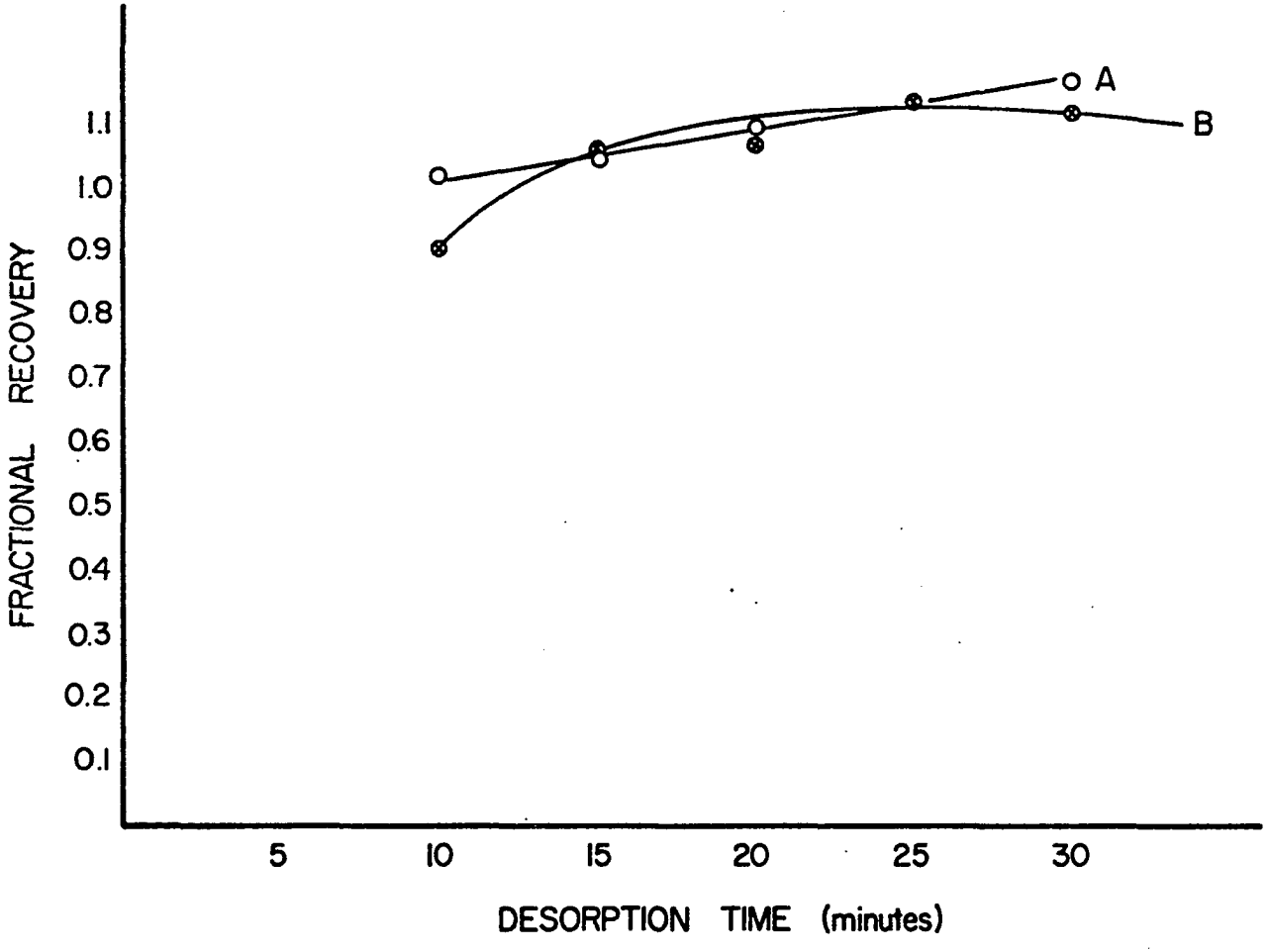


Figure 13. Fractional recovery of phenanthrene (A) and anthracene (B) as a function of desorption time. Data are from Table 9. Fractional recovery was estimated by the quotient of the compound-to-internal standard peak height ratios of thermal desorption and direct injection as in Figures 11 and 12. Chromatographic parameters were as described in Table 8

slightly better than injection directly into the chromatographic injection port, relative to fluorene, since the fractional recovery exceeds 1.0. This is a logical consequence of the nonlinear split which is observed in conventional splitting systems. Nonlinear split is a phenomenon of discrimination by molecular weight caused largely by incomplete volatilization of the sample in the injection port. This phenomenon is absent in thermal desorption as long as desorption of the individual compound is efficient because the compound must be thoroughly volatilized before it can reach the splitter.

Figures 14 and 15 describe the effect of desorption time on the recovery of tritan and pyrene. These compounds are near the upper limit, in terms of the molecular weight and boiling point, of compounds that can be successfully desorbed from XAD-4. The shape of the recovery vs. desorption curve and comparison to direct injection both indicate that these compounds can be desorbed under the condition in Table 9 in a period of about 30 min.

The desorption time study demonstrated the range of the method by proving that even compounds that boil at or about 400°C are thermally desorbable at temperatures well within the stability range of XAD-4. Also, in comparing the data of the two studies, it would appear that desorption time is somewhat more valuable than desorption flow rate in terms of desorption power.

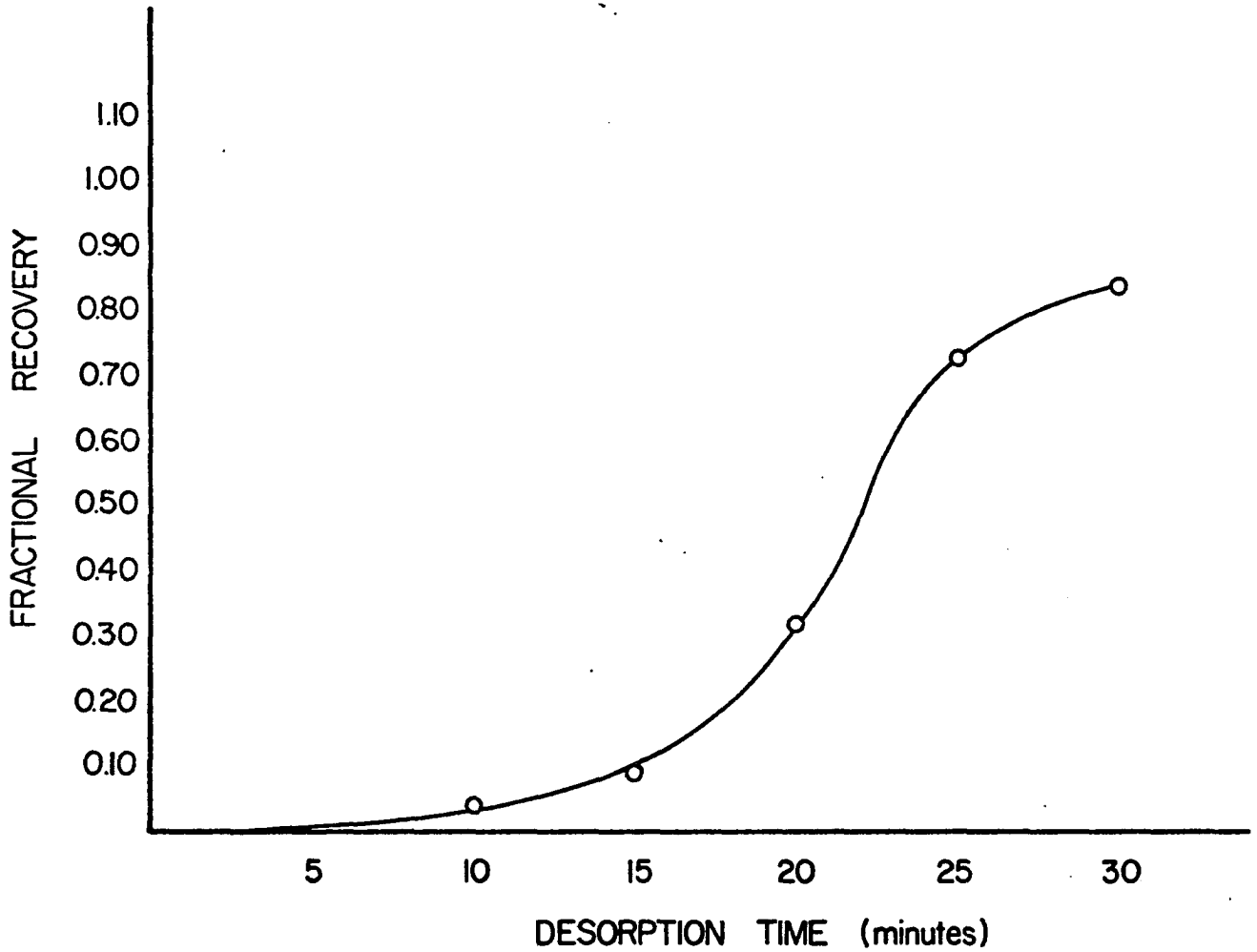


Figure 14. The fractional recovery of tritan as a function of desorption time. Data are from Table 9. Fractional recovery was estimated as in Figures 11-13. Chromatographic and desorption parameters were as described in Table 8

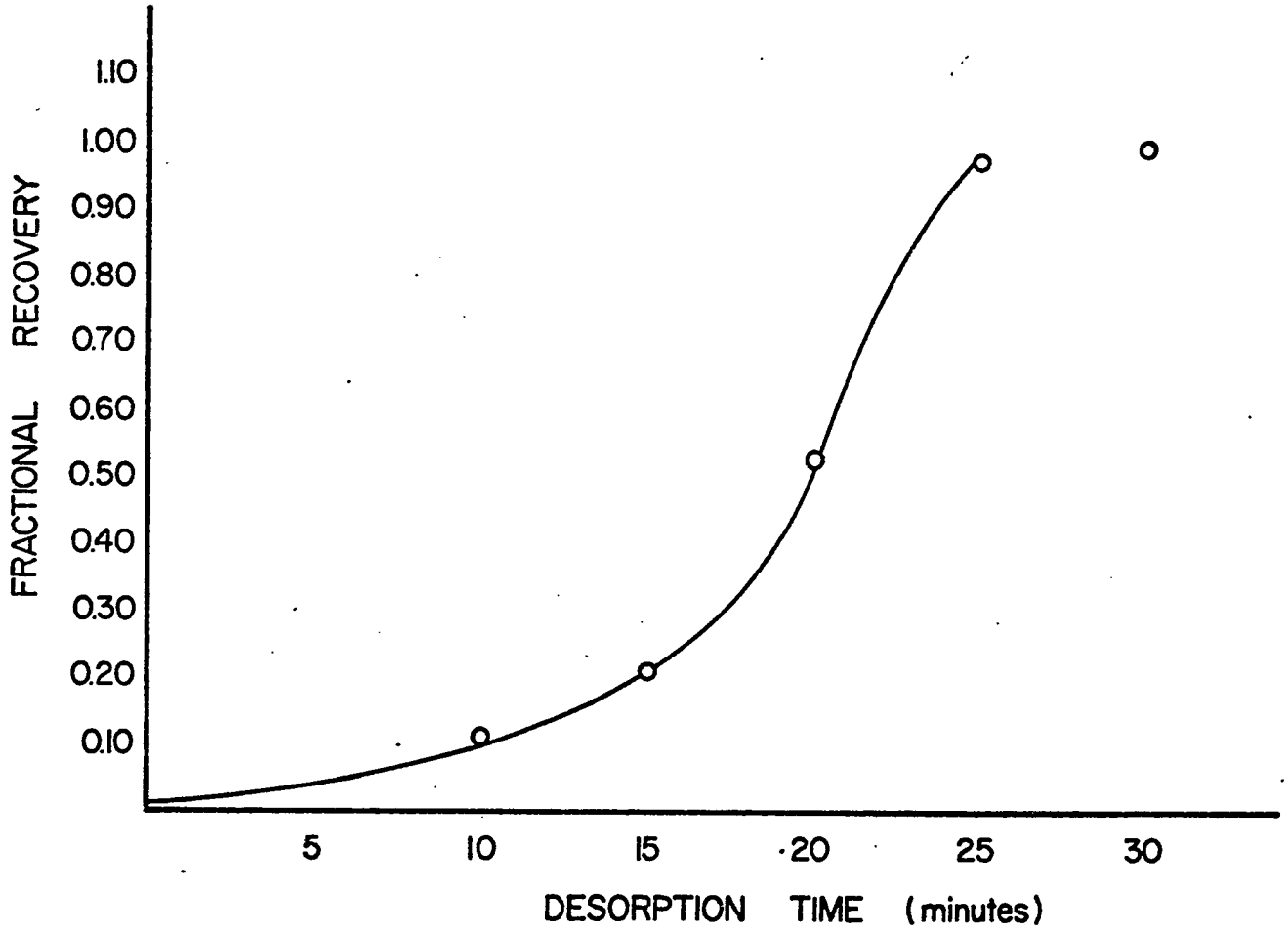


Figure 15. The fractional recovery of pyrene as a function of desorption time. Data are from Table 9. Fractional recovery was estimated as in Figures 11-14. Chromatographic and desorption parameters were as described in Table 8

An important aspect of these investigations is that a way must be found to accommodate longer desorption times and larger flow rates without the additional loss of volatile compounds through the Tenax trap.

Direct injection comparison and sample losses

Sample decomposition It was observed in the desorption efficiency experiments that tritan tended to decompose slightly, producing an extraneous gas chromatographic peak. This phenomena was observed in direct injection experiments and was even more pronounced in the thermal desorption injection experiments. Apparently, tritan is not stable at 300°C, especially in the presence of stainless steel. The magnitude of the effect can be gauged by comparing the efficiency of desorption of tritan with that of pyrene using a direct injection as the standard of comparison as in Table 7 and Figure 14. An approach to solving this problem will be discussed in the section describing an improved thermal desorption instrument.

Split discrimination It has also been established that direct injection in the split mode cannot be directly compared to thermal desorption in the split mode. To get a valid comparison it is necessary to use an internal standard which is of approximately the same volatility as the component of interest. The reason for this is that a nonlinear split

is often observed in the normal split mode when a sample containing compounds that boil near or above the injection port temperature is injected into the chromatograph. In such cases the high-boiling compounds can be severely discriminated against by the conventional inlet splitter system. However, relatively little split discrimination takes place in thermal desorption to the chromatograph because sample components are volatilized well before reaching the injection port and splitter.

Solvent effect Experimentation has also shown that a thermal desorption injection yields lower peak heights than a direct injection of the same amount of material if an injection splitter is being used. This is apparently due to the instantaneous pressure increase caused by the flash vaporization of solvent during direct injection. Since the pressure is momentarily much greater than normal at the head of the column, a larger portion of the sample is forced into the column than would be under the conditions present during a thermal desorption injection. Without the splitter system the peak heights of thermal desorption injections would be the same as those of direct injections, within the range of desorption efficiency, as shown in Table 5.

Volatiles The loss of volatile compounds under strenuous thermal desorption conditions was not investigated with the capillary column system. It was felt that highly

volatile compounds could be analyzed separately under favorable conditions until a complete solution to the problem was implemented, as will be discussed in the section devoted to the improved thermal desorption instrument.

Resolution

The resolution of the thermal desorption-glass capillary chromatographic system is illustrated by the chromatogram of Ames, Iowa, tap water seen in Figure 16. A brief comparison with the chromatograms previously obtained from the packed column system is sufficient to demonstrate the need for capillary columns in the analysis of complex samples. The resolution demonstrated by the chromatogram in the figure was achieved with an old Carbowax 20 M glass capillary column that was only 25 meters long, and yet, the resolution was still sufficient for the identification of some of the major peaks by simply spiking the XAD-4 minicolumn with some of the compounds believed to be in the water sample. Two compounds were eliminated from consideration while four were tentatively identified by this simple process.

Another example of the resolving power of the capillary instrument is seen in Figure 17. Phenanthrene and anthracene, which are resolved to the baseline in the figure, are often extremely difficult, if not impossible, to resolve by the usual chromatographic methods. The high resolution of the thermal desorption-capillary column system makes the

Figure 16. A thermal desorption chromatogram of Ames, Iowa, tapwater, spiked with 300 nanograms each of cumene, cymene, indene, 1-methylnaphthalene, acenaphthene and acenaphthylene. 4.5 liters of water were passed through an XAD-4 minicolumn and then 2 microliters of diethylether containing hydrocarbons in the amounts listed above were injected into the minicolumn and desorption was carried out as usual. The resulting chromatogram (shown here) was compared by an unspiked sample to identify peaks in the water samples by their correspondence to components in the diethylether standard solution. The order of elution is from right to left and each number represents the elution temperature of the peak directly above it. The retention times and elution temperatures of indene, 1-methylnaphthalene, acenaphthene, and acenaphthylene were found to exactly correspond to some of the major contaminants in Ames water. Cumene and cymene were apparently not present in Ames water at the time of sampling (December, 1978) in concentrations sufficient for detection by this method (less than 0.05 ppb).

The chromatography was performed on a wall-coated open tubular (WCOT) 25 meters long x 0.25 mm i.d. coated with Carbowax 20 M. Desorption from XAD-4 was carried out at 180-210°C for 12 minutes with 20 ml/min helium flow. The temperature increased at 2°C/min to 190°C, final temperature held for 10 minutes.

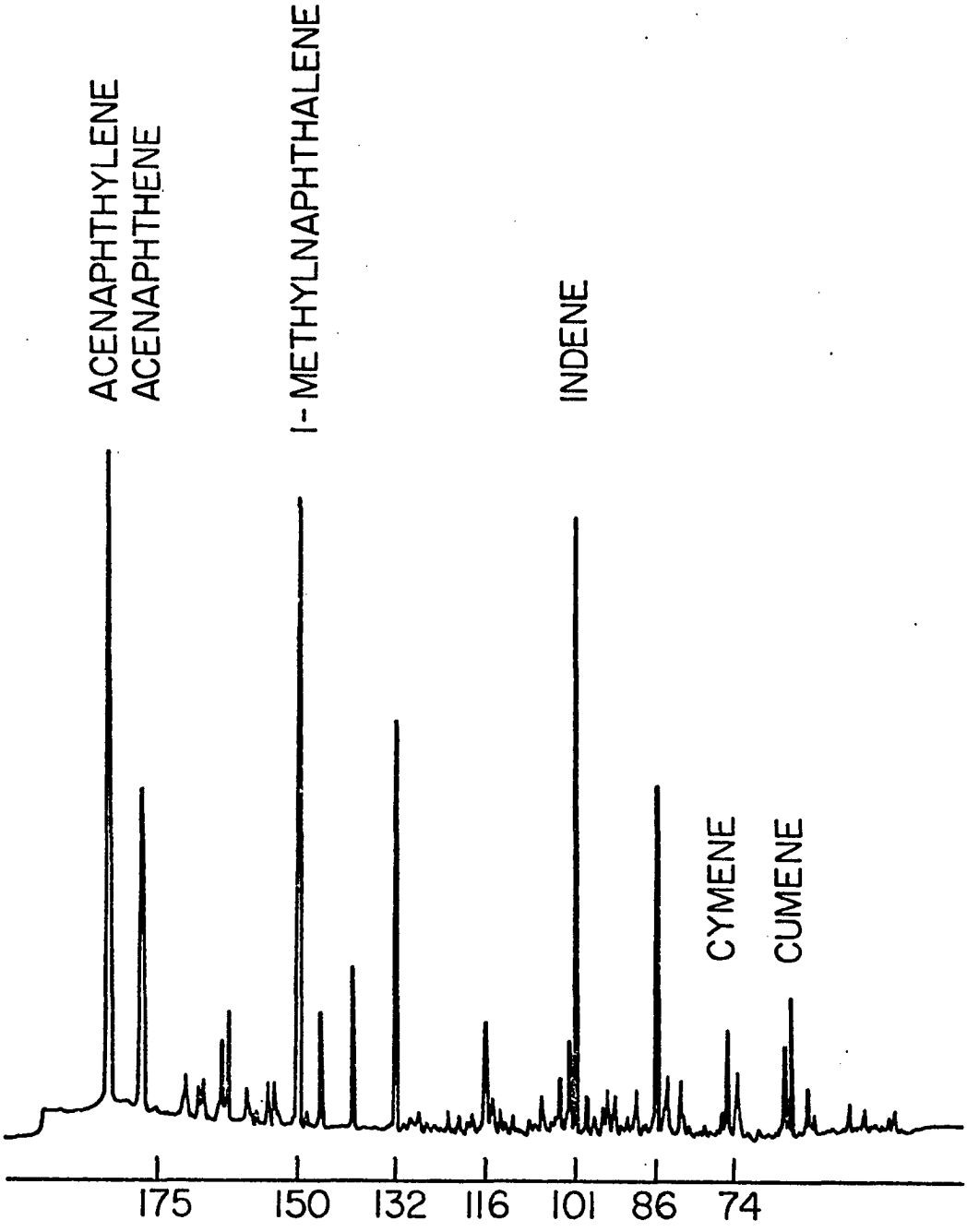
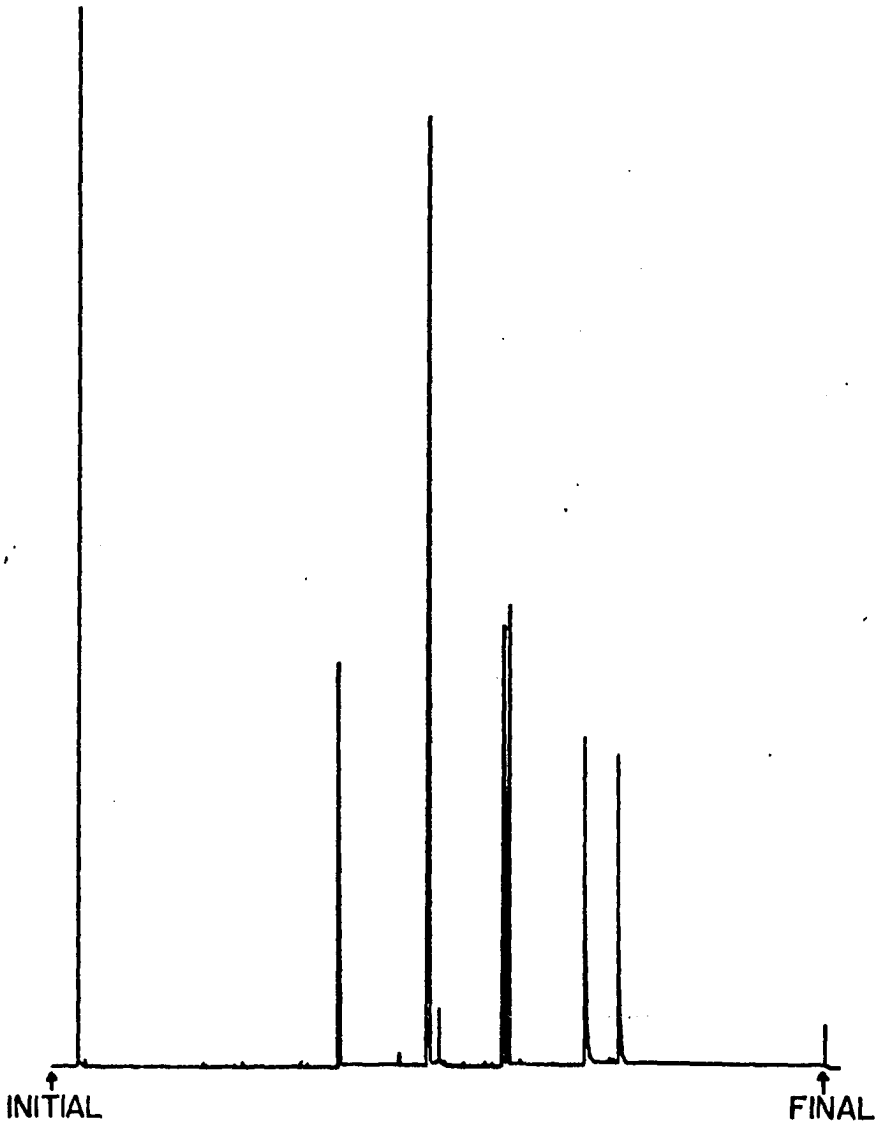

ACENAPHTHYLENE
ACENAPHTHENE
1-METHYLNAPHTHALENE
INDENE
CYMENE
CUMENE
175
150
132
116
101
86
74

Figure 17. The peaks, in order of elution (initial to final), are biphenyl, fluorene, anthracene, phenanthrene, tritan and pyrene, as described in the "Desorption efficiency" section under "Flow rate". Anthracene and phenanthrene were resolved to the baseline in the original chromatogram but some resolution was lost in mechanically reproducing the trace. The tall peak near the initial point of the chromatogram is the standard solution solvent, acetone, most of which was not retained by the Tenax trap under the chosen desorption conditions. The peak at the end of the chromatogram was caused by an inductive spike. The chromatography was performed on a glass capillary wall-coated open tubular column (WCOT) 30 meters long x 0.25 mm i.d. coated with SE-30. The sample was thermally desorbed from XAD-4 at 200 ± 1°C in 15 minutes with a flow rate of 42 ml/min helium. The Tenax desorption temperature was 300°C. The temperature program was as follows: isothermal at 50°C for 2 minutes, temperature increased at 4°C/min to 240°C, then isothermal for 5 minutes before allowing the chromatograph to cool back down to 50°C for the next sample injection.


INITIAL
FINAL

simultaneous determination of these two compounds routine, even in the presence of each other.

Analysis

Identification

As mentioned in the Introduction, the identification of the components in samples as complex as real water sources requires an extremely sophisticated and expensive array of equipment. Therefore, any identification of sample constituents performed in the course of this research was done with the aid of other methods. The analysis of Ames water that had been done previously by Junk et al. (58) was especially valuable in the selection of compounds as candidates for identification and analysis. The object of using this approach was to demonstrate the utility of the thermal desorption method for the analysis of target compounds, as described in the Introduction.

The method used to identify and measure the chosen target compounds was to take duplicate samples of the water to be analyzed and pass each through an XAD-4 minicolumn. One of the columns was subsequently spiked with a standard solution of the target compound(s) in diethylether, or some other appropriate solvent, and then analyzed with the thermal desorption chromatogram of the unspiked sample and exact

correlations in retention time noted. An example is provided in Figure 16.

Tentative identifications can be made in a single such trial with a high-resolution chromatographic system. A second exact retention time correlation on a high-resolution chromatographic column of different polarity is generally considered sufficient evidence for positive identification, although supporting spectroscopic data are always desirable.

The dependence of recovery on sample volume

Distilled water samples The sensitivity of the proposed thermal desorption method is largely determined by the volume of water from which the components of interest can be recovered. Unfortunately, many of the more water-soluble compounds are only recovered well from small volumes of water (see Table 2). Even so, it is generally possible to apply direct adsorption-thermal desorption to the analysis of these compounds at the ppb level, if they can be extracted from volumes as large as 20 ml.

In one of the initial experiments with the high-resolution system, a series of ketones was analyzed to establish the reciprocity of concentration and sample volume. In this case reciprocity means that sample volume and sample concentration are related to detector response in the same way. As long as sample concentration and volume are within an established reciprocal range, a given amount of analyte

in the sample will produce a given detector response. Two chromatographs are shown in Figure 18 which demonstrate that such reciprocity does exist at the ppb level.

It was observed in the reciprocity experiment that an unknown peak (peak a), which eluted earlier in the chromatograms, approximately doubled in height when the volume of water in the sample was doubled (see Figure 18). Since ordinary distilled water directly from the tap was used to make up the ketone standards, the new peak apparently represented a volatile contaminant from the water. A blank determination on a large sample of distilled water (300 ml) gave a still larger unknown peak (see Figure 19). However, the relative height of the peak in the 300-ml sample was only about 60% of that expected from extrapolation of the heights of the same peak in the 20-ml and 40-ml samples. Two other peaks that had not been observed in the chromatograms of the smaller samples can be seen in Figure 19. These are believed to represent other contaminants in the distilled water, probably at concentration levels well below 1 ppb. No attempt was made to positively identify any of these compounds, but the major contaminants probably represent compounds such as morpholine or cyclohexylamine, which are used in many boiler systems to prevent scale.

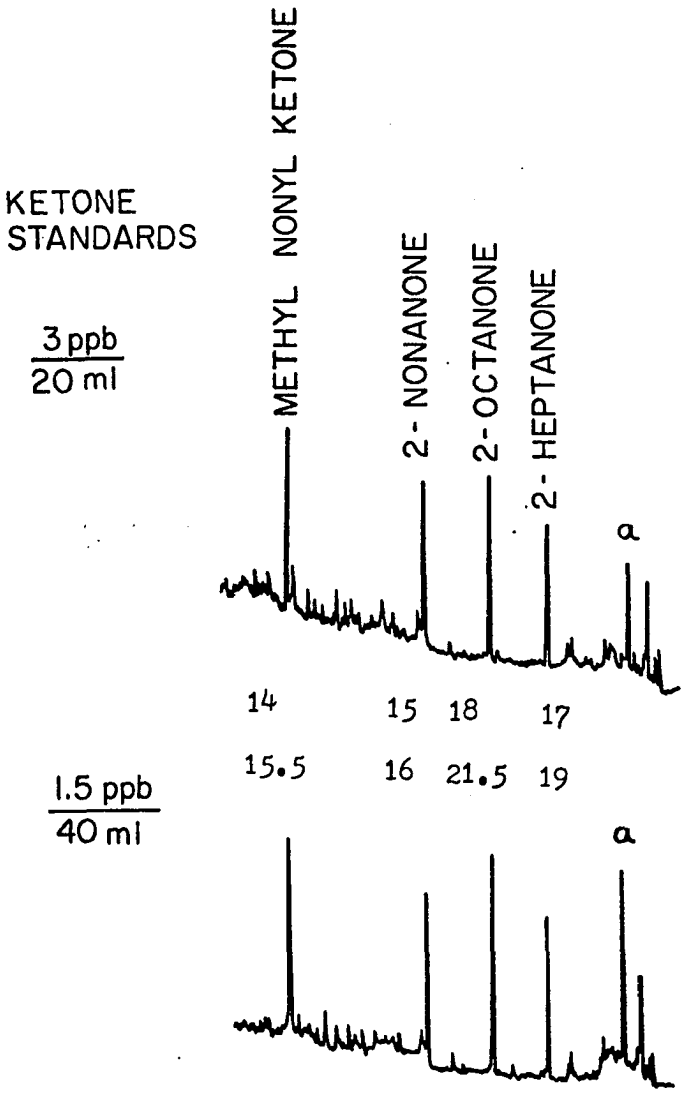


Figure 18. The recovery of ketones. The thermal desorption chromatograms of two standard samples are shown which contained the same amount of each ketone in different volumes of water. Chromatographic elution was from right to left. The numbers between the two chromatograms represent the measured heights of the respective chromatographic peaks. Desorption time was 10 min. The attentuation was 1x4. The column was a new Carbowax 20 M, 25-meter glass capillary. The program was isothermal at 45°C for 2 min, 2°C/min to 175°C, and isothermal at 175°C for 10 min

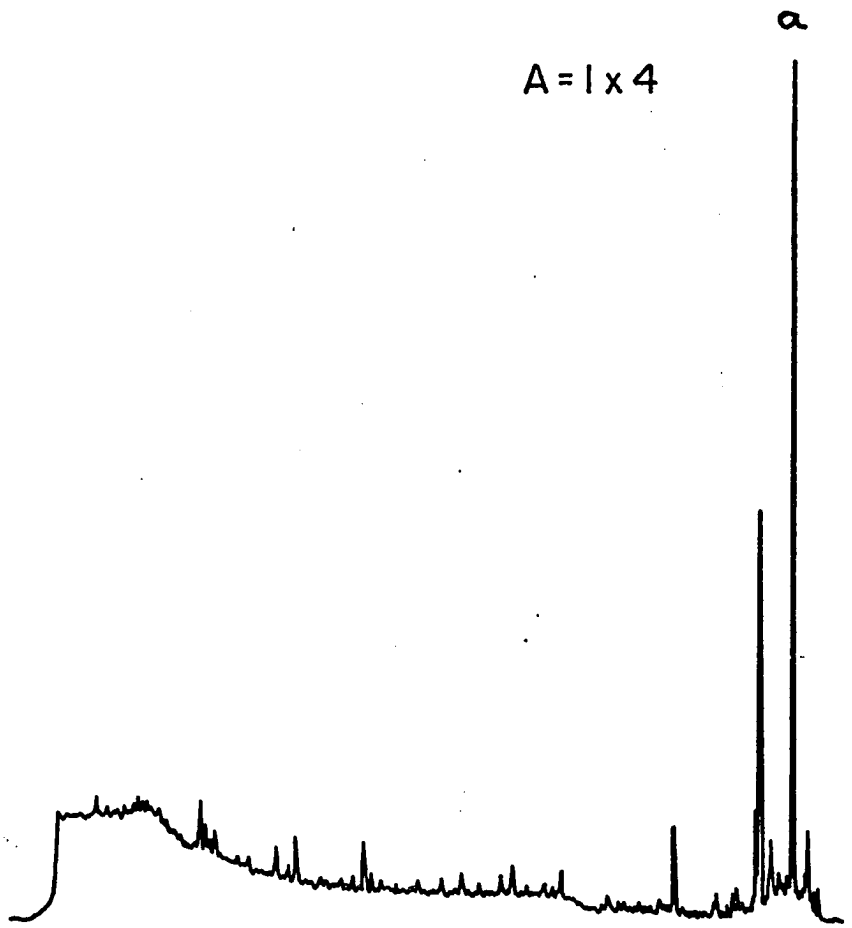


Figure 19. Distilled water, 300-ml sample. Desorption from new XAD-4. Chromatographic and desorption conditions were as in Figure 18

Ames tap water samples Since it was known that aromatic hydrocarbons are adsorbed extremely well by XAD-4, it followed that direct adsorption-thermal desorption was potentially an extremely sensitive method for their determination. Ames tap water was chosen as the subject of experimentation. Numerous samples were taken to determine the dependence of the recovery of the major peaks on sample volume.

Samples ranging in size from 150 ml to about 4.4 liters were taken and analyzed. New or almost new minicolumns were used, and the desorption and chromatographic parameters were reproduced as carefully as possible. The data and conditions of analysis are listed in Table 10. Only those compounds which eluted at or below 150°C were reported, because the desorption parameters were chosen to maximize the recovery and reproducibility of the more volatile components of the sample. The less volatile hydrocarbons would presumably be extracted from water by XAD-4, and would be retained more efficiently than any of the compounds which eluted earlier. The data from Table 10 are plotted in Figures 20, 21 and 22. Based on previous data, the hydrocarbons are assumed to be almost totally recovered from the smaller volumes.

Figure 20 shows graphically the relative recovery of naphthalene as a function of sample volume. No loss of recovery is observed, even for samples as large as 4.4 liters.

Table 10. Peak heights (cm) per 100 ml of Ames tap water (attenuation normalized to 1x4)

Column temperature at peak elution (°C) Sample size (ml)	86°	101° (Indene)	118°	132° (Naphthalene)	150° (1-Methyl-naphthalene)
150	4.7[a]	15	3.0	5.3	8.0
300	4.7	21	5.2	6.0	1.8
1160	6.0	20	4.3	7.6	7.9
3300	4.8	15	3.8	7.0	6.7
4350	5.6	11	2.1	6.8	9.3

Peak elution temperature °C		Compound	Estimated[a] concentration
86	=	Unknown	---
101	=	Indene	0.70 ppb
118	=	Probably an alkyl indane	---
132	=	Naphthalene	0.28 ppb
150	=	1-Methylnaphthalene	0.35 ppb

[a]The concentrations were estimated by comparison with standards desorbed from wet XAD-4 minicolumns and were based on the median values (see Figures 20-22).

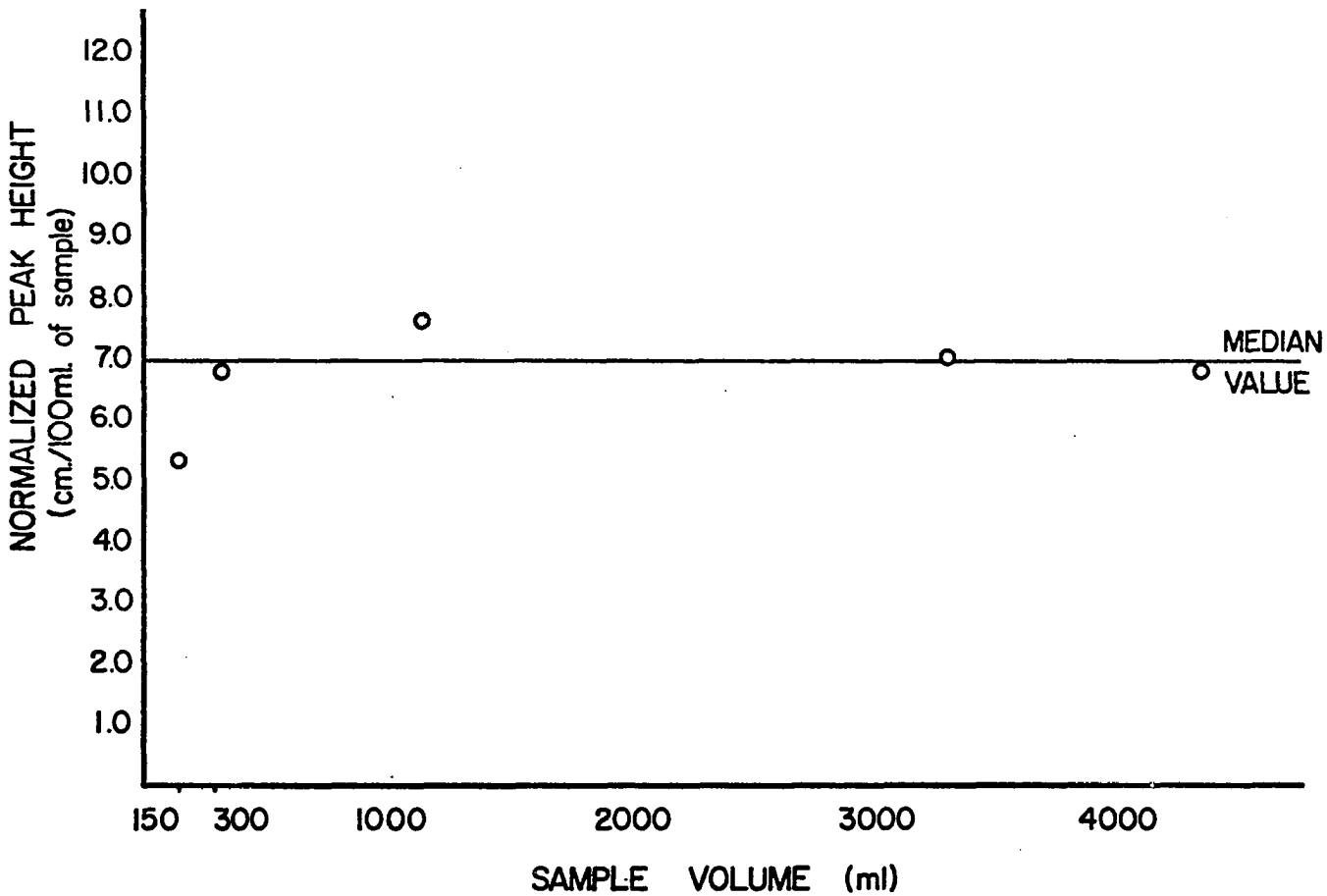


Figure 20. The recovery of naphthalene as a function of sample volume. Data are from Table 10. The ordinate is in units of centimeters of peak height (normalized to an attenuation of 1x4) per 100 ml of sample. The chromatographic and desorption parameters are noted in Table 9

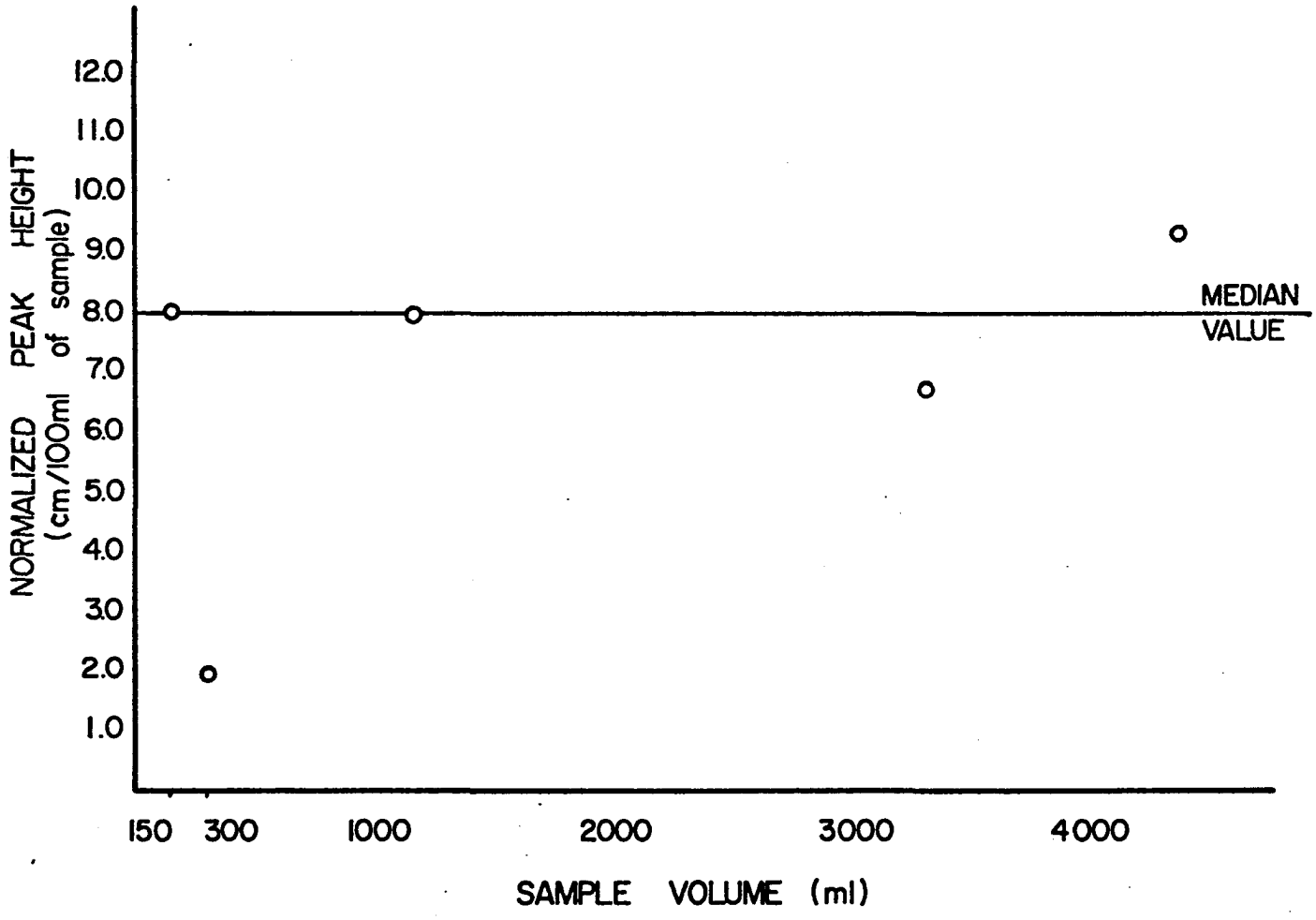


Figure 21. The recovery of 1-methylnaphthalene as a function of sample volume. Data are from Table 10. The ordinate is in units of centimeters of peak height (normalized to an attenuation of 1x4) per 100 ml of sample. The chromatographic and desorption parameters are noted in Table 9

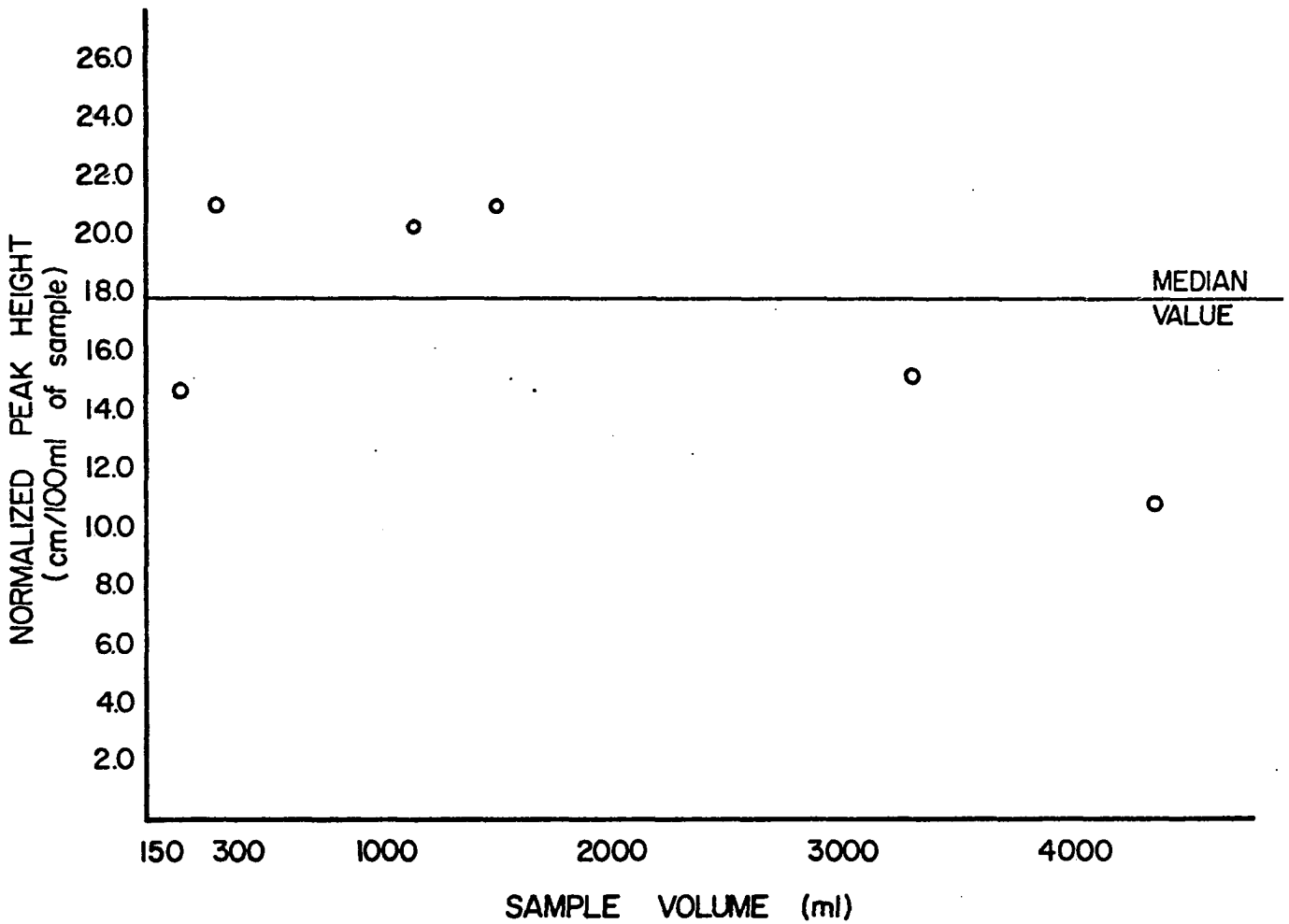


Figure 22. The recovery of indene as a function of sample volume. The ordinate is in units of centimeters of peak height (normalized to an attenuation of 1x4) per 100 ml of sample. Data are from Table 10. The chromatographic and desorption parameters are noted in Table 9

The recovery of 1-methylnaphthalene (Figure 21) is also uniform over the range of sample volumes investigated, except for an apparently deviate analysis of a 300-ml sample. However, the recovery of indene (Figure 22) decreases by about 50% as the sample volume increases from 1.0 to 4.4 liters. According to the data in Figure 22 then, the sample volume should not exceed about 2.0 liters when indene is being determined, unless the lower recovery can be taken into account.

Discussion The results of the recovery-sample-volume study indicate that recovery is linear over a broad range of sample sizes, but only for certain compounds. However, the results of the indene and distilled water determinations show that the recovery of each component must be measured before it can be analyzed quantitatively. This can be done by combining an abbreviated version of the methods just described for determining recovery linearity (like the reciprocity test in Figure 18), with a measure of the absolute recovery. Absolute recovery can be estimated by comparing a spiked water sample with a standard injected directly into the front of a minicolumn (as in Table 2).

A final conclusion to be drawn from these data is that this analytical technique can be successfully applied to the measurement of extremely low concentrations of aromatic hydocarbons in water. For example, the analysis of indene in

water, although apparently limited to sample sizes of 2 liters or less, would be sensitive to 0.1 ppb (g indene/g water), even if other factors caused the detection limit to be as high as 200 ng.

Matrix effects

After a number of samples had been analyzed, it was believed that the direct adsorption-thermal desorption method was virtually without matrix effects. But then recovery studies apparently indicated that indene was poorly retained by XAD-4 in relation to other hydrocarbons. This raised some doubts. It had also been thought that the XAD-4 minicolumns were reusable. Early experiments, performed to determine the fractional recovery of various compounds from water, had shown that the recovery values were quite reproducible, regardless of the number of times the minicolumns had been used. However, the samples had initially been made by spiking distilled water.

When experiments were performed with Ames, or Slater, Iowa, finished waters, the minicolumns were again used repetitively without adversely affecting the analyses. However, these samples did not generally exceed 200 ml in volume.

The earlier recovery studies, involving the analysis of large volumes of Ames finished water, produced some unexpected results. The ratio of the heights of the peaks which eluted at 100°C and 86°C were not constant. This was apparently

caused by differences in minicolumns, as some of them were slightly discolored. Therefore, well-used or discolored minicolumns were not employed in the recovery experiments described in the previous section.

An experiment was performed to assess the effect of using a minicolumn repetitively for the analysis of larger samples. New minicolumns were made and conditioned. These were then used to do repetitive analyses of Ames finished water in a dual minicolumn setup. That is, for each trial, two minicolumns, one new and one used, were connected to the same faucet. The sample volumes and flow rates were measured separately for each minicolumn. Two such trials are recorded in Figures 23-25. The figures are in order, with respect to the condition of the minicolumns, from new to well-used. Blanks corresponding to these analyses are given in Figure 27.

The chromatograms in Figures 23-26 reflect a curious phenomenon. The recovery of indene gradually decreases in relation to naphthalene (which elutes at 132°C) and 1-methylnaphthalene (which elutes at 150°C) as the minicolumn becomes more "used", but it also decreases with respect to the peak (unknown) that elutes at 86°C. That is, indene is poorly recovered with respect to compounds which elute both before and after it on a nonpolar gas chromatographic column. The recoveries of acenaphthene and acenaphthylene were also observed to decline when well-used minicolumns were used to perform the analysis.

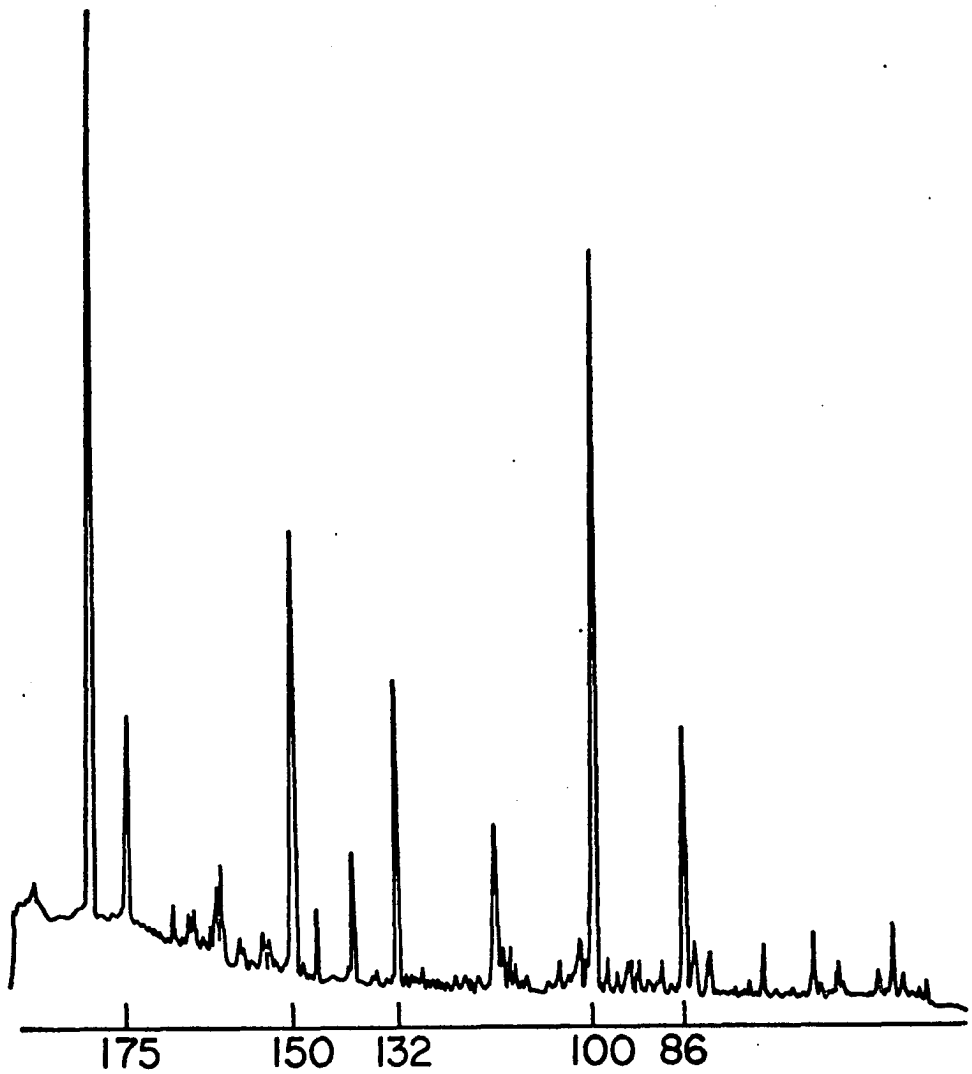


Figure 23. A thermal desorption chromatogram of Ames tap water, 3-liter sample. Sample #1, dual mini-column position A. Sampling flow rate, 12 ml/min; desorption temperature, 180-210°C; desorption time, 10 min. The chromatographic column was a glass capillary WCOT column, 25 meters long x 0.25 mm i.d.; the stationary phase was Carbowax 20 M. The initial temperature of the temperature program was 45°C, held for 2 min, and programmed at 2°C/min to 175°C, held for 10 min and recycled. The attenuation was 2 x 10; split ratio was 25:1

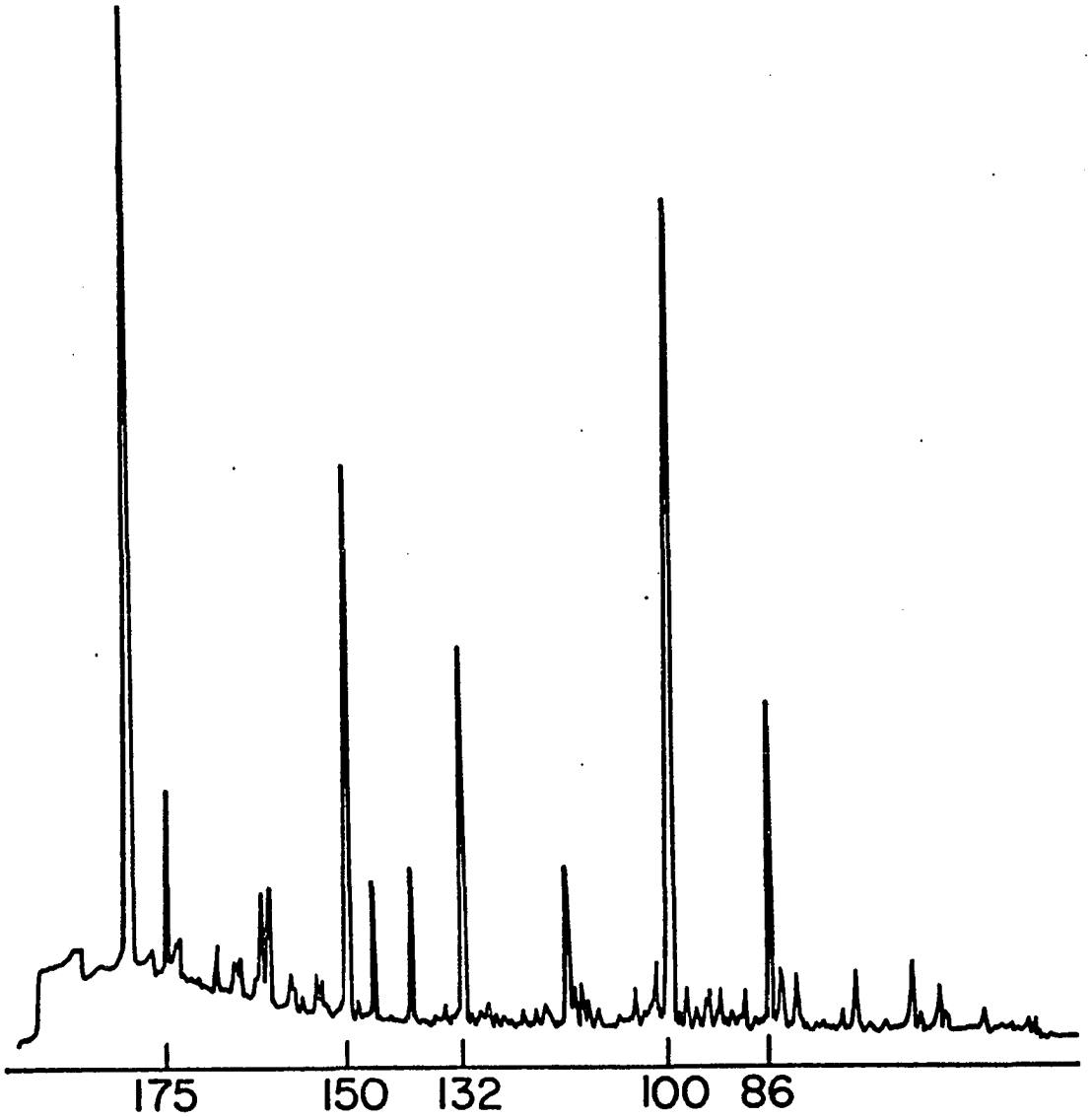


Figure 24. A thermal desorption chromatogram of Ames tap water, 3-liter sample. Sample #2, minicolumn position B. The sampling flow rate was 8.0 ml/min. All chromatographic and desorption parameters were identical to Figure 23. The minicolumn had been used for the previous analysis of 100 ml of Ames tap water

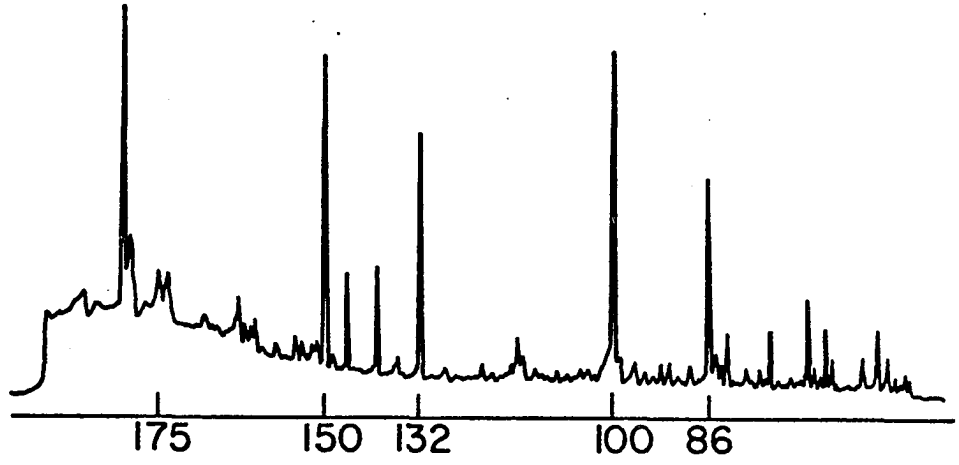


Figure 25. A thermal desorption chromatogram of Ames tap water, 2-liter sample. Sample #2, minicolumn position A. The sampling flow rate was 6.0 ml/min. All desorption and chromatographic parameters were identical to those of Figure 23. The minicolumn had been used for the previous analysis of 300 ml of Ames tap water

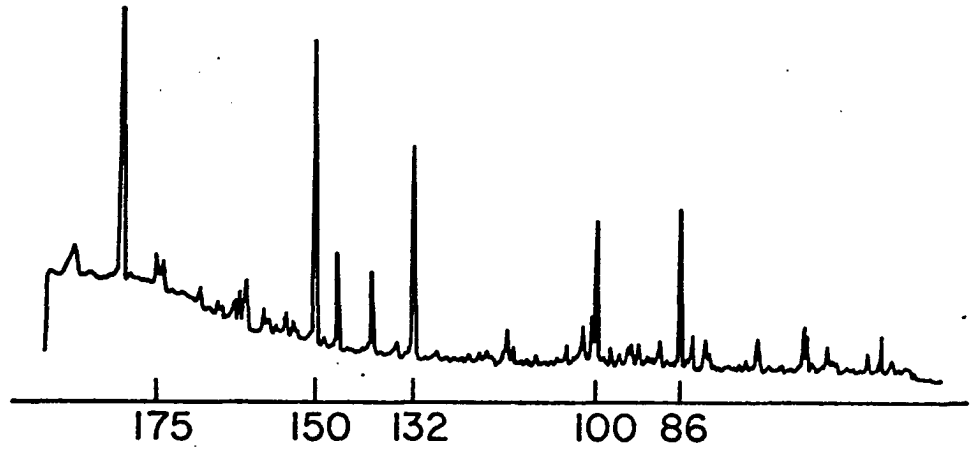


Figure 26. A thermal desorption chromatogram of Ames tap water, 2-liter sample. Sample #1, minicolumn position B. The sampling flow rate was 7.8 ml/min. All desorption and chromatographic parameters were identical to those in Figure 23. The minicolumn was highly discolored and had been used to analyze over 5 liters of Ames water prior to this analysis

Figure 27. Blanks

10-min desorptions of tap water wet XAD-4
Desorption temperature 180-210°C
Attenuation 4 x 10. Program 45/2 - 2 - 200/5

A: After two conditioning periods
1) 8 min at 240°C
2) 8 min at 240-260°C

B: Following a five-day tap water soak after prolonged use

To determine if the loss of recovery was truly a result of the loss of adsorption efficiency, indene standards were injected directly into both new and well-used XAD-4 minicolumns. A significant decrease in desorption efficiency for indene was observed when the recoveries obtained from minicolumns that had been discolored (from the previous analysis of large samples) were compared to these obtained from new minicolumns. Discolored minicolumns also compared poorly with those that had only been used for the analysis of small samples. It was therefore concluded that the anomolously poor recovery of indene was the product of a matrix effect that selectively decreased desorption efficiency, but did not necessarily affect adsorption efficiency. That is, indene may well have been removed from the water but lost in the desorption process.

The nature of the minicolumn discoloration, and presumably the interfering agent, was investigated briefly. The discoloration was between orange and red-brown in color and it developed in a manner similar to a poorly resolved chromatographic band, spreading slowly down the minicolumn as sampling took place. The color and retention behavior of the material indicated that it might be humic material, possibly of an ionic nature. The color suggested either a highly conjugated system or a metal complex, or both.

Attempts at eluting the colored material with neutral organic solvents were entirely unsuccessful. After acidification of the minicolumn with 0.5 M hydrochloric acid, however, most of the color could be eluted from the minicolumn with a few milliliters of acetone, methanol, or acetonitrile. It is therefore hypothesized that the colored material was humic acid, which is known to be present in virtually all water systems to some extent. Gas chromatography and high performance liquid chromatography (HPLC) were used in an attempt to characterize some of the more volatile components of the acidic extracts. Some interesting peak profiles were observed, but the results were inconclusive.

As a result of this investigation, only new XAD-4 minicolumns are now used to analyze real water samples. This eliminates the deliterious effects of humic material accumulation from analysis to analysis. Further experimentation has shown that the recovery of indene from water may be linear somewhat beyond the limit indicated in the recovery studies. This was expected, since some of the minicolumns had been used for small samples prior to the study. However, the effects of humic material are still not negligible and must be minimized in real analyses.

All large or dirty samples should be assessed in terms of the effects of the matrix on analysis. This can be best accomplished by performing an analysis of a spiked sample in

conjunction with an analysis of at least two samples of significantly different volume. (This is consistent with the normal recovery determination procedures recommended in the previous section.) If the samples of different volume give approximately the same estimate of the initial concentration and the spiked sample compares well with a standard, it should be assumed that the analysis can be performed accurately. Future samples can then be run on a routine basis, assuming no dramatic change occurs in the matrix.

Quantitation

Indeterminate error In a recent paper which discussed the nature and sources of indeterminate error in analyses of this kind, Janardan and Schaeffer (73) concluded that the sensitivity of the analysis dominates the error in cases where capture and recovery (i.e., adsorption and desorption efficiencies) are high and precise. Generally speaking, this says that the more sensitive the method is, the lower the indeterminate error will be for a given concentration level determination. However, where capture and recovery are poor or imprecise, they found that the error in any estimate of the sample concentration will be dominated by the error in these factors. Therefore, if an accurate quantitative analysis is to be performed by direct adsorption-thermal desorption, it is important to maximize the precision and

efficiency of both adsorption and desorption, even where the sensitivity of the analysis is not at issue.

Parameters In doing quantitative work, the sample size must be compatible with the volume of resin in the mini-column. The sample should be chosen to achieve an adsorption efficiency as close to 100% as possible. Therefore, smaller samples are preferable to large samples if sufficient sensitivity can be attained. This tends to make adsorption more efficient (see Table 2).

The desorption parameters must be carefully chosen so that a desorption efficiency of approximately unity can be attained. For the basic thermal desorption instrument used in this research, the analysis of volatile compounds requires desorption temperatures on the order of 180°C, desorption times of about 10 min, and flow rates on the order of 24 ml/min. Nonvolatile compounds could not be simultaneously determined (using the basic research instrument) with some of the more volatile compounds, and the temperature programming approach is required to minimize resin artifacts. The temperature of desorption is slowly raised from some lower temperature to 210°C or more, as described in the desorption efficiency studies. The maximum temperature is limited mainly by the allowable background, and does not exceed 220°C if a detection limit of less than 500 ng is desired. Nonvolatile compounds generally require flow rates in the range

of 40-60 ml/min and desorption times on the order of 20-30 min for efficient desorption.

Standards While the precision of an analysis can be enhanced by multiple determinations of the sample, accuracy is best served by closely approximating the sampling conditions with the standards. If small samples (10-50 ml) are being analyzed, then a syringe should be used as the sampling vessel. Quantitation can then be achieved by simply spiking a sample with a standard solution and comparing it to one or more unspiked samples. Either an internal standard or a standard addition method can be used.

If larger samples are being analyzed, it is necessary to take samples of various sizes to establish the linearity (or nonlinearity) of recovery, as was emphasized in the two previous sections. Once recovery efficiency has been estimated, quantitation can proceed. Since it is not generally practical to spike large samples with standards, the minicolumns were spiked with standards after sampling. The standards were injected directly into the minicolumns, followed by about 2 ml of water. These samples were then compared to unspiked samples as before.

Evaluation of Direct Adsorption-Thermal Desorption

Comparison with other methods

Sensitivity The direct adsorption-thermal desorption method is comparable in sensitivity to gas stripping methods for those compounds which can be analyzed by both methods. The detection limit of the direct adsorption-thermal desorption method, however, is limited by artifacts of the resin adsorption substrate. Although these artifacts elute in specific regions of the chromatogram, they cannot be allowed to interfere with any part of the analysis. Therefore, the detection limit of practical analysis is about 100 ng, even though considerably less material can be detected.

Time of analysis The time required to analyze a sample should be considered carefully in the evaluation of a method. The lack of manipulative steps between sampling and chromatography tends to favor the direct adsorption-thermal desorption method in this regard. The time required to take a sample is, of course, totally a function of sample volume, and can vary from 2 min to a matter of hours. In most cases, however, small samples can be used, and only 5-10 min are required. Larger samples can be taken using a syrings pump, some kind of suction pump or the available water pressure. Multiple samples can be taken and the constant attention of the analyst is not required.

The time required for the analysis of a minicolumn sample is determined by the volatility of the components of interest and the required resolution. Assuming that nonvolatile compounds are to be analyzed, the initial desorption period may be as long as 30 min. The chromatographic cycle ranges from 30 min, for a packed-column analysis, to 60 min, for a high-resolution capillary chromatogram. However, since thermal desorption can be carried out during the last part of the chromatographic cycle, the minicolumn analysis time is only slightly longer. Packed column analyses take less than 45 min, while a high resolution analysis cycle is completed in under 70 min.

The time of analysis is therefore a point in favor of the direct adsorption-thermal desorption method, because the total time required is quite short, and the chromatographic analysis can be accomplished within a period of time that approaches the cycle time of the chromatograph.

Range The range of the method is broad enough to encompass almost all of the compounds that can be analyzed by solvent extraction, and a great many of those that cannot. Most of the volatile compounds that represent the entire analytical range of gas stripping can be determined by direct adsorption-thermal desorption. The range of the method is approximately that of the direct adsorption-solvent elution methods, except that thermal desorption tends to be

more efficient for volatile compounds, while the solvent elution methods may be somewhat better for extremely high-boiling compounds (perylene, chricene, etc.).

Reproducibility The reproducibility of the method is determined by the accuracy with which temperatures, flow rates and desorption times can be reproduced. Although these were all manually controlled in the research instrument, precision was generally better than 10% for two analyses with identical parameters.

Sampling One of the strongest points in favor of direct adsorption-thermal desorption is the sampling technique itself. The small sampling columns (minicolumns) and the small sample sizes required for sensitive analysis afford a decided advantage over other methods.

For example, instead of transporting large volumes of water to a laboratory for analysis, samples can be taken by passing them through minicolumns at the sampling site. The minicolumn can then be sealed with Teflon tape and mailed to the laboratory in an ordinary envelope.

On-site sampling with minicolumns also reduces sample losses. By passing the water sample directly through the minicolumn, the volatility and adsorption losses caused by using a separate transporting container are minimized. In effect, the use of minicolumns in this manner approximates the ideal sampling method, because the sample is placed

into a virtually closed analytical system as it is being collected.

Limitations of the basic thermal desorption instrument

Volatility discrimination One of the major difficulties in applying this technique to the simultaneous determination of a large number of compounds has been that some of the more volatile compounds pass through the Tenax trap and are lost. This occurs when high temperatures and long periods of time are required for the effective desorption of some components of a sample. Although this problem can be circumvented by choosing two sets of parameters and running two sets of unknowns, this requires twice the analysis time whenever volatile and nonvolatile compounds are determined together.

Injection splitting Although an injection splitter was successfully used to interface the thermal desorption instrument to a high resolution gas chromatographic system, the method is not ideal. Much of the sensitivity inherent in the method is lost by splitting the sample because fairly large split ratios (greater than 10 to 1, which represents the loss of 90% of the sample) are necessary to maintain adequate desorption flow rates. Without sufficient flow through the Tenax trap, the thermal desorption injection would be too slow and chromatographic resolution would suffer.

The use of an injection splitter did not otherwise limit the power of the system, except for requiring care in reproducing and measuring split ratios. The dead-volume of the splitter was largely compensated for by the flow rate of the desorption carrier gas and the cold-trapping effect of using a low initial column-oven temperature. Although some split discrimination was observed for samples that were injected directly into the injection port, no split discrimination was observed in samples that were thermally desorbed into the gas chromatograph.

Tubing The transfer lines and the Tenax desorption traps were made of 1/8" o.d. stainless steel tubing. The choice of stainless steel may not have been the best, however, because many compounds decompose when chromatographed on stainless steel columns. In thermal desorption experiments with complex samples, it was observed that some compounds were poorly recovered, apparently because of their lack of stability within the thermal desorption system.

It should be recalled that the use of 1/8" tubing was engendered by the desire for compatibility with the packed column system. Although the use of a splitter (in interfacing the desorption instrument to the high-resolution chromatographic system) eliminated any necessity for change, it was anticipated that a splitless system might require significantly lower dead-volumes for efficient sample

transfer, because all volume flow rates would be considerably lower.

Manual control The desorption efficiency studies demonstrated the importance of parameter reproducibility. However, desorption times and temperatures were not reproduced as perfectly as would have been desired because both were controlled manually. With more perfect control of these parameters, the precision of the method should increase.

AN IMPROVED THERMAL DESORPTION INSTRUMENT

Instrument Design and Construction

Design modification

Based largely on the research presented in this dissertation, a more advanced thermal desorption instrument was designed which is expected to enhance the power of the direct adsorption-thermal desorption technique. All of the limitations of the method discussed in the previous section were considered, and some significant changes in design were made to ameliorate them.

The new instrument was designed to retain the use of capillary chromatography but eliminate injection splitting. The Tenax trap was equipped with a cooling system to prevent the loss of volatile compounds. The entire system was made more inert to eliminate sample degradation, and was reduced in scale to minimize dead volume. The instrument was also completely automated for enhanced precision and more convenient operation. Finally, a specially designed exit splitter was acquired for splitting the effluent of the analytical column between two detectors, whenever desirable, thus increasing the power of the analytical system.

Dual cryogenic trapping

In experimentation with the previous device it was observed that Tenax GC does retain most compounds quite well,

but many volatile compounds are partially or completely lost through the Tenax precolumn during the process of thermally desorbing less volatile compounds from XAD-4. However, by cooling the Tenax precolumn after the water vapor has passed through, virtually all of the compounds that can be concentrated from water on XAD-4 could be recovered completely. Therefore, the new thermal desorption instrument design included an automatic cryogenic cooling system for the Tenax precolumn.

In redesigning the thermal desorption instrument for injection into a capillary column without split, the introduction of a second cold trap was indicated. The desorption systems used by those who work with gas purging techniques involve cryogenic trapping on the front of the analytical column (38,51). However, it was considered desirable to develop an instrument that was useable without further modification of existing equipment.

Furthermore, by placing a valve between the cold trap and the analytical column, the major restriction to Tenax desorption flow (the analytical column) is removed. Thus, higher flow rates (and probably more efficient desorption) can be achieved. Therefore, the second cold trap was placed in the new instrument rather than in the gas chromatograph. If the second trap were to present operational difficulties in this configuration, an automated, cryogenic trapping system could

be built into the injection port of the gas chromatograph to trap the sample on the front of the analytical column.

The plan of operation for the second trap was to freeze the sample components there as they eluted from the Tenax pre-column (trap). Then, after they were completely transferred, a valve switch and simultaneous rapid heating would cause them to be injected into the analytical column in a stream of carrier gas. A simple block diagram of the new desorption system is shown in Figure 28. The four steps of the desorption process occur in discrete time intervals which will be exactly reproduced by the automated instrument.

Surface reactivity

Glass-lined stainless steel Glass-lined stainless steel was chosen for the second cold trap on the basis of its inertness. Although it is expected that the glass surface will require specific conditioning procedures (74,75) if it is to be used for the analysis of easily degradable compounds, it has been proven that such traps can be used for the analysis of almost any chromatographable compound (75,76,77). Novotny (74) has written an excellent review of the conditioning procedures that have been applied to glass surfaces for the attainment of an inert surface in gas chromatographic applications. In a more recent article, Farwell et al. (75) described a procedure for deactivating the surface of a glass cryogenic enrichment trap. The trap was then used successfully in the

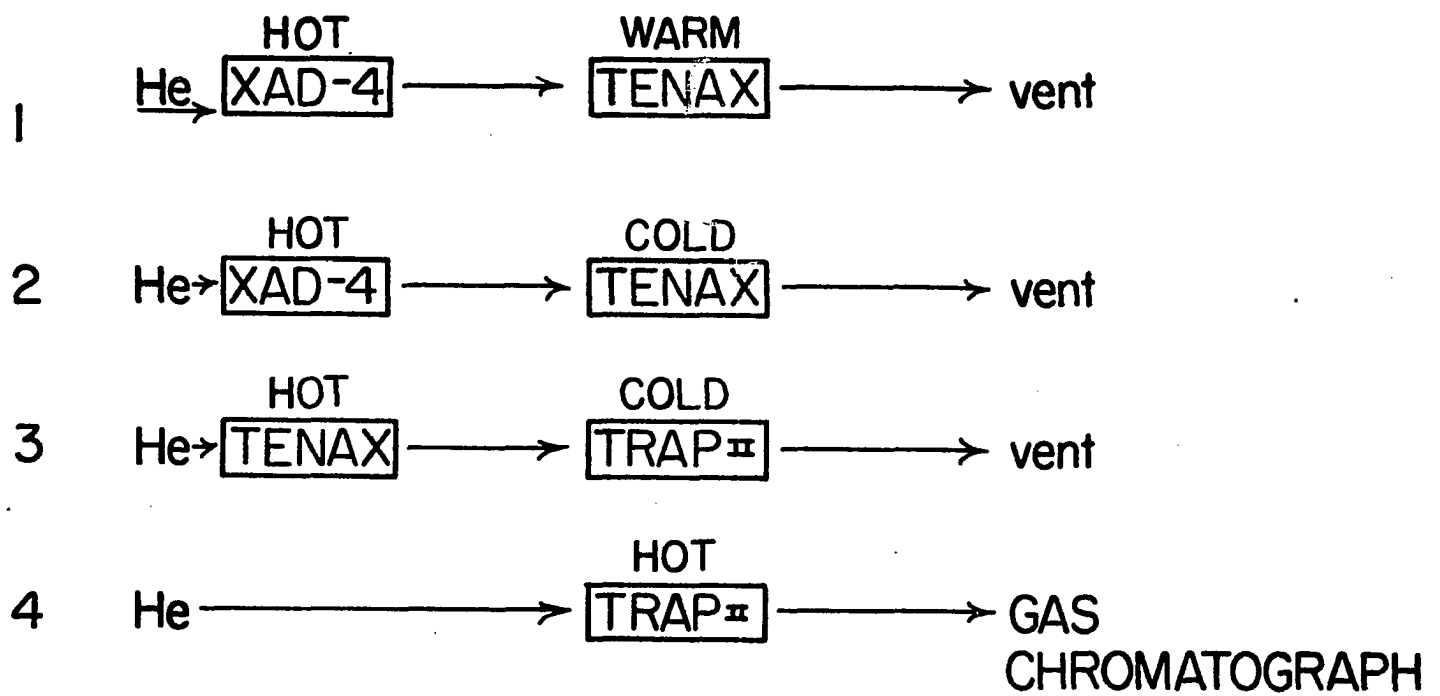
Figure 28. Block diagram of the new thermal desorption instrument

1) The organic compounds are thermally desorbed from the adsorption substrate (XAD-4). They are separated from water on the warm Tenax precolumn.

2) Immediately after the water vapor passes through, the precolumn is cooled with a spray of liquid carbon dioxide, freezing the volatile sample components for the duration of the initial thermal desorption.

3) The Tenax precolumn is heated and, at a switch of a valve, a stream of helium sweeps the sample components to a trap constructed of glass-lined stainless steel capillary tubing (0.3 mm i.d.). This trap is cryogenicly cooled, and is isolated from the rest of the system by a six-port valve.

4) When the Tenax thermal desorption is completed, the six-port valve is switched and the trap is simultaneously heated. The organic compounds are thus transferred to the analytical column, which is connected to the valve with a short length of glass-lined stainless steel capillary tubing.


1
HOT
He
XAD-4
WARM
TENAX
vent
2
HOT
He
XAD-4
COLD
TENAX
vent
3
HOT
He
TENAX
COLD
TRAP II
vent
4
He
HOT
TRAP II
GAS
CHROMATOGRAPH

determination of highly unstable (chromatographically speaking) sulfur-containing organic compounds in gaseous samples. The introduction of the sample to the analytical column was accomplished by a thermal desorption procedure.

Deactivated nickel The Tenax precolumn will be subject to somewhat lower temperatures in the new instrument than in the older version because a rapid desorption from Tenax will no longer be critical to chromatographic resolution. However, it was still necessary to remove active sites from the entire desorption system in order to maintain sample integrity and desorption efficiency. Therefore, the Tenax precolumn and the system transfer lines were made of nickel tubing.

Nickel was chosen on the basis of research done by Fenimore, Whitford, Davis and Zlatkis (78). In this research, a wide variety of sensitive, biologically active compounds were chromatographed on 1/4" o.d. x 6 ft long columns packed with 5% SE-30. These were made of steel, deactivated nickel and silanized glass. A comparison of the chromatograms obtained with these columns proved that both the glass and nickel columns were far superior to those made of stainless steel. Many sample components that decomposed almost entirely on the stainless steel columns were chromatographed quite nicely on both the glass and the nickel columns. In no case did the treated glass prove to be significantly better than the deactivated nickel.

The nickel deactivation treatment was quite simple. After sequential washings with ethyl acetate, methanol, and water, the nickel tubing was filled with 50% nitric acid for 10 min. The tubing was then rinsed with water until neutral and rinsed again with acetone before drying. The result was a chromatographically inert surface that was used successfully to determine sensitive compounds at temperatures as high as 250°C.

Automation and construction

To automate the new desorption instrument a variety of devices had to be either designed and constructed or purchased. Gas switching valves had to be found which could be actuated by a simple relay switch. A trap had to be designed for both cryogenic cooling and high temperature heating. A valve oven had to be built to maintain one or two switching valves at a constant temperature (in the neighborhood of 200-300°C) and temperature controlling devices were needed for the different heated zones. Also, a device was required to automatically actuate the switched devices at preset timed intervals.

Fortunately, it was possible to consolidate all of these by combining a few devices that were commercially available from Valco Instruments Company, Inc., Houston, Texas. Figure 29 is a schematic diagram of the new thermal desorption instrument. For clarity, all actuating and automating devices have been omitted. A similar, but more detailed diagram,

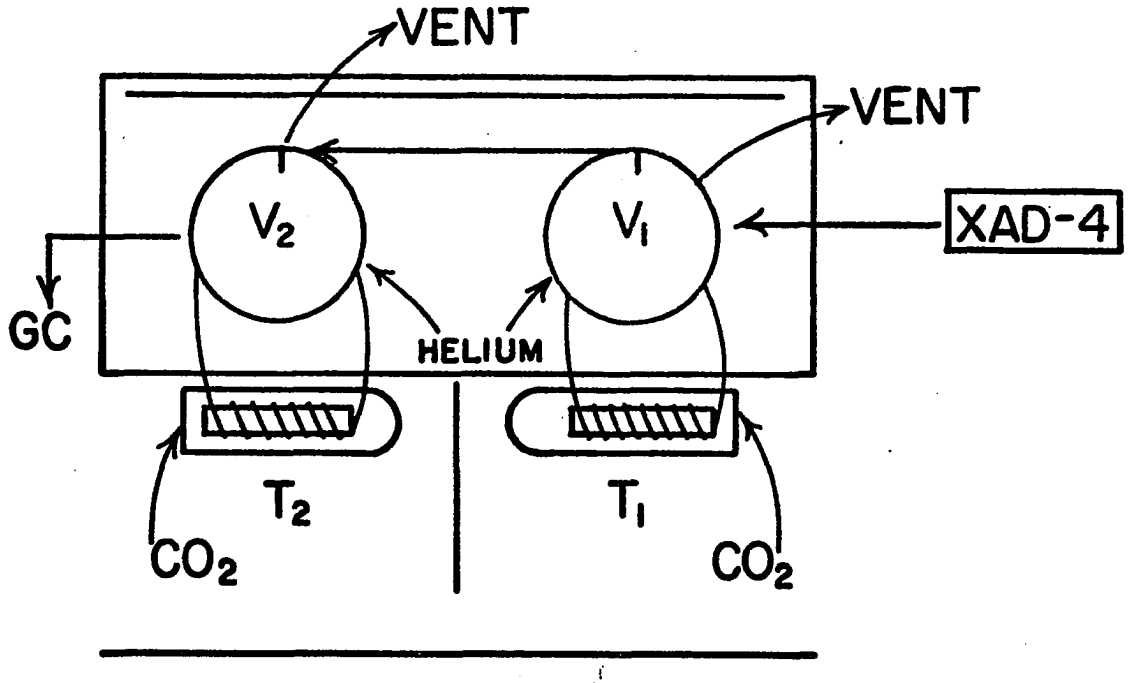
Figure 29. A schematic diagram of the new thermal desorption instrument. The progress of the sample constituents is from right to left, from the XAD-4 minicolumn to the gas chromatograph (GC).

V1 and V2 are six-port valves which contain extremely low volume paths between the ports. They are automatically switched with air pressure, which is controlled by a solenoid-switched valve. The valves are inside a heated valve box that can be accurately maintained at any temperature between ambient and 300°C.

T1 is a 1/16" o.d. tube made of nickel 200, approximately 1.0 mm i.d. x 2 ft long, packed with Tenax GC, 60-80 mesh. This precolumn is wrapped around a heating cartridge and silver-soldered to it as well. The heating cartridge can be heated to any designated temperature from ambient to about 300°C in less than a minute, and is precisely maintained after that time.

CO_2 refers to a stream of liquid carbon dioxide that is released by an automatically controlled solenoid valve. This method is used to cryogenicly cool both T1 and T2.

T2 is a trap made of glass lined stainless steel tubing, 1/16" o.d. x 0.3 mm i.d. x 30 cm in length. This is coiled around a heating cartridge as in T1.


VENT
VENT
XAD-4
V_2
V_1
GC
HELIUM
T_2
T_1
CO_2
CO_2

along with all necessary dimensions, the specific orientation of transfer lines and traps, the valve port connection scheme, the trap sizes and material composition, and a list of the automated devices and their actuation sequences were sent to Valco, where the instrument was constructed.

The automated system is controlled by a Digital Valve Sequence Programmer (DVSP), that is commercially available from Valco. A list of the devices that are controlled by the DSVP is given in Table 11. The logic states of the controlled devices for the four timed intervals of a thermal desorption injection (as described in Figure 28) are listed in Table 12. The DSVP, which is part of a commercially available gas purging instrument, was modified (hard-wired) according to the truth table in Table 12 and the key in Table 11, which were sent to Valco along with the rest of the specifications.

Materials and equipment

The following materials and equipment were used in the construction of the new thermal desorption instrument. Unless otherwise noted, these are commercially available from Valco Instruments Company, Incorporated, Houston, Texas.

Instrument Temperature Controller with digital setpoint, proportional power output and internal standard reference junction (ITC-J10). This instrument operates over a temperature range of 400°C, from 0°C to 399°C, with an absolute accuracy of ±5% of full scale and a repeatability of 0.5°C at constant ambient temperature. The proportional bandwidth is continuously variable from 2°C to 10°C. Four of these were incorporated into the

Table 11. Controlled devices and carrier gas flow paths

(a) V1 - The first valve (as shown in Figure 29). Flows are as follows:

STATE	FLOW
(1)	X[a]---T1---VENT1 /// HELIUM---V2
(0)	X---VENT /// HELIUM---T1 (reverse flow)---V2

(b) COOLT1 - The valve that cools (CO2) T1

(c) T1HEAT1 - Temperature controller that sets T1 at 50-60°C

(d) T1HEAT2 - Temperature controller that sets T1 at 280°C

(e) V2 - Second valve. Flows are

STATE	FLOW
(1)	Helium from V1---T2---VENT /// HELIUM2---GC injection port
(0)	Helium from V1---VENT HELIUM2---T2 (reverse flow)---GC injection port

(f) COOLT2 - Valve that controls CO2 cooling of Trap 2 (T2)

(g) T2HEAT - Temperature controller that sets Trap 2 (T2) to rapid heat cycle to preset temperature (300-400°C)

(h) HELIUM1 - The solonoid valve (Skinner NC) passing helium to valve 1 (V1)

[a]X represents the first thermal desorption trap (XAD-4 in Figure 29).

Table 12. Logic states of the controlled devices for operation of the thermal desorption instrument over four timed intervals

INTERVAL	DEVICE	OPERATION	STATE
I.	V1	Collect/trap/separate	1
	COOLT1	Off	0
	T1HEAT1	On	1
	T1HEAT2	Off	0
	V2	HELIUM2---GC	1
	COOLT2	Off	0
	T2HEAT	Off	0
	HELIUM1	Off	0
II.	V1	Collect/trap/separate	1
	COOLT1	Cooling	1
	T1HEAT1	Off	0
	T1HEAT2	Off	0
	V2	HELIUM2---GC	1
	COOLT2	Cooling	1
	T2HEAT	Off	0
	HELIUM1	On	1
III.	V1	Desorb	0
	COOLT1	Off	0
	T1HEAT1	Off	0
	T1HEAT2	On - heat	1
	V2	HELIUM2---GC	1
	COOLT2	Cooling	1
	T2HEAT	Off	0
	HELIUM1	On	1

Table 12. (Continued)

INTERVAL	DEVICE	OPERATION	STATE
IV.	V1	Desorb	0
	COOLT1	Off	0
	T1HEAT1	Off	0
	T1HEAT2	On - heat	1
	V2	HELIUM2---T2---GC	0
	COOLT2	Off	0
	T2HEAT	On - heat	1
	HELIUM1	On	1

new instrument, one for the valve oven, one for the capillary trap, and one for each setpoint of the Tenax precolumn.

Digital Valve Sequence Programmer (DVSP-4-4). A clock with a quartz crystal time base that can be set to four timed intervals and can actuate a large number of relay-switched devices at these intervals.

Switching Valves (AH2CV-6-HTa-N60). These are 6-port gas switching valves with 1/16" zero dead volume fittings, air operated, Nitronic-60 valve body, operable to 350°C maximum. Two were used.

Air Actuator for Switching Valves (AH2-90). A helical drive air actuator that utilizes solenoid-switched air pressure (about 30 psi) to switch the 6-port valves described above. Two actuators were required, one for each valve.

Valve Oven (HVE-2). A heated valve enclosure for two 6-port gas switching valves.

Rapid Heating and Cooling Trap Assembly (RHCT-1). Two of these were modified for the special application of the thermal desorption instrument. The cooling jet was changed to handle liquid carbon dioxide instead of air, and trapping tubes themselves were custom-made.

The glass-lined stainless steel capillary tubing (used in the construction of the second cold trap and all transfer lines following the Tenax precolumn) was purchased from Scientific Glass Engineering, Austin, Texas.

The XAD-4 desorption section remained essentially untouched. The desorption from XAD-4 to the new section of the thermal desorption instrument was accomplished with the same heated zone. However, the stainless steel transfer lines and fittings were replaced with deactivated nickel lines and fittings, and reduced from 1/8" to 1/16" o.d.

A glass-lined stainless steel exit splitter was specially ordered from Scientific Glass Engineering. The splitter was designed to be infinitely variable, so that from zero to 100% flow could be directed to either an FID or a Hall 700A electroconductivity detector. Both detectors are from Tracor Instruments, Inc., Austin, Texas.

Future Work

Aqueous samples

Since work is still being done with the original thermal desorption instrument, the newest version has not yet been tested. Nevertheless, it is expected that the sensitivity

gained from the elimination of the inlet split (a factor of about 25), the broader analytical range, and the convenience of operation will make it an extremely attractive analytical tool. Once in operation, the new thermal desorption instrument should be ideal for the routine analysis of finished water, processed water, and even effluent streams and surface water. Eventually, such a system could be coupled with spectrometric detection for the rapid analysis of complex and unknown samples.

Recent work with the original thermal desorption instrument has indicated that the lower limit of analyte volatility may be extended by using Tenax GC as the adsorption substrate. High molecular weight compounds could be adsorbed reasonably well by this substrate, and should be desorbed with excellent efficiency. Of course, the use of Tenax in this fashion would represent a relatively specific application of the direct adsorption-thermal desorption technique, since Tenax is not a universally efficient adsorption substrate.

Solid samples

In many cases it is desirable to analyze a solid sample for volatile compounds. Foods, drugs, agricultural chemicals and products, and even cosmetics are subject to such analyses.

To apply the thermal desorption instrument to the problem, a sample could be placed in an empty thermal desorption tube (minicolumn) and heated to a suitable temperature. A stream of inert carrier gas would sweep the volatile constituents onto the Tenax precolumn where they could be separated from any water present in the sample prior to injection into the gas chromatograph. Similar procedures have been used for such analyses (51) but the removal of water has often been a problem.

Heart cutting

Heart cutting is the selective removal of a portion of a sample from a chromatographic system. This is usually accomplished by diverting the effluent flow from a chromatographic column for some fraction of the analysis time. The portion of the sample that is removed in this manner then undergoes further chromatography or is treated in some other way.

The thermal desorption instrument should prove useful in the removal of almost the entire sample from the fraction that contributes the least analytical information, the solvent. A relatively large volume of the sample in question could be injected onto a minicolumn or some other device designed specifically for the purpose. The solvent would then be separated from most of the sample components on the Tenax precolumn. The sample components would subsequently be

thermally desorbed into the gas chromatograph without solvent. A method of this sort could be used to enhance the available sensitivity of other analytical techniques, such as solvent extraction, by analyzing significantly larger samples with no loss of resolution.

A capillary trapping system similar to the one in the new thermal desorption instrument could also be used to trap a fraction of the effluent from one capillary column in order to thermally desorb it onto another. This could be accomplished by essentially replacing the Tenax precolumn with an analytical column. By taking small cuts it would be possible to resolve even the most complex sections of a chromatogram, assuming the proper columns were chosen. Of course, some rather extensive changes would have to be made in the desorption system to accommodate a second capillary column, and such a transition would not be easily reversible.

Selective detection

The greatest potential of the thermal desorption system lies in coupling the new instrument, or one similar to it, to a highly selective detector. The detection limit of the most recently described instrument will probably be established by resin artifacts, rather than by instrumental constraints like detector sensitivity. However, if the detection system were insensitive to these artifacts, or if it could accurately discriminate them, the sensitivity of the method then would

be determined only by sample size, recovery, and the limits of the detector.

Selective detection has the added advantage of simplifying complex samples, and is often inherently more sensitive than the more universal detectors. For instance, both of the common halogen detectors, electron capture and Hall electrolytic conductivity, are approximately three orders of magnitude more sensitive to most halogenated compounds than the commonly used flame ionization detector (FID).

In summation, coupling the thermal desorption system to a selective detector would significantly enhance the sensitivity of the method. Many compounds could be easily determined at the 100 parts per trillion level in a 10-ml sample.

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