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Trace analysis of volatile organic compounds in water by GC and HPLC

by

Ikue Arikawa Ogawa

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TABLE OF CONTENTS

PREFACE

As in any analysis, direct measurement is the simplest. It is toward this end that an investigator strives. If this cannot be attained, then the method containing the least number of processes which gives the best results is preferred. A study of the problem of analysis of trace volatile organic compounds in water begins with existing tools and knowledge.

The literature review explores the traditional methods of concentrating and analyzing volatile organic compunds in water. The division of these methods becomes obscured as the analysis becomes more demanding in terms of scope of compounds and lower amounts quantitated. While impressive gains have been noted in gas and liquid chromatography, concentration is still desirable. There are emerging, a few direct methods of analyses based on fiber optics and very selective methods of detection, such as, fluorescence detection (1) or based on multiple detection systems, such as, tandem mass spectrometry (2).

Sections I and II deal with the problem of analysis low-molecular weight polar compounds in water. It has been shown that the most common method used to disinfect drinking water, chlorination, produces carcinogenic and mutagenic compounds (3). These compounds have escaped detection

because they are highly soluble in water and difficult to concentrate. In order to study the chemistry and the fate of these harmful compounds, an analytical method is necessary. In Sections I and II, a simple method for the analysis of these low-molecular weight polar compounds is described. Section II is more comprehensive and includes a greater variety of compounds. Section I is more limited to the class of low-molecular weight aldehydes and ketones. The analysis of aldehydes and ketones was based on the formation of the 2,4-dinitrophenylhydrazine derivatives, which resulted in high selectivity and high sensitivity.

In recent years, it has been demonstrated that the dumping of toxic wastes have caused these toxic compounds to percolate through various geological rock formations and contaminate the ground and surface waters which are the main sources of drinking water. As a consequence, legislation (4) has been introduced which will affect 50,000 public water supply systems in the USA. These water systems must have their water supplies analyzed within four years by chemists certified by the US Environmental Protection Agency for 8 volatile organic compounds using the prescribed method of purge-and-trap with suitable detection. Section III describes changes that can be made in the purge-and-trap method, so that a greater variety of organic compounds can be analyzed by a single experiment. A single experiment

using both gas purging followed by distillation with continued gas purging is used to concentrate organic compounds. In this way the analysis is simplified, and the cost is reduced.

REFERENCES

1. Chudyk, W. A.; Carrabba, M. M.; Kenny, J. E. Anal. Chem. 1985, 57, 1237.

2. Hunt, D. F.; Shabonowitz, J.; Harvey, T. M.; Coates, M. Anal. Chem. 1985, 57, 525.

3. Coleman, W. E.; Munch, J. W.; Kaylor, W. H.; Streicher, R. P.; Ringhan, H. P.; Meier, J. R. Environ. Sci. Technol. 1984, 18, 674.

4. Federal Register 1985, 50, 46880.

REVIEW OF THE LITERATURE

INTRODUCTION

In the analysis of organic compounds at trace levels, it is often necessary to concentrate the analytes so they can be detected and quantitated by conventional gas chromatography (GC) or high performance liquid chromatography (HPLC). "Trace Organic Analysis," by Klaus Beyermann (1), is a valuable textbook giving general observations about the subject, and containing many diagrams of unique apparatus and ample tables listing references of specific compounds, the matrices, the concentration levels, and results expected. Unfortunately, the literature references are current only up to 1980. Many other texts are available on related topics, such as, chromatography (2-5) and environmental analysis (6,7) contain useful information on organic trace analysis. An examination of original papers listed in the application sections of books on related topics is also useful (8).

Annual publications of reviews can be found in the special April issue of Analytical Chemistry. The "Fundamental Reviews" (9), published in even years, contain detailed sections on gas chromatography, liquid chromatography, thin-layer and paper chromatography. The section on sample preparation of analysis of organic compounds in water analysis can be found on page 73R of the

"Application Reviews" (10), published in odd years. Hertz et al. (11) discussed the difficulties in achieving accuracy, and the lack of appropriate standard reference material in trace organic analysis. Karasek et al. (12) reviewed preconcentration for trace analysis of organic compounds.

Recent reviews published by the Journal of Chromatography are on derivatization in liquid chromatography (13), detectors in liquid chromatography (14) and headspace analysis (15). Novak (16) discussed the problems of trace analysis using gas chromatography.

The major methods of concentrating volatile organic compounds in water for trace analysis are concentration on solid sorbents (resin sorption and molecular sieves), solvent extraction, headspace analysis, distillation and direct injection into GC columns. Derivatives in GC and HPLC enhance detection, or improve chromatography. Each topic will be explored in greater detail. These methods have been skillfully combined, in some cases, to produce methods of analysis that exhibit all the advantages of each method.

CONCENTRATION ON SOLID SORBENTS

Resin Sorption

There are a wide variety of methods in which the analytes are concentrated on solid sorbent particles or membranes. In the first variety, the analytes are predominantly adsorbed on the solid (resin sorption), and in the second variety, the analytes are predominately sorbed in the pores of molecular dimensions of the solid (molecular sieve). The more common type of materials for resin sorption are XAD (copolymer of poly(styrene and divinlybenzene)), and its derivatives, activated carbon and other carbonaceous material, Tenax, polyurethan foam, Speron MD, Ambersorb XE-340, Porapak (N, R, Q), Carbopak, silica and its derivatives, alumina and florisil (magnesium silicate). Polar compounds are readily sorbed on the inorganic sorbents, non-polar compounds on the engineering resins and small molecules in the pores of molecular sieves.

Junk et al. (17) reported that the average recovery of test compounds from aqueous solution on amberlite XAD-2 was 78%. The analytes were desorbed with diethyl ether and further concentrated by microdistillation. The test compounds included alcohols, aldehydes, acids, aromatic halides, aklylbenzenes, phenols, chlorinated phenols, ester, ethers, ketones, polynuclear aromatic compounds, herbicides,

pesticides, and nitrogen and sulfur containing compounds. This work initiated rapid growth in the number of reports using amberlite XAD-type resins for the concentration of organic compounds from water, including the study of large molecules, such as, fulvic and humic acids (18). The method has been extended to 1 ppb level and simplified so that no microdistillation step was necessary by Tateda and Fritz (19). The determination of nitro-compounds on XAD-7 using ethyl acetate to desorb the analytes has been reported (20).

Richard and Fritz modified the XAD resins to produce anion exchange resins for the determination of acidic components (21) and a cation resin for the determination of basic components (22). An acidic eluent (hydrogen chloride gas dissolved in methanol or diethyl ether) and a basic eluent (ammonia dissolved in methanol or diethyl ether) were used to desorb the analytes from the acidic and basic XAD resins, respectively. Selective concentration of aromatic bases, pyridines, acridines, quinolines and aminoanthracenes was achieved on XAD-2 and XAD-8 (23). The analytes were eluted with 1 mL of 0.1 N HCl. Sixteen chlorophenols at 0.01 to 1 ppm level were determined in human urine on XAD-4. The phenols were eluted with a solution of 2-propanol and hexane (24).

Thurman et al. (25) correlated the capacity factor with the aqueous molar solubility of aromatic, aliphatic and

cyclic compounds with carboxyl, hydroxyl, amine and methyl groups on XAD-8, a porous acrylic resin. Giabbai et al. (26) tested 22 model compounds under varying pH on XAD-8, AG-MP-50 and Carbopack B.

The copolymer, poly(styrene-divinylbenzene), has been packed into an HPLC column (PRP 1) which was used to concentrate chlorophenols at the 2 ppb level in drinking and rain water (27). The use of macroreticular resins for the broad spectrum analysis of organic compounds in drinking water was evaluated by Gibbs and co-workers (28).

Activated charcoal has been known as an excellent sorbent for removing unwanted organic compounds from many matrices. However, the problem of quantitative desorption from activated charcoal still remains, except for a few special cases (29). In addition, charcoal has high water adsorption properties and high temperature is necessary if thermal desorption is the mode of concentrating the analytes from the solid sorbent (30). A simple collection tube of silicone polycarbonate membrane and activated carbon was used to collect 23 volatile organic compounds (C_1 to C_7) on activated carbon. Permeation constants varied from 1 to 16 μg/ppm-h. The tube was placed in the sample at the sampling site. The advantages of this method are the problems at sampling, such as, pumps and refrigeration are not needed. Concentration takes place at the sampling site, not at the

laboratory (31). A novel technique for the rapid thermal desorption from activated charcoal by microwave at 700°C has been reported (32). Carbon dispersed in glass fibers has been used as an adsorbent for the enrichment of polychlorinated dibenzofurans in water. The analytes were eluted with a mixture of methylene chloride and cyclohexene (33).

Another sorbent Porapak N was used to concentrate arenes and volatile halogenated compounds at microgram per cubic meter levels by elution with methanol and GC quantitation (34).

An extensive work on trace enrichment of polar compounds on chemically bonded silica and pyrocarbon modified silica sorbents was given by Werkhoven-Goewie et al. (35). On-line separation and trace enrichment on octadecylsilane (C_{18}), PRP 1, and cation-exchange materials were investigated by Nielen et al. (36).

Picker and Sievers (37) reported the synthesis of an unusual adsorbent of europium and bis(β-diketonate) ligand. They were able to accumulate volatile compounds, including acetaldehyde from air samples.

Molecular Sieve

Until recently zeolites have been used in ion exhange and in the separations and storage of very small molecules,

such as, gases and water (38). Zeolites are crystalline aluminosilicates with framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. Thermal desorption of organic compounds from aluminosilicates are known to produce hydration and isomerization of organic compounds (39).

Of the infinite arrangements of corner linked tetrahedra (oxygen atoms at corners and small atoms, such as, Al and Si at the centers), only 40 are known. These tetrahedra are arranged to produce linear, sheets, supercages and channels. The crystals are only 1 to 10 micrometers in length and binders (clay, inorganic gels) are used to produce more manageable sizes (40).

Recently a class of hydrophobic zeolites (silicon dioxide) with discrete pores in the crystal structure has been synthesized. The zeolites were prepared by hydrothermal precipitation of saturated solutions using appropriate additives. There are a bewildering number of manufacturing techniques and numerous proprietory methods for the synthesis (41). The crystal structure and selective sorption properties of these zeolites, ZSM-5 (42, 43) and Silicalite (44) have been reviewed by several authors. These zeolites contain intersecting bent-orthogonal channels that are precisely formed with two similar cross-sectional

geometries: circular 6 Å in diameter and elliptical 5.1 Å to 5.7 Å. These zeolites sorb linear organic compounds that are able to invade the linear and zig-zag channels.

Extensive work on distribution coefficients of organic compounds in the gaseous and aqueous phases with Silicalite has been reported by Chriswell and co-workers (45). Several desorption methods were investigated including solvent elution, soxhlet extraction, high pressure soxhlet extraction, adsorbent dissolution with HF, microwave desorption and thermal desorption. Shultz-Sibbel et al. reported that temperature had little effect on the distribution coefficient of the analyte in the aqueous phase (46). The alumina binder increased the capacity of Silicalite for polar organic compounds.

Using Silicalite, Chriswell and Gjerde (47) concentrated SO_2 from stack gases, Burkholder (48) recovered ethanol from water, Milestone and Bibby (49) concentrated ethanol and 1-butanol from water and Hoering and Freeman (50) separated n-alkanes from monomethylalkanes. Linde 5A was used to remove the the n-alkanes.

HEADSPACE ANALYSIS

A method of analysis of the gaseous portion of a sample (headspace) has recently gained in popularity. Because only the gaseous portion of the sample is injected on a gas chromatographic column, there is no danger of damaging the column. However the procedure works well only for analytes that exhibit vapor pressures large enough so that the amount injected can be detected. Ioffe and Vitenberg discussed the merits of reverse headspace analysis, in which volatile substances are allowed to equilibrate with less volatile solvents (51). The resulting solution is easier to inject into GC columns or treat further. This is an extensive work (book) on the theory and applications of headspace analysis, covering analysis of water, volatile compounds in biological systems and gases in solutions. Ample tables of distribution coefficients with effects of dissolved substances are given. A table of simple experiments is given listing reagent, reagent preparation and result of the treatment, for example, addition of hydrogen iodide to remove ethers from the headspace.

In order to enhance detection and extend the analysis to a wide variety of compounds, the headspace sample is increased by dynamic methods and by concentrating the analytes by gas sparging of the aqueous sample and

collection of the analytes on solid sorbents or in cold traps. Recent reviews are given by Nunez and co-workers (30) in which they discussed the designs of sparging apparatus, types of solid sorbents, and kinds of solvent and thermal desorption. The disadvantage of the solvent desorption is the possible interference of the solvent peak in the GC analysis, but the advantage is that the investigator has the opportunity to do many injections from a single sample. The advantage of thermal desorption is that all of the sample is injected, increasing sensitivity. There is no handling, decreasing errors in evaporation and transfer.

McNally and Grob (52,53) reviewed static and dynamic headspace analyses. A recent application of headspace analysis is the determination of tetrahydrothiophene (54) in water by gas chromatography-mass spectrometry (GC-MS). In this experiment 1 mL of 10 to 250 ng of tetrahydrothiophene was placed in a vial producing 8 mL of headspace at 60^{o}C for 15 minutes and 500 μL of the vapor was injected into a capillary column.

A kind of dynamic head space analysis that has gained wide-spread acceptance is the purge-and-trap method. An inert gas, such as, helium, is bubbled into the aqueous sample. The organic compounds must be volatile, and the gas transports these volatile organic compounds out of the water

and onto an adsorbent usually a column containing Tenax GC. Then the compounds are desorbed thermally or by solvent elution. The concentrated compounds are analyzed by GC or GC-MS. In the extensive work of Bellar and Lichtenberg (55) nitrogen at 20 mL/min was bubbled into 5 mL of sample containing benzene, toluene, methylene chloride and 2-butanone at 1000 to 1 ppb level at 65°C for 11 minutes. With Tenax GC as the adsorbent they concluded that compounds with GC retention indices above 500, with boiling points less than 200°C and with solubility in water of less than 2%, could be successfully quantitated by this method. Repetitive purging and trapping has been applied successfully in the quantitation of benzene, toluene, n-decane, n-undecane, and n-dodecane in water at ppb level (56). Gershey designed a sampling device which employed a bubble adsorptive technique to produce aerosols from seawater that were enriched with respect to surface active organic matter. Concentration factors of greater than 100-fold were obtained (57). A dynamic headspace method to eliminate errors in quantiation due to matrix effects has been reported by Gregoire (58).

PURGE-AND-TRAP

The most widely used adsorbent in the purge-and-trap experiment is Tenax GC (porous poly(2,6-diphenyl-p-phenylene oxide)), a trade mark registered by Enka N. V. and developed by AKZO Research Laboratories, Arnham, The Netherlands. Tenax GC can be differentiated from the macromolecular resins of the Amberlite XAD-type polymers by the fact that it does not suffer oxidation and thermal fragmentation at 250°C or greater (59).

Low blank level is a result of its high thermal stability. However, artifacts have been found as a result of the reaction of inorganic oxidizing gases (nitrogen oxides, chlorine, sulfur dioxide, ozone) with easily reducible compounds, such as, olefins to form a variety of corresponding oxidized compounds. Thermal desorption was the mode of concentrating the organic compounds in this experiment (60). Comparative assessment of the artifact background on thermal desorption of Tenax GC and Tenax TA have been made (61).

Raymond and Guiochon evaluated graphatized carbon black as trapping material for organic compounds in light gases. They predicted that the homogeneous surface and routine use at 400°C would make this sorbent suitable for the concentration of high molecular weight polycyclic aromatic

compounds (62). Murray compared the breakthrough volumes of some aqueous volatile compounds on Chromsorb 102, 105, 106 and Tenax GC (63). Similar studies with other polymeric adsorbents to determine their retention behavior have been performed on Porapak series (64), Chromsorb series (65), and Tenax GC (60).

Adsorption of organic compounds on polyurethan foam followed by solvent extraction gave comparable results as adsorption on Tenax GC followed by thermal desorption (66). The authors found degradation products, benzaldehyde and acetophenone in the Tenax GC experiments. The capacity of Tenac GC has been compared with a new adsorbent, Thermosorb, by Zlatkis and co-workers (67). They found that, in general, the capacity of many compounds was lower on Thermosorb than on Tenax GC.

Tenax is soluble in low-molecular weight chlorinated hydrocarbons, tetrahydrofuran, carbon disulfide, dioxane, pyridine and cyclohexanone. It is insoluble in cyclohexene, alcohols, acetone, diethyl ether and ethyl acetate (59). A few μL of methylene chloride injected into a Tenax GC column caused the resin particles to clump together.

The popularity of Tenax has led to extensive studies characterizing this sorbent. One study included the interference of the sorption of benzene on Tenax GC in the presence of varying quantities of n-butanol, n-pentane and xylene (68).

The most common type of purge-and-trap experiment is an on-line process, in which initial sparging of the organic compounds from water, the desorption of the compounds and the separation and analysis are completed in one operation. Hence, the sparging apparatus is connected to the concentration column which is usually placed in the inlet of a gas chromatograph where the column can be easily heated to release the concentrated organic compounds. The compounds released in this manner are concentrated in a liquid nitrogen cryotrap. The concentrated sample is quickly swept to the head of a GC column, where the analytes are separated. The gas chromatograph is interfaced with a mass spectrometer where the analytes are detected and quantitated. In this way, the entire sample can be swept into the GC column. The result is very high sensitivity.

In order to accomodate this arrangement, the adsorbent must be thermally stable, producing a low blank level. Another requirement is that great care must be taken to keep water away from the concentration column. Large quantities of water that emerge from the concentration column can freeze and plug the cryotrap or result in too large an ion pressure in the mass spectrometer. The cryotrap is necessary to focus the analytes at the head of the GC column. So that a minimum of water enters the Tenax column, the concentration apparatus is carefully designed, the flow

rate of the sparging gas is controlled and the temperature of the aqueous solution is generally kept at or below 80°C (69).

With these constraints this method has been appropriately applied to the analysis of halocarbons (with the novel use of a Nafion permeation dryer (70)) and other volatile hydrophobic compounds (71), such as, acrylonitrile, chlorobenzene, 1,2-dichloroethane, ethylbenzene (72,73) and methylnaphthalenes (74). These compounds were readily purged from aqueous solutions.

Grob and Habich described charcoal particles melted into the surface of capillary columns and the use of thick stationary phases, to replace conventional traps that lack conformity with capillary GC columns in terms of carrier gas flow rates (75). Crogenic traps have been reviewed in great detail by Brettell and Grob (76,77).

A commercial apparatus (Tekmar) is available for compounds of boiling points less than 150°C and water solubility of less than 3% (78). For this apparatus a needle was used to introduce the purge gas instead of a frit for foaming samples. Another apparatus (Chemical Data Systems) can be heated to 85°C for the concentration of more polar compounds. Tenax is mixed with Ambersorb XE 340 to concentrate methanol (79).

Chiba and Haraguchi used an ice bath to cool a short Tenax precolumn to concentrate trihalomethanes that exhibited low breakthrough volumes (80).

The use of high temperatures in the purge-and-trap method has been investigated by several groups. By heating the sample to 80°C Spraggins and co-workers were able to obtain high molecular weight aromatic compounds, naphthalene and acenaphthene (81). No recovery or comparison of recovery with other methods were given. By this method the amount of aniline was 7% and of nitrobenzene was 3% of the amount obtained by solvent extraction. They were able to detect aniline and nitrobenzene in mud samples. Ramstad and Nicholson were able to determine acryonitrile at 10 ppb at elevated temperature (82). Other applications of higher temperatures for the analysis of soils and glues have been reported by Ramstad et al. (83).

Kopfler et al. suggested fractional purging to simplify identification process during subsequent GC-MS analysis (84). They purged the sample at 6°C for 30 minutes followed by two 30-minute purging at 95°C.

The work of Ryan and Fritz showed that phthalates and polynuclear aromatic compounds could be conveniently concentrated on 2 mm I.D. mini-columns containing XAD-4. The organic compounds were thermally desorbed and trapped by a Tenax column. A splitter was used to focus the analytes

on the capillary GC column (85). Continuing this work, Hyde (86) improved the sensitivity by replacing the splitter with a carbon dioxide cryotrap, so that all of the sample could be delivered to the GC column. He extended the range of organic compounds to include alcohols. Organophosphorous compounds at the ppb level were initially concentrated on XAD-4 (87). The analytes were eluted with ethyl acetate and the entire solution was vaporized with gas purging. The analytes were collected on Tenax. The sample was transferred to the GC column by the usual thermal desorption.

Of the three designs of sparging vessels investigated by Kuo et al., the stripping flask was the most efficient (88). By sparging 200 mL of solutions containing analytes at 16 ppm level at 95°C at 120 mL/min helium flow for 30 minutes, less than 6% of acetone, 2-pentanone, 1-butanol, propionaldehyde, and butyraldehyde remained in the stripping flask. However, quantitative amounts of the more polar compounds, acetic and butyric acids were found in the stripping flask. These results for polar compounds are in sharp contrast to the fact that methylene chloride and chloroform can be sparged from the stripping flask at 23°C in 15 minutes.

The method of direct on-line analysis does not allow sample clean up, such as, for pesticide analysis using electron capture detection (89).

Recently Freeman and Lautamo prepared a new stationary phase for capillary columns, DB-624, which contained methyl, phenyl and cyano groups on large bore silica columns. They reported separation of 23 compounds in 22 minutes. The column was interfaced directly with a purge-and-trap apparatus. At desorption flow rate of 8 mL/min no cryogenic trap was needed. When the analysis of the large bore column was less than 100°C, water accumulated in the column, and the column was heated to 100°C for 30 to 40 minutes each day (90).

Curvers et al. presented an equation to predict the recovery in purge-and-trap experiment (91). The recovery was dependent on the flow rate of the sparging gas, the process time, the gas-liquid distribution coefficient, the volume of the headspace, and the volume of the sample. The gas-liquid distribution coefficient was dependent on the vapor pressure and the activity coefficient of the analyte. The vapor pressure was estimated from the boiling point and the heat of vaporization using the Clausius-Clapeyron equation. The activity coefficient was estimated from water solubility. The equation was used to calculate vapor pressure and activity coefficient of toluene, 1-heptanol and o-dichlorobenzene. These calculated values agreed with literature values. The equation predicted that large gas volumes will be necessary for polar and nonvolatile compounds.

DISTILLATION

Grob was able to purge C_{18} to C_{24} compounds from water with high efficiency at 80°C using inert gas in a closed system (92). When water was used as the purging gas (steam distillation), polar organic compounds were volatilized from the water and there was no limitation on the molecular weight of the compounds recovered from water. But unfortunately by using steam as the purging gas in his experiment more volatile compounds up to C_{14} were lost. This method of recycling the sample is called closed loop stripping and has been studied by many investigators (93) because it has the potential of very high sensitivity. It was used by Gschwend et al. (94) to concentrate heptanal, decanal, dodecanal and tridecanal. A similar apparatus has been reported by Westendorf (95). The sample at 40°C was purged for two hours and the analytes were collected on 1.5 mg activated charcoal. Saevenhed and co-workers (96,97) reported that recoveries of compounds increased substantially at elevated purging temperatures and polarized purging times. At higher temperature the use of an open loop rather than a closed loop stripping system simplified the analysis.

Higher molecular weight hydrocarbons, such as, pesticides and more polar organic compounds, such as, acids,

amines, acetone and acetaldehyde have been successfully concentrated by Richard and Junk (98) using steam distillation. The authors included a good recent review of steam distillation as a viable method for the isolation of fatty acids and phenols, neutral hydrophilic compounds and basic nitrogen compounds. In their method the pH of 100 mL of sample was adjusted to 11 and the sample was steam distilled to give 50 mL of distillate containing basic and neutral compounds. Then the sample was adjusted to pH of 2 and 100 mL of the acidic fraction was obtained. Test solutions containing 2 to 500 ppm of butanoic acid, heptanoic acid, phenol, acetonitrile, propionitrile, formaldehyde, propanone and butanone were quantitatively recovered. The steam distillation results were compared with solvent extraction and ion exchange methods of concentration. According to the authors the disadvantages were the long distillation times and the possibility of acid or base catalyzed hydrolysis. They obtained a concentration factor of 2.

Godefroot and co-workers (99,100) developed a microdistillation apparatus in which 10 ppb to 10 ppm organic compounds were recovered in 80% to 100% from water using 1 mL of methylene chloride or pentane to extract the aqueous distillate in a continuous manner. The compounds studied included alcohols, ketones and chlorinated

pesticides. Alkanes up to C_{26} were recovered quantitatively in 60 minutes, but the recovery for phenol was less than 50% using methylene chloride.

For the more hydrophobic analytes, 3-pentanone, 2-methyl butanoate, α-pinne, D-limonene, n-decanal, methyl-N-methyl anthranilate, β-caryophylene and geranyl butanoate the steam distillation apparatus was modified with the addition of hexane to extract the organic compounds from the distillate (101). A Tenax trap was positioned above the distillate to concentrate volatile compounds that passed through the hexane layer for the analysis of mud samples. Nunez and Bemelmans used steam distillation and solvent extraction with pentane and diethyl ether to extract fruit juice aromas. The compounds included 3-pentanone (vapor pressure 356 mmHg at 100°C, soluble in water) to 1-decanal (vapor pressure 76.2 mmHg at 100°C, insoluble in water). The same procedure using steam distillation and hexane solvent extraction with 3 hours processing time was used by Onuska and Terry (102) to obtain an average of 81% recovery of chlorobenzenes in sediment samples. Similar apparatus was used to recover acrylonitrile from water at the ppb level (22).

Rijks and co-workers presented a theoretical model that described the recovery of different classes of compounds as a function of process time for the simultaneous steam

distillation and solvent extraction process (103). The mathematical model predicted that 100% recovery can be expected for 10 to 15 minute process time for volatile and nonpolar compounds. The recovery for phenol was 17% (experimental value) at 20 ppb level for 30 minute process time.

Amin and Narang (104) determined chlorinated, brominated and fluorinated alkanes and benzenes from sediments by heating the sample to 120°C for 30 minutes while using a metabellows pump using air as the purging gas.

In a novel experiment using vacuum distillation, Kozloski was able to concentrate hexane, carbon tetrachloride, chloroform, benzene, 1,2-dichloroethane and diethyl ether at the 40 ppb level from large quantities (1 L) of water in 11 minutes collecting 4.4 mL distillate (105). The flow of gas using the distillation method was estimated at 350 mL/min. Rapid stirring was essential. The distillate was subjected to the usual purge-and-trap experiment. The recoveries of more polar compounds were 12.3% for methyl isobutyl ketone, 11.8% for methyl acetate and 3.7% for tetrahydrofuran. For samples that contain moderately low quantities of water, such as, fish samples, vacuum distillation was used to initially remove the water and finally to concentrate the volatile organic compounds (106).

A unique microdistillation apparatus (1.3 mL distillate from 500 mL sample) was designed by Peters (107). Headspace analysis of the distillate (with the addition of sodium sulfate) resulted in detection limit of 4 ppb for volatile polar organic compounds. Good recovery (80%) was achieved for the compounds tested. The remainder (20%) was found in the reflux condensor.

Phenolic compounds in water at 0.1 to 3 mg/L level by continuous steam distillation and liquid extraction at pH 1 amd 40% sodium chloride solution required 1.5 hours (108). These authors also reviewed recent methods of concentration of phenolic compounds, including liquid-liquid extraction, sorbent and ion exchange, and derivative formation for electron capture detection. Phenolic compounds in beer was determined by steam distillation and aluminum oxide column chromatography (109).

Kuo and co-workers (110) recovered 67% methanol, 79% ethanol, 83% acetone, 83% 2-propanol, 40% diethyl ether and 78% 2-butanone at ppm level from 1 L water by collecting the first 10 mL of the distillate and distilling the 10 mL. From the second distillation they collected 1.5 mL of distillate.

SOLVENT EXTRACTION

Solvent extraction has been widely used because of its simplicity. In many cases it requires no special instrumentation. A wide variety of readily available solvents can usually be found in most laboratories. Many designs of the extracting vessels to enhance detection have been reported for batch extractions (111-114) and an evaluation of several continuous extractors has been investigated (115,116).

Among the disadvantages are loss of volatile analytes during concentration and transfer, incomplete extraction of the analytes, cumbersome process of handling large sample sizes, and interference of solvent peak with the analyte peak during separation and quantitation by gas chromatography. In some cases emulsions are formed that hinder quantitation. It was noticed that samples that produce emulsions during simple solvent extractions produced foaming in steam distillation. In some severe cases foam filled the entire distillation apparatus (116).

Colgrove and Svec used liquid-liquid extractions to fractionate complex mixtures of organic compounds into basic, acidic and neutral components at the ppm level (117). The neutral fraction was further divided into aldehydes, ketones, polar and nonpolar compounds. Eichelberger *et al.*

determined 80 compounds in the 30 ng/L level by extraction with methylene chloride, microdistillation and quantitation by GC-MS (118). The method was applied to groundwater and surface water. Other recent work using solvent extractions is the work of Castello et al. (119).

Continuous flow extraction with on-line capillary GC has been designed for automated monitoring of alkanes and aromatic hydrocarbons at the 2 ppb level by Roeraade (120).

Because much of the work has been done on packed or glass capillary columns coated with a stationary phase, the solvents have been restricted to alkanes, diethyl ether, methylene chloride and carbon disulfide. With the introduction of more stable stationary phases (cross-linked), solvent extraction with analysis by GC using other solvents offers new areas of research that can be explored.

DIRECT GAS CHROMATOGRAPHIC ANALYSIS

Because direct aqueous injection appears to be the simplest method, requiring no sample preparation, much research as been reported in this area. In the early years of GC analysis MacAulife packed firebrick and Ascarite into the injection port to separate dissolved hydrocarbons from water (121). He was able to make three 50 μL injections before replacing the Ascarite packing material. Mieure and Dietrich used GC columns packed with Chromsorb 102 (1/8" x 4") for the analysis of surface waters. Recoveries of model compounds varied from less than 5% for methanol to 85% for phenol, 79% for pyridine, and 97% for o-ethylphenol (122). More recently quantitative analysis of 68 polar compounds from 10 chemical classes at the ppm level by direct aqueous injections on a column packed with Tenax GC has been reported (123).

Steam as carrier gas for preparative scale separation of close isomers and isotope-substituted compounds has been reviewed by Zabokritsky and co-workers (124). Rudenko *et al.* used ammonia, sulfur dioxide, freons, and steam to separate fatty acids, amines, sterols and alkaloids with flame ionization detection. Nonaka reported that the retention time of the analytes were reduced using steam as carrier gas in comparison with nitrogen and the peak shapes were improved (125,126).

Recently Zlatkis used a cross-linked fused silica column to concentrate 5 ng of benzaldehyde, 2-octanone, 5-nonanone, 2-decanone, and 2-undecanone from 400 μL of water (127). Then the column was used as the analytical column. Meharan used a capillary column to concentrate organohalogen compounds in water (128). Hussein and MacKay recycled 20 mL of aqueous solution containing aromatic test compounds through a column (24' x 0.186" I.D., 19 μm thick, SE-30) four times (129). When solutions containing sodium sulfate were used, the column was rinsed with distilled water. Recovery (0.1% to 114%) was dependent upon column length, residence time of the sample in the column, sample size and concentration. The analytes were thermally desorbed onto Tenax GC and thermally desorbed from the Tenax. A packed column was used for GC quantitation.

Grob summarized the problems of direct aqueous injections (130). The possible deposition of nonvolatile materials on the inlet section of the capillary column and possible hydrolysis of the stationary phase have a detrimental effect on column performance.

Lee and co-workers warned of serious consequences of too large a sample volume resulting in tailing peaks, dissolution of the stationary phase, retention time shifts and non-linear splitting (discrimination) at the injection port. An equation was given to calculate the maximum volume

of sample (V_{max}) which will increase peak variance by more than a fraction (θ):

$$V_{max} = 2.72\theta(1+k)(Lhd_c).$$

In this equation k is the capacity factor, L is the length of the column, h is the reduced plate height (plate height/diameter) and d_c is the diameter of the column (131). From this equation it is evident that the maximum volume that can be injected into a GC column is a complex function of column length, column diameter, film thickness, column efficiency and retention time of the analyte (132).

Adding to the confusion are the puzzling effects of injection port design, speed of injection, and type of solvent used on peak shape. In some cases, peak shape was so distorted that splitting of the peaks was noted. In some way the eluting band of analyte was separated into two parts. Other authors have studied the effects of repeated injections of large quantities of water and other solvents on the performance of a GC column (133-135). After 50 to 100 injections (2 μL) of water, Grob noticed column damage (134).

Grob and co-workers reviewed several methods of injecting large samples into a GC column. When large samples were injected into a capillary column, the liquid formed a thin film. The volatile solutes migrated behind the solvent layer and were release immediately after the

solvent. The nonvolatile solutes with high boiling points were deposited on the walls of the capillary. Hence a retention gap (capillary that is uncoated or coated with a different phase) placed before the analytical column was proposed. In this way the solutes with high boiling points were quickly focused at the head of the analytical column by slightly raising the temperature. The technical aspects, such as, wettability of the retention gap, surface (phenyldimethylsilylated phase recommended for water and methanol) of the retention gap, required length of the retention gap, symptoms of poor connection between the retention gap and the analytical column, cleaning the retention gap, choice of solvent, initial temperature and rate of temperature increase, proper use of fused silica needle for injection and rate of injection were discussed. Preparation of the retention gap was also discussed because the authors felt that there were too many parameters (type of stationary phase for given solvent, film thickness, deactivation, length and inner diamter) that required optimization for successful injections of large samples. A summary of recommended conditions was given. For methanol 50 μL was injected into a 15 meter retention gap. No specific instruction were given for injection of large water samples (136).

Wide-bore thick film (5 μm, methyl silicone) capillary columns were used in the analysis of compounds with low retention volumes, such as, ethane, ethylene, propene, and butenes (137).

Other developments of interest in gas chromatography include "Super Caps" available from Quadrex Corp. (P. O. Box 3881, New Haven, CT 06525). Aluminum was bonded to the exterior of the capillary column instead of the polyimide coating. The columns exhibited excellent heat transfer and was heated to high temperature (500^{o}C).

Gas chromatography on a chip has been reported by several authors (138-140). The capillary column (1.5 meters) was etched on a silica chip. The entire gas chromatograph (excluding gas supply) was 5 cm in diameter.

DERIVATIZATION

Derivatization is used to improve detection or chromatography or both. There is a vast number of work in the area of chemical derivatization for organic analysis (141-144). Some of the qualities of a good derivatization procedure are (1) the reaction of analyte and reagent yield reproducible, preferrably quantitative amounts of product, (2) the reaction is rapid, usually complete in less than one hour and (3) the products are stable enough to allow sufficient time for analysis.

In gas chromatography highly polar compounds that exhibit severe tailing, such as, alcohols, acids, and amines are converted to ethers, esters, and tertiary amines (145). Because electron capture detection offers very high sensitivity, the analytes are converted to halognated derivatives. Other methods are used to increase selectivity and thermal stability or improve separation of the analytes. Subtraction methods are used to precipitate or destroy a functional class of compounds from the sample before they enter the GC column. An example is the removal of pyridine using copper salts by Chriswell and co-workers (146).

In liquid chromatography the analytes are derivatized with chromophores (usually conjugated systems) that increase the ultraviolet extinction coefficient or alter the maximum

absortion wavelength, so that the analyte can be detected without interference from the solvent. Highly rigid cyclic derivatives are prepared for fluorescence detection (147). Fluorescence detection offers high selectivity because it is possible to vary both excitation wavelength and emission wavelength.

Gandelmann and Birks used the photochemical reduction of anthraquinone (in the mobile phase) with aliphatic alcohols (4 ng), aliphatic amines and compounds with allylic and benzylic hydrogen (C-H bond less than 95 kcal/mole) to hydroquinone. The resulting hydroquinone was detected by a fluorometer (148). Rosenfeld et al. impregnated XAD-2 with benzyl and pentafluorobenzyl bromide to simultaneously extract and derivatize acids in water (149). Krull et al. reviewed derivatization for improved analyte detection (precolumn and post column chemical, photochemical, enzymic oxidative reactions) in liquid chromatography using electrochemical detection (150).

New derivatives that have been reported recently include formation of p-bromophenylacyl esters with acids (151), formation of oxazolidine derivative with formaldehyde (152), and reaction of acetaldehyde with diazotized orthanilic acid (153).

If the derivatization procedure is rapid, then an on-line procedure of analysis can be obtained. Bed reactor and

reaction loops have been proposed for reactions that require longer reaction times (154).

Tanaka and Fritz determined acetic, propionic, butyric, valeric, formic, maleic, oxalic, fumaric, malonic, tartaric, citric and succinic acids at 0.2 to 5 ppm level in drinking water, tap water, surface water and agal suspension in buffered solution (155). A conductivity detector was used for this ion exclusion experiment.

There is an abundance of derivatization procedures but the procedures are appropriate for a given class of compounds and in some cases, for only a single compound. Considerable effort would be required to optimize and test the procedures for low-molecular alcohols, ethers, acids, esters, amines, etc. at trace levels.

REFERENCES

1. Beyermann, K. "Trace Organic Analysis"; Chalmers, R. A., Translation Ed.; Ellis Horwood Limited: Chichester, 1984.

2. Grob, R. L. "Modern Practice of Gas Chromatography"; 2nd Edition; John Wiley & Sons: New York, 1985; Chapter 10, p. 478.

3. Jennings, W. "Gas Chromatography with Glass Capillary Columns"; 2nd Edition; Academic Press: New York, 1980; Chapter 12, p. 203.

4. Onuska, F. I.; Karasek, F. W. "Open Tubular Column Gas Chromatography in Environmental Sciences"; Plenum Press: New York, 1984; Chapter 5, p. 121.

5. Poole, C. F.; Schuette, S. A. "Contemporary Practice of Chromatography"; Elsevier: Amsterdam, 1984; Chapter 7, p. 429.

6. Novotny, M. In "Analytical Aspects of Environmental Chemistry"; Natusch, D. F. S.; Hopke, P. K.; Eds.; John Wiley & Sons: New York, 1983; p. 61.

7. Marr, I. L.; Cresser, M. S. "Environmental Chemical Analysis"; International Textbook Company: New York, 1983; p. 37.

8. Lee, M. L.; Yang, F. J.; Bartle, K. D. "Open Tubular Column Gas Chromatography. Theory and Practice"; John Wiley & Sons: New York, 1984; p. 174.

9. Anal. Chem. 1984, 56. 1R.

10. Anal. Chem. 1985, 57, 46R.

11. Hertz, H. S.; May, W. E.; Wise, S. A.; Chesler, S. N. Anal. Chem. 1978, 50, 428A.

12. Karasek, F. W.; Clement, R. E.; Sweetmean, J. A. Anal. Chem. 1981, 53, 1050A.

13. Frei, R. W. J. Chromatogr. 1979, 165, 75.

14. DiCesare, J. L.; Ettre, L. S. J. Chromatogr. 1982, 251, 1.

15. Nunez, A. J.; Gonzales, L. F.; Janak, J. J. Chromatogr. 1984, 300, 127.

16. Novak, J. In "Advances in Chromatography"; Giddings, C. C.; Grushka, E.; Cazes, J.; Brown, P. R.; Eds.; Marcel Dekker, Inc.: New York, 1983; Vol. 121, p. 303.

17. Junk, G. A.; Richard, J. J.; Grieser, M. D.; Witiak, D.; Witiak, J. L.; Arguello, M.; Vick, R.; Svec, H. J.; Fritz, J. S.; Calder, G. V. J. Chromatogr. 1974, 99, 745.

18. Josefsson, C. M.; Johnston, J. B.; Trubey, R. Anal. Chem. 1984, 56, 7648.

19. Tateda, A.; Fritz, J. S. J. Chromatogr. 1978, 152, 329.

20. Junk, G. A.; Richard, J. J. Anal. Chem. 1986, 58, 723.

21. Richard, J. J.; Fritz, J. S. J. Chromatogr. Sci. 1980, 18, 35.

22. Kaczvinsky, J. R., Jr.; Saitoh, K.; Fritz, J. S. Anal. Chem. 1983, 55, 1210.

23. Struber, H. A.; Leenheer, J. A. Anal. Chem. 1983, 55, 111.

24. Edgerton, T. R.; Moseman, R. F.; Lores, E. M.; Wright, L. H. Anal. Chem. 1980, 52, 1774.

25. Thurman, E. M.; Malcolm, R. L.; Aiken, G. R. Anal. Chem. 1978, 50, 775.

26. Giabbai, M.; Roland, L.; Ghosal, M.; Reuter, J. H.; Chian, E. S. K. J. Chromatogr. 1983, 279, 373.

27. Prippel P.; Maasfeld, N.; Kettrup, A. Int. J. Environ. Anal. Chem. 1985, 23, 97.

28. Gibbs, J.; Najar, B.; Suffet, I. H. "Water Chlorination: Chemical and Environmental Impact on Health Effects"; Jolley, R. L., Ed.; Proc. Conf., 5th, 1984; Lewis: Chalsea, MI, 1985; 1099.

29. Grob, K.; Grob, K., Jr.; Grob, G. J. Chromatogr. 1975, 106, 299.

30. Nunez, A. J.; Gonzalez, L. F.; Janak, J. J. Chromatogr. 1984, 300, 1.

31. Blanchard, R. D.; Hardy, J. K. Anal. Chem. 1985, 57, 2349.

32. Neu, H.-J.; Merz, W.; Panzel, H. J. High Resolut. Chromatogr. Chromatogr. Commun. 1982, 5, 1033.

33. Smith, L. M. Anal. Chem. 1981, 53, 2152.

34. Van Tessel, S.; Amalfitano, N.; Narang, R. S. Anal. Chem. 1981, 53, 2130.

35. Werkhoven-Goewie, C. E.; Brinkman, U. A. Th.; Frei, R. W. Anal. Chem. 1981, 52, 2072.

36. Nielen, M. W. F.; Brinkman, U. A. Th.; Frei, R. W. Anal. Chem. 1985, 57, 806.

37. Picker, J. E.; Sievers, R. E. J. Chromatogr. 1981, 217, 275.

38. Barr, R. M. In "Inclusion Compounds. Structural Aspects of Inclusion Compounds Formed by Inorganic and Organometallic Host Ligands"; Atwood, J. L.; Davies, J. E. D.; MacNicol, O. D.; Eds.; Academic Press: London, 1984; Vol. 1, p. 190.

39. Raymond, A.; Guichon, J. J. Chromatogr. 1975, 13, 173.

40. Roberts, C. W. In "The Properties and Applications of Zeolites"; Townsend, R. P., Ed; Special Publication No. 33; The Chemical Society: London, 1980; p. 109.

41. Haggin, J. Chem. & Engr. News Dec. 12, 1982; p. 9.

42. Dessau, R. M. In "Adsorption and Ion Exchange with Synthetic Zeolites"; Flank, W. H., Ed.; ACS Symposim Series 135; American Chemical Society: Washington, DC, 1980; Chapter 6, p. 123.

43. Olson, D. H.; Haag, W. O.; Lago, R. M. J. Catalysis 1980, 61, 390.

44. Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. Nature 1978, 271, 9.

45. Chriswell, C. D.; Gjerde, D. T.; Shultz-Sibbel, G. M. W.; Fritz, J. S.; Ogawa, I. "Evaluation of the Adsorption Properties of Silicalite for Potential Application in Isolating Polar Low-Molecular-Weight Organics from Drinking Water", Report (1983) EPA-600/1 -83-001. Order No. PB83-148501. National Technical Information Service, Springfield, VA 22161.

46. Shultz-Sibbel, G. M. W.; Chriswell, C. D.; Fritz, J. S.; Coleman, E. W. Talanta 1982, 29, 447.

47. Chriswell, C. D.; Gjerde, D. T. Anal. Chem. 1982, 54, 1911.

48. Burkholder, H. "Recovery of Ethanol from a Molecular Sieve Using Dielectric Heating"; IS-J 1436; Ames Laboratory Document Library: Ames, IA 50011.

49. Milestone, N. B.; Bibby, D. M. J. Chem. Tech. Biotechnol. 1981, 31, 932.

50. Hoering, T. C.; Freeman, D. H. J. Chromatogr. 1984, 316. 333.

51. Ioffe, B. V.; Vitenberg, A. G. "Head-Space Analysis and Related Methods in Gas Chromatography"; Mamontov, I. A., Translator; John Wiley & Sons: New York, 1984.

52. McNally, M. E.; Grob, R. L. Am. Lab. (Fairfield) 1985, 17(1), 20.

53. McNally, M. E.; Grob, R. L. Am. Lab. (Fairfield) 1985, 17(2), 106.

54. Carlucci, G.; Airoldi, L.; Fanelli, R. J. Chromatogr. 1984, 287, 425.

55. Bellar, T. A.; Lichtenberg, J. J. J. Am. Water Works Assoc. 1974, 66, 739.

56. Drozd, J.; Vodakova, Z,; Novak, J. J. Chromatogr. 1986, 354, 47.

57. Gershey, R. M. Limnol. Oceanogr. 1983, 28, 395.

58. Gregoire, J. In "Proceedings of the Sixth International Symposium on Capillary Chromatgraphy"; Sandra, P., Ed.; Heuthig: Heidelberg, 1985; p. 353.

59. Van Wijk, R. J. Chromatogr. Sci, 1970, 8, 418.

60. Pellizzari, E. D.; Krost, R. J. Anal. Chem. 1984, 56, 1813.

61. MacLead, G.; Ames, J. M. J. Chromatogr. 1986, 335, 393.

62. Raymond, A.; Guiochon, J. J. Chromatogr. 1975, 13, 173.

63. Murray, K. E. J. Chromatogr. 1977, 135, 49.

64. Rakshieva, N. R.; Wicar, S.; Novak, J.; Janak, J. J. Chromatogr. 1974, 91, 59.

65. Simpson, R. F. Chromatographia 1979, 12, 733.

66. Ligocki, M. P.; Pankow, J. F. Anal. Chem. 1985, 57, 1138.

67. Zlatkis, A.; Ghaoui, L.; Weisner, S.; Shanfield, H. Chromatographia 1985, 19, 343.

68. Vejrosta, J.; Mikesova, M.; Novak J. J. Chromatogr. 1986, 354, 59.

69. Pellizzari, E. D.; Sheldon, L. S.; Bursey, J. T.; Hargrove, W.; Michael, L. C.; Zweindinger, R. A. "Experimental Development of the Master Analytical Scheme for Organic Compounds in Water: Part 1. Text"; Report (1985) EPA/600/4-85/007a; Order No. PB85-153096. National Technical Information Service, Springfield, VA 22161.

70. Simmonds, P. G. J. Chromatogr. 1984, 287, 117.

71. Novak, J.; Zlutcky, Z.; Kubelka, V.; Mostecky, J. J. Chromatogr. 1973, 76, 45.

72. Warner, J. M.; Beasley, R. K. Anal. Chem. 1984, 56, 984.

73. Otson, R.; Williams, D. T. Anal. Chem. 1982, 52, 984.

74. Voznakova, Z.; Popl, M.; Gerka, M. J. Chromatogr. Sci. 1978, 16, 123.

75. Grob, K.; Habich, A. J. Chromatogr. 1985, 321, 45.

76. Brettell, T. A.; Grob, R. L. Am. Lab. (Fairfield) 1985, 17(10), 19.

77. Brettell, T. A.; Grob, R. L. Am. Lab. (Fairfield) 1985, 17(11), 50.

78. Westendorf, R. G. Am. Lab. (Fairfield) 1981, 13(10), 88.

79. Liebman, S. A.; Wampler, T. P.; Levy, E. J. "Proceddings: National Symposium in Pollutant Monitoring of Ambient Air and Stationary Sources"; Report (1983) EPA 600/9-83-007. United States Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

80. Chiba, K.; Haraguchi, H. Anal. Chem. 1983, 55, 1504.

81. Spraggins, R. L.; Oldham, R. G.; Prescott, K. J.; Baughman, K. J. In "Advances in the Identification & Analysis of Organic Pollutants in Water"; Keith, L., Ed.; Ann Arbor Press: Ann Arbor, 1981; Vol. 2, p. 747.

82. Ramstad, T. J.; Nicholson, L. W.; Anal. Chem. 1985, 57, 1191.

83. Ramstad, T. J.; Nestrick, T. J.; Peters, T. Am. Lab. (Fairfield) 1981, 13(7), 65.

84. Kopfler, F. C.; Melton, K. G.; Lingg, R. D.; Coleman, W. E. In "Identification and Analysis of Organic Pollutants in Water"; Keith, L. H., Ed.; Ann Arbor Science: Ann Arbor, 1976; Chapter 6.

85. Ryan, J. P.; Fritz, J. S. In "Advances in the Identification & Analysis of Organic Pollutants in Water"; Keith, L. H., Ed.; Ann Arbor Science: Ann Arbor, 1981; Vol. 1, p. 317.

86. Hyde, W. G. Ph. D. Dissertation, Iowa State University, Ames, IA, 1986.

87. Verweij, A.; Van Liempt-Van Houten, M. A.; Boter, H. L. Int. J. Environ. Anal. Chem. 1985, 21, 63.

88. Kuo, P. P. K.; Chian, E. S. K.; DeWalle, F. B.; Kim, J. H. Anal. Chem. 1977, 49, 1023.

89. Leuenberger, C.; Pankow, J. F. Anal. Chem. 1984, 56, 2518.

90. Freeman, R. R.; Lautamo, R. M. A.; Am. Lab. 1986, 18(5), 60.

91. Curvers, J.; Noy, T.; Cramers, C.; Rijks, J. J. Chromatogr. 1984, 289, 171.

92. Grob, K. J. Chromatogr. 1973, 84, 255.

93. Marchand, M.; Capraid, J. C. Analusis 1983, 11, 216.

94. Gschwend, P. M.; Zafiriou, O. C.; Fauzi, R.; Mantora, C.; Schwarzenbach R. P.; Gagosian R. B. Environ. Sci. Technol. 1982, 16, 31.

95. Westendorf, R. G. Am. Lab. (Fairfield) 1982, 14(12), 44.

96. Saevenhed R.; Boren, H.; Gimvall, A.; Tjeder, A. Water Sci. Technol. 1983, 15, 138.

97. Boren, H.; Gimvall, A.; Palmborg, J.; Saevenhed, R.; Wigilius, B. J. Chromatogr. 1985, 348, 67.

98. Richard, J. J.; Junk, G. A. Anal. Chem. 1984, 55, 1625.

99. Godefroot, M.; Sandra, P.; Verzele, H. J. Chromatogr. 1981, 203, 325.

100. Godefroot, M.; Stechele, M.; Sandra, P.; Verzele, H. J. High Resolut. Chromatogr. Chromatogr. Commun. 1982, 5, 75.

101. Nunez, A. J.; Bemelmans, J. M. H. J. Chromatogr. 1984, 294, 361.

102. Onuska, F. I.; Terry, K. A. Anal. Chem. 1985, 54, 801.

103. Rijks, J.; Curves, J.; Noy, T.; Cramers, C. J. Chromatogr. 1983, 279, 395.

104. Amin, T. A.; Narang, R. S. Anal. Chem. 1985, 57, 648.

105. Kozloski, R. P. J. Chromatogr. 1985, 346, 408.

106. Haitt, M. H. Anal. Chem. 1983, 55, 506.

107. Peters, T. L. Anal. Chem. 1980, 52, 211.

108. Janda, V.; Krijt, K. J Chromatogr. 1984, 283, 309.

109. Bukee, G. K.; Long, D. E. In "Developments in Chromatography"; Knapman, C. E. H., Ed.; Applied Science Publishers Ltd: London, 1980; Vol. 2, p. 124.

110. Kuo, P. P. K.; Chian, E. S. K.; DeWalle, F. B. Water Research 1977, 11, 1005.

111. Grob, K.; Grob, K., Jr.; Grob, G. J. Chromatogr. 1975, 106, 299.

112. Junk, G. A.; Ogawa, I.; Svec, H. J. In "Advances in the Identification & Analysis of Organic Pollutants in Water"; Keith, L. H., Ed.; Ann Arbor Science: Ann Arbor, 1981; Vol. 1, p. 281.

113. Thurn, K. E.; Oberholtzer, J. E. In "Advances in the Identification & Analysis of Organic Pollutants in

Water"; Keith, L. H., Ed,; Ann Arbor Science: Ann Arbor, 1981; Vol. 1, p. 283.

114. Thomsason, M. M.; Bertsch, W. J. Chromatogr. 1983, 279, 383.

115. Zolteck J.; Earle, J. F. K. Report (1985) AFESC/ESL-TR-84-84; Order No. AD-A150 882/9/GAR. National Technical Information Service, Srpingfield, VA 22161.

116. Peters, T. L. Anal. Chem. 1982, 54, 1913.

117. Colgrove, S. G.; Svec, H. J. Anal. Chem. 1981, 53, 1737.

118. Eichelberger, J. W.; Kerns, E. H.; Olynyk, P.; Budde, W. L. Anal. Chem. 1983, 55, 1471.

119. Castello, G.; Gerbino, T. C.; Kanitz, S. J. Chromatogr. 1986, 351, 165.

120. Roeraade, J. J. Chromatogr. 1985, 330, 263.

121. MacAuliffe, C. J. Phys. Chem. 1966, 70, 1267.

122. Mieure, J. P.; Dietrich, M. W. J. Chromatogr. Sci. 1973, 11, 559.

123. Knuth, M. L.; Hoglund, M. D. J. Chromatogr. 1984, 285, 153.

124. Zabokritsky, M. P.; Chizhkov, V. P.; Rudenko, B. A. J. High Resolut. Chromatogr. Chromatogr. Commun. 1985, 8, 170.

125. Nonaka, A. Anal. Chem. 1972, 44, 271.

126. Nonaka, A. Anal. Chem. 1973, 45, 483.

127. Zlatkis, A.; Wang, F.-S.; Shanfield, H. Anal. Chem. 1983, 55, 1848.

128. Meharan, M. J. Chromatogr. Sci. 1985, 23, 5468.

129. Hussein, M. M.; MacKay, D. A. J. Chromatogr. 1982, 243, 43.

130. Grob, K. J. Chromatogr. 1984, 299, 1.

131. Lee, M. L.; Yang, F. J.; Bartel, K. D. "Open Tubular

Column Gas Chromatography. Theory and Practice"; John Wiley & Sons: New York, 1984; p.42.

132. Ettre, L. S. Chromatographia 1984, 18, 477.

133. Schomberg, G.; Bastian, E.; Behlau, H.; Husmann, H.; Weeks, F.; Oreans, M.; Muller, F. J. High Resoult. Chromatogr. Chromatogr. Commun. 1984, 7, 4.

134. Jennings, W.; Meharan, M. F. J. Chromatogr. Sci. 1986, 24, 34.

135. Etweiler, F. J. High Resolut. Chromatogr. Chromatogr. Commun. 1985, 8, 436.

136. Grob, K., Jr.; Karrer, G.; Riekkola, M.-L. J. Chromatogr. ("Chromatographic Reviews") 1985, 334, 129.

137. Adland, E. R.; Davies, R. E. Chromatographia 1985, 20, 195.

138. Angell, J. B.; Terry, S. C.; Bortle, P. W. Sci. Am. 1983, 248, 44.

139. Hagiwara, S.; Takayama, Y. Jpn. Kokai Tokkyo Koho JP, 60,142,255 (85,142,253).

140. Hagiwara, S.; Takayama, Y. Jpn. Kokai Tokkyo Koho JP, 60,142,254 (85,142,254).

141. Frei, R. W.; Lawrence J. F. "Chemical Derivatization in Analytical Chemistry"; Plenum Press: New York, 1978.

142. Knapp, D. P. "Handbook of Analytical Derivatization Reactions"; John Wiley & Sons: New York, 1979.

143. Crippen, R. C. "Identifying Pollutants and Unknowns"; Pergamon Press: New York, 1983.

144. Drozd, J. "Chemical Derivatization in Gas Chromatography"; Elsevier Scientific Publishing Company: Amsterdam, 1981.

145. Jennings, W. "Gas Chromatography with Glass Capillary Columns"; 2nd Edition; Academic Press: New York, 1980.

146. Chriswell, C. D.; Kissinger, L. D.; Fritz, J. S. Anal. Chem. 1976, 48, 1123.

147. Olsen, E. D. "Modern Optical Methods of Analysis"; McGraw-Hill Book Company: New York, 1975; p. 387.

148. Gandelmann, M. S.; Birks, J. W; Anal. Chem. 1982, 54, 2131.

149. Rosenfeld, J. M.; Marieka-Russell, M.; Phatak, A. J. Chromatogr. 1984, 283, 127.

150. Krull, I. S.; Selavka, C. M.; Duda, C.; Jacobs, W.; J. Liq. Chromatogr. 1985, 8, 2845.

151. Kawamura, K.; Kaplan, I. Anal. Chem. 1984, 56, 1616.

152. Kennedy, E. R.; Hill, R. H., Jr. Anal. Chem. 1982, 54, 1739.

153. Flamerz, S. Anal. Chem. 1982, 54, 1734.

154. Frei, R. W. In "Analytical Techniques in Environmental Chemistry 2"; Albaiges, J.; Ed.; Pergamon Press: Oxford, 1982; p. 193.

155. Tanaka, K.; Fritz, J. S. J. Chromatogr. 1986, 361, 151.

SECTION I. DETERMINATION OF LOW-MOLECULAR WEIGHT ALDEHYDES AND KETONES IN WATER BY HPLC

INTRODUCTION

The analytical technology for preconcentration of trace organic compunds from aqueous samples has improved tremendously in recent years. However, the determination of very low concentrations of volatile, hydrophilic organic compounds in water has been carried out only with great difficulty. The determination of polar organic compounds of low-molecular weight in drinking water is of importance in order to better understand the complicated chemistry involved in the chlorination of water. Coleman et al. believe that mutagenic organic compounds can be produced by chlorination of humic matter that occurs naturally in water (1). Chloroacetone was included in the list of compounds that might be produced.

Organic compounds in drinking water, except for humic matter, usually are found in such low concentrations that a concentration step is needed prior to analysis (2). With recent advances in capillary columns used in gas chromatography, direct injection of aqueous samples has become a viable method for trace analysis of some organic compounds with a favorable FID (flame ionization detection) response (3,4). However, Richard and Junk (5) indicated that a concentration of at least 1 ppm is necessary for the direct injection of samples containing low-molecular weight polar compounds.

The usual methods for preconcentration of organic compounds, such as, concentration on XAD-2 (6) or Tenax (7,8) do not work for small, polar molecules. These compounds can sometimes be sorbed on activated charcoal, but desorption has not been reproducible (9). While compounds, such as, aniline and chlorophenols have been reported to be effectively sorbed by reversed-phase LC (liquid chromatography) columns (10, 11), many others are not taken up. Multiple fractional distillation or steam distillation (12) have been used for certain specialized cases.

A novel method for accumulation of aldehydes and ketones was reported by Takami et al. (13) in which an ion-exchange column loaded with 2,4-dinitrophenylhydrazine was employed. The authors were able to determine low concentrations of aldehydes and ketones in rain water and river water, although the method was not applied to drinking water.

The physical and chemical characteristics of a zeolite, ZSM-5, have been reported (14). A unique property of ZSM-5 is that it has channels that are about 5 Å to 5.6 Å in diameter. Organic molecules of the proper size and shape are able to invade these channels and these organic molecules are retained due to the unusual hydrophobicity of ZSM-5. Recently investigations with Silicalite (15,16), a member of the ZSM-5 substitutional series (17), have reported that Silicalite has high capacity for low-molecular weight polar organic compounds.

The use of the zeolite, ZSM-5, for the preconcentration of polar organic compounds from aqueous samples is examined. Low-molecular weight aldehydes and ketones, with the exception of formaldehyde, are strongly retained by the zeolite and can be subsequently eluted by a small volume of methanol or acetonitrile. The effluent is then reacted with 2,4-dinitrophenylhydrazine and the resulting derivatives are then separated by conventional liquid chromatography.

EXPERIMENTAL

Solvents and Reagents

Water was produced using the Barnstead NANOPure II System (Barnsted, Division of SYBRON Corp., Boston, MA 02132). All organic solvents were distilled in glass UV grade (Burdick and Jackson laboratories Inc., Muskegon, MI 49442). Unless otherwise specified, these solvents were used as received.

Acetonitrile and pentane were further purified by adding 0.5 mL of a dilute solutin of 2,4-dinitrophenylphydrazine and HCl to 100 mL of acetonitrile or pentane and then distilling. In each case 75 mL of distillate was collected.

Test Solutions

For breakthrough experiments, 100 μL of the aldehyde or ketone to be tested was dissolved in 100 mL of pure water. For accumulation experiments, a stock solution containing 1 μL of aldehyde or ketone in 10 mL of water was diluted to the desired concentration with pure water.

Preparation of ZSM-5 Column

The zeolite, ZSM-5, was in the ammonium form and was used as received. However, classification of particle size was accomplished by slurrying 1 g of the zeolite with 60 mL

of water and decanting the fine particles that has not settled after 15 min. This process was repeated twice. The remaining zeolite was collected and dried overnight.

For capacity experiments dry zeolite was added to a small glass tube and held in place by a plug of glass wool. For accumulation of carbonyl compounds from aqueous samples, a 4.6 mm by 5 cm stainless steel column was packed with about 0.5 g of the dry zeolite by the tap and fill method (18). After use, the column was filled with methanol or acetonitrile for storage.

Chromatographic Instruments

A Tracor 550 Gas Chromatograph (Austin, TX 78721) with flame ionization detection (FID) was used. For aqueous injections a 1 mm I.D. x 6 ft glass column (made by house glass shop) was packed with 50-80 mesh Porapak Q (Supelco, Inc., Belefonte, PA 16823). For hexane and methylene chloride solutions a 12.5 m x 0.2 mm I.D. dimethyl silicone capillary column (Hewlett Packard, Canonga Park, CA 91304) was used.

The loading apparatus consisted of a Milton Roy minipump, pressure gauge, pressure relief valve, Valco injector and a 2 μm solvent filter.

The analytical liquid chromatograph was a Spectra-Physics 8000 (Santa Clara, CA 95051) with fixed (254 nm)

wavelength detector or a Tracor 970A variable wavelength (UV-VIS) detector. A 10 μL sample loop was used with a 4.5 mm X 5 cm column filled with 3 μm spherisorb C_{18} ("Little Champ").

Procedure for Determination of Capacity

Breakthrough curves were obtained by passing an aqueous solution containing 1 mg analyte/mL solution through 0.5 g ZSM-5. Using gravity flow at ambient temperature, fractions at 1 mL intervals were collected and analyzed by GC on Porapak Q.

Procedure for Determining Aldehydes and Ketones in Aqueous Samples

The ZSM-5 column was washed with 3 mL of purified acetonitrile, which was added by means of a hand-held syringe. Then 200 mL of pure water was pumped through the column to remove the acetonitrile. A water sample of appropriate volume (100 mL for recovery experiments, 1 to 3 L for drinking water) was passed through the column at a flow rate of approximately 4 mL/min.

The ZSM-5 column was removed from the loading apparatus and eluted with 3 mL of purified acetonitrile directly into the bottom of a centrifuge tube containing 2,4-dinitrophenylhydrazine (DNP) for derivatization. The tube

contained 0.5 to 0.7 mL of a solution of 1.7 mg of DNP per milliliter of purified acetonitrile. Perchloric acid catalyst (0.02 mL of 1 M aqueous solution) was added just before the elution. The ZSM-5 column was immediately washed with water to avoid later plugging.

After 15-20 min reaction with the DNP reagent, 50 mL of water was added and the resulting solution was extracted twice with 10 mL portions of purified pentane. Each pentane layer was extracted twice with 15 mL of water to remove traces of unreacted DNP. The combined pentane extracts were dried over anhydrous sodium sulfate. The pentane solution was then concentrated in a Kuderna-Danish apparatus and then carefully evaporated to dryness.

The residue was dissolved in 1 to 2 mL of 50% acetonitrile-50% water. Nitrobenzene or acenaphthene was used as an internal standard, by addition to the DNP solution used for derivatization. A 10 μL aliquot of the 50% acetonitrile solution of the residue was injected into the HPLC apparatus. Gradient elution was used, going from 40% methanol (60% water) to 70% methanol (30% water) over 30 min and continuing to 100% methanol over the next 25 min. The temperature was 25^{o}C and the flow rate was 1 mL/min. Quantitation was based either on peak height or peak area using external standards at 254 nm, or at 331 nm if spectral interferences were encountered at 254 nm.

RESULTS AND DISCUSSION

Capacity Experiments

Dilute aqueous solutions (1mg/mL) of several aldehydes and ketones were passed through a column of ZSM-5 to ascertain the feasibility of using this material to accumulate carbonyl compounds. Each solution was passed through the ZSM-5 column at gravity flow until breakthrough occurred. Results are given in Figure 1.

The capacity of the zeolite for aldehydes and ketones increased with higher molecular weight. ZSM-5 showed good retention for all of the carbonyl compounds tested with the exception of formaldehyde and acetaldehyde. From the data in Figure 1, the estimated distribution coefficients ranged from 1.2 for formaldehyde to 100 for 2-pentanone. Exploratory experiments showed that smaller amounts of most aldehydes and ketones were well retained by the zeolite column, even after washing with rather large volumes of water.

Elution

Several investigators have selected derivatization with 2,4-dinitrophenylhydrazine (DNP) and liquid chromatographic separation for quantitative determination of aldehydes and ketones (19,20). The improved derivatization method of

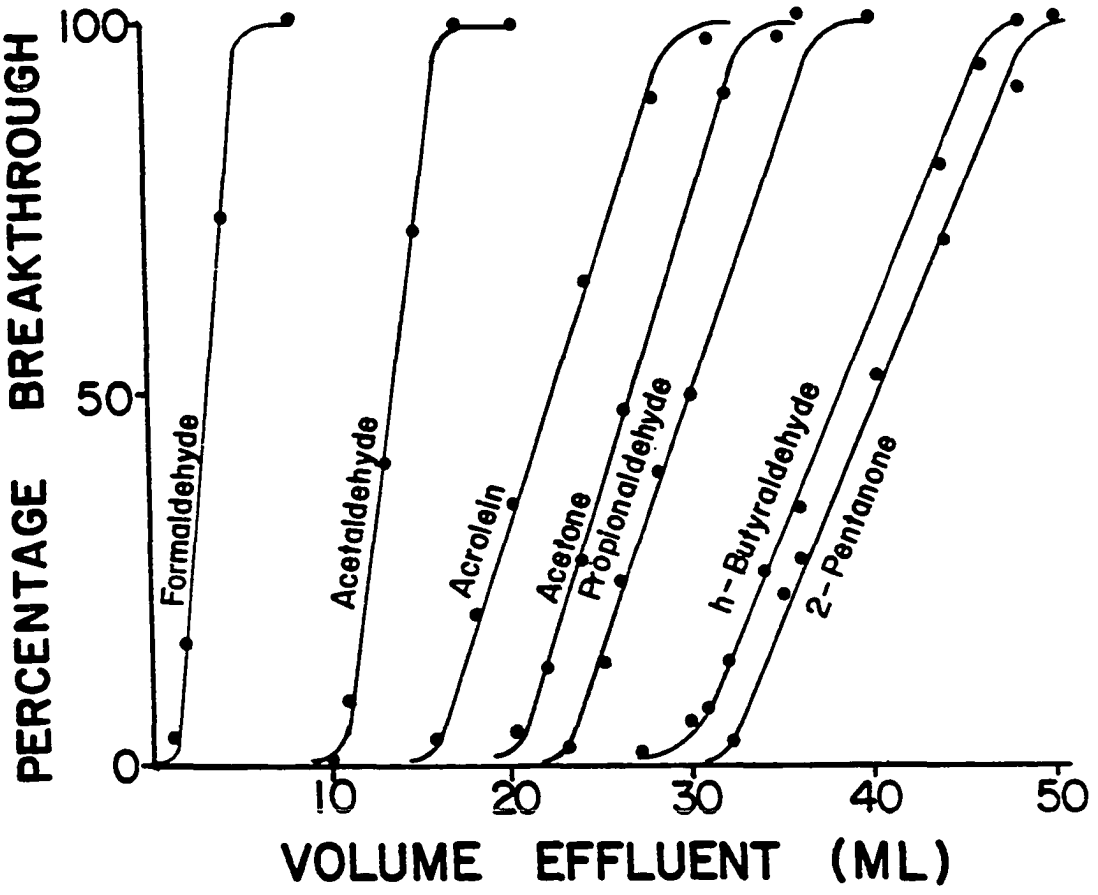


Figure 1. Breakthrough curves of aldehydes and ketones

Aqueous solutions containg 1 mg/mL of carbonyl compounds were passed through a mini-column containing 0.50 g of ZSM-5.

Lipari and Swarin (21) was convenient and effective. An on-line derivitization and elution procedure was investigated first. The ZSM-5 column containing the sorbed carbonyl compounds from an aqueous sample was connected to a liquid chromatographic column. An elution gradient beginning with 100% water and ending with 100% methanol was started. Immediately after starting the gradient, a DNP reagent with catalyst was injected to react with the carbonyl compounds on the zeolite column. However, this method gave unfavorable results, possibly because of insufficient reaction time of DNP with the sorbed carbonyl compounds.

The next approach was to elute the carbonyl compounds from the zeolite column with an organic solvent and then form 2,4-dinitrophenylhydrazones in a post-column reactor. Experimental work demonstrated that all of the carbonyl compounds studied could be completely eluted from the ZSM-5 column with a small volume of either methanol or acetonitrile. Acetonitrile was selected because a smaller volume was required for elution and because acetonitrile was found to contain fewer carbonyl impurities than methanol.

Derivatization of Carbonyl Compounds and Solvent Extraction of the 2,4-Dinitrophenylhydrazones

Reaction of the aldehydes and ketones (eluted with acetonitrile) with the DNP was complete within a few minutes. During the elution step it was found necessary to run the acetonitrile effluent directly into the DNP solution, which was contained in a small test tube. If this was not done losses were sometimes noted for volatile compounds, such as, acetone.

When the derivatization reaction was complete, it was necessary to separate the derivatives from the acetonitrile and from the excess of DNP. Some concentration was also desirable. These aims were accomplished by adding water, extracting twice with pentane, and carefully evaporating to dryness. The dinitrophenylhydrazones were then taken up in a small volume of 50% acetonitrile and aliquots injected into a liquid chromatograph for separation of the individual dinitropheylhydrazones (Table 1). The unusually high recovery for acetone was due to traces of acetone in solvent. The solvent was purified by distillation over DNP.

Chromatography and Recovery Studies

Some effort was needed to work out an effctive combined procedure for derivatization, solvent extraction and subsequent separation by HPLC. Using the derivatization and

Table 1. Extraction of 2,4-dinitrophenylhydrazones with pentane[a]

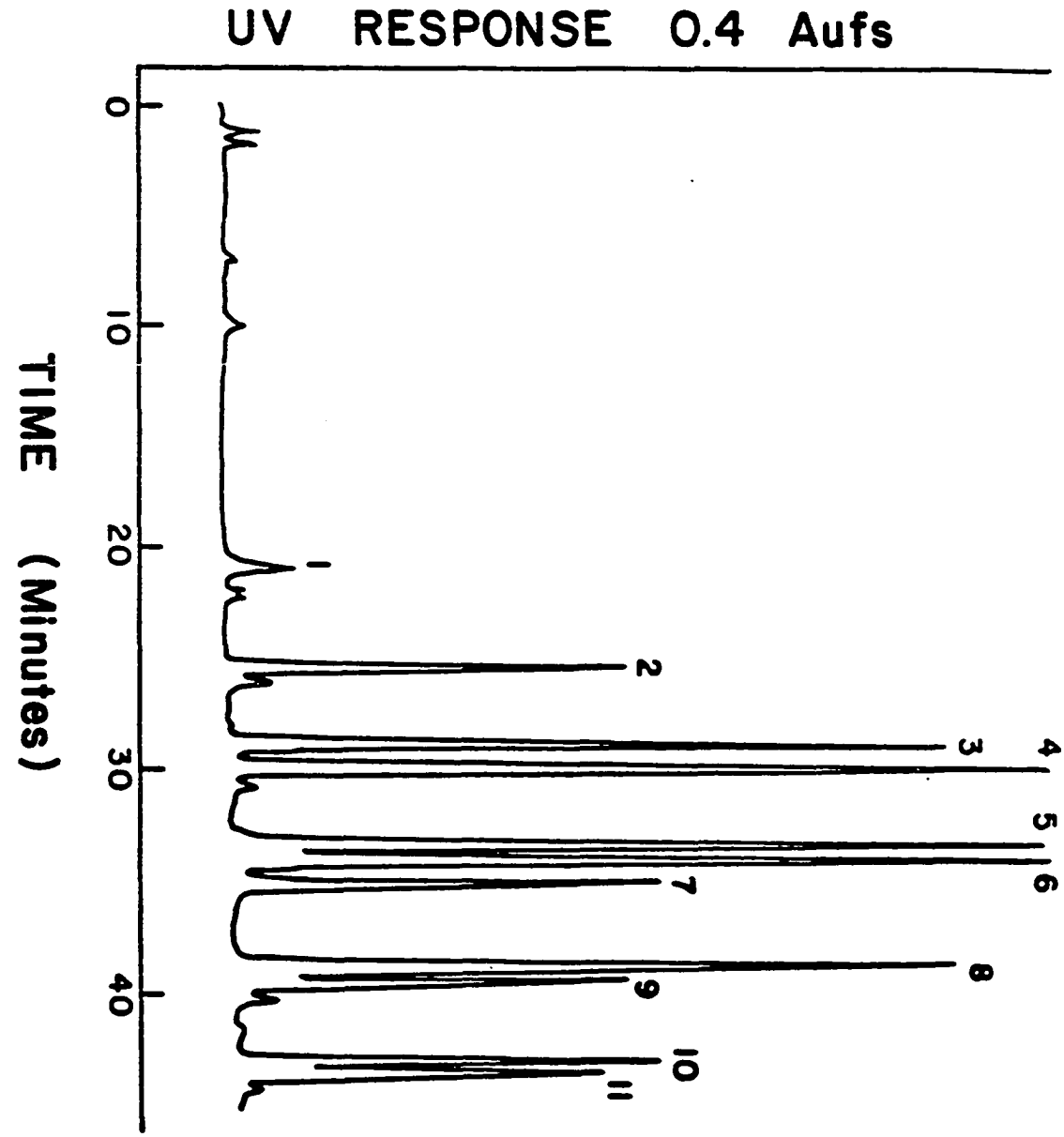
Compound	Percentage Recovery First Extraction	Second Extraction
Formaldehyde	45.2, 51.6	79.6, 84.8
Acetaldehyde	60.9, 68.6	90.3, 96.5
Acrolein	73.1, 85.1	75.1, 76.1
Acetone	54.1, 92.2	112.0, 112.8
Propanal	77.6, 87.6	96.8, 100.0
Crotonaldehyde	82.7, 94.9	99.7, 103.1
Butanal	78.8, 94.6	100.9, 103.3
Butanone	55.0, 97.6	98.8, 107.8
Pentanal	84.3, 98.3	100.1, 102.2
2-Pentanone	56.8, 96.4	95.5, 106.1
Hexanal + 2-Hexanone	64.9, 92.3	98.4, 103.6

[a]2 runs using 10μg of aldehyde or ketone and 0.65 mL of DNP reagent.

Figure 2. HPLC chromatogram of 2,4-dinitrophenylhydrazones

Conditions: Column: Little Champ.
Temperature: 25°C.
Detector: UV 254nm 0.4Aufs.
Gradient Elution: methanol-water (40:60) to methanol-water (70:30) in 30 minutes, then 100% methanol in 25 minutes.

Components: 2,4-dinitrophenylhydrazones of formaldehyde (1); acetaldehyde (2); acrolein (3); acetone, 1-propanal, (4); crotonaldehyde (5); 1-butanal (6); butanone (7); 1-pentanal (8); 2-pentanone (9); 1-hexanal (10); 2-hexanone (11).


UV RESPONSE 0.4 Aufs
TIME (Minutes)
0
10
20
30
40
1
2
3
4
5
6
7
8
9
10
11

extraction procedure described, liquid chromatography on a very short column ("Little Champ") with a methanol-water gradient was found to give good resolution of the derivatives studied. The chromatogram in Figure 2 is for known carbonyl compounds added to acetonitrile and carried through the procedures described above.

Recoveries of test compounds were made by passing 100 mL of an aqueous solution containing 100 μg/L of aldehyde or ketone through the zeolite column and following the procedure described. Only 50 mL of the aqueous solution containing acetaldehyde was used. The results in Table 2 show excellent recoveries for all compounds investigated with the exception of formaldehyde. A larger volume (500 to 900 mL) of a more concentrated solution (1000 μg/L) also gave good recoveries in two cases. The low recovery of acetone (at 1000 μg/L) could be due to volatility losses from the method that was used (no derivatization but direct GC injection on Porapak Q).

In these experiments the residue from the pentane extraction and evaporation was taken up in 2 mL of 50% acetonitrile and 10 μL was injected into the LC column, monitored at 254 nm at 0.4 AUFS. A very conservative estimate of the detection limit is less than 10 ng of aldehyde or ketone.

Table 2. Percentage recovery of model compounds[a]

Compound	1000 ppb[b]	100 ppb[c]
Formaldehyde		0.2, 2.2
Acetaldehyde		81, 99[d]
Acrolein		92, 104
Acetone	39, 49	78, 90
Propanal		94, 102
Crotonaldehyde		97, 99
Butanal		100, 106
Butanone	98, 102	96, 104
2-Pentanone	94, 100	91, 103
Hexanal + 2-Hexanone		92, 98

[a]2 runs.

[b]A volume of 900 to 500 mL of 1000 μg/L solution was loaded on 0.5 g of ZSM-5. Analysis of effluent was by GC.

[c]A volume of 100 mL of 100 μg/L solution was loaded on 0.5 g of ZSM-5. Analysis of DNP derivative was by HPLC.

[d]A volume of 50 mL of 100 μg/L solution was loaded on 0.5 g of ZSM-5. Analysis of DNP derivative was by HPLC.

Application to Drinking Water

Samples ranging from 1 L to 3 L of both raw and finished drinking water were passed through a ZSM-5 column and analyzed for possible low-molecular weight carbonyl compounds by the new procedure. A blank, carried out with pure distilled water, is shown in Figure 3. Nitrobenzene was added as an internal standard. The other peaks are believed to come from residual DNP and accompanying impurities.

Figure 4 shows the chromatogram obtained in the analysis of water from Des Moines, IA. Peak 3 was identified as butanone and peak 2 is believed to be the derivative of formaldehyde. The retention times differ somewhat from those in Figure 2 owing to some deterioration of the LC column. However, the butanone product was confirmed by GC-MS analysis. This water was estimated to contain 1.6 ppb (ug/L) of butanone. No aldehydes or ketones were found in water samples from Ames, IA, and from the nearby Skunk River.

Figure 3. HPLC chromatogram of blank

Conditions: Same as Figure 2.
Components: Nitrobenzene (internal Standard, 1).

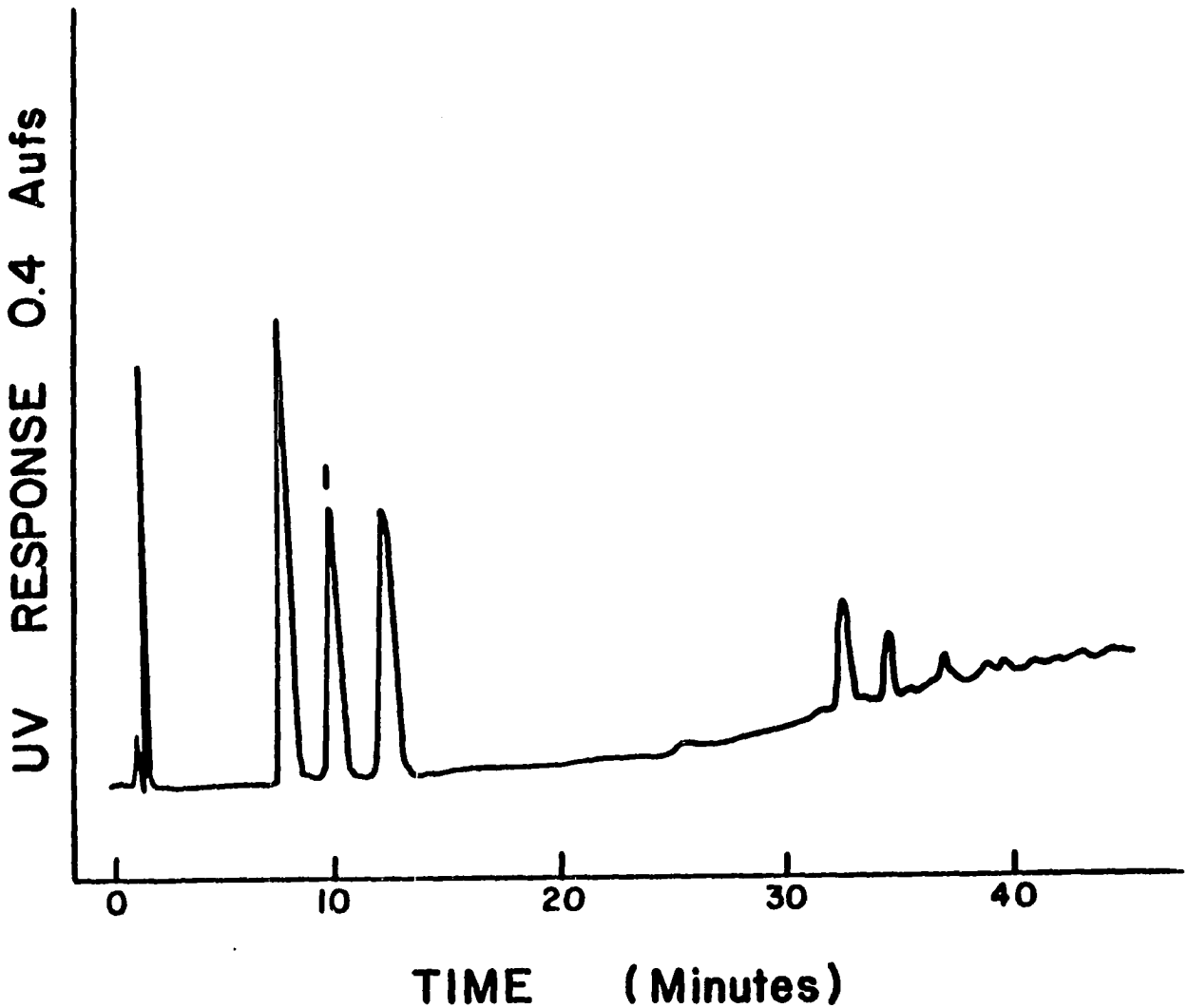
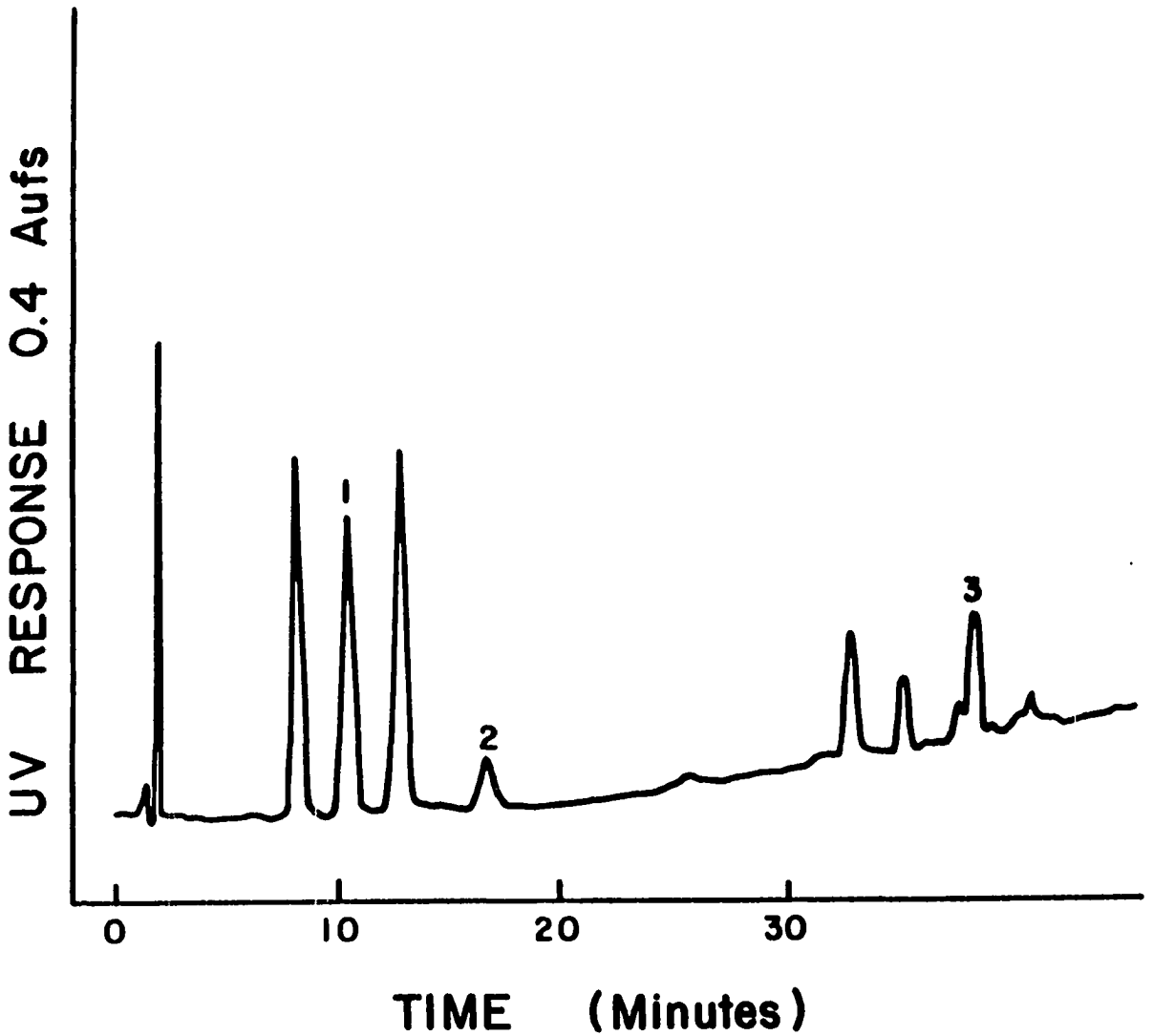

UV RESPONSE 0.4 Aufs
0
10
20
30
40
TIME (Minutes)

Figure 4. HPLC chromatogram of Des Moines Water

Conditions: Same as Figure 2.
Components: Nitrobenzene (internal standard, 1); formaldehyde (2); butanone (3).


UV RESPONSE 0.4 Aufs
1
2
3
0
10
20
30
TIME (Minutes)

CONCLUSION

Low concentrations of aldehydes and ketones in aqueous samples were concentrated on a small column containing a zeolite known as ZSM-5. The carbonyl compounds were then eluted with a small volume of acetonitrile and converted to the 2,4-dinitrophenylhydrazones, which were then separated by liquid chromatography. Excellent recoveries were obtained for all of the carbonyl compounds studied with the exception of formadehyde. The method was used in the analysis of drinking water.

REFERENCES

1. Coleman, W. E.; Munch, J. W.; Kaylor, W. H.; Streicher, R. P.; Ringhand, H. P.; Meier, J. R. Environ. Sci. Technol. 1984, 18, 674.

2. Dressler, M. J. Chromatogr. 1979, 165, 167.

3. Zlatkis, A.; Wang, F.-S.; Shanfield, H. Anal. Chem. 1983, 55, 1848.

4. Knuth, M. L.; Hoglund, M. D. J. Chromatogr. 1984, 285, 153.

5. Richard, J. J.; Junk, G. A. Anal. Chem. 1984, 55, 1625.

6. Junk, G. A.; Richard, J. J.; Grieser, M. D.; Witiak, D.; Witiak, J. L.; Arguello, M. D.; Vick, R.; Svec, H. J.; Fritz, J. S.; Calder, G. V. J. Chromatogr. 1974, 99, 745.

7. Barnes, R. D.; Law, L. M.; MacLeod, A. Analyst 1981, 106 412.

8. Tai, D. Y. Report (1978) USGS/WRQD/WRI-79/002, US/WRI-78-123; Order No. PB291-151. National Technical Information Service, Springfield, VA 22161.

9. Grob, K,; Grob, K., Jr.; Grob, G. J. Chromatogr. 1975, 106, 299.

10. Golkiewicz, W.; Werkhoven-Gowie, C. E.; Brinkman, U. A. Th.; Frei, R. W.; Colin, H.; Guiochon, G. J. Chromatogr. Sci. 1983, 21, 27.

11. Chladek, E.; Marano, R. S. J. Chromatogr. Sci. 1984, 22, 313.

12. Garrison, A. W.; Pellizzari, E. D. In "Analytical Techniques in Environmental Chemistry 2"; Albaiges, J.; Ed.; Pergamon Press: Oxford, 1982; p. 87.

13. Takami, K.; Kuwata, K.; Sugimae, A.; Nakamoto, M. Anal. Chem. 1985, 57, 243.

14. Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. J. Phys. Chem. 1981, 85, 2238.

15. Chriswell, C. D.; Gjerde, D. T.; Shultz-Sibbel, G. M. W.; Fritz, J. S.; Ogawa, I. "Evaluation of the Adsorption Properties of Silicalite for Potential Application in Isolating Polar Low-Molecular-Weight

Organics from Drinking Water"; Report (1983) EPA-600/1-83-001; Order No. PB83-148501. National Technical Information Service, Springfield, VA 22161.

16. Shultz-Sibbel, G. M. W.; Chriswell, C. D.; Fritz, J. S. Coleman, E. W.; Talanta, 1982, 29, 447.

17. Dessau, R. M. "Adsorption and Ion Exchange with Synthetic Zeolites"; ACS Symposium Series 135: American Chemical Society: Washington, DC, 1980; p. 123.

18. Snyder, L. R.; Kirkland, J. J. "Introduction to Modern Liquid Chromatography"; John Wiley & Sons, Inc.: New York, 1979; p. 206.

19. Kuwata, K.; Uebori, M.; Yamasaki, Y. J. Chromatogr. Sci. 1979, 17, 264.

20. Johnson, L.; Josefsson, B.; Marstop, P.; Eklund, G. Int. J. Environ. Anal. Chem., 1981, 9, 7.

21. Lipari, F.; Swarin, S. J. J. Chromatogr. 1982, 247, 297.

SECTION II. DETERMINATION OF LOW-MOLECULAR WEIGHT POLAR COMPOUNDS IN WATER BY GC

INTRODUCTION

The success of the method for concentrating low-molecular weight aldehydes and ketones spurred on research to extend this concentration method (on hydrophobic molecular sieve) to other low-molecular weight compounds, such as, ether, esters, nitriles and acids. In Section I a derivatization method was found that was quantitative and rapid. However, it would require considerable effort to find such a procedure for each of the functional classes under consideration.

To solve this problem rapidly, a gas chromatographic method of quantitation was developed. It relied on the use of large-bore thick-film capillary column. Large volume injections could be made without serious deterioration of resolution. By using thick-film columns, the retention volumes of solutes with low retention volumes were increased, so that subambient temperatures were not needed. It was discovered that the polar phase selected to separate the polar compounds was not as stable as the nonpolar phases (methyl silicone), especially at high temperature. However, the stationary phase was more firmly attached (cross-linked) so that more different kinds of solvents were at the disposal of the experimenter. Hence solvents were selected which were efficient in eluting the analytes from the

molecular seive and which did not interfere with the subsequent quantitation. For GC purposes the solvents were selected so that the analytes eluted before or sufficiently after the solvent tail to produce a reasonably stable baseline. To achieve this end it was found that the solvents, in some cases, required extensive purification.

EXPERIMENTAL

Solvents and Reagents

Water was produced using the Barnstead NANOPure II System (Barnstead, Division of SYBRON Corp., Boston, MA 02132). All organic solvents were distilled in glass UV grade (Burdick and Jackson Laboratories Inc., Muskegon, MI 49442). Unless specified, these solvents were used as received.

Instrumentation

Tracor 550 GC with flame ionization detection (FID) and injector and detector modified for capillary column was used. Nitrogen was the make up gas and the split ratio was 1:15. For low-molecular weight polar compounds a 0.525 mm x 15 m with 1 μm film thickness (DBWax) fused silica column (J & W, Cordova, CA) was used. The flow rate was about 1 mL/min.

Capacity Experiments

ZSM-5 For capacity experiments dry zeolite (Mobile Research and Development Corporation, New York) was added to a small glass tube and held in place by a plug of glass wool. Breakthrough curves were obtained by passing an aqueous solution containing 1 mg analyte/mL water at ambient

temperature. Fractions at 1-mL intervals were collected and analyzed by GC on Porapak Q or DBWax column.

ELZ-115 The ELZ-115 (Union Carbide Corporation, New York) was ground and sized (60-170 mesh). The fines were removed by washing with water. Breakthrough curves were obtained in the same way as for ZSM-5.

Accumulation Experiments

Pump Loading Method For aldehydes and ketones 0.5 to 0.9 g ZSM-5 or ELZ-115 was used as received. Fines were removed and the zeolite was packed into 4.6 mm I.D. (internal diameter) x 5 to 8 cm stainless steel columns. The columns were washed and loaded with 100 mL of aqueous solution (100 ppb) as described in the experiment for ZSM-5. The column was eluted with 3.3 mL acetonitrile into the 2,4-dinitrophenlyhydrazine derivatizing solution. The hydrazones were extracted with pentane and analyzed as described in Section I.

Gravity Flow Method For the remaining low-molecular weight compounds the ELZ-115 was ground and sized to 60-170 mesh. The zeolite (0.5 g to 0.25 g) was packed into a column (disposable pipette) with a glass wool plug to retain the zeolite. The column was regenerated by eluting with 15 mL of solvent followed by 100 to 200 mL water or by heating the column to 100^{o}C for 1 hour (to prevent loss of the

zeolite due to rapid evolution of solvent) and then to 400°C for at least 4 hours or at 800°C for 2 hours. The column was attached to a reservoir using a teflon connector.

Preparation of Test Solutions To prepare 100 ppb solution 20 μL of 0.5 μg analyte/μL water stock solution was added to 100 mL water (in reservoir). For 10 ppb test solution 20 μL of 0.05 μg analyte/μL water stock solution was added to 100 mL water. For 1 ppb test solution 20 μL of 0.05 μg analyte/μL water stock solution was added to 1 L water which had previously been eluted through an ELZ-115 column.

Desorption of Test Compounds The columns were eluted with 1.5 to 2 mL of solvent (methanol, distilled acetonitrile, distilled 1-propanol, acetone, diethyl ether). Analysis was by GC with FID on fused silica (DBWax, 0.525 mm I.D., 1 μm thickness, 10 m) column.

RESULTS AND DISCUSSION

Capacity Experiments

The breakthrough curves in Figure 5 show the capacity of ZSM-5 for methanol, phenol, acetonitrile, 1-propanol, ethyl acetate and crotonaldehyde. As in Section I a solution of 1 mg analyte in 1 mL of water was passed through 0.5 g ZSM-5 for each breakthrough curve. The effluent (at 1 mL intervals) was analyzed by packed column (Porapak Q) GC. The zeolite retained these analytes to varying degrees. A conclusion is that ZSM-5 can be used to concentrate these low-molecular weight polar compounds. The small particle size of the ZSM-5 resulted in very narrow band width by frontal chromatography, especially for methanol and acetonitrile.

Breakthrough experiments for acetic and butyric acids under the same conditions but using ELZ-115 (60-170 mesh) in Figure 6 show that these acids were retained by ELZ-115. Exploratory experiments with acetaldehyde indicated that the particle size of ELZ-115 as received was too large and caused early breakthrough and distorted breakthrough curve. After grinding and sizing there was great improvement in the band width of acetaldehyde. Capacity measurements on ELZ-115 impregnated with concentrated solutions of uranium, cesium, rhodium and thorium salt solutions, gave no improvement in the retention of acetaldehyde.

Figure 5. Breakthrough curves of low-molecular weight compounds

Aqueous solutions containing 1 mg/mL of analytes were passed through a mini-column containing 0.50 g of ZSM-5.

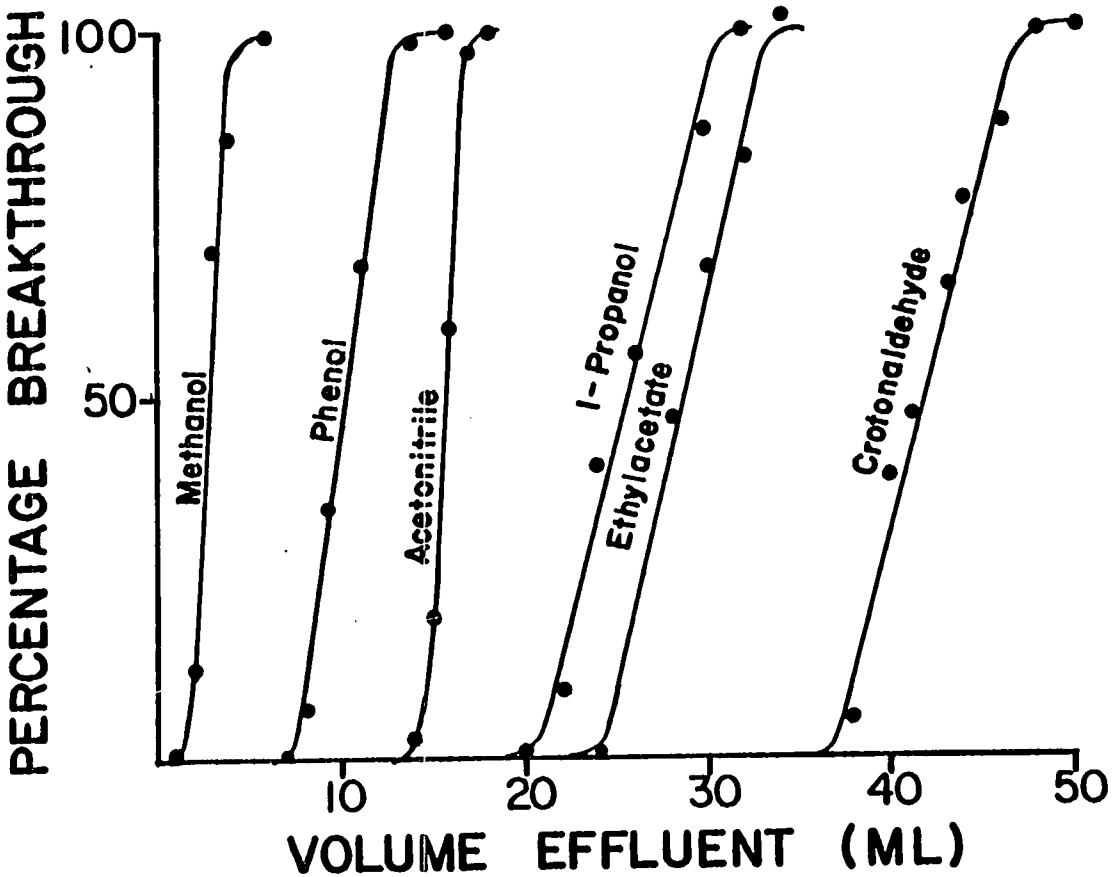
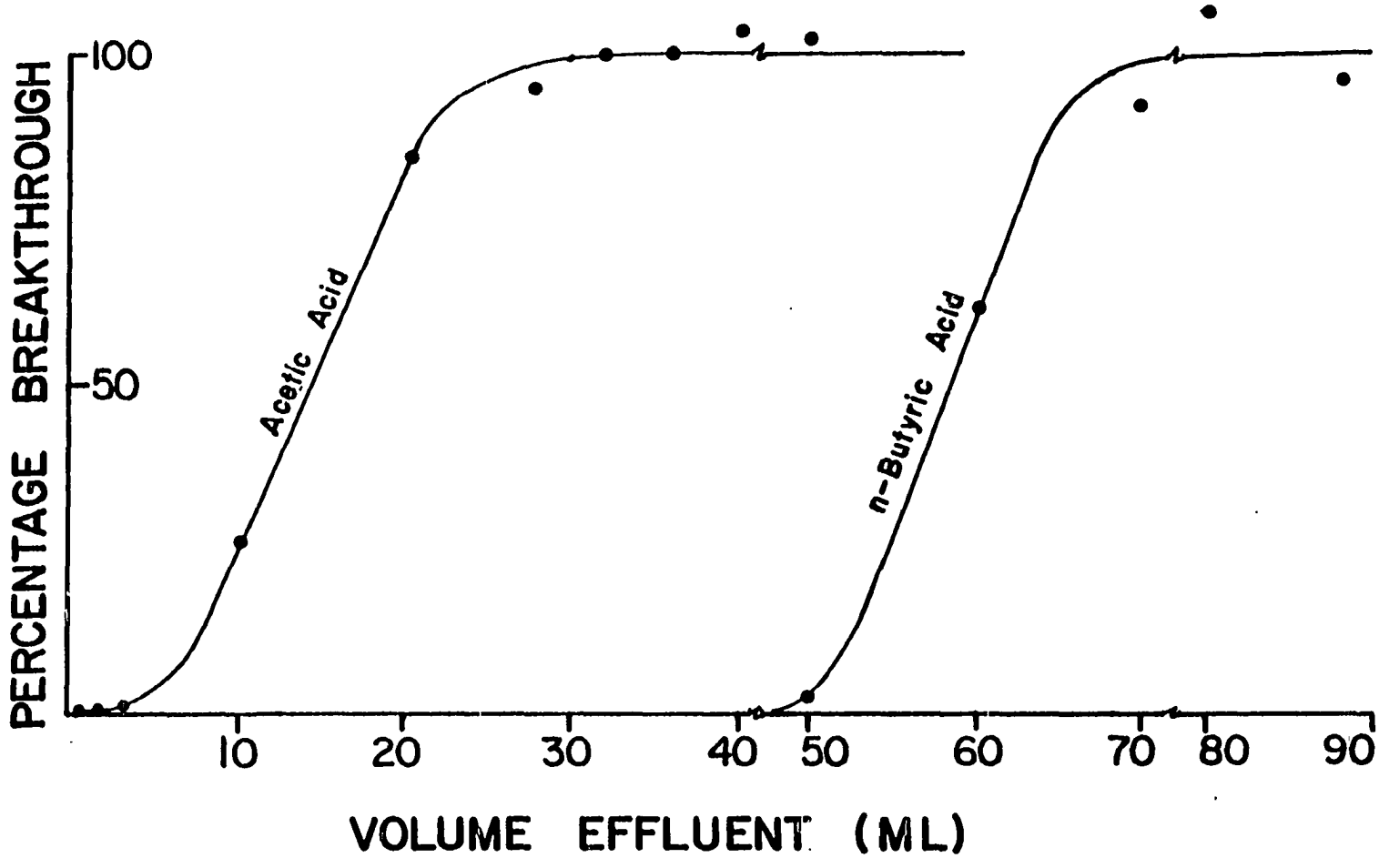

PERCENTAGE BREAKTHROUGH
100
50
Methanol
Phenol
Acetonitrile
I-Propanol
Ethylacetate
Crotonaldehyde
10
20
30
40
50
VOLUME EFFLUENT (ML)

Figure 6. Breakthrough curves of acids

Aqueous solutions containing 1 mg/mL of acids were passed through a mini-column containing 0.5g of ELZ-115.


PERCENTAGE BREAKTHROUGH
100
50
Acetic Acid
n-Butyric Acid
10
20
30
40
50
60
70
80
90
VOLUME EFFLUENT (ML)

An estimation of the maximum volume of aqueous solution (1 mg analyte/ml water) that the mini-column can sample quantitatively, V, was calculated from the equation (1):

$$V = V_r - W/2.$$

In this equation, V_r is the retention volumne (volume at 50% breakthrough in frontal chromatography) and W is the band width (minimum volume at 100% breakthrough minus maximum volume at 0% breakthrough).

The peak width for acetonitrile is unusually small and for acetic acid it is very large. Apparently acetonitrile molecules are able to find sorption sites very quickly. The maximum volume, V, increased with increasing carbon number. The maximum volume was low for phenol and very high for butyric acid. The coefficient of determination for V and number of carbon atoms was 0.77 for all analytes on ZSM-5 and ELZ-115. For formaldehyde, methanol, acetaldehyde, acetone, 1-propanol, and n-butyraldehyde the coefficient of determination was 0.97 (Figure 7). An improvement in the coefficient of determination may be possible if each class of compounds were considered individually, for example only n-alcohols.

Table 3. Capacity Measurements and Calculations

Compound	Peak Width (W in mL)	Maximum Volume (V in mL)
Methanol	2.2	1.9
Acetonitrile	2.3	15.85
Formaldehyde	3.6	1.6
Acetaldehyde	5.2	11.0
Phenol	6.0	7.4
Propionaldehyde	7.4	26.3
Ethyl Acetate	9.4	24.6
Crotonaldehyde	10.4	36.
1-Propanol	10.6	20.3
Acetone	13.2	19.9
Acrolein	13.6	15.6
n-Butyraldehyde	17.0	29.7
2-Pentanone	18.0	31.2
Acetic Acid	17.6	5.7
Butyric Acid	15.2	50.65

In these experiments, V is only an estimation because the void volume was not measured. Also the concentrating material for acids was ELZ-115 of very large mesh size in comparison to the small mesh size of ZSM-5 which was used in the capacity experiments of all other analytes. In addition

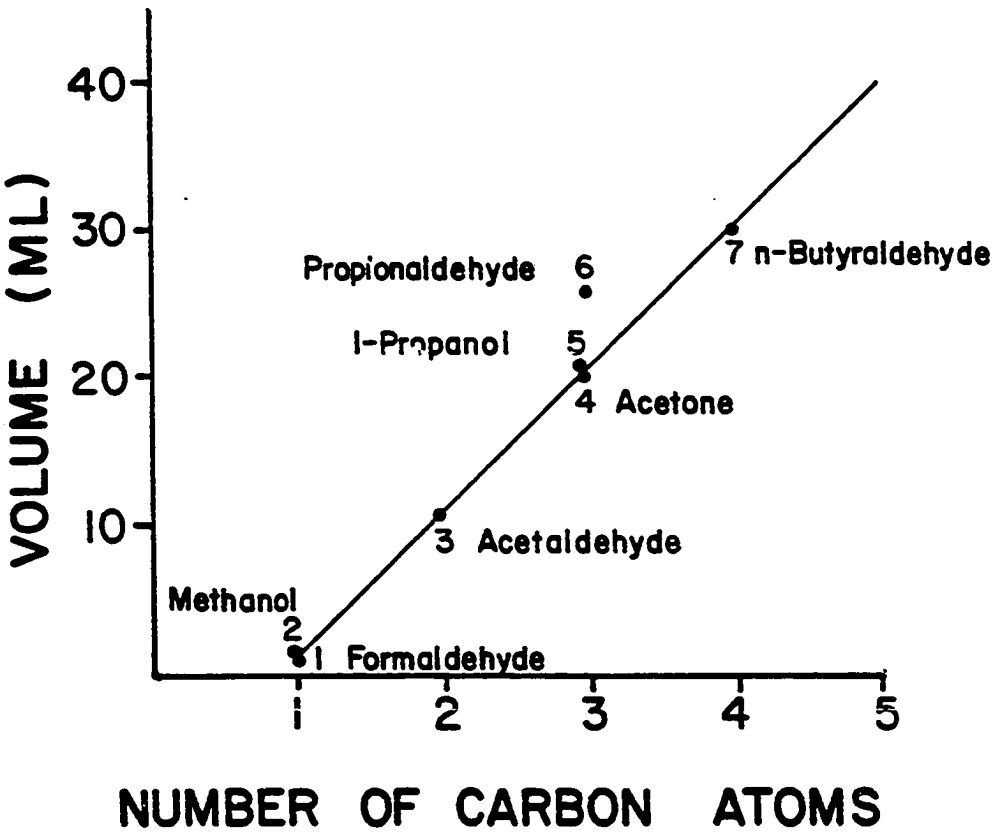


Figure 7. Number of carbon atoms vs. maximum volume

chemical interaction with surface groups may also play an important role for the concentration of acids with ELZ-115.

As in gel chromatography, in molecular sieves, molecules that cannot invade the pores of the sorbent have low retention volumes. These large molecules elute with the void volume. However in gel chromatography, with relatively greater range in pore sizes and shapes, the smallest molecules elute last. The explanation is that these molecules are able to invade most of the pores, resulting in the longest path length through the column. For ZSM-5 and ELZ-115 with highly uniform pores of molecular dimensions, however, the smallest molecules are able to move in and out of the channels unhindered (2). The larger molecules must reorient themselves as they approach a pore (large peak width). They must also reorient themselves as they exit through the channels (large retention volume). The behavior of very long molecules that might extend throughout the channels was not tested.

Application of Concentration Method of Section I on Alcohols and Ethyl Acetate

Recovery The analyte loading method of Section I was applied to alcohols using ZSM-5 and ELZ-115. Good recoveries (Table 4) were obtained for the alcohols and ethyl acetate indicating that the concentration method of

Table 4. Application of concentration method of Section I on alcohols and ethyl acetate

Compound	Percentage Recovery 100 ppm[a]	1ppm[b]	100 ppb[c]
1-Propanol	60	21.4, 39.8	
Ethyl Acetate	99	90.3, 97.1	109
1-Butanol	103	96.6, 98.2	117
1-Pentanol	110	88.2, 107.6	98
1-Hexanol	103	93.4, 102.2	
i-Propanol			73
i-Butanol			130
i-Pentanol			100

[a]Single run using 0.4 g of ZSM-5 and 200 mL of 100 ppm solution. Eluted with 4 mL methanol.

[b]2 runs using 0.4g ZSM-5 and 500 mL of 1 ppm solution. Eluted with 5.5 mL methanol.

[c]Single run using 0.5g of 60-170 mesh ELZ-115 and 100 mL of 100 ppb solution. Eluted with 2 mL acetonitrile.

Section I could be applied to alcohols and ethyl acetate. In addition the experiment on ELZ-115 confirmed the results of the breakthrough experiments that ELZ-115 was as efficient as ZSM-5 in concentrating low-molecular weight alcohols and acetates.

The ZSM-5 column was sensitive to pressures above 300 psi and once a column of ZSM-5 was subjected to these higher

pressures the column became clogged and could not be restored. The ELZ-115 was more resistent to drastic pressure changes. But a method of simple gravity flow using very short columns was used. This method is a modification of that used by Tateda and Fritz (3).

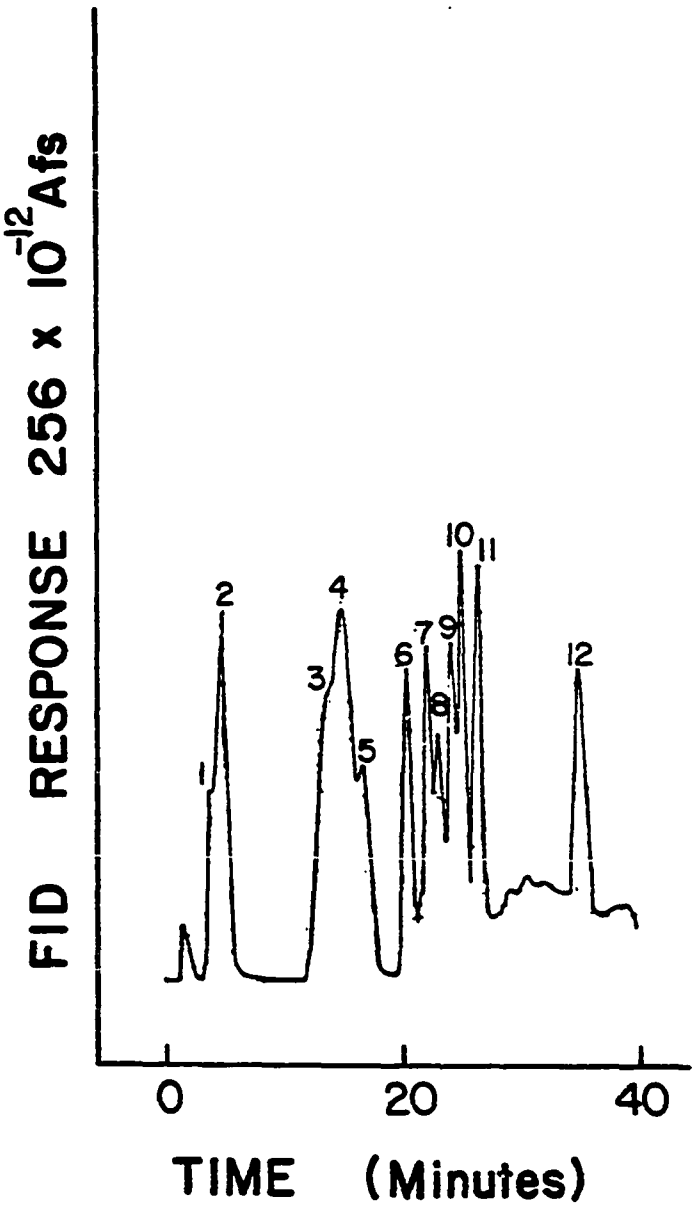
Using up to 1 liter reservoirs, several experiments could be run simultaneously. The test samples (100 mL) eluted through the column in less than 15 minutes and solution change over was complete in less than 5 minutes. This was much simpler and less time was needed than the extensive cleaning required for solvent change over in a pumping system for the investigation of trace amounts of analytes in water.

Gas Chromatography For many years in gas chromatography, water and other polar solvents were avoided because these compounds had a tendency to dissolve the stationary phase. In addition it was difficult to find a stationary phase polar enough so that the early eluting volatile components were well separated from the solvent tail. Twelve compounds were injected in Porapak Q column. The shape of the peaks were reasonable, for example, phenol (12) in Figure 8. But when retention times were about the same severe overlapping of the peaks occurred, for example, the peak containing ethanol (3); acrolein, propionaldehyde (4); and acetone (5). The result of this low resolution is that many test mixtures were necessary so that component

Figure 8. Typical GC chromatogram on packed column

Conditions: Tracor 550 GC
Column: 1 mm I.D. x 18 m glass column packed with 60-80 mesh Porapak Q.
Carrier gas: 15 mL/min N_2.
Temperature Program: Initial hold of 2 minutes at 50°C and programmed at 15°C/min to 230°C and held at 230°C for 4 minutes.
Detector: FID at 256 x 10^{-12}Afs.
Sample: 1.7 μL of 1 μg/μL.

Components: Methanol, Formaldehyde (1); Acetaldehyde (2); Acetonitrile, Ethanol (3); Acrolein, Propionaldehyde (4); Acetone (5); 1-Propanol, Chloroform (6); Butyraldehyde (7); Ethyl Acetate (8); Crotonaldehyde (9); t-Butanol (10); 2-Pentanone (11); Phenol (12).


FID RESPONSE 256 x 10^{-12}Afs
1
2
3
4
5
6
7
8
9
10
11
12
0
20
40
TIME (Minutes)

peaks did not overlap. Identification of compounds based on retention times would be unreliable for real samples.

The chromatogram (Figure 9) of 20 components show good peak shapes and separation within 20 minutes on large-bore (0.525 mm I.D.) column. Some overlapping of peaks occurred. Although the large-bore column did not have the high resolving power of the usual (0.2 mm I.D.) capillary column, it was a vast improvement over the packed column in terms of resolution and time of analysis.

Because of the high capacity of thick-film large-bore columns, these columns have been predicted to be suitable for trace analysis. A complex sample must be diluted so that the major components do not exceed the capacity of the 0.2 mm I.D. capillary column. But by dilution, the trace components cannot be detected.

Figure 10 show the capablility of the gas chromatograph to detect 0.5 ng of low-molecular weight compounds in aqueous solution using the large-bore column. The baseline was satisfactory at this sensitivity and column temperature. Because direct aqueous injection of the DBWax large-bore column gave good results at 0.5 ng/μL no further work on concentrations greater than 1 ppm (1mg/L water) was carried out.

Figure 9. Typical GC chromatogram of polar compounds on DBWAX megabore column

Conditions: Tracor 550 GC.
Column: Hewlett Packard 0.525 mm I.D. x 15 m polyethylene glycol (1 μm thick).
Flow rate: 1.2 mL/min He.
Split: 1:15.
Make up gas: N_2 15 mL/min.
Detector: FID 265 x 10^{-12} Afs.
Temperature Program: Initial nold of 2 minutes at 40°C and programmed at 5°C/minute to 150°C and held at 150°C for 10 minutes.
Sample: 0.3 μL of 5 to 2.5 μg/mL.

Components: Diethyl Ether (1); Acetaldehyde (2); 1-Propanol (3); Acetone (4); Methyl Acetate (5); Acrolein (6); Butyraldehyde (7); Ethyl Acetate (8); Methanol, t-Butanol, Butanone (9); 2-Propanol (10); Ethanol (11); Propyl Acetate, Valeraldehyde, 2-Pentanone (12); Acetonitrile, i-Butylnitrile (13); Propylnitrile, t-Pentanol (14); 2-Butanol (15); Crotonaldehyde, 1-Propanol (16); Butyl Acetate (17); i-Butanol (18); 1-Butanol (19); i-Pentanol (20); 1-Pentanol (21).

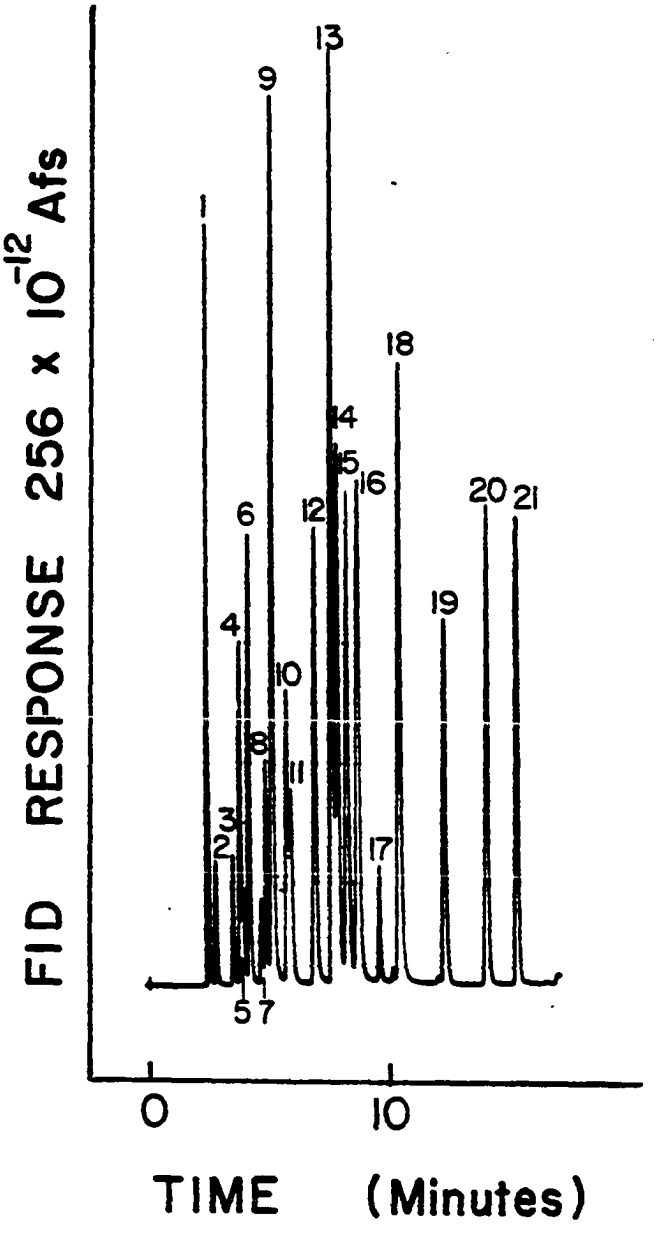
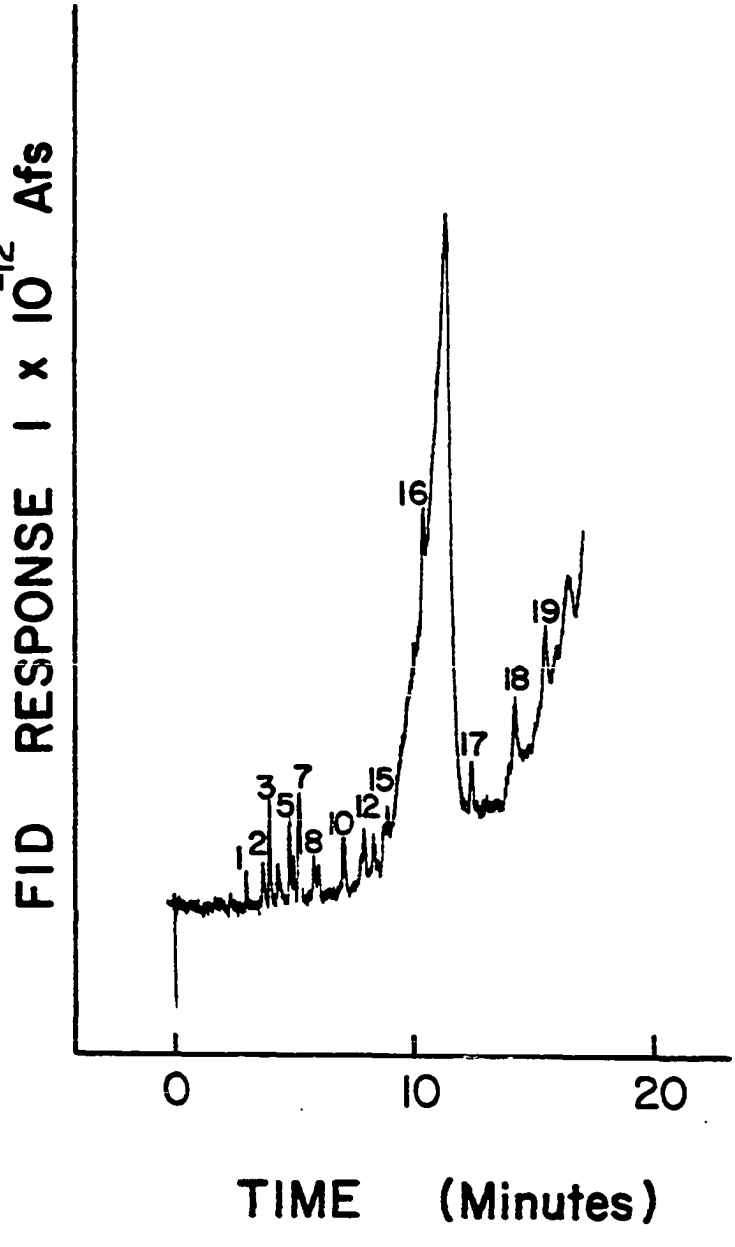

FID RESPONSE 256 x 10^{-12} Afs
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
0
10
TIME (Minutes)

Figure 10. GC chromatogram at high sensitivity

Conditions: Same as Figure 9.
Detector: FID 1 x 10^{-12} Afs.
Sample: 0.8 μL of 0.5 ng/μL.

Components: Acetaldehyde (1); Propionaldehyde (2); Acetone (3); Acrolein (4); Butyraldehyde (5); Ethyl Acetate (6); Methanol, t-Butanol, Butanone (7); 2-Propanol (8); Ethanol (9); 2-Pentanone (10); 1-Propanol (11); t-Pentanol (12); 2-Butanol (13); Acetonitrile (14); Crotonaldehyde (15); i-Butanol (16); 1-Butanol (17); i-Pentanol (18); 1-Pentanol (19).


FID RESPONSE I x 10^-12 Afs
1
2
3
5
7
8
10
12
15
16
17
18
19
0
10
20
TIME (Minutes)

Solvents for Desorption Next the effect of solvent (Table 5) to elute alcohols from the ELZ-115 column was tested. Methanol gave good recoveries for all compounds tested except 1-butanol at 100 ppb level. This is probably due to impurities in the solvent that interfered with quantitation. The solvent tail interfered with the analysis of 1-propanol and 2-butanol when acetonitrile was the solvent. Except for 1-pentanol low recoveries were obtained when diethyl ether was the solvent.

Table 5. Effect of eluting solvent on recovery of low molecular weight alcohols

Compound	Percentage Recovery[a] Methanol[b] 100 ppb	Acetonitrile[c] 100 ppb	Diethyl ether[d] 200 ppb
1-Propanol	100.6, 102.8		
2-Butanol	93.8, 100.6		76.5, 87.5
i-Butanol	93.4, 105.4	104.5, 104.9	76.0, 86.4
1-Butanol	115.9, 124.1	92.5, 100.9	33.4, 40.4
i-Pentanol	96.6, 103.5	95.4, 101.0	100.2, 100.6
1-Pentanol	102.0, 102.6	72.4, 89.2	48.3, 53.9

[a]2 runs on 0.3 to 0.5g of 60-170 mesh ELZ-115.

No difference in the recoveries of alcohol was evident for 0.5 to 0.25 g ELZ-115 (60-170 mesh) in Table 6. Lower mesh sizes may result in still lower amounts of zeolite needed for the retention of alcohols.

Table 6. Effect of amount of ELZ-115 on recovery of low molecular weight alcohols at 100 ppb level

Compound	Percentage Recovery 0.5g[a]	0.3 to 0.25g[b]
1-Propanol	100.6, 102.8	
2-Butanonal	93.8, 100.6	
i-Butanol	93.4, 105.4	90.0, 95.0
1-Butanol	97.9, 106.1	96.5, 102.9
i-Pentanol	96.7, 103.5	92.3, 99.5
1-Pentanol	102.0, 102.6	86.3, 87.9

[a] 2 runs eluted with 2 mL methanol.

[b] 2 runs eluted with 2 mL acetonitrile.

Range of Sample Concentration Table 7 gives the effect of concentration on the accumulation of low-molecular weight alcohols at 1 ppb level. At 1 ppb level 1-butanol, i-pentanol and 1-pentanol and were recovered.

Table 7. Sample concentration range for the recovery of low-molecular weight alcohols

Compound	Percentage Recovery 100 ppb[a]	10 ppb[b]	1 ppb[b]
1-Propanol	102		
2-Butanol	97		
i-Butanol	99		
1-Butanol	99	99.5, 102.9	99.9, 101.3
i-Pentanol	98	90.6, 93.0	90.9, 91.5
1-Pentanol	90	99.6, 100.8	63.0, 65.4

[a]Average of all runs at this level of concentration.

[b]2 runs using 0.3 to 0.2 g of ELZ-115 and eluted with 1.6 mL methanol.

Diethyl Ether, Esters and Nitriles

Recovery The investigation was extended to other low-molecular weight compounds, diethyl ether, acetates and nitriles. With acetonitrile as desorbing solvent good results were obtained for diethyl ether, methyl acetate, ethyl acetate, n-propyl acetate and acetonitrile. The solvent tail interfered with the analysis of n-propylnitrile and n-butyl acetate using acetonitrile as solvent. Using acetone as solvent, reasonable results were

Table 8. Effect of eluting solvent on recovery of diethyl ether, acetates, nitriles

Compound	Percentage Recovery		
	Acetonitrile or 1-Propanol 100 ppb	Acetone 200 ppb	Diethyl ether 200 ppb
Diethyl Ether	97.6, 101.9		
Methyl Acetate	93.2, 100.0		
Ethyl Acetate	100.0, 103.2		
n-Propyl Acetate	96.9, 104.3	95.0, 103.2	
Acetonitrile	76.4, 93.0	70.3, 78.7	
n-Propylnitile		96.0, 99.4	
n-Butyl Acetate		91.9, 99.9	43.0, 54.2

obtained for n-propyl acetate, acetonitrile, n-propylnitrile and n-butyl acetate. Diethyl ether gave poor recovery of n-butyl acetate and the solvent tail interfered with the analysis of all other compounds listed in Table 8.

Sample Volume The recovery of diethyl ether and acetates were used to test the effect of large sample sizes on the recovery of these compounds using 1-propanol as the solvent. At very large sample size (1000 mL) good

Table 9. Effect of large dilute aqueous samples on the recovery of acetates, diethyl ether and acetonitrile

Compound	Percentage Recovery 100 mL[a]	1000 mL[b]
Diethyl ether	99.1, 101.5	91
Methyl Acetate	100[c]	89
Ethyl Acetate	94.4, 99.2	
Propyl Acetate	85.2, 95.2	88
Acetonitrile	31.9, 33.3	

[a]2 runs at 4 ppb level using 0.3 to 0.25 g ELZ-115 and eluted with 2 mL 1-propanol.

[b]Single run at 1 ppb level using 0.3 g ELZ-115 and eluted with 2 mL 1-propanol.

[c]Single run.

recoveries were obtained for diethyl ether, methyl acetate and propyl acetate (Table 9).

Gas Chromatography While 1-propanol was an excellent solvent for the elution of the analytes from ELZ-115, Figure 11 shows the problems of interference of impurities in 1-propanol. In order to obtain a good blank (Figure 11 (B)) the 1-propanol was distilled three times through a vigreux column, using only the middle fractions of each distillation. Then the distillate was passed through ELZ-115 that had been cleaned by heating it to 800°C for 2 hours. The filtered water (Barnstead) was also passed through clean ELZ-115. Other treatment using florisil or activated carbon to purify 1-propanol showed more impurities in the blank. Figure 11 (C) shows the chromatogram of the test sample with analytes eluting before 1-propanol for experiments at the 1 ppb level.

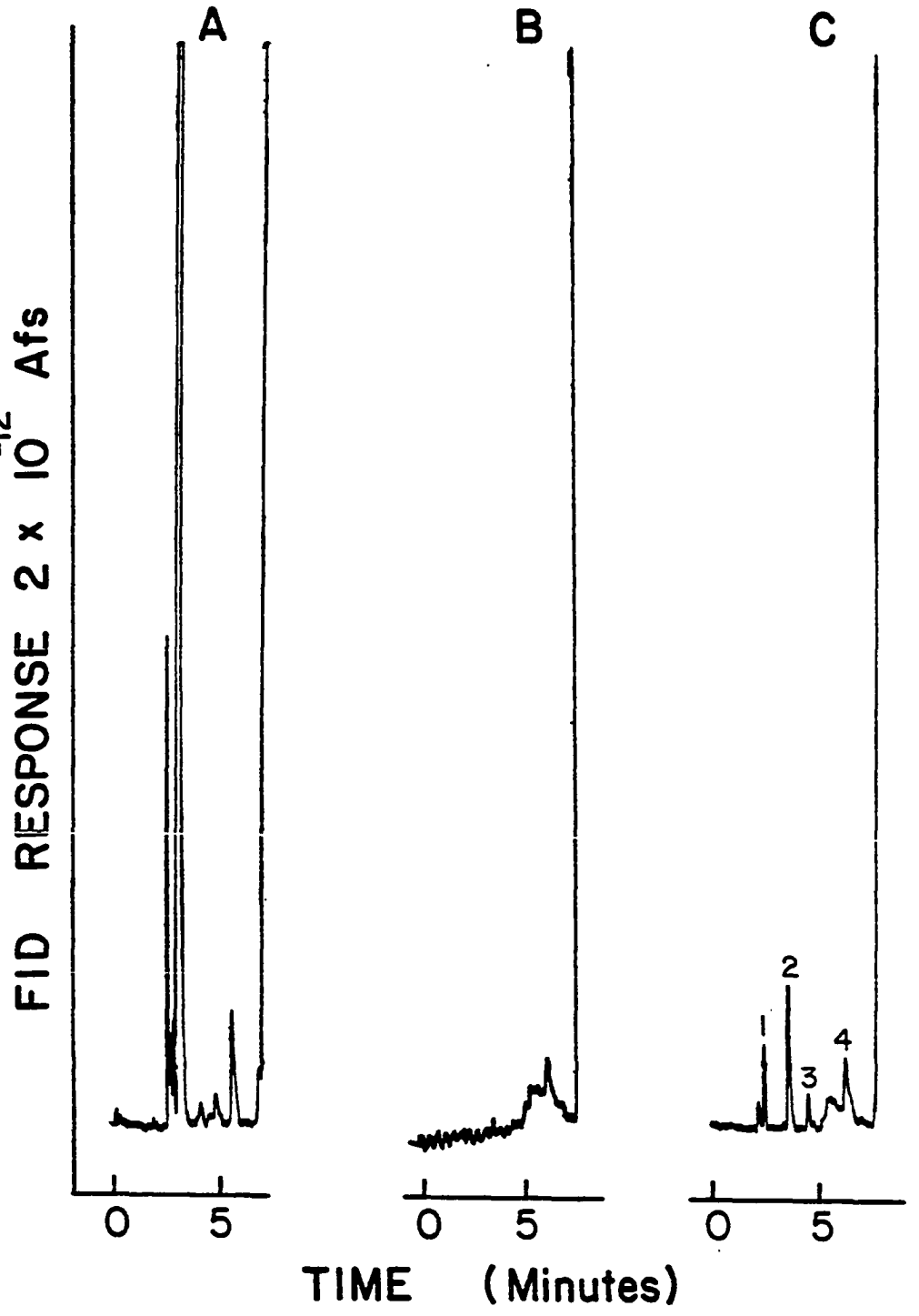
Aldehydes and Ketones

Good recoveries were obtained for aldehydes and ketones using ELZ-115 (Table 10) at 200 ppb level. In agreement with the capacity experiments and recoveries from ZSM-5 in Section I low recovery of acetaldehyde was obtained. All other compounds gave good recoveries.

Thermal desorption of aldehydes and ketones from ELZ-115 at 100°C to 300°C using nitrogen, carbon dioxide, helium, helium saturated with methanol and helium saturated with

Figure 11. GC chromatogram of volatile components in 1-propanol

Conditions: Same as Figure 9.
1.4 μL injection for each case.
A: Middle fraction of distilled 1-propanol.
B: Blank. 1 L H_2O eluted with 1-propanol (distilled and eluted through heat treated ELZ-115).
C: Diethyl Ether (1), Methyl Acetate (2), Propyl Acetate (3) analyzed at 1 ppb level.


A
B
C
FID RESPONSE 2 x 10^-12 Afs
0
5
0
5
0
5
1
2
3
4
TIME (Minutes)

acetonitrile resulted in poor recovery of aldehydes and ketones. Although acetaldehyde was not a test compound, large amounts of acetaldehyde were obtained. The presence of acetaldehyde was confirmed by the GC-MS of the 2,4-dinitrophenylhydrazine derivative of acetaldehyde. The poor recovery is in agreement with literature reports of gas phase conversions of oxygenated compounds, including ketones to other compounds, predominantly hydrocarbonds using ZSM-5 (4,5).

Table 10. Recovery of aldehydes and ketones at 200 ppb level on ELZ-115 and eluted with 1-propanol

Compound	Percentage Recovery
Acetaldehyde	14.0, 14.4
Propionaldehye	81.2, 84.8
Acetone	99.1, 101.5
Butyraldehyde	81.7, 91.5
Butanone	97.6, 102.4
2-Pentanone	96.3, 98.7

Silicalite-1 (prepared from tetrapropyl ammonium fluoride) was used recently as a column packing for the separation of methanol, ethanol, p-xylene, acetone and propanol using steam-solid chromatography by Campbell et al. (6). This crystal form of Silicalite according to the authors was extremely stable to steam.

Acids

Recovery Capacity experiments on ELZ-115 indicated that low-molecular weight acids could be concentrated on ELZ-115. Methanol, 1-propanol, ethyl acetate and acetone were some of the solvents that were successful in desorbing the analytes from ELZ-115. A dilute HCl solution was also effective in desorbing the analytes, but HCl would cause irreversible damage to the capillary column. The recovery data (Table 11) was obtained using 1-propanol as the desorbing solvent.

The effect of esterification was tested by adding acetic, propionic, butyric, and valeric acids at the 1 ppm level to 1-propanol. No change in peak height ratio of the acids to an internal standard (1,2,4-trimethylbenzene) was evident for two hours. This is sufficient time for elution of the acids from the ELZ-115 column and injection into the gas chromatograph. The acids formed esters with methanol

Table 11. Dependence of recovery of acids on the amount of water passed through ELZ-115 column[a]

Acid	Percentage Recovery			
	2 mL H_2O	100 mL H_2O	400 mL H_2O	1000 mL H_2O
Acetic	4, 6	0	0	0
Propionic	85, 89	0	0	0
Butyric	101, 105	93, 101	66, 92	6, 87
Valeric	104, 104	102, 108	104, 106	44, 44

[a]2 runs of 80 μg of acid on 0.3 g of ELZ-115.

more quickly than with 1-propanol. Traces of HCl increased the rate of formation of the ester and the peak height ratios of acid to internal standard were no longer constant.

Sample Volume The effect of large sample volumes considerably reduced the recovery of acids from ELZ-115. Hence this method of concentration of acetic, propionic, butyric and valeric acids is useful only for small sample sizes. The effect of larger amounts of ELZ-115 or of smaller mesh size maybe beneficial when large sample volumes must be analyzed. The importance of fatty acids has been emphasized by Lee et al. by the fact that 25% of research

reports published on GC deals with fatty acids. The shorter chain fatty acids are more difficult to analyze by GC (7).

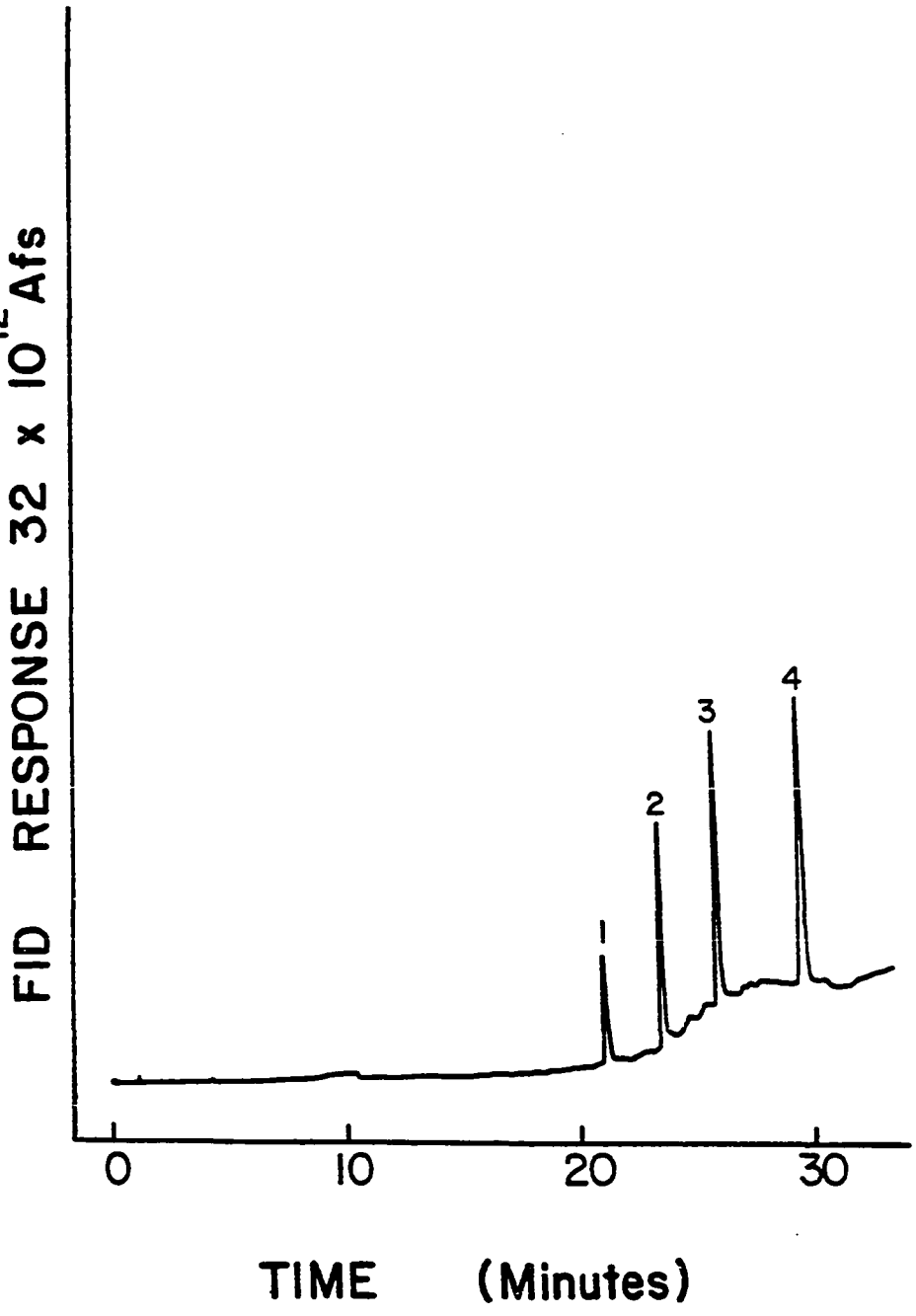
Baseline Problems of the DBWax Column

While alcohols, esters, acetates and nitriles eluted at lower temperature from the DBWax column, acids required higher temperature. The best isothermal conditions for the elution of all four acids with highest sensitivity for valeric acid and with acetic acid away from the solvent tail showed the same problem as those of the temperature programmed experiment. At high analyte concentration of 1 μg/uL (Figure 12) the baseline instability was already noticeable from retention time of 20 to 30 minutes. Approximately 500 injections of test compound in water, methanol and other solvents had been made on this column.

The immediate solution to this problem was to obtain a new DBWax column. But after only 7 injections of water, the baseline had already deteriorated (Figure 13 (A)) so that the column could not be used for trace analysis. The baseline was restored (Figure 13 (B)) by using high carrier gas flow rate (15 mL/min) at high temperature (150^{o}C) for 10 minutes. Although this procedure solved the baseline problem, it was an inconvenience to the chromatographer. After the high flow rate (15 mL/min) to restore the baseline, sufficient time was required for the gas flow rate

Figure 12. Typical GC chromatogram of acids

Conditions: Same as Figure 9.
0.35 μL of 0.5 μg/μL.
Components: Acetic (1), Propionic (2), Butyric (3), Valeric (4).


FID RESPONSE 32 x 10^-12 Afs
1
2
3
4
0
10
20
30
TIME (Minutes)

to be restored to the level of 1 mL/min used in the analysis. A valve system would be beneficial in maintaining constant flow rate for successive analyses. It is common practice to subject packed columns to high temperatures overnight to produce satisfactory baselines. The usual (0.2 mm I.D.) capillary columns do not require this treatment.

As a last resort the column was backflushed with 5 mL of freshly distilled Barnstead filtered water. The column was connected to a hand-held syringe. It required considerable effort to pass the first few drops through the column. After the emergence of brown droplets of water, the water flowed through the column at 1 mL/ min. Then the column was connected to the inlet of the gas chromatograph and flushed with helium at 15 mL/min. Finally the column was slowly programmed to 150°C and held at 150°C for 4 hours. In this final step to dry the column great care must be taken to preserve the polymer (which now has the consistency of gelatine (8)) on the silica and to keep water from entering the split valving system of the gas chromatograph. In addition Grob (9) noted that a few percentage of extractable phase was sufficient to increase the viscosity of the washing solvent and result in permanent plugging of the capillary column. He recommended washing apolar silicone capillary column with acetone, a poor solvent (up to 50 mL) overnight.

The benefits of backflushing are clearly evident in the "before" and "after" backflushing chromatograms in Figures 14 and 15. In Figure 15 the "before" chromatogram (A) shows tailing alcohol preaks, but in the "after" chromatogram (B) tailing has been eliminated restoring resolution. Peak shape is an important parameter in determining the number of peaks that can be adequately separated. In Figure 15 the "before" chromatogram (A) shows a missing peak, 2,6-dimethylaniline (5). This is probably the result of large quantities of acid injected on the column before the injection of 2,6-dimethylaniline. It maybe prudent to use a different column for different classes of compounds. On the other hand, one might be able to concentrate amines on acid loaded DBWax column.

Other Concentration Methods

Test solutions were recycled through 30 cm of DBWax column. Poor recoveries were obtained for the polar low-molecular weight compounds.

Methyl ketones and aldehydes (1 ppm) were retained on strong anion exhange column loaded with sodium bisulfite. Aldehydes and methyl ketones were eluted with methanol and acetonitrile. This method appears to have some potential in separating methyl ketones and aldehydes from a complex mixture.

Figure 13. Effect of high flow rate and temperature programming on baseline

Conditions: Same as Figure 9.
A: Before treatment.
B: After treatment.

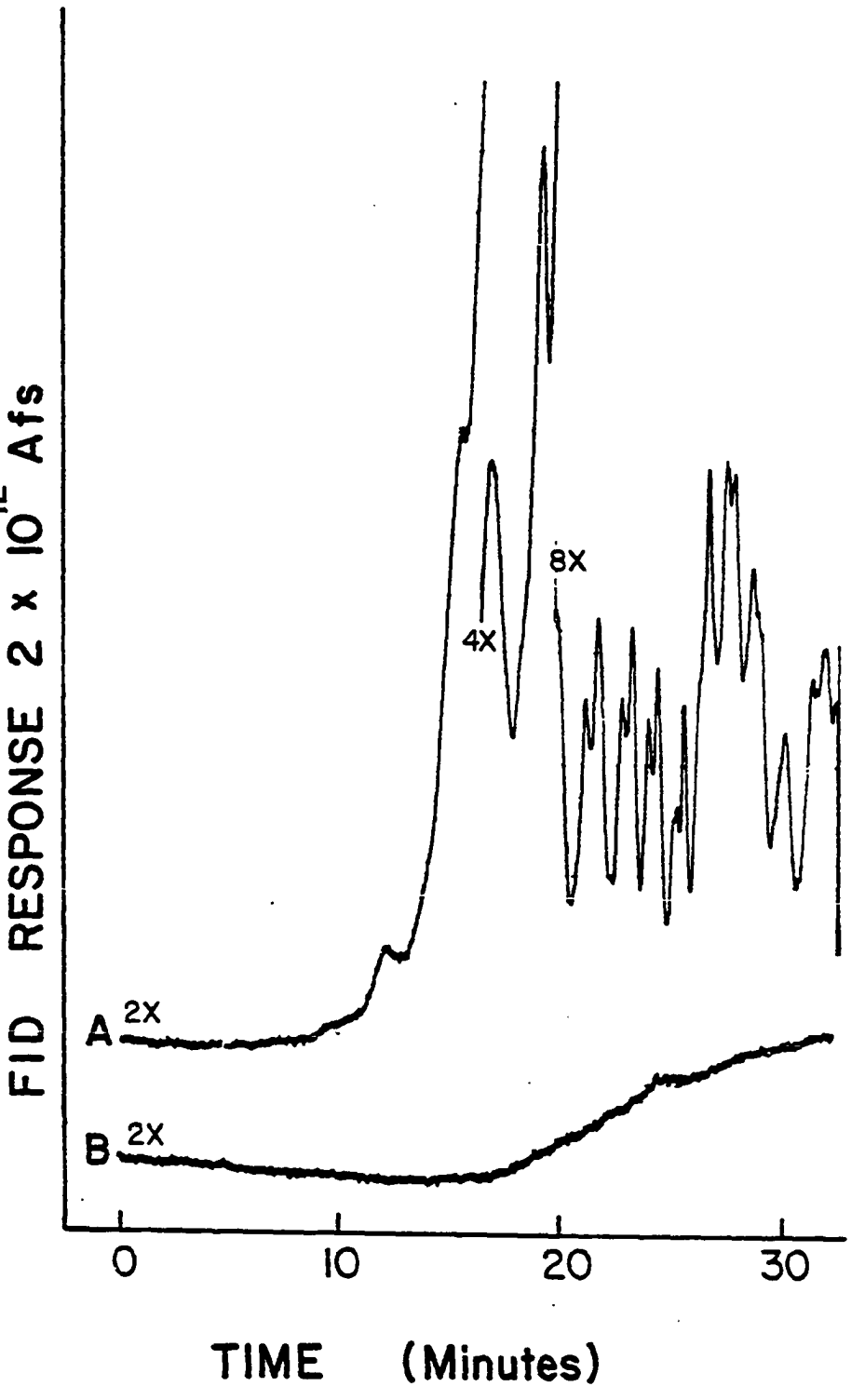

FID RESPONSE 2 x 10^-12 Afs
8X
4X
A 2X
B 2X
0
10
20
30
TIME (Minutes)

Figure 14. Effect of backflushing

Conditions: Same as Figure 9.
Components: Diethyl Ether (1); Acetone (2); Methanol, t-Butanol, Butanone (3); Ethanol, 2-Propanol (4); 2-Pentanone (5); Acetonitrile, i-Butylnitrile (6); 1-Propanol (7); i-Butanol (8); 1-Butanol (9); i-Penatanol (10); 1-Pentanol (11).
A: Deterioration of column showing tailing of alcohol peaks.
B: Restoration of column performance after backflushing with water.

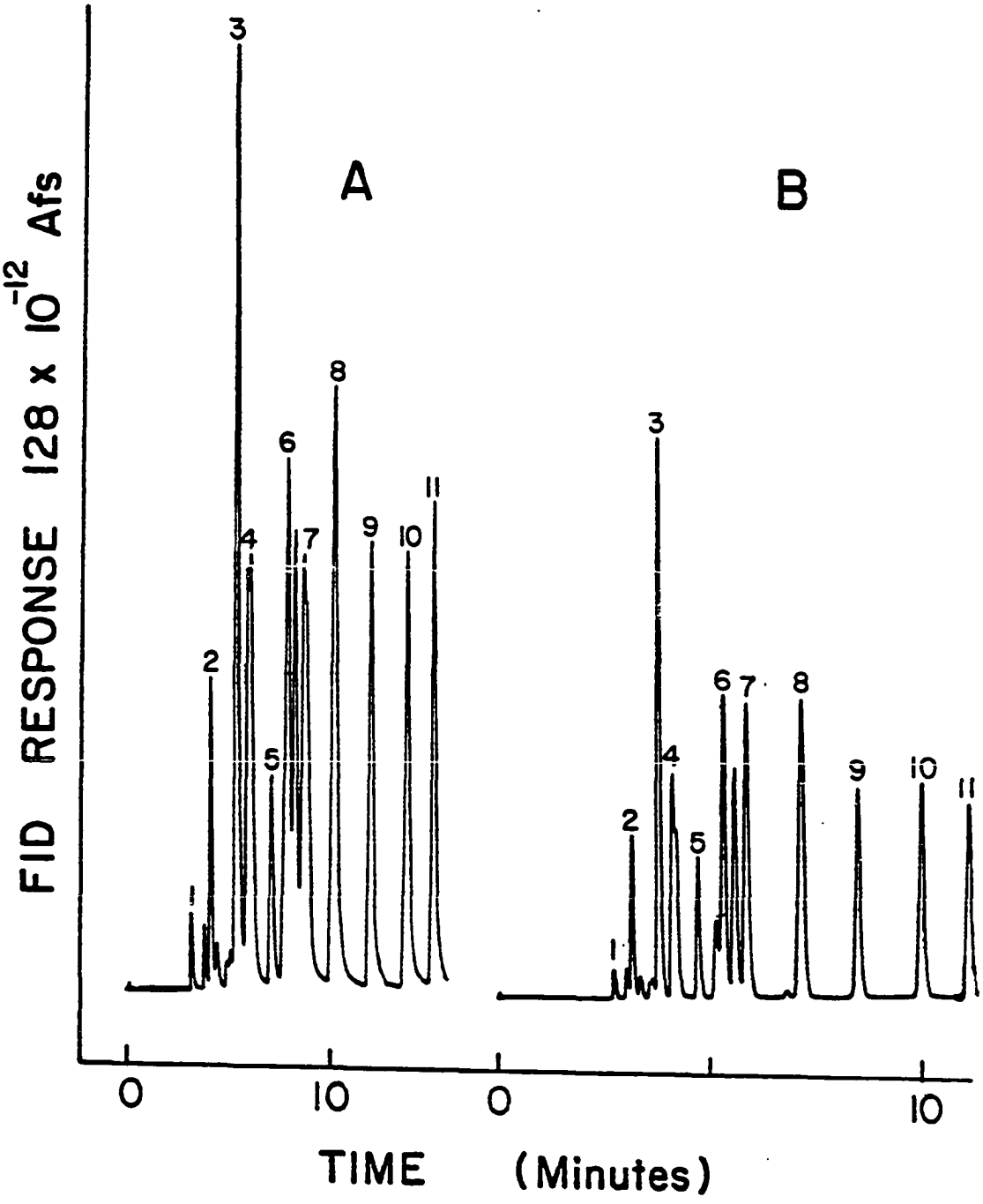
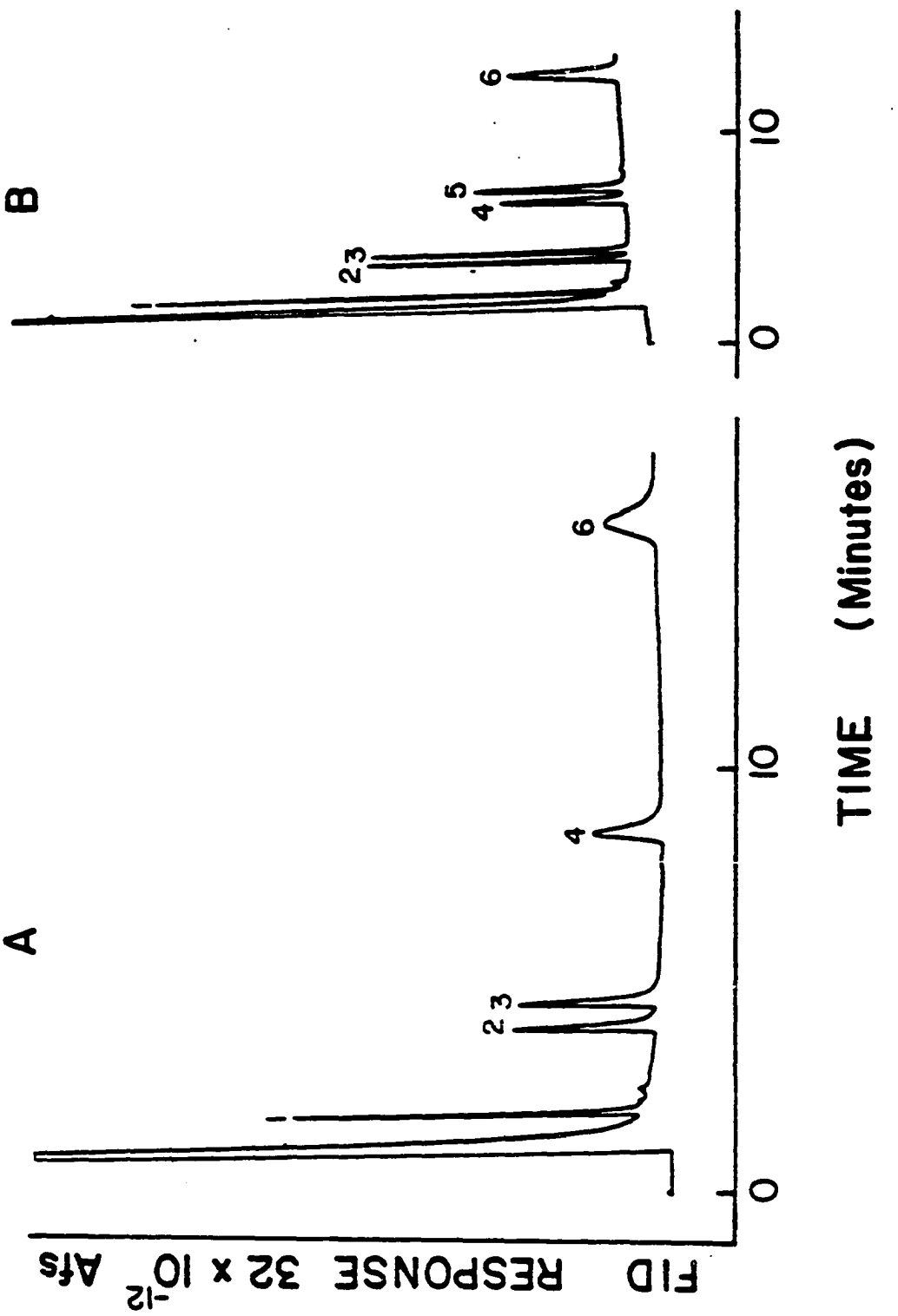

FID RESPONSE 128 x 10⁻¹² Afs
A
B
1
2
3
4
5
6
7
8
9
10
11
0
10
0
10
TIME (Minutes)

Figure 15. Restoration of a peak

Conditions: Same as Figure 9.
Isothermal at 130°C.
Components: 2-Octanone (1), 1-Octanol (2); Methyl Decanoate (3); 1-Decanol (4); 2,6-Dimethylaniline (5); 2,6-Dimethylphenol (6).
Concentration: 1 μg/μL hexane.
A: Before backflushing.
B: After backflusing.


A
B
23
4
5
6
0
10
TIME (Minutes)
FID RESPONSE 32 x 10⁻¹² Afs

CONCLUSION

The shape-selective zeolites, ZSM-5 and ElZ-115 were used to concentrate low-molecular weight polar compounds. The solvents used to desorb all the analytes tested were 1-propanol, acetone, methanol and acetonitrile. 1-Propanol was used for those analytes with low GC retention times. Acetone was used for those with intermediate retention times and methanol was used for those with high GC retention times. It is propable that 1-propanol and acetone would constitute the desorbing solvent system for all of the analytes tested. The desorption using acetone on alcohols was not tested.

Diethyl ether and methyl acetate were desorbed with 1-propanol. Acetonitrile was desorbed with 1-propanol or acetone. N-propyl acetate, n-propylnitrile, n-butylnitrile, and n-butyl acetate were desorbed with acetone. 1-Propanol was desorbed with methanol. 2-Pentanol, i-butanol, 1-butanol, i-pentanol and 1-pentanol were desorbed with either methanol or acetonitrile. The above order of analytes is given in terms of increasing retention times on DBWax GC column. The desorbing solvents were selectd so that the solvent did not interfere with GC quantitation.

1-Propanol was the desorbing solvent for propionaldehyde, acetone, n-butyraldehyde, butanone 2-

pentanone, n-butyric acid, and n-valeric acid. Concentration factors of 50 at 100 ppb level and 500 at 1 ppb level were acheived. Except for methanol, formaldehyde, acetaldehyde, acetic acid and propionic acid good recoveries were obtained at the 100 ppb level.

The small particle size and the fragile nature of ZSM-5 made it prone to problems of column plugging. The very large particle size of ELZ-115 resulted in premature breakthrough. A solution to this problem was to grind the ELZ-115 to smaller mesh size. Detailed optimization of the use of ELZ-115, such as, best mesh size, column dimensions, amount of zeolite and amount of desorbing sorbent was not investigated.

From the measurements by frontal chromatography the maximum volume at analyte concentration of 1 mg/mL that could be concentrated on 0.5 g ZSM-5 was calculated. The maximum volume of analyte that can be concentrated on the ZSM-5 column increased linearly with carbon number. The coefficient of determination of the maximum volume to carbon number was 0.97 for n-alcohols, n-aldehydes and acetone. From the recovery studies of Section I acetaldehyde with maximum volume of 11.0 mL could not be quantitatively recovered from 100 mL of solution at 100 ppb level. The sampling solution was reduced to 50 mL for quantitative recovery. It is apparent that for analytes with maximum

volume less than 11.0 mL, adjustments in the amount of zeolite or in the amount of sampling solution will be necessary for quantitative recovery. Although n-butyric acid had a high maximum volume (50.65 mL) and could be quantitatively recovered from 100 mL of water at 100 ppb level, only 7% was recovered from 1 L of water at 1 ppb level. Direct comparison of maximum volume of the acids cannot be made with other analytes because the capacity measurements of the acids was carried out using ELZ-115, but capacity measurements of all other analytes was made using ZSM-5.

The method of using pumps to load concentrating columns maybe useful where multiple runs from single sample is required. It would be prudent to design the instrument so that the process can be terminated if clogging occurs. The disadvantage of this method was that extensive cleaning of the apparatus was necessary each time a new solution was analyzed.

The gravity flow method of concentration was used for the majority of the experiments. A column was fashioned from a disposable pipette and connected to a reservoir. With 60-170 mesh ELZ-115, 100 mL of aqueous test solution eluted in 15 minutes. Unlike the pump loading method, different solutions were tested by simply cleaning the reservoir. The zeolite column was regenerated by washing

with methanol and water or by heating at 400°C for 4 hours or at 800°C for 2 hours.

A DBWax large-bore GC column was used for quantitation with flame ionization detection. At the temperature used the column showed good baseline stability for the determination of analytes at the ppm level by direct aqueous injection. The cross-linked stationary phase was stable to injections of polar solvents, such as, water, alcohols, acetonitrile. These solvents cannot be used in capillary columns with coated stationary phases. The thick-film of the column increased retention times so that subambient temperatures were unnecessary for the analysis of diethyl ether and methyl acetate. These characteristics together with the large diameter made it possible to inject large quantities of dilute solutions without serious loss of resolution. Column stability due to large number of injections of aqueous samples at analyte concentration of 1 ppm was not investigated. The DBWax large-bore column showed great improvement over packed column in terms of resolution and speed of analysis. In comparison with the usual (0.2 mm I.D.) columns the DBWax column exhibited greater sensitivity. For these experiments 1.4 to 0.3 μL were injected. The carrier gas flow rate was 1.2 mL/min and the split ratio was 1:15. Nitrogen was the make up gas. The instrument used did not have the valve system for

splitless injections. Even greater sensitivity may be achieved by using the splitless mode of injection.

For the analysis of acids, the baseline interfered with quantitation using DBWax column. One solution was to subject the column to high temperature (150^{o}C) at high flow rate (15 mL/min) of carrier gas. Another was to backflush the column with water. After this treatment, peak shape of alcohols was restored. A peak missing in the test mixture to evaluate column performance was also restored.

Shape selective zeolites, ZSM-5 and ELZ-115, have been demonstrated to be capable of extracting polar low-molecular weight compounds from water at the ppb level. Quantitation can best be carried out using gas chromatography with recently available large-bore columns. It is a method that can be extended to low-molecular weight compounds that are heat sensitive and cannot be distilled or thermally desorbed. It is a convenient method for field sampling because only the mini-column need to be transported to the laboratory for later analysis.

REFERENCES

1. Raymond, A.; Guichon, J. J. Chromatogr. 1975, 13, 173.

2. Haggin, J. Chem. & Engr. News Dec. 13, 1982, 11.

3. Tateda, A; Fritz, J. S. J. Chromatogr. 1978, 152, 329.

4. Wu, M. M.; Kaeding, W. W. J. Catal., 1984, 88, 478.

5. Deane, S.; Wilshire, K.; Western, R.; Mole, T.; Seddon, D.; J. Catal., 1984, 88, 499.

6. Campbell, D. J.; Lowe, B. M.; Rowley, a. G.; Williams, R.; Anal. Chim. Acta. 1985, 172, 345.

7. Lee, M. L.; Yang, F. J.; Bartle, K. D. "Open Tubular Column Gas Chromatography. Theory and Practice"; John Wiley & Sons: New York, 1984; p. 279.

8. Jennings, W. J & W Scientific, Inc., 3871 Security Park Drive, Rancho Cordova, CA 95670, private communication, Sept. 19, 1985.

9. Grob, K. J. Chromatogr., 1984, 299, 1.

SECTION III. CONCENTRATION OF ORGANIC COMPOUNDS IN WATER BY GAS PURGING AND BOILING

INTRODUCTION

As indicated in the Review of Literature, the volatile hydrophobic compounds can be sparged from water. From the discussion on steam distillation, there appears to be a large number of more polar compounds that can also be steam distilled. It was the intention of this work to concentrate both types of compounds, those that can be volatilized by gas purging and those that can be volatilized by steam distillation. The test compounds were selected to represent various classes of organic compounds having a variety of solubilities, molecular weights, and those compounds (such as, cyclohexanone) that are known to be poorly concentrated on XAD-type resins. Precautions were taken to avoid interferences (chemical and chromatographic). Hence the aldehyde test mixture was separate from those containing amines.

In this experiment aqueous test samples containing organic compounds were sparged with helium. The sample was heated and boiled (distilled) with helium purge. The vapors passed through a small Tenax column, which retained the organic compounds in the vapors. The heating was stopped. Then the Tenax column was removed and eluted with approximately 1 to 2 mL of organic solvent (methanol or acetonitrile). A portion of the organic solution was

injected into a GC capillary column where the analytes were separated and quantitated.

The experiment differs from the usual purge-and-trap experiment in that in the purge-and-trap experiment the sample is generally heated to 85°C or less. Boiling is avoided because too much water vapor will freeze and plug the liquid nitrogen trap (to focus the analytes at the head of the GC capillary column) or will produce too great an ion pressure in the mass spectrometer.

However, by boiling the sample, polar compounds (such as, heptanol, nitrobenzene) and high molecular weight compounds (such as, acenaphthene, fluorene) were also recovered from the test samples in addition to the usual volatile hydrophobic componds (such as, ethylbenzene, o-dichlorobenzene).

The analysis has been futher simplified by the injection of methanol solutions containing the concentrated organic compounds and some water directly on the rugged (cross-linked) fused silica column. The usual solvent exchange and solvent drying steps have been eliminated. In addition sensitivity has been greatly improved by large sample injection on the thick-film large-bore column. No additional concentration of the methanol solution was necessary for the analysis of organic compounds at the ppb level. For the large-bore column, resolution was better

than on packed column and sensitivity was better than on the usual (0.2 mm I.D.) capillary column.

The method appears to be especially attractive in analysis of volatile compounds in messy samples (containing large quantities of nonvolatile compounds) that cannot be directly injected into a capillary column.

EXPERIMENTAL

Chemicals

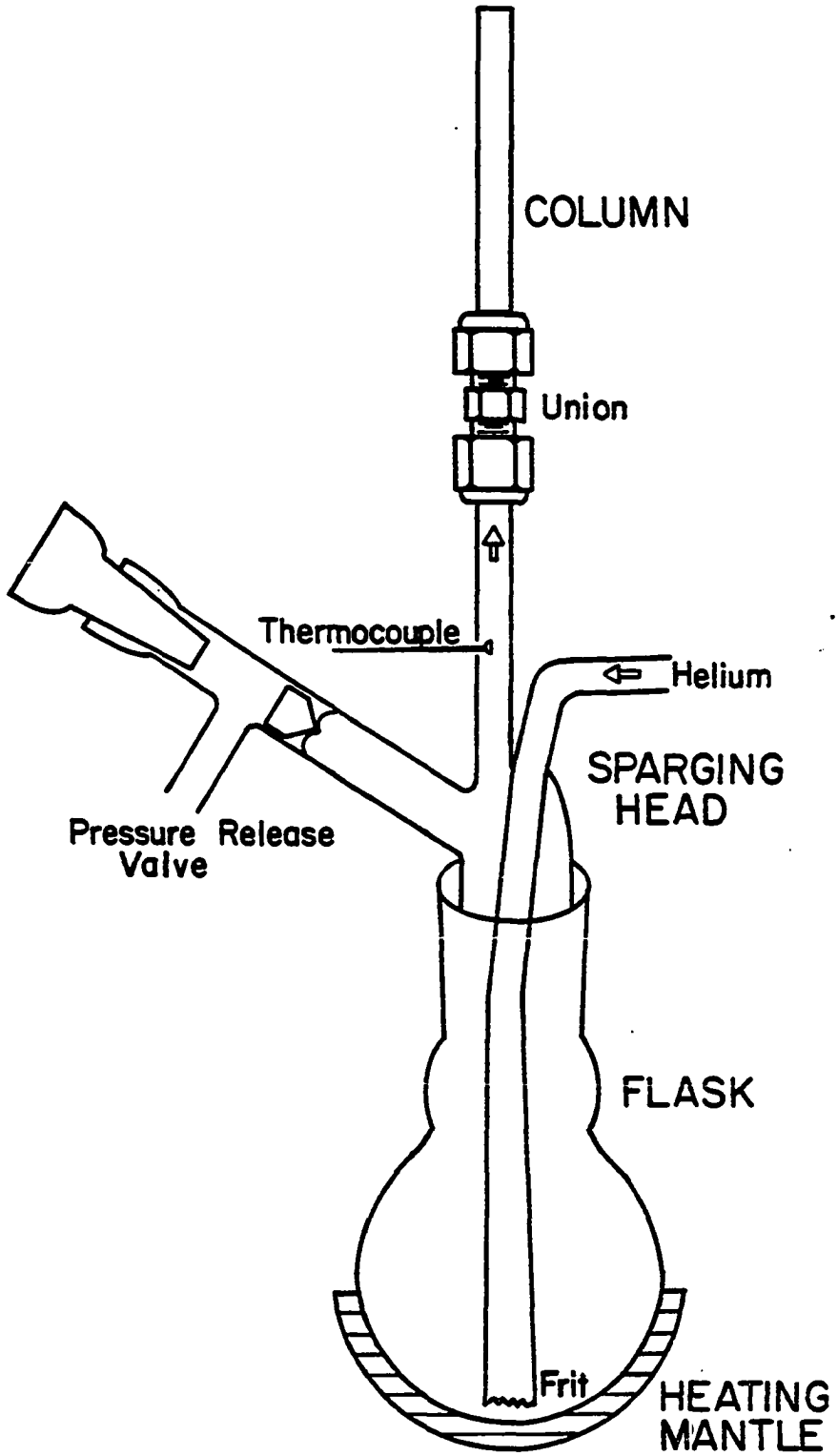
Water from Barnstead NANOpure II system (Barnstead, Division of SYBRON Corp.; Boston, MA 02131) was used. The Solvents were HPLC grade methanol and acetonitrile (Fisher Scientific, Fair Lawn, NJ 07418). Zero helium (Alfagaz, Specialty Gases Division, Liquid Air Corporation, One Embarcadero Center, San Francisco, CA 94111) was used in the concentration experiments.

Instrumentation

A Tracor 550 GC with flame ionization detectin (FID) and injector and detector modified for capillary column was used. Nitrogen was the make-up gas. For concentration experiments at 25 ppm and 2.5 ppm an HP (Hewlett Packard) 0.2 mm I.D. x 12 m FSOT (fused silica open tubular) methyl silicone (cross-linked) column was used. The flow rate through the column was 1 mL/min helium and the split ratio was 1:32. For other experiments a 0.53 mm (megabore) x 10 m column (1 μm thickness, FSOT, cross-linked) methyl silicone column (HP) was used. The split ratio was 1:7 and with a flow rate of 3.7 mL/min and the inlet pressure was 8 psi.

Figure 16. Apparatus for gas purging and distillation

Column: 2 mm I.D. 1/4" O.D. x 9 cm with 0.035 g of 80-100 mesh Tenax held in place by silanized glass wool.
Sparging head: 2 mm I.D. 1/4" O.D. gas inlet and outlet, pressure release valve, 10 mm medium frit, and thermocouple attached to S 24/40 inner joint.
Pot: 100 mL S 24/40 round bottom flask.


COLUMN
Union
Thermocouple
Helium
SPARGING HEAD
Pressure Release Valve
FLASK
Frit
HEATING MANTLE

Columns for Concentration of Organic Compounds

Preparation of Tenax Column In a typical experiment 0.036 g of 80-100 mesh Tenax GC resin (Alltech Associates, Arlington Heights, IL 60004) was packed into a 2 mm I.D. x 9 cm glass tube and held in place with silanized glass wool plugs. The column was cleaned by elution with 15 mL of methanol, followed by purging with helium at 15 mL/min at 70°C for 20 minutes.

Preparation of XAD Column The XAD-4 column (80-100 mesh, Rohm & Haas, Philadelphia, PA 19105) was prepared in a similar manner as the Tenax column. Another batch of XAD-4 resin was ground and sized. This batch required removal of fines by washing the resin several times with methanol and acetonitrile.

Concentration of Organic Compounds on Tenax Column

Fast Heating The apparatus in Figure 16 was used. The sparging head was fashioned from a 24/40 inner joint, 2 mm I.D. 1/4" O.D. glass tubing to receive 1/4" Swagelok fittings with graphite ferrules, 10 mm medium frit sealing tube, and a pressure release valve (Ace Glass, Incorporated, Vineland, NJ 08360) by the house glass shop. A thermocouple was embedded in the gas outlet of the sparging head to monitor temperature. The temperature monitored by this thermocouple was 80°C or higher for all successful

experiments. Organic compounds in methanol or acetonitrile stock solutions were added into 100 mL Barnstead filtered water in a S 24/40 100-mL round bottom flask. Helium was bubbled through the sparger at 20 mL/min and 10 psi head pressure.

In a typical experiment the water was heated to boiling in 15 to 20 minutes using a heating mantle and boiled for 2 minutes (variac setting of 70 V at 7.5 A). This method consistently gave good results, but was abandoned because the rate of pressure increase was too large at times and blew off the sparging head. An ice condensor was used especially for experiments involving short columns or long heating times (more than 30 minutes). It was fashioned from a plastic bottle by cutting off the bottom and securing it to the column with a cork.

Slow Heating For the slow heating experiments the pot variac (7.5 A) was set to 70 V and reduced to 65 V after 15 minutes. The initial helium flow rate was set at 20 mL/min and reduced as necessary (usually after 15 minutes) to reduce the internal pressure. The final helium flow rate was 1 mL/min. The total heating time for a typical experiment was one to 1.5 hours. The sparging head up to the union was heated so that at boiling the thermocouple registered 80°C to 95°C. The amount of water emitted from the column was collected. Good results were obtained when at least 1.5 mL of water was collected.

Removal of Organic Compounds from Concentrating Column

The Tenax column was removed from the apparatus and helium was passed through the column at 15 mL/min for one minute to flush out most of the water. The column was eluted with 0.14 to 2 mL (1 mL for typical experiment) of HPLC grade methanol or acetonitrile into a 2-mL receiving vessel or the Kuderna-Danish concentrator (Supelco, Inc., Bellefonte, PA 16823) containing 10 μL methanol or acetonitrile. Organic compounds were removed from the XAD-4 column in the same manner as in the fast heating experiment.

Quantitation

Quantitation of the analytes in the methanol effluent was determined by measuring the peak heights of the GC chromatograms using external standard.

Aqueous Sampling

In aqueous sampling experiments at ambient temperature 0.036 g of 80-100 mesh Tenax GC (as in accumulation experiment above) was packed into a disposable pipette which was attached to a 100-mL reservoir by a Teflon connector. The concentrated stock solution was added to the reservoir containing 100 mL H_2O. The water containing the organic test compounds was allowed to precolate through the column by gravity flow. Organic compounds were removed from the

concentrating column in the manner similar to the gas purging and steam distillation experiments using 1 mL methanol. Gas pressure was occasionally used to initiate flow. Quantitation was carried out as in the accumulation experiments above.

RESULTS AND DISCUSSION

Result of Aqueous Sampling

The simplest experiment involved aqueous sampling in which water containing 25 to 50 ppb organic compounds was allowed to percolate through the Tenax column at room temperature. The analytes were desorbed with methanol and the methanol solution was analyzed by GC. Table 12 gives the results of this experiment. Low recoveries of 50% or less were obtained for all compounds tested. Extensive investigations by Pankow and co-workers (1) have led them to conclude that poor recovery of nonpolar organic compounds from aqueous sampling on Tenax GC was due to poor transport rather than poor retention. They noted early breakthrough but once the analytes were retained on the column, elution with additional volumes of water did not result in additional breakthrough. The breakthrough process was not caused by exhaustion of a fixed amount of sorbing surface area but by diffusional limitation of the transfer of analyte through the sampling fluid to sorbing beads. The explanation of the results was based on a diffusion film that prevented the analytes from coming in contact with the surfaces of the Tenax particles before the analytes were swept from the column. These investigators were able to

Table 12. Accumulation of organic compounds at 25 to 50 ppb level on Tenax[a] by aqueous sampling

Compound	Percentage Recovery
1-Hexanol	51.1, 53.4
Ethylbenzene	21.3, 23.7
1-Heptanol	27.5, 32.5
o-Dichlorobenzene	43.6, 47.6
Ethyl Malonate + n-Butylbenzene	32.5, 41.0
1-Octanol	36.0, 42.2
Naphthalene	40.0, 40.0
1-Decanol	47.2, 61.2
2-Undecanone	45.3, 90.0
Biphenyl + 1-Undecanol	49.1, 70.4
Acenaphthene	27.0, 33.8
Fluorene	27.0, 45.0
Phenanthrene	50.0, 50.0

[a]Disposable piptette (5 mm I.D. x 14.6 cm) containing 0.036 to 0.40 g of 80-100 mesh Tenax.

obtain quantitative recovery for chlorinated aromatic and aliphatic hydrocarbons using aqueous samples by using two cartridges of 4.5 mL volumes of 60-80 mesh Tenax (2). An elaborate apparatus using large quantities (15 mL) of solvent was then necessary for the desorption of the analytes from the Tenax columns. Microdistillation and nitrogen assisted evaporation was necessary to concentrate the effluent from the Tenax column.

Leoni and co-workers (3) also obtained quantitative recovery of pesticides (hexachlorobenzenes, heptachlor, ronnel, parathion and methylparathion, etc.) at 1 ppb level by aqueous sampling of 8 to 15 liters on Tenax. As in the above example, large quantities of Tenax (48 cm x 1 cm column containing 1.5 g Tenax) were used. The analytes were eluted from the column with diethyl ether.

Result of Gas Purging and Heating

Table 13 shows the result of purging the aqueous test solution with helium. Heat was applied but was quickly removed just as the water began to boil. Only a single experiment was conducted for each compound tested. The results show that the more polar compounds, the alcohols and the heavier aromatic compounds (fluorene, biphenyl and phenanthrene) were poorly recovered. Only the volatile

Table 13. Accumulation of organic compounds at 25 to 50 ppb level on Tenax[a] by gas purging and heating

Compound	Percentage Recovery
1-Hexanol	0
Ethylbenzene	94
1-Heptanol	13
o-Dichlorobenzene	94
n-Butylbenzene	92
1-Octanol	14
Naphthalene	92
1-Decanol	0
2-Undecanone	96
Biphenyl + 1-Undecanol	58
Acenaphthene	100
Fluorene	27
Phenanthrene	0
Cyclohexanone	46
Benzaldehyde	61
Phenol	0

[a]Single run using 2 mm I.D. x 9 cm column containing 0.035 g of 80-100 mesh Tenax.

Table 13. (Continued)

Compound	Percentage Recovery
Ethyl Hexanoate	103
Acetophenone	48
Nitrobenzene	61
Methyl Benzoate	73
Phenylacetonitrile	15
p-Ethylphenol	4
Methyl Salicylate	42
Ethyl Cinnamate	46

nonpolar compounds were quantitatively recovered. The results are in agreement with the usual purge-and-trap experiments in which the temperature is kept below the boiling point of water resulting in the quantitative concentration of only volatile hydrophobic organic compounds.

Sample Concentration Range

Recovery Table 14 gives the results of the accumulation experiments of organic compounds at 25 ppm to 25 ppb level from water using gas purging and boiling the sample. Good recoveries were obtained for most of the compounds in this concentration range. The recoveries for the more polar compounds, such as, alcohols and higher molecular weight aromatic compounds were lower. The recovery of ethyl malonate was only 57% due to its high solubility in water. Results are not reported where water solubility has been exceed, for example for biphenyl, acenaphthene, fluorene and phenanthrene at 25 ppm.

Gas Chromatography The experiments at test sample concentrations of 25 ppm and a few at 2.5 ppm were analyzed using a regular GC (0.2 mm I.D.) capillary column. Comparison of Figures 17 and 18 show the change in sensitivity of at least 17 times using a 10 m large-bore GC

Table 14. Sample concentration range for the accumulation of organic compounds at 25 to 50 ppb level on Tenax[a] by gas purging and distillation

Compound	Percentage Recovery 25 ppm	2.5 ppm	25 ppb
1-Hexanol	81.4, 85.4		89.0, 101.8
Ethylbenzene	105.5[b]	96.4, 96.8	74.5, 87.9
1-Heptanol	103.1, 105.9	96.3, 96.9	77.1, 83.1
o-Dichlorobenzene	84.2, 90.2	78.7, 80.9	91.6, 101.4
Ethyl Malonate	53.7, 62.1	64.0, 72.0[c]	
n-Butylbenzene	82.1, 84.7	64.0, 72.0[c]	
1-Octanol	101.1, 103.1	96.1, 96.9	80.7, 83.7
Naphthalene	102.5[b]	99.8, 100.0	96.4, 100.6
1-Decanol	53.8, 63.4	94.3, 96.5	99.6, 102.2
2-Undecanone	95.8[b]	94.5, 104.3	97.3, 109.7
1-Undecanol + Biphenyl		80.3, 83.5	91.7, 96.7
Acenaphthene		98.1, 111.1	84.8, 85.0
Fluorene		66.0, 72.6	93.2, 98.8
Phenanthrene		61.9, 62.9	78.4, 89.2

[a]2 runs on 2 mm I.D. x 9 cm columns containing 0.035 g of 80-100 mesh Tenax.

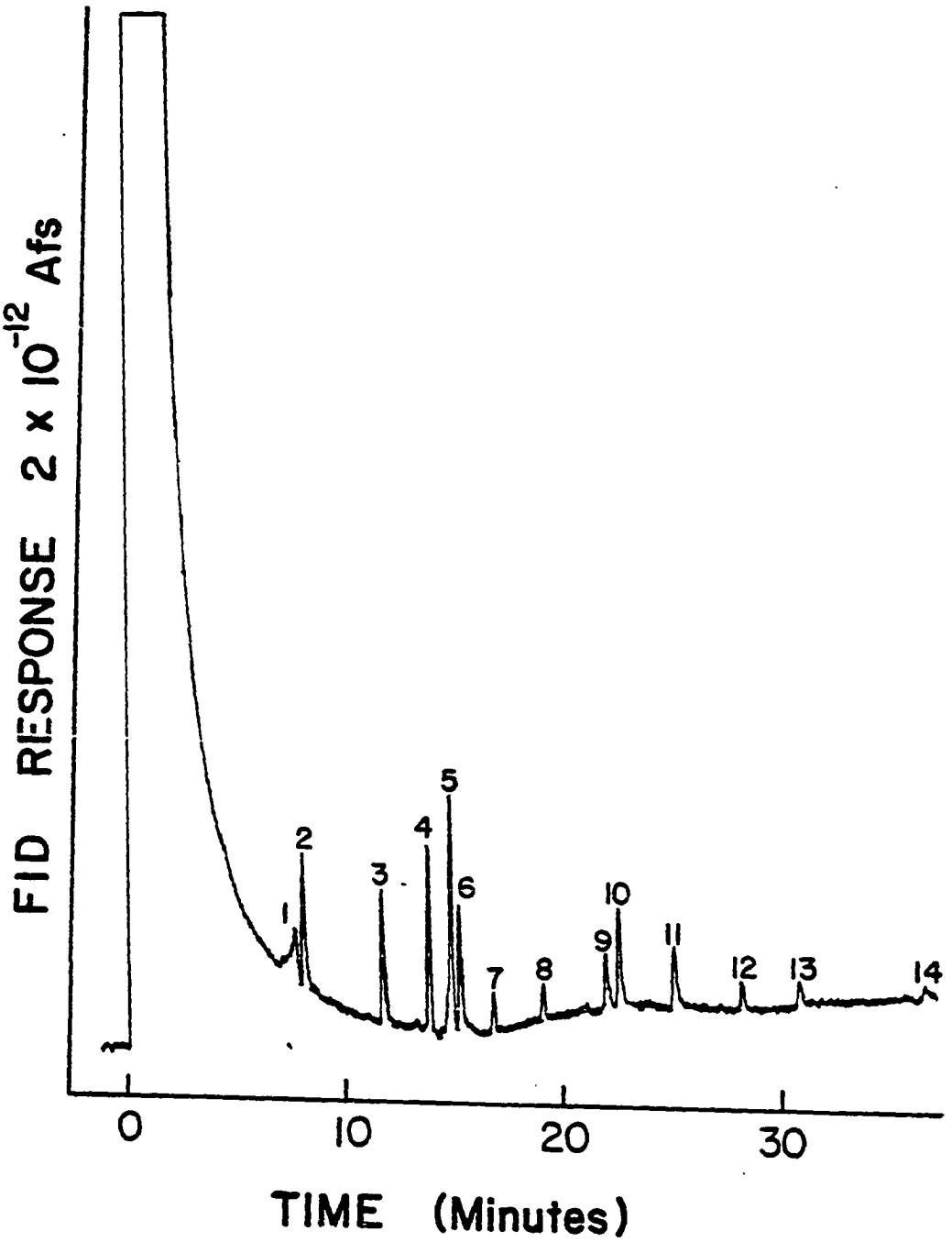
[b]Single run.

[c]Ethyl Malonate + n-Butylbenzene.

Figure 17. Typical GC chromatogram using narrow bore column

Conditions: Tracor 550 GC.
Column: Hewlett Packard 0.2 mm I.D. x 12 m methyl silicone.
Flow rate: 1 mL/min He.
Split: 1:32.
Make up gas: N_2 15 mL/min.
Detector: FID 2 x 10^{-12} Afs.
Temperature Program: Initial hold of 2 minutes at 40°C and programmed at 5°C/minute to 220°C and held at 220°C for 10 minutes.
Sample: 1.7 µL of 5 to 2.5 µg/mL.

Components: 1-Hexanol (1); Ethylbenzene (2); 1-Heptanol (3); o-Dichlorobenzene (4); Ethyl Malonate, n-Butylbenzene (5); 1-Octanol (6); Naphthalene (7); 1-Decanol (8); 2-Undecanone (9); Biphenyl, 1-Undecanol (10); Acenaphthene (11); Fluorene (12); Phenanthrene (13); n-Butylphthalate (14).


FID RESPONSE 2 x 10⁻¹² Afs
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12
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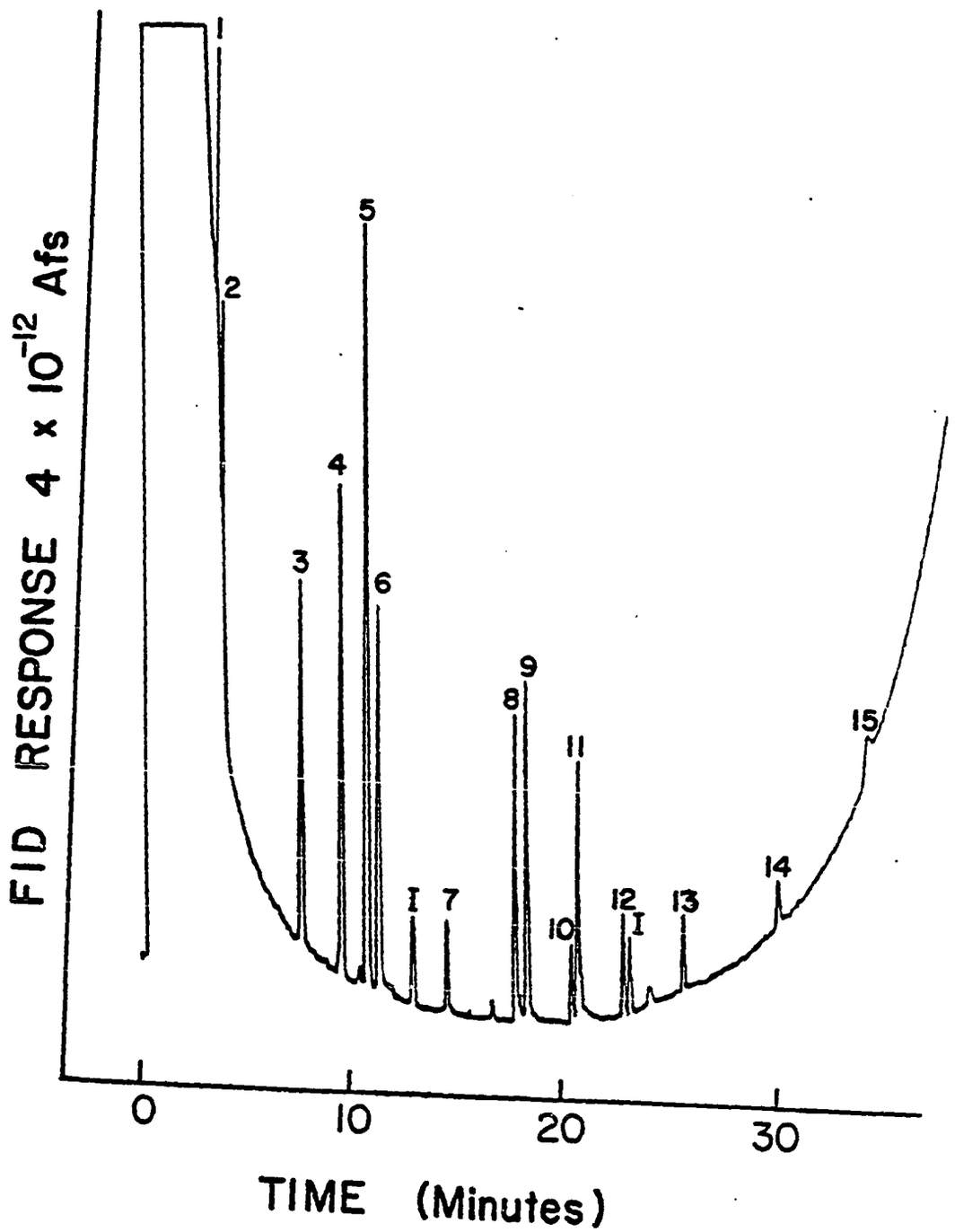
10
20
30
TIME (Minutes)

Figure 18. Typical GC chromatogram using megabore column

Conditions: Tracor 550 GC.
Column: Hewlett Packard 0.53 mm I.D. x 10 m methyl silicone (1 μm thick).
Flow rate: 3.7 mL/min He.
Split: 1:7.
Make up gas: N_2 15 mL/min.
Detector: FID 4 x 10^{-12} Afs.
Temperature Program: Initial hold of 2 minutes at 40°C and programmed at 5°C/minute to 220°C and held at 220°C for 10 minutes.
Sample: 0.3 μL of 5 to 2.5 μg/mL.

Components: 1-Hexanol (1); Ethylbenzene (2); 1-Heptanol (3); o-Dichlorobenzene (4); Ethyl Malonate, n-Butylbenzene (5); 1-Octanol (6); Naphthalene (7); 1-Decanol (8); 2-Undecanone (9); Biphenyl (10); 1-Undecanol (11); Acenaphthene (12); Fluorene (13); Phenanthrene (14); n-Butylphthalate (15); Impurity (I).


FID RESPONSE 4 x 10⁻¹² Afs
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14
15
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30
TIME (Minutes)

column. The increase in sensitivity made possible recovery studies at lower analyte concentration without concentration of the methanol effluent.

Effect of Tenax Column Dimensions

Table 15 gives the results for 2 mm x 9 cm, 1 mm x 9 to 14 cm, and 2 mm x 2.6 cm columns. There was no difference in results for these column. More work is needed to assess the merits of the 1 mm X 4.8 cm column. In early experiments, it was noted that water emitting from the column was cool when good results were obtained. Hence, subsequent experiments were carried out with an ice condensor to cool the column. The gas at the column inlet at 80°C to 95°C would desorb the analytes on the column as was noted in a similar case by Grob (4).

Hence a long column (9 cm) was preferred, because the outlet would be cooler and more likely to retain the organic compounds. However, a short column would decrease the back pressure simplifying the heating process. A device could be designed using carbon dioxide gas to cool the column more efficiently. It would require skillful manipulation and design, as too much cooling would freeze the water and plug the column and not enough cooling would allow the analytes to pass through the column.

Table 15. Effect of column dimensions on the accumulation of organic compounds at 25 to 50 ppb level on Tenax[a] by gas purging and distillation

Compound	Percentage Recovery 9 cm[b]	9 - 14 cm[c]	2.6 cm[d]	4.8cm[e]
Ethylbenzene	97, 97	74, 74	91, 97	19
1-Heptanol	97, 97	78, 94	92, 98	64
o-Dichlorobenzene	79, 81	79, 95	62, 103	82
Ethyl Malonate[f]	64, 72	63, 67	19, 49	64
1-Octanol	97, 97	73, 83	100, 104	115
Naphthalene	100, 100	89, 89	99, 105	111
1-Decanol	94, 96	93, 101	77, 97	109
2-Undecanone	94, 104	85, 87	121, 163	115
1-Undecanol[g]	80, 84	96, 98	71, 83	81
Acenaphthene	99, 111	77, 79	84, 84	62
Fluorene	66, 72	63, 69	63, 73	64
Phenanthrene	61, 63	60, 60	62, 62	60

[a]80-100 mesh Tenax. Eluted with 2 to 0.2 mL methanol.

[b]2 mm x 9 cm column.

[c]1 mm x 9 to 14 cm column.

[d]2 mm x 2.6 cm column.

[e]Single run for 1 mm x 4.8 cm column.

[f]Ethyl Malonate + n-Butylbenzene

[g]1-Undecanol + Biphenyl

A small diameter column was selected because it contained less resin which required less solvent to elute the analytes from the column. The main disadvantage of the small diameter column was that the back pressure was drastically increased. Thus a short, small diameter column appears to be an optimum. In this case the column containing only 0.0004 g of Tenax GC was used. There was drastic reduction in recovery for ethylbenzene (19%). However, the use of minute amounts of Tenax maybe useful for those analytes for which Tenax has a high capacity. The amount of solvent required for desorption of the analytes was not investigated. Hughes (5) discussed equations to predict on the basis of the intercept of the graph of recovery vs. solvent used whether irreversible sorption had occurred. These are useful data for the chemist in trying to devise a solvent system to desorb analytes from solid concentrating columns.

Evaluation of Losses

In an effort to study the losses that occurred during gas purging and distillation, the experiment was interrupted before completion of the entire heating process and the analytes were recovered from various sections of the apparatus. Table 16 summarizes the results.

Table 16. Study of losses of organic compounds at 50 ppb level on Tenax[a] by gas purging and distillation

Compound	Percentage Recovery on Tenax column	in aqueous effluent	on sparging head	in pot
Cyclohexanone	40	56		
Benzaldehyde	72			
Phenol	7	9		50
Ethylhexanoate	102			
Acetophenone	67		5	
Nitrobenzene	77		3	
Methyl Benzoate	78		3	
p-Ethylphenol	53	6		16
Methyl Salicylate	29	10		53
2-Methoxynaphthalene	66		4	
Ethyl Cinnamate	55		2	

[a]Single run using 2 mm I.D. x 9 cm column containing 0.035 g of 80-100 mesh Tenax.

Cyclohexanone was found in the water distilled through the column showing that breakthrough had occurred.

Because acetophenone, nitrobenzene, methyl benzoate, phenylacetonitrile, 2-methoxynaphthalene and ethyl cinnamate were found in the sparging head, this part of the apparatus was heated either by adjusting the pot variac (fast heating method) or by a separate heating tape (slow heating method).

Under the conditions of this experiment the phenols did not steam distill. The pot contents were extracted with methylene chloride, concentrated and submitted for GC-MC analysis. The results confirmed the presence of phenol, p-ethylphenol and methyl salicylate.

The results on phenol is in agreement with Grob (4), who recovered 67% phenol at 8 ppt level on activated carbon only after prolong (20 hours) closed loop stripping with steam.

Effect of pH

Table 17 gives the results of studies on other classs of compounds, phenols, amines, and other compounds of moderate water solubility. Highly water-soluble compounds, cyclohexanone and aniline were less than 50% recovered.

The pH of the test solution was changed to 2 in anticipation of high recovery for the acidic phenolic compounds. But no difference in recovery was noted for

Table 17. Effect of pH on the accumulation of organic compounds at 25 to 50 ppb level on Tenax[a] by gas purging and distillation

Compound	Percentage Recovery pH = 7	pH = 2[b]
Cyclohexanone	45.8, 53.8	
Benzaldehyde	88.4, 106.8	
Phenol	13.1, 17.7	13.7
Ethyl Hexanoate	102.4, 103.6	51.5
Acetophenone	80.0, 104.8	
Nitrobenzene	79.1, 105.9	
Methyl Benzoate	83.8, 86.2	86.1
Phenylacetonitrile	73.0, 85.0	
p-Ethylphenol	23.5, 26.9	23.6
Methyl Salicylate	26.8, 29.0	27.0
2-Methoxynaphthalene	93.2, 104.4	
Ethyl Cinnamate	76.2, 84.6	61.0
Aniline	24.3, 40.5	
Methylaniline	84.8, 104.4	
N,N-Dimethylaniline	100.8, 110.0	
Methyl Decanoate	99.2, 100.0	
Naphthylamine	6.5, 13.3	

[a]2 runs on 2 mm I.D. x 9 cm columns containing 0.035 g of 80-100 mesh Tenax.

[b]Single run.

phenols at pH 7 and pH 2. In fact at pH 2 ethyl hexanoate, a compound that was repeatedly quantitatively recovered, was only 51.5% recovered possibly due to hydrolysis. The results show that pH changes may be useful only if a particular class of compound, such as, phenols is being analyzed. Low pH affected the recovery of ester.

Effect of Heating Rate

The fast heating experiments consistently gave good results. However, the rapid and unpredictable pressure increase could not be controlled. This presented a danger to the experimenter. The rate of vaporization of water molecules was dependent on a number of factors, such as, ionic strength, volume of headspace, and volume of water. This rate must be precisely controlled for the success of the experiment. In addition, the pressure drop for the sorbent was dependent upon the bed packing diameter, bed length, particle mesh size and range, the adsorbent and the flow rate of the gas. Pressure drop data on Tenax GC are given by Krost et al. (6). The maximum pressure drop of 1400 mmHg was found for a 0.5 cm x 3 cm column packed with 60-80 mesh Tenax at helium flow rate of 9 mL/min. Unfortunately no data was given for 80-100 mesh Tenax GC.

A device that would respond rapidly and accurately to pressure changes would be beneficial, so that the

experimenter can make appropriate changes in heat input and gas flow rate. Knowledge of the maximum pressure drop that can be tolerated by the apparatus would also be desirable. Because the above were not available, an experimental procedure of slower heating rate was sought. A comparison of the fast heating rate and slow heating rate (Table 18) shows that the recoveries for slow heating rate were consistently lower for the slow heating method. However, the results of the slow heating method (Table 17) are considerably better than the results for the usual purge-and-trap experiment (Table 13) especially for alcohols, benzaldehyde, fluorene, acetophenone, nitrobenzene, phenylacetonitrile and ethyl cinnamate.

Effect of Another Adsorbent: XAD-4

The Tenax column was used successfully because the experiment was designed so that initially those compounds that accumulate on the resin were in the vapor state. But as more compounds which had lower retention on Tenax were tested, it was necessary to cool the column so that the analytes were not thermally desorbed from the column. Thus it was likely that the fluid passing through the column was to a greater extent in the liquid state. However, very dilute solutions of analytes in water were only poorly

Table 18. Effect of heating rate on the accumulation of organic compounds at the 25 to 50 ppb level on Tenax[a] by gas purging and distillation

Compound	Percentage Recovery Fast Heating	Slow Heating[b]
1-Hexanol	89.0, 101.8	86.2
Ethylbenzene	74.5, 87.9	73.2
1-Heptanol	77.1, 83.1	78.8
o-Dichlorobenzene	90.7, 100.5	78.8
Ethyl Malonate + n-Butylbenzene	77.8, 94.8	78.6
1-Octanol	80.7, 83.7	76.7
Naphthalene	96.4, 100.6	87.5
1-Decanol	99.6, 102.2	65.5
2-Undecanone	97.4, 109.8	91.4
Biphenyl + 1-Undecanol	91.7, 96.7	82.9
Acetophenone	82.4, 99.0	75.0
Fluorene	93.2, 98.8	83.3
Phenanthrene	78.4, 89.2	50.0

[a]2 runs on 2 mm I.D. x 9 cm columns containing 80-100 mesh Tenax.

[b]Single run.

Table 19. Accumulation of organic compounds at 50 ppb level on XAD-4[a] by gas purging and distillation by slow heating method

Compound	Percentage Recovery
1-Hexanol	96.6, 99.0
Ethylbenzene	79.1, 81.7
1-Heptanol	79.4, 86.6
o-Dichlorobenzene	87.7, 88.3
Ethyl Malonate + n-Butylbenzene	81.4, 86.2
1-Octanol	79.9, 82.9
Naphthalene	90.4, 95.2
1-Decanol	91.0, 96.4
2-Undecanone	96.8, 99.0
Biphenyl + 1-Undecanol	83.7, 88.5
Acenaphthene	76.6, 79.4
Fluorene	79.9, 87.3
Phenanthrene	65.3, 69.9

[a]2 runs on 2 mm x 9 cm column containing 0.065 g of 80-100 mesh XAD-4.

recovered by Tenax as shown in the experiments on aqueous sampling. While it may be possible that analytes can be sorbed onto dry Tenax resin, if the concentration of the analyte is sufficiently high, or if the surface of the Tenax can be modified to be more hydrophilic, a polymer that is amenable to aqueous sampling was sought. The results using XAD-4 (Table 19) by the slow heating method show that the recoveries using XAD-4 were comparable to those using Tenax. The XAD-type resins have not been as popular as Tenax because the former exhibit poor stability at high temperatures resulting in high bleed that obscured quantitation when thermal desorption was used.

Correlation of Recovery with Water Solubility and Molecular Weight

Table 20 and Table 21 list literature values of molecular weight, vapour pressure and water solubility (7,8,9). The available vapor pressure data at ambient temperature are similar and no correlation is apparent. No simple correlation between recovery and boiling points (bp) is apparent. An example is that phenol (bp 180^{o}C) was only 15% recovered, but o-dichlorobenzene (bp 182^{o}C) was quantitatively recovered. They have about the same boiling points.

Table 20. Molecular weight, boiling point and vapor pressure of organic compounds[a, b, c]

Compound	Molecular Weight (Daltons)	Boiling Point (°C)	Vapor Pressure (mm Hg)
Acenaphthene	154.21	279	
Aniline	93.12	184 - 186	1 (35°C)
Acetophenone	120.15	202	1 (15°C)
Benzaldehyde	106.12	179	1 (26°C)
Biphenyl	154.2	254 - 255	
n-Butylbenzene	134.21	183.1	1 (23°C)
Cyclohexanone	98.14	155.6	4 (20°C)
1-Decanol	158.28	236.9	1 (70°C)
o-Dichlorobenzene	147.01	180.5	1 (20°C)
N,N-Dimethylaniline	121.8	192 - 194	1.1 (30°C)
Ethylbenzene	106.18	136.12	7 (20°C)
Ethyl Cinnamate	176.21	271	
Ethyl Hexanoate	144.21	166 - 167	
Ethyl Malonate	160.17	198 - 199	
p-Ethylphenol	122.16	219	
Fluorene	166.21	295	
1-Heptanol	116.2	175.8	

[a]Windholz (7).

[b]Verachueren (8).

[c]Huang et al. (9).

Table 20. (Continued)

Compound	Molecular Weight (Daltons)	Boiling Point (°C)	Vapor Pressure (mm Hg)
1-Hexanol	102.17	157	0.98 (20°C)
2-Methoxynaphthalene	158.19	272	
Methylaniline	107.15	194 - 196	0.3 (20°C)
Methyl Benzoate	136.14	198 - 200	1 (37°C)
Methyl Decanoate			
Methyl Salicylate	152.14	220 - 234	1 (54°C)
Naphthalene	128.16	217.9	1 (53°C)
2-Naphthylamine	143.18	306	
Nitrobenzene	123.11	210 - 211	0.15 (20°C)
1-Octanol	130.22	194 - 195	1 (54°C)
Phenanthrene	178.32	340	
Phenol	94.11	182	0.2 (20°C)
Phenylacetonitrile	117.14	233.5	0.1 (20°C)
1-Undecanol	172.31	243	
2-Undecanone	170.30	231 - 232	

Table 21. Solubility of organic compounds[a, b, c]

Compound	Solubility
Acenaphthene	0.0255 mol/m^3
Aniline	34,000 mg/L
Acetophenone	5500 mg/L
Benzaldehyde	3300 mg/L
Biphenyl	7.5 mg/L (25°C)
n-Butylbenzene	1.56 mol/m^3
Cyclohexanone	23,000 mg/L (20°C)
1-Decanol	
o-Dichlorobenzene	145 mg/L (25°C)
N,N-Dimethylaniline	
Ethylbenzene	152 mg/L
Ethyl Cinnamate	
Ethyl Hexanoate	
Ethyl Malonate	1 g/50 mL
p-Ethylphenol	
Fluorene	0.0119 mol/m^3
1-Heptanol	2000 mg/L (20°C)

[a]Windholz (7).

[b]Verachueren (8).

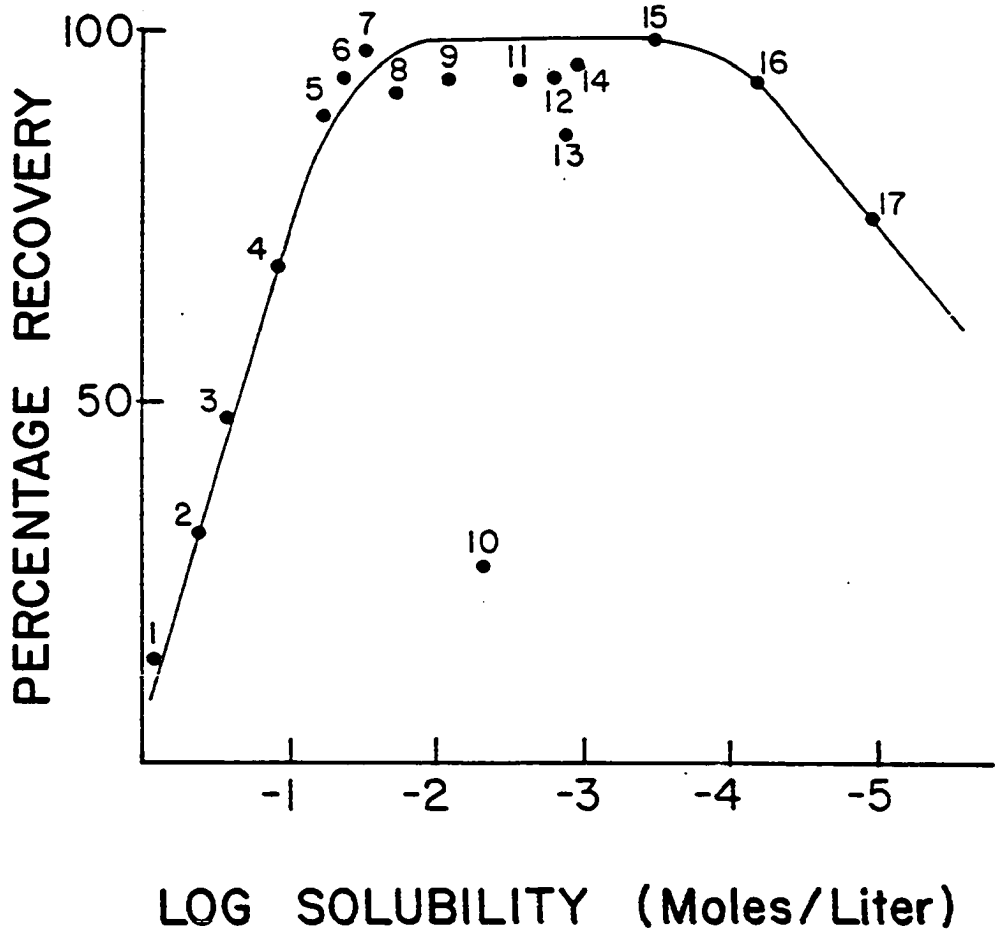
[c]Huang et al. (9).

Table 21. (Continued)

Compound	Solubility
1-Hexanol	5900 mg/L (20°C)
2-Methoxynaphthalene	
Methylaniline	
Methyl Benzoate	
Methyl Salicylate	5000 mg/L
Naphthalene	30 mg/L
2-Naphthylamine	
Nitrobenzene	1900 mg/L (20°C)
1-Octanol	
Phenanthrene	1.6 mg/L (15°C)
Phenol	82 g/L (15°C)
Phenylacetonitrile	
1-Undecanol	
2-Undecanone	

Figure 19. Correlation of recovery with water solubility and molecular weight

Components: Phenol (1), Aniline (2), Cyclohexanone (3), Ethyl Malonate (4), 1-Hexanol (5), Acetophenone (6), Benzaldehyde (7), Nitrobenzene (8), 1-Heptanol (9), Methyl Salicylate (10), 1-Octanol (11), Ethylbenzene (12), Metnyl Benzoate (13), o-Dichlorobenzene (14), Naphthalene (15), Biphenyl (16), Phenanthrene (17).


100
50
PERCENTAGE RECOVERY
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
-1
-2
-3
-4
-5
LOG SOLUBILITY (Moles/Liter)

The available solubility data were used to obtain Figure 18. As water solubility decreases the recovery increases until a plateau (nitrobenzene to naphthalene in Figure 19) at 100% is attained. The experimental data which do not fall in the 100% region may be due to high vapor pressure that resulted in loss during sample transfer or due to interference in GC quantitation. Finally, as molecular weight increases the recovery decreases (biphenyl to phenanthrene). A more precise correlation can be obtained if data for a given class of compounds, such as, alcohols or alkanes, could be treated in the above manner. The correlation can be used to predict recoveries of compounds not tested in this work on the basis of literature values of water solubility and molecular weight. The extremely low recovery of methyl salicylate is not clear.

With the advancements in chromatographic methods more accurate data on water solubility can be found. McNally and Grob (10,11) suggested a simple method for measuring solubility using headspace analysis. The GC signal from the headspace was plotted against the concentration of the analyte in water at a given temperature. The signal increased linerarly and then leveled off. The lowest concentration at which the signal was constant (also the maximum signal) corresponded to the limiting concentration (solubility) of the analyte in water.

For compounds that are not volatile, the method of Mays and co-workers (12,13) can be used. A column of glass beads coated with the analyte was connnected to an HPLC column. Solubility was calculated from the volume of water pumped through the glass bead column and the amount of analyte eluted from the HPLC column.

Real Samples

The experimental procedure was applied to real samples. Figure 20 to Figure 24 show the GC chromatograms for blank (Barnstead water), tap water, instant decafffeinated coffee, strawberry jello and shale retort water. Except for Barnstead and tap water, the samples produced foam and the amount of sample was reduced to 95 mL. Other investigators have added anti-foaming agents (14,15), decreased the gas sparging (introduced the gas through a needle rather than a frit (16) or introduced the gas over the sample (17) or reduced the sample volume by 40% (18) to alleviate foaming.

The chromatogram of the strawberry jello showed a single intense peak. Although this peak was not identified, Nunez and Bemelmans (19) have reported the major volatile compounds of fresh strawberry as 3-pentanone, methyl butanoate, α-pinene, D-limonene, n-decanal methyl-N-methylanthranilate, β-caryophyllene and geranyl butanoate.

Figure 20. GC chromatogram of Barnstead water (blank)

Conditions: Same as Figure 18.
1.3 μL injection.

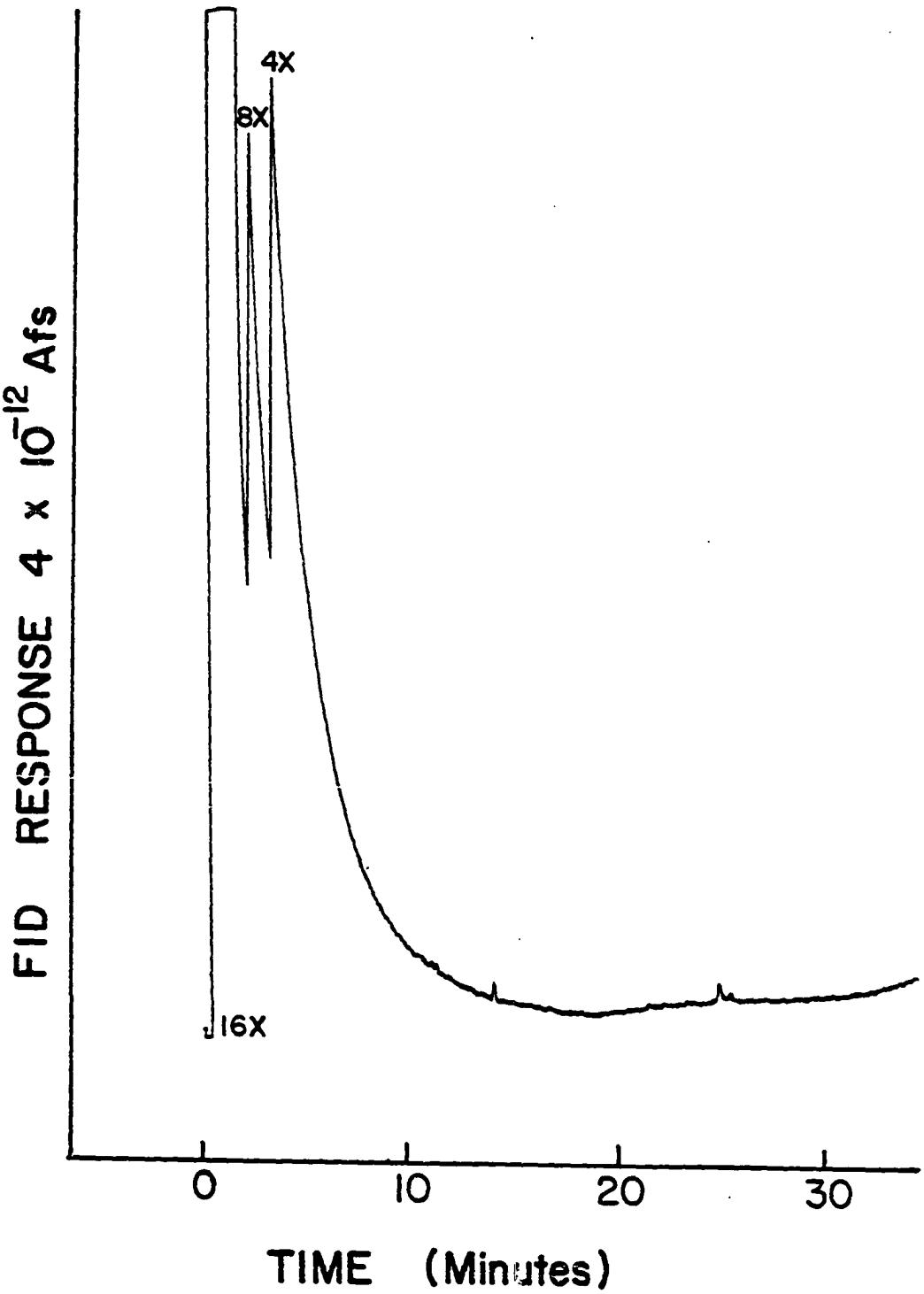

4X
8X
16X
FID RESPONSE 4 x 10⁻¹² Afs
0
10
20
30
TIME (Minutes)

Figure 21. GC chromatogram of Iowa State University tap water

Conditions: Same as Figure 18.
1.3 μL injection.

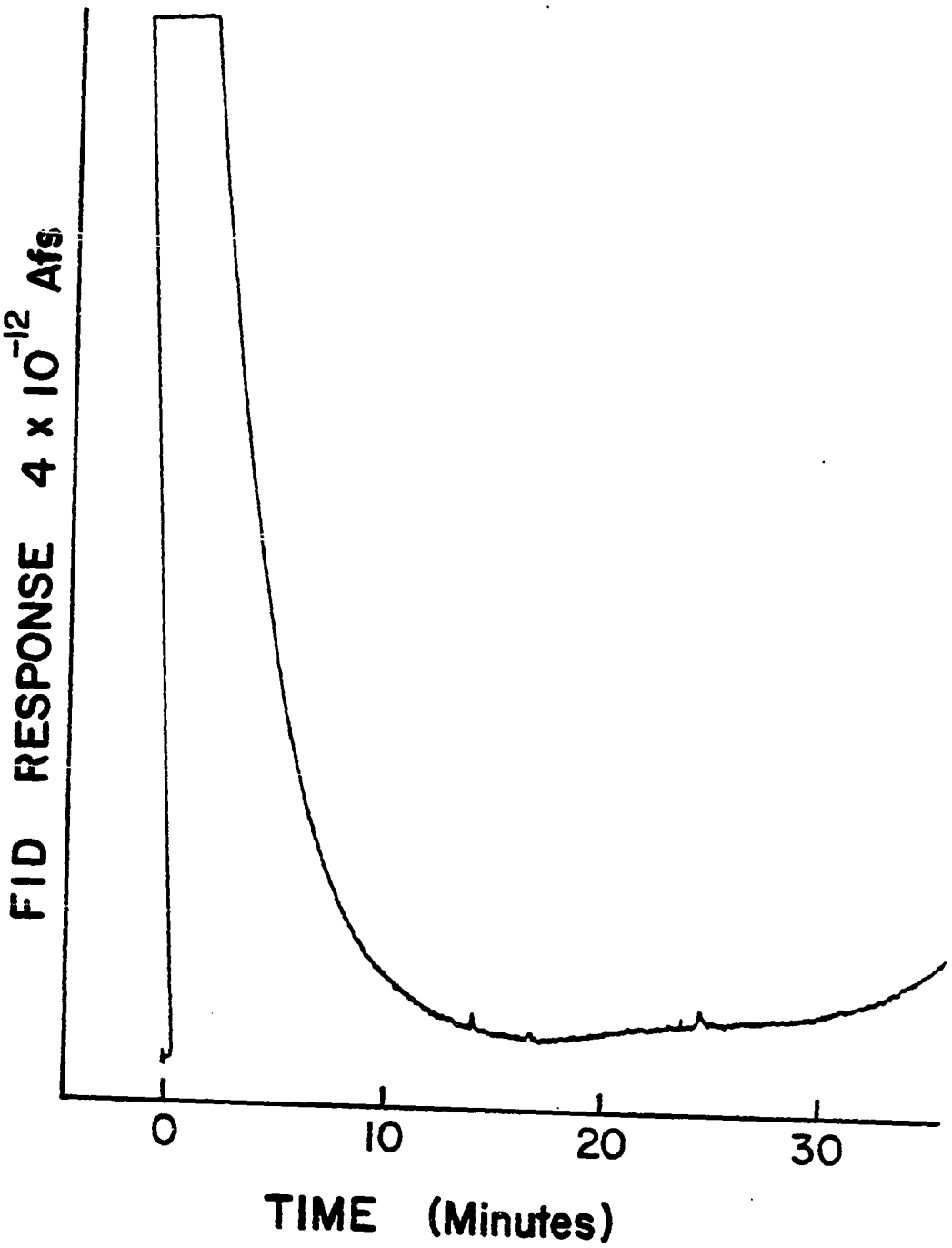

FID RESPONSE 4 x 10⁻¹² Afs
0
10
20
30
TIME (Minutes)

Figure 22. GC chromatogram of instant decaffeinated coffee (1 cup, pH 8)

Conditions: Same as Figure 18.
1.3 μL injection.

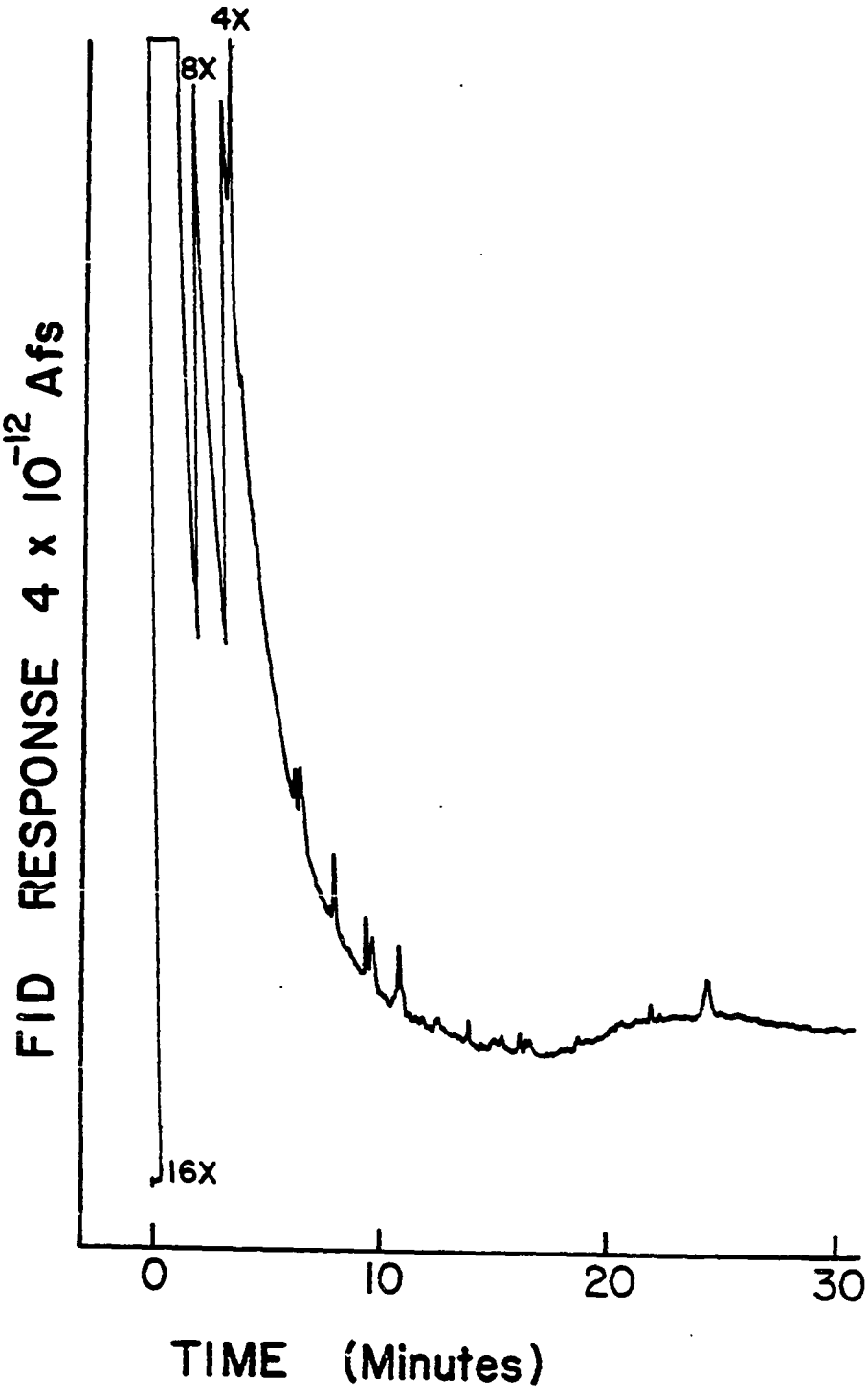

4X
8X
16X
FID RESPONSE 4 x 10⁻¹² Afs
0
10
20
30
TIME (Minutes)

Figure 23. GC chromatogram of strawberry jello (1g)

Conditions: Same as Figiure 18.
1.2 μL injection.

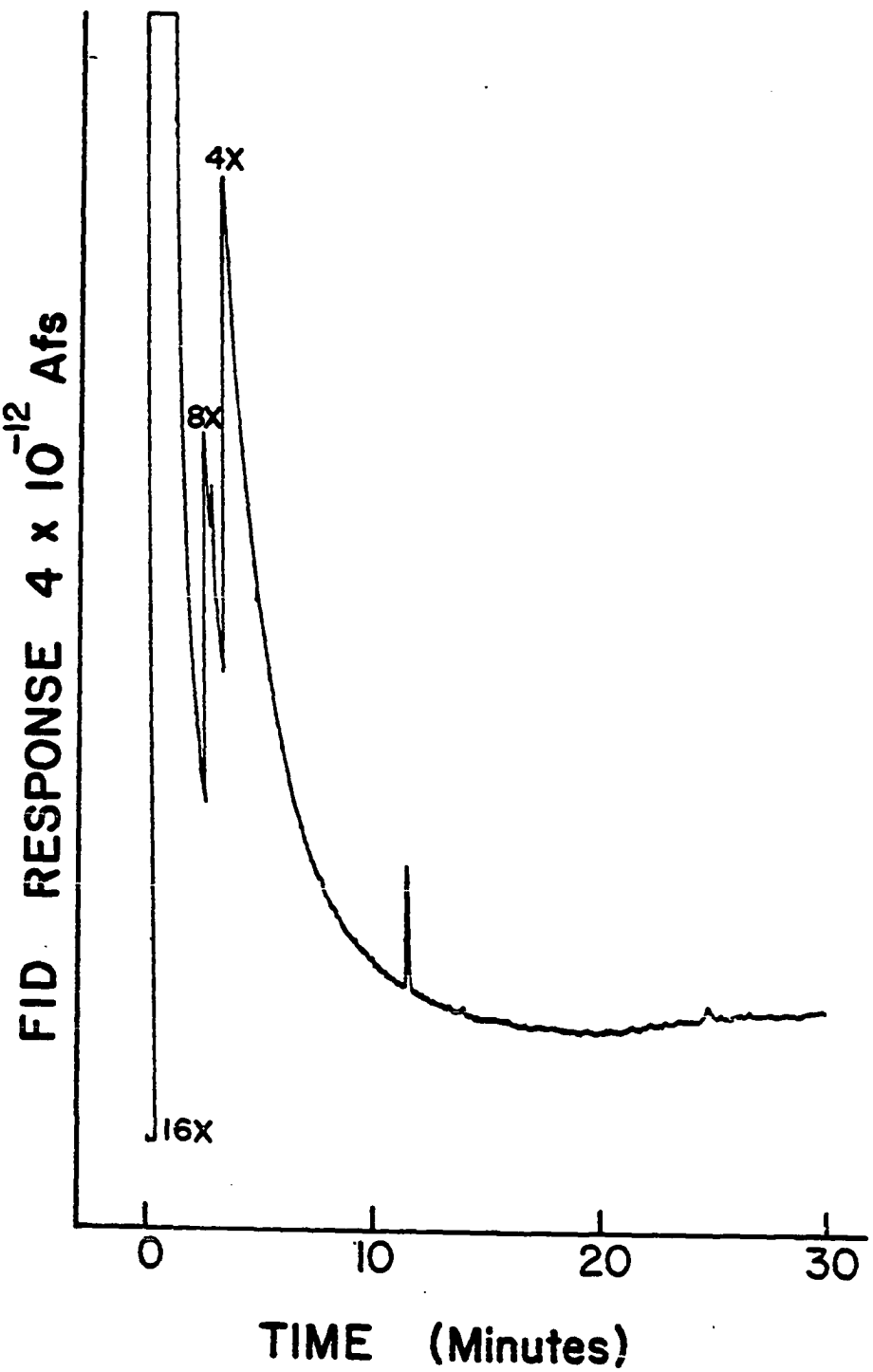

FID RESPONSE 4 x 10⁻¹² Afs
4X
8X
16X
0
10
20
30
TIME (Minutes)

Figure 24. GC chromatogram of shale oil retort water (pH 7.5)

Conditions: Same as Figure 18.
1.3 μL injection.
Components: 4-Ethylpyridine (1); benzonitrile (2); 2,3,5-trimethylpyridine (3); n-nonanoic acid (4); n-decanoic acid (5).

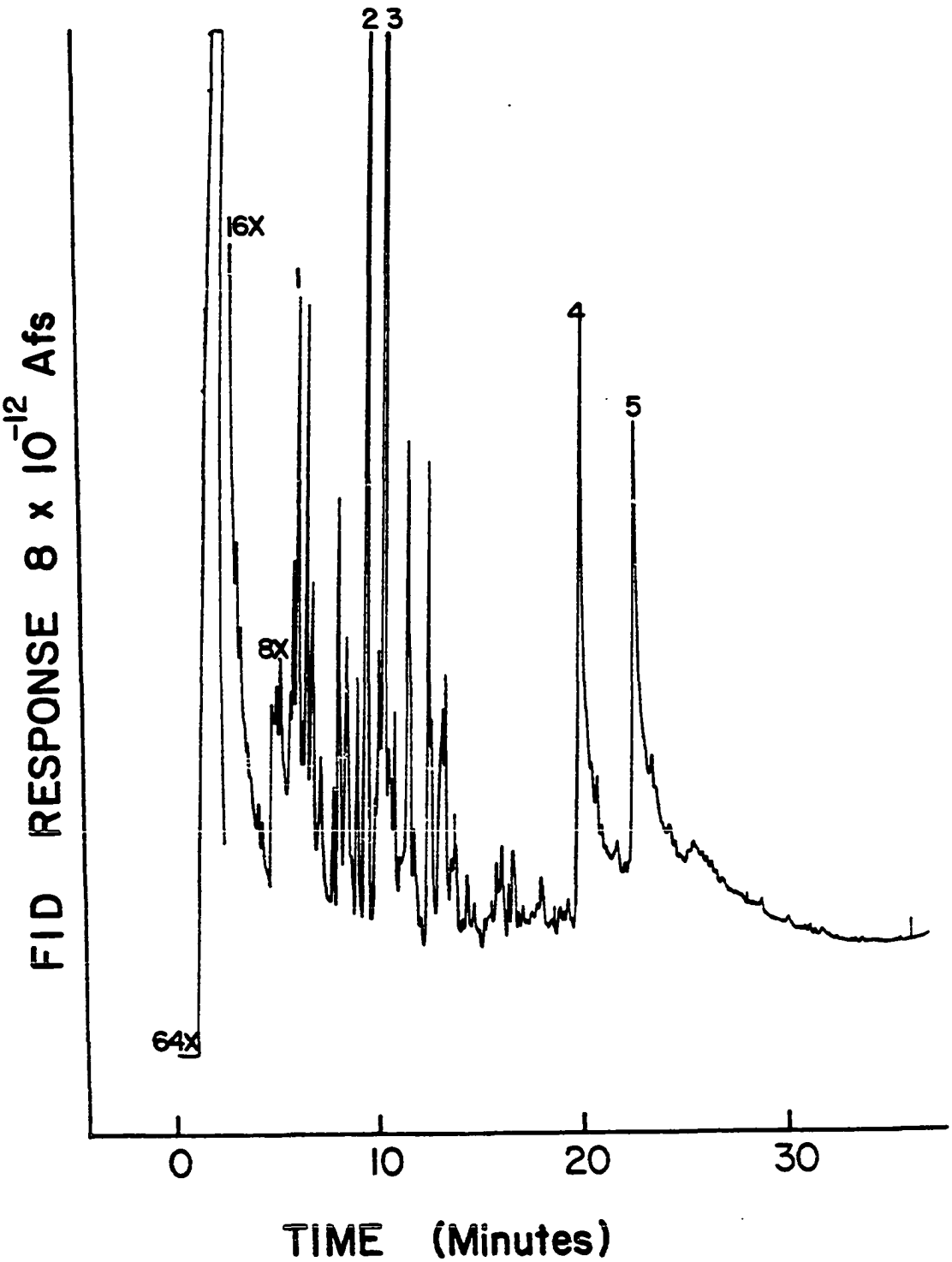
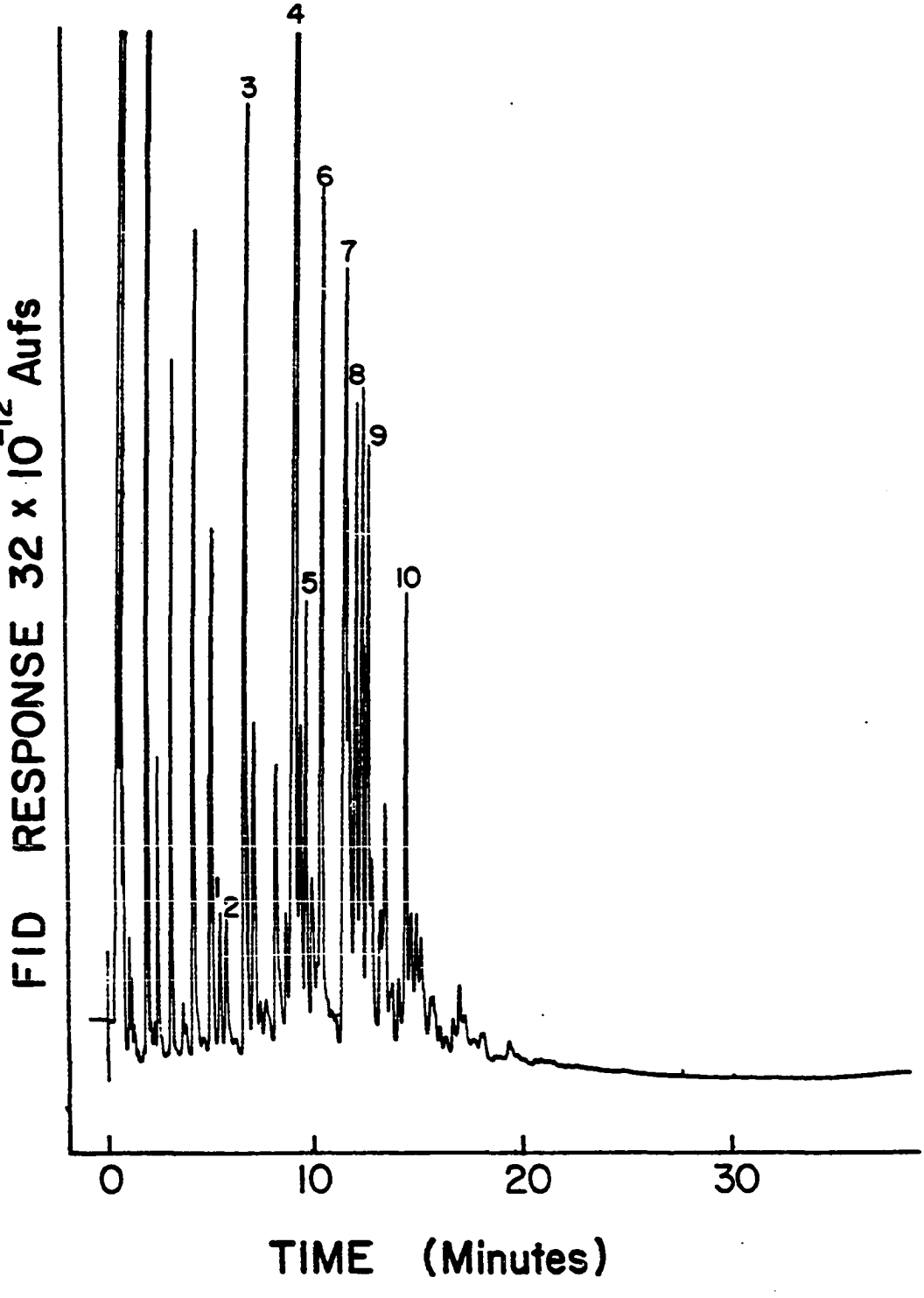

FID RESPONSE 8 x 10⁻¹² Afs
64X
16X
8X
1
2 3
4
5
0
10
20
30
TIME (Minutes)

Figure 25. GC chromatogram of breakthrough of compounds in shale oil retort water

Conditions: Same as Figure 18.
Components: Pyridine (1); 2-Methylpyridine (2); 4-Methylpyridine (3); Cyclohexanone (4); 4-Ethylpyridine (5); Aniline (6); 2,3,4-Trimethylpyridine (7); 4-Octyne (8); 2,3,4-Trimethy-2-cyclopenten-1-one (9); 1-Ethoxyethylbenzene (10).


FID RESPONSE 32 x 10⁻¹² Aufs
1
2
3
4
5
6
7
8
9
10
0
10
20
30
TIME (Minutes)

Volatile organic acids have also been identified in gelatine (20).

Because breakthrough was noticed for the shale oil retort water experiment, another experiment was carried out using the retort water diluted ten times. There was no change in the profile of the gas chromatogram of this experiment indicating no change in the relative amounts of compounds retained by Tenax or in the kinds of compounds accumulated. The concentrated methanol solution for the shale oil retort water sample was submitted for GC-MS analysis. The results were compatible with the experimental data. Highly soluble compounds (in this case, the pyridines) were not completely retained. They were also found in the water that emerged from the concentrating column (Figure 25). The C_9 and C_{10} acids that are not normally determined by the usual purge-and-trap methods were found by this method of gas purging and boiling. These acids required the high temperature of boiling. A method to prevent breakthrough is to use a resin, such as, XAD-4, that has been demonstrated to have high capacity for the compounds that were not retained by Tenax GC.

CONCLUSION

Organic compounds were poorly recovered on Tenax by aqueous sampling, in agreement with other authors. The bed volume of Tenax must be increased to obtain quantitative recovery.

In the purge-and-trap experiment, volatile hydrophobic compounds were easily concentrated from water using helium as the sparging gas and heating the sample up to the boiling point of water. The vapors passed through a concentrating column (Tenax) where the organic compounds are retained. In this experiment the water was boiled (distilled) with continued gas purging of the water.

The experiment was quantitative in the concentration range of 25 ppm to 25 ppb. The effect of column dimensions was studied in an attempt to reduce column volume as much as possible. A column containing a small volume of Tenax would require a small volume of desorbing solvent, increasing sensitivity. The goal of these experiments was to find the dimensions of a small diameter Tenax column containing a minimum of Tenax so that this concentrating column could be directly interfaced with the large-bore GC analytical column. The small diameter column that was used increased the pressure considerably during the final stages of the sparging experiment.

The experiment on the evaluation of losses was in agreement with other investigators. Losses occurred in cooler zones of the apparatus. Most of the phenols remained in the boiling flask. Other strategies to volatilize the phenols were investigated. The ionic strength was increased considerably. Losses occurred during the addition and dissolution of large quantities (30% w/v) of sodium sulfate. At pH 2 the recovery of phenols was the same as at pH 7. At pH 2 only 51% of ethyl hexanoate was obtained. The merits of another adsorbent should be investigated for the concentration of phenols at low pH.

A procedure was found in which the sample was heated quickly up to the boiling point. Then the rate of heating was decreased so that the rate of vaporization of water was decreased to reduce the pressure in the headspace. Simultaneously the flow rate of the carrier gas was decreased. For this slow heating method, the results of recovery were consistently lower than those of the fast heating method in which the rate of heating was not reduced. Automation of this process would be a great benefit to the experimenter.

The effect of XAD-4 in concentrating volatile organic compounds was tested. The results using XAD-4 were comparable to those using Tenax for hydrophobic volatile organic compounds using the slow heating method. Because

XAD-4 has been used successfully in aqueous sampling, XAD-4 should be tested for the recovery of other more polar compounds that can be distilled with gas purging.

The percentage recovery of the analytes increased linearly with the negative logarithm of the water solubility up to solubility of 2 g/L. Quantitative recovery was obtained for those compounds for which the solubility was less than 2 g/L. However, when the molecular weight exceeded 125 daltons, the percentage recovery again decreased linearly with the negative logarithm of the water solubility. The results are not surprising because the concentration of analytes above a solution is dependent on the solubility of the analyte in the given solution. The anomalous behavior of methyl salicylate is not clear.

The method of gas purging and distillation was applied to real samples. For drinking water no organic compounds were found. The volume of the sample was reduced 5% to increase the headspace to dissipate the foam for jello, instant decaffeinated coffee and shale oil retort water.

Pyridines in the shale oil retort water were not concentrated on Tenax GC, in agreement with the experimental results for aniline. But large amounts of polar compounds, n-nonanoic and n-decanoic acids were obtained by the gas purging and distillation method. These acids cannot be concentrated by the usual purge-and-trap method. The

pyridines were found in the water that passed through the Tenax column.

By sparging an aqueous sample initially at room temperature, the volatile hydrophobic compounds were concentrated on Tenax GC. As the temperature was increased and kept at the boiling point, more polar compounds and hydrophobic higher molecular weight compounds were concentrated. The basic nitrogen compounds were found to be easily volatilized, but could not be concentrated on Tenax. Hence a suitable adsorbent, other than Tenax, would be more appropriate for these compounds.

REFERENCES

1. Pankow, J. F.; Isabelle, L. M.; Kristnsen, J. T. J. Chromatogr. 1982, 245, 31.

2. Leuenberger, C.; Pankow, J. F. Anal. Chem. 1984, 56, 2518.

3. Leoni, V.; Puccetti, G.; Colombo, R. J. Ovidio, D. J. Chromatogr. 1976, 125, 399.

4. Grob, K. J. Chromatogr. 1974, 84, 255.

5. Hughes, D. R. Anal. Chem. 1983, 55, 78.

6. Krost, K. J.; Pellizzari, E. D.; Walburn, S. G.; Hubbard, S. A. Anal. Chem. 1982, 54, 810.

7. Windholz, M. "The Merck Index", 9th Edition; Merck & Co., Inc.: Rahway, New Jersey, 1976.

8. Verachueren, K. "Handbook of Environmental Data on Organic Chemicals"; Van Nostrand Reinhold Company: New York, 1977.

9. Huang, G.-L.; Shih, W.-Y.; Mackay, D. Environ. Sci. Technol. 1985, 19, 522.

10. McNally, M. E.; Grob, R. L. J. Chromatogr. 1984, 284, 105.

11. McNally, M. E.; Grob, R. L. J. Chromatogr. 1983, 260, 23.

12. May, W. E.; Wasik, S. P.; Freeman, D. H. Anal. Chem. 1978, 50, 175.

13. May, W. E.; Wasik, S. P.; Freeman, D. H. Anal. Chem. 1978, 50, 997.

14. Rose, M. E.; Colby, B. N. Anal. Chem. 1979, 51, 2176.

15. Erickson, M. D.; Alsup, M. K.; Hyldburg, D. A. Anal. Chem. 1981, 53, 1256.

16. Westendorf, R. G. Am. Lab. (Fairfield) 1981, 13(10), 88.

17. Pellizzari, E. D. Anal. Chem. 1980, 52, 1936.

18. Bellar, T. A.; Lichtenberg, J. J. J. Am. Water Works Assoc. 1974, 66, 739.

19. Nunez, A. J.; Bemelmans, J. M. H. J. Chromatogr. 1984, 294, 361.

20. Hausser, E. E.; 190th American Chemical Society National Meeting; Sept. 8-13, 1985; Chicago, IL; ANYL No. 70.

SUMMARY

In Section I, low-molecular weight aldehydes and ketones were concentrated by a hydrophobic zeolite (ZSM-5) which contained discrete (6 Å circular and 5.1 Å to 5.7 Å elliptical) channels. The organic compounds are believed to be retained in these channels. The carbonyl compounds at 100 ppb level were desorbed with a small volume of acetonitrile and converted to the 2,4-dinitrophenylhydrazones. The derivatized analytes were recovered by solvent extraction with pentane followed by microdistillation. The 2,4-dinitrophenylhydrazones were analyzed by reversed phase HPLC on C_{18} column at 254 nm.

Good recoveries were obtained for the model compounds, except formaldehyde. External standards were used because isomerization, degradation and other reactions have been reported using ZSM-5. The method was applied to the analysis of drinking water. No aldehydes or ketones were found in drinking water from Ames, IA. The drinking water from Des Moines, IA contained 1.6 ppb butanone.

In Section II, other polar low-molecular weight compounds, diethyl ether, acetates, nitriles, alcohols, aldehydes, ketones and acids were concentrated by the ZSM-5 and a similar zeolite, Silicalite. Except for methanol, formaldehyde, acetic acid, and propionic acid good

recoveries were obtained for model compounds at the 100 to 200 ppb levels. Concentration factors of 50 at 100 ppb and 500 at 1 ppb were achieved. Satisfactory desorbing solvents were 1-propanol, acetone, methanol and acetonitrile.

A fused silica capillary column (DBWax) was used for the quantitation. The stationary phase (cross-linked) and the film thickness (1 μm) and large diameter (0.525 mm I.D.) made it possible to inject large samples of dilute solutions of water and polar solvents without serious deterioration of column performance. Subambient temperatures were necessary for analytes with low GC retention volumes. Concentration of the solutions containing the analytes desorbed from the zeolites was not needed. For the determination of acids, the column was subjected to high carrier gas flow rate (15 mL/min) and high temperature (150^{o}C) or backflushed with water to obtain a baseline satisfactory for trace analysis.

In Section III, the method of distillation with gas purging concentrated a variety of classes of organic compounds. The compounds were selected so that amines, alcohols, ketones, aldehydes, esters, phenols, nitriles, chlorinated compounds and polynuclear aromatic compounds were represented.

Good recoveries were obtained for the sample concentration range 25 ppm to 25 ppb. Unlike normal gas purging experiments, the sample was heated and boiled. The

entire apparatus was heated to 85°C or greater, so that the analytes would not be lost on the walls of the apparatus. The concentrating column (Tenax) was cooled to prevent thermal desorption of the analytes. The helium gas flow rate was maintained at as high a level as possible to prevent plugging. For safety a slow heating procedure was devised. The heating rate and helium flow rate were reduced as necessary to prevent loss of sample. The analytes were desorbed from the concentrating column by solvent elution with methanol or acetonitrile. The concentrated solution was injected into a large-bore (0.525 mm I.D.) capillary column and the analytes were quantitated by GC with FID.

Acidification (pH 2) of the sample solution showed no improvement in the recovery of phenols. The XAD-2 concentrating column gave results comparable to the Tenax column using the slow heating method.

Recovery of the analytes was primarily dependent on the water solubility and molecular weight of the analyte.

The analytes from very "dirty" samples were concentrated and analyzed directly by gas chromatography. Less sample (more headspace) was necessary for the strawberry jello, instant decaffeinated coffee, and shale oil retort water, all foaming samples. This is a minor imconvenience in view of the fact that usual sample preparation require filtration, extraction and distillation.

The broad range in capacity and the inertness of the GC capillary column allowed large volumes of the concentrated solution to be injected directly into the GC column. Concentration by microdistillation was unnecessary. This combination of the solvent elution of the concentrating column and analysis on large-bore GC column greatly simplified the analysis of organic compounds in water at trace levels.

The large-bore fused silica column was not as flexible as the normal (0.2 mm I.D.) column, but it was easily installed in a normal gas chromatograph. Additional flow regulators at the inlet were an advantage because the gas chromatograph was used for packed column originally. For temperature programmed experiments the high temperature regions of the chromatogram exhibited some bleed reminscent of packed columns. The short (10 m) column was suitable for the compounds studied reducing retention times, so that the compounds did not elute in the high bleed region.

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