STUDIES OF SELECTED PRIORITY POLLUTANTS

AND THEIR PRESENCE IN

THE KAW RESERVOIR

By

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1977

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PREFACE

This study is concerned with the determination of the extraction efficiencies of selected Priority Pollutants and their presence in the Kaw reservoir. The primary objective is to evaluate the usefulness of purge and solvent extraction procedures and to determine the potential of the Kaw water to contain halogenated compounds after being chlorinated.

The author expresses his appreciation to his major adviser, Dr. Louis P. Varga, for his assistance and guidance throughout this study. Appreciation is also extended to the other committee members, Dr. Horatio Mottola and Dr. Sterling Burks, for their assistance in preparing the final manuscript.

Special thanks are given to Mr. Dave McCartney for his help in sampling and chlorinating the Kaw reservoir water, and to Mr. Jerry Caplinger for his invaluable assistance throughout this study.

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CHAPTER I

INTRODUCTION

In recent years, much attention has been given to the presence of halogenated organic compounds in raw and treated drinking waters. Because many such compounds are known or suspected to be toxic or carcinogenic, and since one city's wastes often become another city's drinking water, the presence of these compounds is undesirable. The problem is increased by the apparent formation of such compounds from precursors, either naturally-occurring or introduced into the environment by man, during chlorination for the purpose of disinfection. Therefore it is not only desirable but necessary to develop analytical methods for detecting, identifying, and quantitating halogenated organic compounds, and to determine their presence in existing and potential water supplies.

In 1976, largely as a result of the so-called Consent Decree, the Environmental Protection Agency began compiling a list of Priority Pollutants; that is, pollutants which warrant priority attention for analytical methodology development and determination in natural, treated, and waste waters. The pollutants on this list, which now number 129 and include many halogenated organics, pesticides, and cer-

tain inorganics, were chosen on the basis of known occurrence in the environment and evidence of toxicity or carcinogenicity to aquatic life or humans. Since the development of the Priority Pollutants list, much progress has been made toward improving analytical methods, especially gas chromatography-mass spectrometry.

The studies of the effect of storage on phenolic compounds and the purge and extraction efficiencies reported in this work were largely the result of another project in which this lab was involved (EPA project number R805242, Dr. Anthony Gaudy, head). In that project, the effects of selected priority pollutants on sewage treatment were studied, and this lab performed gas chromatographic analyses. During the course of the project, these experiments were made.

The city commission of Stillwater is desiring to increase the city's water supply by piping water from the Kaw reservoir, a man-made lake on the Arkansas river about 45 miles north of Stillwater. Local groups opposing the plan have arisen, citing among other reasons the presence of toxic or potentially toxic compounds in the reservoir. At the time of this work, however, no actual study had been done to determine the presence (or absence) of such compounds. In the belief that such a study might be beneficial, it was made and is reported here.

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CHAPTER II

LITERATURE REVIEW

Introduction

There are basically seven steps involved in trace organic analysis: sampling, preservation, extraction, concentration, isolation, identification, and quantitation. All seven steps have their own sources of error, which must be minimized to ensure accurate analyses. Several steps can be combined into one procedure; for example, gas chromatography can perform isolation, identification, and quantitation.

Sampling and Preservation

One of the largest problems in trace analysis is ensuring that a sample remains unchanged between sampling and analysis. For phenolic compounds, the commonly recommended method of preservation has been the addition of copper sulfate (1 g/L) and phosphoric acid (pH \lt 4), followed by storage at 4^oC until analysis (no more than 24 hours) (1). However, a study by Carter and Huston (2) showed that the addition of a strong acid or base alone preserved phenolics for as long as or longer than the copper sulfate-phosphoric

acid treatment. It was found that samples preserved with 2 mL/liter of concentrated sulfuric acid and stored at $4^{\circ}C$ were stable (less than 5% loss) for at least 28 days.

There is very little or no information pertaining to the preservation of non-phenolic nonvolatiles. However, since the major cause of loss in a sample is bacterial decomposition, the preservation method used for phenolics should also be applicable to neutral and basic compounds.

The preservation of chlorinated water for volatile analysis is usually limited to low temperature ($4^{O}C$ or less) and the addition of a reducing agent to destroy residual chlorine and prevent further reaction during storage. Kissinger and Fritz (3) recommend the addition of ascorbic ac-d, while the Environmental Protection Agency (4) suggests the use of sodium thiosulfate or sodium bisulfite.

For all organic analyses, glass containers are recommended for sampling and storage, to minimize interaction of any pollutants with container walls and to avoid problems of leaching of chemicals from plastic containers.

Extraction and Concentration

Nonvolatiles

The two most common methods used for extracting nonvolatiles from water are solvent extraction and adsorption. The most commonly used solvents for solvent extraction are

dichloromethane, chloroform, diethyl ether, and hexane Of these, dichloromethane and chloroform are most (5,6).suitable because of their relatively low solubilities, high densities, and high extraction efficiencies. Dichloromethane is recommended over chloroform because of the toxic effects of chloroform. To increase extraction efficiencies, the addition of acid or base may be necessary to convert dissociated species to molecular form (6). Concentration is best achieved by solvent evaporation in a Kuderna-Danish apparatus, shown in Figure 1. The Snyder column above the flask provides a reflux action which continually washes down the sides of the flask, as well as preventing higherboiling compounds from evaporating with the solvent. The Kuderna-Danish apparatus gives much higher recoveries than concentration in a Rotavap or under a stream of air, down to a final volume less than 1 mL(5).

The method recommended by the Environmental Protection Agency (4) for solvent extraction of nonvolatiles is as follows. A sample is first adjusted with 6N sodium hydroxide to a pH \geq 11. It is serially extracted with one-eighth, one-twentieth, and one-twentieth its volume of dichloromethane. The extracts are filtered through anhydrous sodium sulfate and combined. The combined extract is then concentrated in a Kuderna-Danish apparatus to 1.0 mL. The extracted water sample is next acidified with 6N hydrochloric acid to a pH \leq 2, and extracted as before, this time using one-tenth, one-twentieth, and one-twentieth its vol-



ume of dichloromethane.

The two solids most commonly used for adsorption methods of extraction are activated carbon and macroreticular Macroreticular refers to the relatively large, resins. controlled pore size of the resin beads; each grain of resin is formed from many microbeads cemented together during the polymerization process. Because of such problems as irreversible adsorption and compound degradation on activated carbon, macroreticular resins have become the more widely used and have shown the most success in trace environmental analysis. The XAD series of resins manufactured by Rohm and Haas is the most popular. The XAD resins are styrene-divinylbenzene (XAD-1, 2 and 4) and methacrylate (XAD-7, 8) polymers, with pore sizes ranging from 50 to 250 Angstroms and specific surface areas ranging from 100 to 750 m²/g (7). The basic procedure for using these resins is to pass a water sample over a bed of the resin, followed by elution with a small amount of a suitable solvent (methanol, dichloromethane, etc.). If necessary, concentration can be performed in a Kuderna-Danish apparatus. The sample is then ready for analysis.

Many studies of the use of these resins have been made by a group of researchers at Iowa State University (8,9). In general, phenol itself had a low recovery (about 40% on XAD-4), while other phenols were higher. The resin XAD-7 gave the highest recovery of phenol at 86%. The recoveries of nitrobenzene, naphthalene, and fluorene on XAD-2 were

reported to be 91%, 98%, and 84%, respectively. A later work by Rossum and Webb (10) reported values of 46% for phenol and 86% for naphthalene on a mixture of XAD-4 and 8.

One other resin that has been studied for phenolic extractions is the anion-exchange resin A-26 (Rohm and Haas) (11). The recoveries of phenol and <u>p</u>-chloro-<u>m</u>-cresol from basic solutions were given as 93% and 100%, respectively, at high concentrations (500 and 800 ppb, respectively), and 95% for both at lower concentrations (25 and 40 ppb, respectively).

Volatiles

There are two basic techniques for extracting volatile compounds from water: liquid-liquid extraction, and purging with an inert gas ("gas sparging" or "dynamic headspace analysis"). Headspace analysis, the taking of a sample of the water-volatile organic vapor mixture above a water sample, is not actually an extraction method and will only be discussed later for comparison purposes.

By far the more widely used technique is purging, that is, bubbling an inert gas through a water sample to strip out volatile compounds, which are trapped on an appropriate solid adsorbent (for example, Tenax GC). The trapped compounds can then be thermally desorbed from the trap into a gas chromatograph. The basic technique was first reported by Swinnerton and co-workers (12,13) in the determination of dissolved gases, and was applied to volatile organic

analysis by Bellar and co-workers (14-17). Since then the Environmental Protection Agency (4) has adopted this technique as the standard method for extracting volatiles.

The two major drawbacks of the purging technique are the equipment needed and the time involved (usually about 16 minutes purge and desorb time per sample). Liquidliquid extraction can have advantages in these areas. Several recent papers have reported such procedures (18-21). The solvents studied were pentane and methylcyclohexane, and the solutes used were chloroform, bromodichloromethane, dibromochloromethane, and bromoform. A comparison of these techniques (22) reported the extraction efficiencies listed in Table I. Overall, the method employing methylcyclohexane was recommended as the quickest (about 1 minute) and Table II shows a comparison of this the most accurate. technique with the purge method of Bellar et al. (15). The two were found to be of comparable accuracy and precision.

Finally, a comparison of gas sparging, headspace analysis, and liquid-liquid extraction methods (23) found that the purging technique was the most sensitive, although the solvent extraction method again had comparable precision. Solvent extraction was recommended as the most suitable for routine monitoring of water for trihalomethanes because of its precision, accuracy, simplicity, and speed. The purging technique was more sensitive, but required extensive equipment.

Extractant	Solvent:Water Ratio	Time Required	Aver	age Recove	eries, perc	cent	Ref.
			CHC13	CHBrCl ₂	CHBr ₂ C1	CHBr3	
Pentane	1:23	15 minutes	72.0 1 5.4	72.6±5.6	78.0±6.0	82.5±4.3	18
Pentane	1:10	30 seconds	80.3±8.4	81.8±7.2	87.5±8.0	92.8±6.0	19
Methylcyclohexane	e 1:5	1 minute	86.4±3.7	87.9±4.5	89.5±4.2	92.2±3.7	20

COMPARISON OF SOLVENT EXTRACTION METHODS

TABLE I

*based on concentrations ranging from 1 to 200 ppb

TABLE II

COMPARISON OF PURGE AND LIQUID EXTRACTION METHODS

				Amount Fo	ound, ppb			<u>.</u>	
City	<u>purge</u>	$\frac{C1_3}{LLE}$	<u>CHB</u> purge	LLE	<u>purge</u>	<u>r2C1</u> LLE	<u>purge</u>	LLE	
1	9.5±0.2	9.5±0.8	0.9±0.0	3 1.6±0.5	٢0.1	0.3±0.05	N.D*	N.D.	
2	98.6±3.1	89.1±2.8	17.0±0.9	15.2±0.9	2.6±0.9	2.0±0.3	N.D.	N.D.	
3	2.1±0.1	3.3±0.2	N.D.	0.2±0.05	N.D.	N.D.	N.D.	N.D.	
4	40.4±1.8	34.7±1.2	0.9±0.1	0.8±0.1	< 0.1	N.D.	N.D.	N.D.	
5	37.0±1.7	36.0±0.9	1.8±0.1	1.9±0.1	< 0.2	N.D.	N.D.	N.D.	
6	141.3±1.7	128.0±7.7	65.3±0.8	74.7±3.3	35.9±0.3	36.8±3.4	5.7±0.3	5.3±0.1	
7	139.1±6.4	131.3±4.2	34.7±1.4	36.3±1.5	6.3±0.5	6.4±0.4	N.D.	N.D.	
8	46.2±1.6	37.7±1.1	24.8±1.8	31.6±2.9	16.8±0.6	19.4±1.2	0.5±0.1	1.5±0.6	
				· · · · · · · · · · · · · · · · · · ·					

*N.D. = none detected

Isolation, Identification,

and Quantitation

These three steps are usually performed simultaneously on a gas chromatograph or a gas chromatograph-mass spectrometer. The gas chromatograph performs isolation, identification by retention time, and quantitation by detector response relative to a standard. Mass spectrometry is useful for final identification, usually by comparing an unknown spectrum to reference spectra in a computer (24).

The column recommended by the Environmental Protection Agency (4) for separating nonvolatiles is composed of 1% SP 2250 on 100/120 mesh Supelcoport in a 6-foot x 2 mm i.d. glass column. Recommended carrier gas is helium at 30 mL The temperature program is 50⁰C for 4 minutes, per minute. then 8^o/minute to 260^oC and hold. The SP 2250 column gives bad tailing for acidic compounds, however. Another recommended column is composed of 60/80 mesh Tenax GC, programmed from 180°C to 300°C at 8° per minute, but problems are reported with this column, also. One of the best columns for separating most phenols is composed of the stationary phase FFAP (Free Fatty Acid Phase, a condensation product of Carbowax 20M and 2-nitroterephthalic acid) on a suitable support, usually Chromosorb T or W (25). The main problem encountered with this column is that p-chloro-mcresol takes a very long time (about 40 minutes) to elute and gives a low, broad peak. There are, of course, many

other columns which can be used to separate both acidic and non-acidic compounds, but the above-mentioned are among the most commonly reported for applications in environmental analysis.

The column recommended by the Environmental Protection Agency (4) for separating volatile organics is composed of 0.2% Carbowax 1500 on 60/80 mesh Carbopack C in an 8-foot x 1/8 inch o.d. stainless steel column. The carrier gas used is helium at 33 mL/minute. The temperature program is room temperature during desorb, rapidly heat to 60° C, hold for 4 minutes, then increase 8° /minute to 170° C and hold. This column gives good separation and peak shape for most of the volatiles studied. As with the nonvolatiles, there are other columns which can be used, but this column is one of the most widely used.

Analysis of Drinking Waters for Organics

It has long been known that halogenated compounds cause disagreeable tastes and odors in drinking waters; phenolics are a well-known example of this (26). In recent years, however, many halogenated organics have become suspect as possibly being toxic or carcinogenic. The improvment of existing techniques and the development of new methods have made possible the detection of trace amounts of many of these compounds. Because of their known or suspected toxicity, much work has been done in their detection, identification, and quantitation in municipal drinking waters. Burnham and co-workers (8) in 1972 found trace amounts of various nonvolatiles in a well supplying water to Ames, Iowa. Also in 1972, Kleopfer and Fairless (27) analyzed the drinking water of Evansville. Indiana, and found among other compounds bromodichloromethane, dibromochloromethane, toluene, tetrachloroethene, bromoform, and hexachloroethane. They also found bis(2-chloroisopropyl)ether, a contaminant from an industrial outfall about 150 miles upstream of the city. Work by Novak et al. (28) in Czechoslovakia and Grob and Grob in Switzerland (29) indicated that European cities have similar problems, with both volatiles and nonvolatiles being found. In 1974 Bellar et al. (14,16) reported the presence of chloroform, bromodichloromethane, and dibromochloromethane in various municipal water supplies. The levels found ranged from 1.7 to 152 ppb of chloroform, 1.1 to 20.8 ppb of bromodichloromethane, and 0.1 to 2.0 ppb of dibromochloromethane.

In 1975 Dowty and co-workers (30) reported the finding of various volatile organics in New Orleans drinking water. Among the compounds found were dichloromethane, trichloroethane, tetrachloroethene, and dibromochloromethane. Many of these same compounds, as well as benzene and several derivatives, were also found in commercially bottled artesian water and commercially deionized, charcoal-filtered water. In the same year Bertsch and co-workers (31) found many of the same volatiles, as well as various benzene derivatives, in the drinking water supplies of Tuscaloosa, Alabama, and

Houston, Texas.

In late 1974 a nation-wide study was undertaken by the Environmental Protection Agency to determine the presence and concentrations of certain volatile organics in the raw and treated drinking waters of 80 cities across the United States (32). The compounds selected for study were chloroform, bromodichloromethane, dibromochloromethane, bromoform, carbon tetrachloride, and 1,2-dichloroethane. The 80cities studied were chosen to represent a wide variety of raw water sources and treatment methods. In general, it was found that the four trihalomethanes were not present or were present only in very low concentrations (1 ppb) in the raw waters. Carbon tetrachloride was found in 5% of the waters, at concentrations of 4 ppb or less. Dichloroethane was found in 14% of the waters, at concentrations of 3 ppb or less. In the treated waters, the median concentrations (and ranges) of the trihalomethanes were: chloroform, 21 ppb (0.1-311 ppb); bromodichloromethane, 6 ppb (0-116 ppb); dibromochloromethane, 1.2 ppb (0-100 ppb); and bromoform, 3 ppb (0-92 ppb). Carbon tetrachloride was found in 12.5% of the waters, with a maximum concentration of 3 ppb, and dichloroethane was found in 32.5% of the waters, with a maximum concentration of 6 ppb. The following conditions seemed to give higher concentrations of trihalomethanes: surface water as source water, raw water chlorination practiced, and >0.4 ppm free chlorine residual present after treatment.

Since the EPA study, many more studies have been performed (33-42). These have largely supported the findings of the EPA; manely, most of the water supplies using chlorination contain at least traces of the trihalomethanes and other halogenated organic compounds.

Finally, of local interest is a study done by Slimak (43) in 1975. In this study, Stillwater tap water (source: lake Carl Blackwell) was found to contain traces of bromodichloromethane, dibromochloromethane, and bromoform, as well as other unidentified compounds. However, no attempt was made to determine the levels of the trihalomethanes.

Formation of Halogenated Organics

There are two possible sources of halogenated compounds in drinking water: those present in the raw water, and those formed during treatment. Those formed during treatment evidently arise from the reaction of chlorine (as hypochlorous acid) with naturally-occurring humic matter (44) or similar substances introduced by man. Although by no means conclusive, evidence indicates that this formation occurs via alternate hydrolysis and halogenation steps (45), resulting in the formation of CX_3 . If chlorine were the only halogen present, then chloroform would be the only product; the presence of bromide and iodide leads to the formation mostly of mixed trihalomethanes. This was illustrated by Kissinger and Fritz (3), who demonstrated the formation of bromodichloromethane, dibromochlorometh-

ane, and bromoform from humic acid or a chlorine-containing trihalomethane, chlorine (Cl_2) , and bromide. Table III shows a summary of their results. Kleopfer (36) suggests that mixed haloforms occur by reaction of the separate hypohalites with humic matter, but the results of Kissinger and Fritz indicate that the process is more complex, with some type of exchange occurring between the chlorine-containing trihalomethanes and the other hypohalites.

The influence of bromide on the formation of trihalomethanes may involve more than just the production of brominated compounds: evidence indicates that bromide may also affect the rate and extent of reaction as well. This was illustrated by Trussell and Umphres (45). It is clear that, if bromide is present and is oxidized by chlorine or hypochlorite to hypobromite, the overall trihalomethane concentration will be higher, due to the presence of brominated compounds that would not be present otherwise. It is reported that levels of bromide greater than 0.1 ppm result in bromoform being the predominant trihalomethane formed; this seems to indicate that hypobromite is more active in the haloform reaction than hypochlorite. Thus the possibility exists that bromide may affect the rate of reaction as well. Data reported by Trussell and Umphres indicate such an effect, but more work needs to be done before any definite conclusions can be drawn. Because of the apparent importance of bromide in the formation of trihalomethanes, the level of bromide in the Kaw reservoir was determined.

TABLE III

FORMATION OF TRIHALOMETHANES FROM PRECURSORS

Reactants*	CHC13	CHBrC12	CHBr2C1	CHBr3	
HA,Br-,C1 ₂	+	+	+	· +	
HA,Br $_2$				+	
HA,Br2,Cl-				+	•
CHCl ₃ ,Br ⁻ ,Cl ₂	+	+	+	+	
CHCl ₃ ,Br ₂	+				•
CHCl3,Br-	+				
CHC13,C12	+				
CHBrCl ₂ ,Br ⁻ ,Cl ₂		+	+	+	
$CHBrCl_2, Br_2$		+			

*HA = humic acid source: reference no. 3 Other factors affecting trihalomethane formation are pH, temperature, chlorine dosage used, and the levels and characteristics of the precursors in the water. Clearly, the formation of halogenated compounds during chlorination is a complex process, and as yet is not well understood.

Trace Determination of Bromide

The standard method of trace bromide determination (46) uses the reaction of bromide with phenol red; the resulting dye is measured spectrophotometrically at 590 nm. Sensitivity is reported to be 0.1 ppm. A method reported by Zitomer and Lambert (47) involves the inhibition by bromide of the reaction converting ammonia to trichloramine; the resulting trichloramine is reacted with nitrite and iodide to form triiodide, which can be measured as the starch-triiodide complex. Sensitivity was reported to be 0.02 ppm.

A method involving catalysis by bromide was reported by Fishman and Skougstad (48). In that report, it was found that traces of bromide catalyze the oxidation of iodide or iodine to iodate by acid-permanganate; the extent of oxidation is proportional to the amount of bromide present. By extracting unreacted iodine into carbon tetrachloride and measuring at 515 nm, an applicable range of concentration of 0-0.1 ppm was reported. Similar to this method was one reported by Nikoleis et al. (49), which involves the catalysis by bromide of the reaction between

iodide and iodate to form iodine. Sensitivity was reported to be about 8 ppm.

A colorimetric method was reported by Elbeih and El-Sirafy (50), involving the oxidation of bromide to bromine, followed by reaction with Chromotrope 2B to form a color-The extent of bleaching was measured at less product. 511 nm. Sensitivity was reported to be 5 ppm. Another method involving bleaching was reported by Tamarchenko and Toropova (51). Here, the bromine formed by oxidation of the bromide is reacted with methyl orange to form a colorless product, and the extent of bleaching is measured at 490 nm. Sensitivity is reported to be about 8 ppb. Finally, a colorimetric method involving oxidation of the bromide to bromate, followed by reaction with excess bromide and rosaniline to form a colored product, was reported by Moldan and Zyka (52). The sensitivity was reported to be 0.4 ppm.

Similar to the methods involving bleaching of a dye is a technique reported by Axelrod et al. (53). Bromide is reacted with excess fluorescein to form a non-fluorescent product, and the remaining fluorescein is measured by fluorimetry. The applicable concentration range reported was 0-0.16 ppm.

X-ray fluorescence techniques have been reported by several workers (54-56). Tungsten target tubes (50 kV, 40-50 mA) were used to excite the K \propto line, and LiF analyzing crystals were used for resolution. A concentration limit

of 0.05 ppm was reported by Radcliffe (55), whose method included a concentration step.

A gas chromatographic method was reported by Nota et al. (57). Here bromide is reacted with chlorine and cyanide to form cyanogen bromide, which is separated by gas chromatography and detected with electron-capture detection. Concentrations as low as 0.05 ppm are reported detectable.

CHAPTER III

EXPERIMENTAL

Equipment

Purge and Trap

A tekmar model LSC-1 Liquid Sample Concentrator was used for purging the volatile compounds from water. The instrumental settings used are given in Table IV. The sample concentrator was connected to the gas chromatograph as shown in Figure 2. Copper tubing, 1/8th inch o.d., was used to connect the carrier gas line of the gas chromatograph to the desorb gas inlet of the LSC-1. Teflon tubing, 1/8th inch o.d., connected the desorb outlet of the LSC-1 back to the carrier gas line, just before the injection port. In this way, the carrier gas was used to desorb the purged volatile compounds from the trap.

Gas Chromatography

The gas chromatograph used for the storage and purge and extraction efficiency studies was an F&M model 810 Research Chromatograph with a flame ionization detector. The instrumental settings used are given in Table V. The entire set-up, including the LSC-1, is shown in Figure 3.

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TABLE IV

LSC-1 CONDITIONS

Purge Gas	Helium, 20 psi
Purge Flow	40-45 mL/minute
Purge Time	12 minutes
Desorb Time	4 minutes
Desorb Temperature	180 ⁰ C
Desorb Gas	Helium, 40 psi
Trap	2/3 Tenax GC 1/3 Silica Gel

TABLE V

GC CONDITIONS

Carrier Gas	Helium, 40 psi
Detector Gases	H_2 , 8 psi; air, 17 psi
Carrier Flow	20-25 mL/minute
Hydrogen Flow	25 mL/minute
Air Flow	250 mL/minute
Inj. Port Temp.	240 ^o C
Detector Temp.	250°C
Recorder Range	-0.2 to +1.0 mV full scale



Figure 2. Gas Chromatograph-Sample Concentrator Interface





For the volatile compounds, the column used was 8-foot by 1/8th inch o.d. stainless steel, containing 0.2% Carbowax 1500 on 60/80 mesh Carbopack C, preceded by a 1-foot by 1/8th inch o.d. stainless steel column containing 3% Carbowax 1500 on 60/80 mesh Chromosorb WAW-DCMS. For the three phenolics studied for storage effects, the column used was 6-foot by 1/8th inch o.d. stainless steel, containing 5% FFAP on 80/100 mesh Chromosorb W-HP. For the extraction efficiency studies, the column used was 6-foot by 1/8th inch o.d. stainless steel, containing 3% SP 2250 on 100/120 mesh Supelcoport.

Gas Chromatography-Mass Spectrometry

The system used for analyzing samples for volatile compounds was a Finnigan model 4000 Gas Chromatograph-Mass Spectrometer, with a Data General Nova 3 data system. The instrumental settings used are given in Table VI. The column used in the gas chromatograph was 6-foot by 2 mm i.d. glass, containing 0.2% Carbowax 1500 on 80/100 mesh Carbopack C. The instrument was operated by Garmon Smith and is located at the Robert S. Kerr laboratory in Ada, Oklahoma.

The system used for analyzing samples for nonvolatile compounds was a Hewlett-Packard model 5992 Gas Chromatograph-Mass Spectrometer. The instrumental settings used are given in Table VII. The column used in the gas chromatograph was a 30-meter by 0.25 mm i.d. glass capillary

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TABLE VI

GC-MS CONDITIONS FOR VOLATILES ANALYSIS

Parameter	Setting
GC	
Desorb Time	5 minutes
Desorb Temperature	180 ⁰ C
Program	Room temp. during desorb, then 60°C for 4 minutes, then 8°C per minute to 170°C and hold
Carrier Gas	Helium, 20 mL/minute
MS	
Ionizer temperature	250 ⁰ C
Separator temperature	210 ^o C
Manifold temperature	82°C
Filament current	300 µA
Electron multiplier voltage	1700 volts
Pre-amp sensitivity	1×10^{-7}
Energy	70 eV
Vacuum	1×10^{-6} torr during run
TABLE VII

GC-MS CONDITIONS FOR NONVOLATILES ANALYSIS

Parameter Setting		
GC		
Carrier Gas	Nitrogen, 2 mL/minute	
Program	30 ⁰ C for 2 minutes, then 10 ⁰ C per minute to 150 ⁰ C and hold	
MS		
Electron multiplier voltage	1800 volts	
Repeller	250	
Gain	174	
Offset	31	
Entrance lens	100 volts	
X-ray shield	90 volts	
Mass gain	43.7	
Mass offset	37.1	

column, containing 3% SP 2100. The instrument is located in the Reservoir Research laboratory of Oklahoma State University, under the direction of Dr. Sterling Burks, and was operated by Elaine Stebler.

Bromide Determination

The instrument used for the bromide determination was a Perkin-Elmer model 552 Spectrophotometer. The wavelength used was 515 nm, and the slit width was 0.25 nm.

Procedures

Storage Studies

Standards were prepared containing approximately 100 to 150 ppm of phenol, 2-chlorophenol, and 2-nitrophenol. 1.0 mL samples were placed in 2 mL serum vials with Teflonlined caps; a set of vials was stored at -10° C and another set was stored at room temperature (27°C). After a selected time interval, a vial for each compound was removed from storage, the refrigerated vials were allowed to come to room temperature, and the samples were analyzed against newly-prepared standards. The column temperatures used were: phenol, 145° C; 2-chlorophenol and 2-nitrophenol, 135° C.

Purge Efficiency Studies

A standard mixture was prepared containing approxi-

mately 1 to 10 ppb of the compound of interest. 1.0 µL injections of this standard were made directly into the gas chromatograph, using the following temperature program: room temperature during injection, rapidly heat to 60°C and hold for 4 minutes, then increase 8° / minute to 160°C and hold as long as necessary. The area of the resulting peak was calculated by triangulation. Next, a 5 mL sample syringe (Figure 4) was filled with distilled water, air bubbles were removed, and the volume was adjusted to 5.0 mL. 1.0 µL of the standard mixture was added through the Teflon valve, the sample was injected through a septum into the purging vessel (Figure 4), and purging was started. After purging, the trap was quickly heated to 180°C and the trapped compound was desorbed onto the head of the gas chromatographic column, which was being held at room tem-After desorbing, the programmed run was made as perature. Again, the peak area was calculated by triangulabefore. tion, and the purge efficiency of the compound was calculated. Finally, the above procedure was repeated for each of the volatile compounds studied (Table VIII).

Extraction Efficiency Studies

A standard mixture was prepared containing the following compounds: nitrobenzene, naphthalene, fluorene, and hexachlorobenzene. 1.0 mL samples of this standard were diluted to 100 mL with distilled water. For neutral ex-





tractions, the water was not treated and the pH was about 7. For acidic extraction, the water was acidified with 3 mL of concentrated hydrochloric acid, giving a pH ≤ 2 . For basic extraction, the water was treated with 3 mL of approximately 12N sodium hydroxide, giving a pH ≥11. The treated water samples were serially extracted with 12.5, 5, and 5 mL portions of distilled dichloromethane. The extracts for each water sample were filtered through anhydrous sodium sulfate and combined. The combined extracts were collected in Kuderna-Danish flasks, and the sample volumes were reduced to 1.0 mL. The samples were stored in 2 mL serum vials equipped with Teflon-lined caps, and kept at $<0^{\circ}$ C until analysis. The above procedure was repeated on a standard mixture containing phenol and p-chloro-mcresol, and on a standard mixture containing 2-chlorophenol and 2-nitrophenol. As a reference, 1.0 mL samples of these original standards were stored in 2 mL vials along with the extracted samples.

For the gas chromatographic runs, 1.0 μ L injections of the extracted samples were made using the following temperature program: 50°C for 4 minutes, then 8°/minute to 260°C and hold as long as necessary. Calibration curves were obtained by injecting various sample sizes of the unextracted standards, and the extraction efficiencies were calculated.

Kaw Reservoir Sample

A 5 gallon sample was taken from the Arkansas river

from a bridge 6 miles east of Newkirk, Oklahoma (Figure 5). The sample was packed in ice and transported to the laboratory. 5 liters of the sample were removed for immediate analysis, and the rest was treated as follows.

TABLE VIII

VOLATILE COMPOUNDS STUDIED

Dichloromethane Chloroform Carbon Tetrachloride 1,2-Dichloroethane 1,1,2-Trichloroethane Trichloroethene 1,1,2,2-Tetrachloroethane Tetrachloroethene Bromoform Benzene Toluene Ethylbenzene Chlorobenzene

12 liters of the water were chlorinated by adding 200 mg of calcium hypochlorite, then treated with 300 mg of alum and 67 mg of lime to remove solids. After flocculating for 1½ hours, the solution was allowed to settle for 1 hour. At this point, the solids removal was determined by the following procedure: 100 mL of the treated and untreated water were filtered through Millipore type HA mem-



Figure 5. Kaw Reservoir and Sampling Site

brane filters which had been preweighed, the filters were dried at 103° to 105° C, and reweighed. Also at this point the residual chlorine was determined by the following method: 25 mL of the water were placed into a test tube containing 1 mL of orthotolidine reagent (Hach testing kit, Hach Chemical Company, Ames, Iowa). After allowing the color to develop, the test tube was placed in a color comparator and compared to standards. Using these methods, the solids removal was found to be 84.4% (90 mg/liter before treatment, 14 mg/liter after treatment), and the chlorine residual was 2.2 mg/liter. The treated water was allowed to stand, first at 4^oC and then at room temperature, for a total of 12 hours. After standing, the treated water was analyzed. Both raw and treated water samples were analyzed by the following procedures.

<u>Nonvolatiles</u>. A 1 liter sample of the water was placed in a separatory funnel, and the pH was adjusted by the addition of 5 mL of 12N sodium hydroxide to \geq 11. The sample was extracted serially with 125, 50 and 50 mL portions of dichloromethane, and the extracts were filtered through anhydrous sodium sulfate and combined. Next, the same water sample was acidified to a pH \leq 2 by the addition of 10 mL of concentrated hydrochloric acid. The solution was again extracted, this time with 100, 50 and 50 mL portions of dichloromethane, and the extracts were filtered and combined. Another 1 liter sample was treated in the

same way, and the two sets of extracts were combined, giving the equivalent of a 2 liter extraction. The base-neutral and acid extracts were then concentrated in Kuderna-Danish flasks to 1.0 mL, and stored in 2 mL serum vials at -10° C. Finally, the entire procedure was repeated, to give a duplicate run. For a blank, 400 mL of dichloromethane were concentrated to 1.0 mL and stored along with the samples.

Gas chromatographic analyses were performed as before, for the extraction efficiency studies. The conditions used were the same as those listed there.

<u>Volatiles</u>. A 25 mL sample of the water was purged and run by gas chromatography to provide an initial indication of compounds present. A standard containing the compounds believed present was purged and quantitated to estimate the amounts present. Finally, two 25 mL samples of the water were purged and trapped on separate Tenax/silica traps, the traps were removed, and stored in glass tubes under a nitrogen atmosphere at -10° C (58). Blank traps were also prepared and stored along with the samples. The overall separation scheme for both volatiles and nonvolatiles is shown in Figure 6.

<u>GC-MS Analysis of Volatiles</u>. The purged and stored samples were analyzed by gas chromatography-mass spectrometry as follows. A trap was placed into an LSC-1 which was connected to the GC-MS instrument as described before.





Separation Scheme

The trap was desorbed and run according to the program listed in Table VI. After the run was completed, a printout of the ion chromatogram and the mass spectra of the significant peaks was obtained. A computer library search was made for all peaks, with most being identified.

<u>GC-MS Analysis of Nonvolatiles</u>. The acid extracts of the treated water were analyzed as follows. The column oven was cooled to 30° C, and 2 µL of the sample were injected. There was a 5 minute delay before the temperature program began and the valve to the MS opened, to allow most of the solvent to vent. After the run, the spectra of any significant peaks were reproduced and a library search was made to attempt identification.

<u>Bromide Determination</u>. A standard solution containing 0.1 mg/L of bromide was prepared. For the calibration curve, 2.5, 5.0, 7.5, and 10 mL aliquots of the standard solution were placed into 250 mL separatory funnels, and distilled water was added as necessary to give a final volume of 10 mL. These dilutions corresponded to solutions containing 25, 50, 75, and 100 ppb of bromide. For a blank, 10 mL of distilled water were placed into another separatory funnel. Because the reaction had to be precisely timed, the following procedure was performed on each flask sequentially, not simultaneously.

To each flask 1.0 mL of a solution containing 1.31 g/L of potassium iodide and 350 mL/L of concentrated sulfuric

acid was added. The solution was mixed, and placed in an ice bath at 0.5° C. The temperature was monitored constantly to ensure reliability. After cooling for exactly 30 minutes, 1.0 mL of 4.0N potassium permanganate was added, the solution was mixed well, and timing was started. After reacting for exactly 10 minutes, 5.0 mL of carbon tetrachloride were added, each solution was shaken for exactly 12 seconds, and the CCl₄ layers were drawn out with Pasteur pipets and placed in capped vials. For the Kaw water sample, a 100:1 dilution was first made by diluting 1.0 mL of the water to 100 mL. Then the above procedure was repeated on two 10 mL samples of the dilution, to give a duplicate.

After all solutions were treated, the extracts were measured at 515 nm, using pure CCl_4 as reference. The calibration curve was obtained by plotting As/Ao vs. concentration on semi-log paper, where As was the absorbance of each solution, and Ao was the absorbance of the blank.

CHAPTER IV

RESULTS AND DISCUSSION

Storage Study

Figure 7 shows the results of the study of the effect of storage on phenol, 2-chlorophenol, and 2-nitrophenol. As can be seen, while there is no obvious pattern of sample decomposition, it is not safe to assume that there is no degradation taking place. The sometimes large day-to-day variations in concentration seem to preclude either the decomposition of the samples or the evaporation of the solvent, which should cause consistently high results. Also, since the standards for comparison were prepared daily, the variations should not be due to fluctuations in the gas chromatograph or electrometer. All precautions were taken to prevent evaporation, but it is possible that only some of the vials lost solvent, which could cause some of the fluctuation seen. But whatever the case, there appears to be no actual compound decomposition over a period of at least a week, and so if proper precautions are taken to prevent solvent evaporation, instrument fluctuation, and other systematic and random errors, extracted samples of at least these three compounds can be stored even at room tem-





perature for up to a week with no loss. Since most loss is due to reactions of the compounds of interest with other substances in the actual water sample, then barring any reaction with the solvent itself it is probable that other nonvolatile compounds can be stored in the same way.

Purge Efficiencies

Figure 8 shows the separation obtained for the 13 volatiles studied. The order of elution is given in Table The major problem encountered was that benzene and IX. trichloroethene eluted together, although this was not reported by the EPA (4). The purge efficiencies of the compounds are also listed in Table IX, as are the corresponding values reported by the EPA (4). The main thing to note is that the purge efficiencies found in this study were lower than those found by the EPA, in some cases considerably lower. There are several possible explanations for this. One possibility is that some of the sample was left behind in the 5 mL syringe when the spiked water was injected into the purging vessel. Although the method used was that of the EPA, a test was made to see if this were the cause of the lower values. 5 mL of distilled water were placed directly into the purging vessel, and to this 1 uL of the standard was added. The sample was then checked for purge efficiency as before. No difference in the efficiency was found.

Another possible cause of the difference is that, dur-



Figure 8. Chromatogram of 13 Volatile Compounds

*43

TABLE IX

RETENTION TIMES AND PURGE EFFICIENCIES OF VOLATILE ORGANICS

Compound	RRT*	A**	B***
Dichloromethane	1.00	63.2	76
Chloroform	2.49	52.2	95
1,2-Dichloroethane	2.61	75.7	98
Carbon Tetrachloride	3.17	51.6	87
Trichloroethene	3,96	52.8	89
Benzene	3.96	47.5	no data
1,1,2-Trichloroethane	4.26	39.6	88
Bromoform	5.05	56.4	71
Tetrachloroethene	5.74	39.3	88
1,1,2,2-Tetrachloroethane	5,93	9.5	58
Toluene	6.15	42.5	no data
Chlorobenzene	7.07	36.7	89
Ethylbenzene	8.57	17.3	no data
	1		

*Relative to dichloromethane, absolute r.t. = 3.6 minutes
**Percent purged

***Percent purged as reported by the EPA (reference no. 4)

ing the purge or desorption or both, some of the volatile compound condensed in the tubing which connects the purging vessel, the Tenax/silica trap, and the GC injection port. If this were the case, however, it might be expected that these condensed compounds would be at least partially volatilized during subsequent runs by the action of the purge and/or desorb gases passing over them. This should show up as either a "ghost peak" effect or successively larger peaks in subsequent runs. But, neither of these effects were seen during later runs, at least at detectable levels.

A third possibility is that these actually were the amounts purged. The purge efficiency is related to various factors, among them being temperature, purge rate, vessel geometry, and solution matrix. Room temperature throughout most of this work was about 28^oC, which is slightly higher than normal and so should not cause a decrease in purge efficiency. The purge rate (40-45 mL/minute), vessel geometry (Figure 4), and sample matrix (distilled water containing the compound in methanol) were all similar to or the same as the ones reported by the EPA, and also should not contribute to the difference.

An experiment was done to determine if any purgable compound remained in the water after the initial purge. This was done by first purging, then twice repurging a sample. However, dichloromethane showed no detectable peak after the first purge. This indicates that the remaining compound either could not be stripped from the water, or

was lost somehow during the first purge.

One final possibility is that the Tenax/silica trap had lost some of its retention capabilities, due to age and heavy use. In this case, the breakthrough volume (the volume of purge gas required to begin pushing the trapped compounds completely through the trap) might be greatly lowered, and this could account for the lower purge efficiencies. This possibility was not investigated, but of those mentioned it seems the most likely.

There are, of course, other possible reasons for the differences. A leak at a joint, electrometer problems, and recorder problems are also possibilities, although these were investigated and did not seem to be the cause.

The above points out the dependency of the purge efficiency on the various factors affecting it, and it is clear that the term "purge efficiency" is somewhat relative. It would be difficult to reproduce all conditions from lab to lab, and so reported purge efficiencies should be used with caution.

Table X lists the purge efficiencies found under various different conditions (sample matrices). Column A gives the percent of each compound purged from a solution containing that compound and dichloromethane. Column B lists the purge efficiency of dichloromethane corresponding to column A. Column C gives the percent of each compound purged from a mixture of all 13 compounds. In most cases, there was no great difference between these values and the

TABLE X

PURGE EFFICIENCIES OF VOLATILES UNDER VARIOUS CONDITIONS

Compound	A*	B**	C***
Dichloromethane		_	51,1
Chloroform	43.8	54.9	62.3
1,2-Dichloroethane	43.3	58.7	50.9
Carbon Tetrachloride	24.4	52.3	37
Trichloroethene	24.9	51.5	50.6
Benzene	44.7	52.7	
1,1,2-Trichloroethane	44.7	54.8	46.9
Bromoform	41.7	46.8	52.5
Tetrachloroethene	29.4	55.7	41.1
1,1,2,2-Tetrachloroethane	18.6	50.9	8.4
Toluene	43	56.9	41.2
Chlorobenzene	38.7	54.5	32.2
Ethylbenzene	16.9	54.6	21

*Percent purged in presence of dichloromethane

Percent dichloromethane purged in presence of compound *Percent purged from mixture of all 13 compounds values obtained for each compound alone (Table IX), although those in Table X tend to be slightly lower.

Extraction Efficiencies

Figure 9 shows the separation of the 8 nonvolatiles studied. Although all compounds were distinguishable, there was considerable overlap between 2-chlorophenol and phenol, and between 2-nitrophenol and nitrobenzene. The retention times are listed in Table XI, along with the extraction efficiencies found under neutral, acidic, and No references could be found in the litbasic conditions. erature to other studies of extraction efficiencies for these compounds, so no comparisons were made. As would be expected, the acidic phenols were not recovered from the basic solutions, which is the underlying principle in the separation scheme used (Figure 6). Although nitrobenzene might be expected to be slightly acidic, no evidence was seen in its extraction efficiencies.

Kaw Reservoir Sample

GC Analysis

The initial gas chromatographic analyses for volatiles and nonvolatiles are shown in Figures 10 to 12. Figure 10 is the chromatogram of a purged 25 mL sample of the raw water, Figure 11 is the chromatogram of a purged 25 mL sample of the treated water, and Figure 12 is the chromatogram



* 49

TABLE XI

RRT* Compound NEUT ACID BASE 2-Chlorophenol 0.72 94.7 92.6 Phenol 0.77 76.2 78.9 Nitrobenzene 102 97.7 1.00 102 2-Nitrophenol 1.08 96.7 104 94.2 Naphthalene 1.12 91.4 90.7 p-Chloro-m-cresol 1.32 97.3 106 Fluorene 1.73 95.5 102 101 Hexachlorobenzene 1.86 84.8 95.3 94.4

RETENTION TIMES AND EXTRACTION EFFICIENCIES OF NONVOLATILE COMPOUNDS

*Relative to nitrobenzene, abs. r.t. = 11.4 min. Neut = percent extracted from neutral solution Acid = percent extracted from acidic solution Base = percent extracted from basic solution



Figure 10. Chromatogram of Purged Untreated Kaw Water







Figure 12. Chromatogram of Acid Extract of Treated Kaw Water

of the acid extract of the treated water. No peaks were seen in either of the base-neutral extracts or in the acid extract of the raw water.

The first peak in Figure 10 was tentatively identified as dichloromethane, and standards placed the amount at about 0.18 mg/L, or 180 ppb. The source of this dichloromethane is unknown, but it is unlikely that this amount was absorbed from the air if dichloromethane vapor were present. The second peak in Figure 10 did not correspond to any of the volatile standards; see Figure 8.

Only two peaks were identified in the treated water (Figure 11), and they were dichloromethane (60 ppb) and chloroform (80 ppb). The remaining peaks were identified later by GC-MS. These early results indicated that some products had been formed during chlorination, but aside from the chloroform no definite conclusions could be made. The single peak in Figure 12 did not correspond to any of the nonvolatile standards (Figure 9).

GC-MS Analysis

Figures 13 and 14 are the reproduced ion chromatograms of purged samples of the untreated and treated water, respectively. The peaks that were identified in each run are listed in Tables XII and XIII. Also listed are the average ion current values (duplicate samples) and the amount of each compound, if determined. The main thing to notice, of course, is the presence of chloroform, four other trihalo-



Figure 13. Ion Chromatogram of Purged Untreated Kaw Water



methanes, and carbon tetrachloride, none of which was found in the untreated water in significant amounts. Of these, only chloroform was quantitated.

TABLE XII

VOLATILE COMPOUNDS IDENTIFIED IN UNTREATED KAW WATER

Compound	Ion Current	Concentration	(ppb)
Dichloromethane	720960	180	
Acetone	99882		•
Bromodichloromethane	2672		• *
Trichloroethene	569	ngan alam again	
Benzene	1904		
Tetrachloroethene	534		
Toluene	6082		

The mass spectra of the compounds listed in Table XIII are shown in Figures 15 to 26. Figure 17 is the mass spectrum of the second peak in Figures 10 and 11, and it is believed that this is acetone, although the spectrum was not complete enough to verify this. All other spectra were identified by library search with the exception of Figure

TABLE XIII

VOLATILE COMPOUNDS IDENTIFIED IN TREATED KAW WATER

Compound	Ion Current	Concentration (ppb)
Dichloromethane	85824	60
Acetone	68896	·
Chloroform	391072	80
Carbon tetrachloride	2440	
Bromodichloromethane	356376	
Trichloroethene	2932	
Benzene	2132	 ,
Dibromochloromethane	90048	
Dichloroiodomethane	847	
Bromoform	5218	
Tetrachloroethene	862	· · · · · · · · · · · · · · · · · · ·
Toluene	1674	







Figure 16. Mass Spectrum of Dichloromethane














Figure 20. Mass Spectrum of Bromodichloromethane

























15. A computer search for this spectrum turned up no likely matches, but the peaks at 210 and 127, as well as the base peak of 83, led to the conclusion that this was probably dichloroiodomethane. Table XIV lists the most abundant peaks from this spectrum and the possible fragments corresponding to the peaks. Also listed are the ten most abundant peaks found by Kleopfer (36) for dichloroiodomethane. The differences could be due to the very low level of the compound in the water (ion current = 847), so that impurities become significant. Based on the ion current, the level is estimated to be less than 1 ppb.

Figure 27 is the reproduced ion chromatogram of the acid extract of the treated water. The mass spectra of the two peaks are shown in Figure 28. The first compound is believed to be styrene, whose spectrum is shown in Figure 29; compare also the mass spectrum of benzene, Figure 22. Table XV lists the most abundant peaks from each spectrum, along with the possible fragments corresponding to each peak. The source of the styrene is unknown, since all samples were treated the same and styrene only showed up in the acid extract of the treated water. It might be noted, however, that styrene was also found in the drinking water of Cleveland, Ohio (59). The raw water for Cleveland is taken from Lake Erie, and the extraction method used was adsorption on activated carbon.

The second compound in Figures 27 and 28 is unidentified, but may be a pesticide metabolite or a naturally-

TABLE XIV

COMPARISON OF MASS SPECTRUM OF FIGURE 15 WITH MASS SPECTRUM OF DICHLOROIODOMETHANE

Figure 15		Fragment	Dichloroiodomethane	
Mass	Percent Abundance		Mass	Percent Abundance
83	100	CHCl ₂ (base)	83	100
44	72.7	CO ₂ (impurity)		
85	54.6	CHC12	85	63.27
127	42.4	I	127	34.58
47	27.3	CC1	47	19.81
48	25.9	CHC1	48	22.73
50	11.7	CHC1	50	6.79
49	8.3	CC1		· · · · · · · · · · · · · · · · · · ·
87	6.3	CHC12	87	11.07
210	5.9	CHC12I	210	12.62
175	4.4	CHClI	175	11.07
84	3.4	CCl ₂		



Figure 27. Ion Chromatogram of Acid Extract of Treated Kaw Water



Figure 28. Mass Spectra of Acid Extract Unknowns



Figure 29. Mass Spectra of Acid Extract Unknown **#1** and Styrene

TABLE XV

COMPARISON OF MASS SPECTRUM OF FIGURE 28, FIRST UNKNOWN, WITH MASS SPECTRUM OF STYRENE

Mass	Unknown Percent Abundance	Fragment	Mass	Styrene Percent Abundance	
104.1	100	mol. ion	104	100	
103.2	48.5	m-1	103	45	
78.1	42.8	C ₆ H ₆	78	32	
77.1	22.7	C ₆ H ₅	77	17	
51.0	21.0	C_4H_3	51	21	
50.1	10.5	C_4H_2	50	7	
105.0	9.7	m+1	105	9	
76.1	6.1	$C_{6}H_{4}$			
63.0	6.0	$C_{5}H_{3}$			
52.0	6.0	C_4H_4	52	7	

occurring substance. Because of the low level, it was not seen on the F&M chromatograph, and so could have been present in some or all of the other samples. It was present in both acid extracts of the treated water.

Bromide Determination

The method used was that reported by Fishman and Skougstad (48). Figure 30 shows the calibration curves obtained for two different runs. Table XVI lists the absorbances obtained for the standards and water samples for the two runs. The average amount of bromide found was 7.7 ppm, with a standard deviation of 0.3.

TABLE XVI

Concentration (ppb)	Run 1 Absorbance	Run 2 Absorbance	
0 (blank)	0.336	0.399	
25	0.191	0.234	
50	0.120	0.150	
75	0.089	0.117	
100	0.167	0.089	
Unknown	0.085	0.118	
Unknown	0.086	0.112	

RESULTS OF BROMIDE DETERMINATION



Because a reaction time of 10 minutes is required at the temperature of the test (about $0^{O}C$), it might be possible to run the reaction at room temperature for a much shorter time (say, 30 seconds or 1 minute). This would make the method more suitable for routine or on-site analysis. The major drawback to this method is that a particular calibration curve is applicable only at the temperature at which it was run, since the reaction is very temperature dependent. This makes the method somewhat limited in applicability, and requires standards to be run along with samples.

CHAPTER V

CONCLUSIONS

Storage Study

For the compounds phenol, 2-chlorophenol, and 2-nitrophenol, there appears to be little or no decomposition for up to a week when stored in dichloromethane at room temperature. The day-to-day variations found appear to be due more to solvent evaporation or other error than to actual sample degradation. Thus, once a sample has been extracted, it may not be imperative that the sample be analyzed immediately, if proper precautions are taken to prevent sample loss due to evaporation, handling, etc. Although only the three compounds were studied, it seems likely that other nonvolatile compounds would behave similarly.

Purge and Extraction Efficiencies

Purge efficiencies are dependent on many variables, and so it would be difficult to determine the actual cause of the low values found here. The most likely explanations are that either the compounds condensed in the tubing, or the Tenax/silica trap did not retain all of the compound being purged. Of the two, the second seems the more like-

ly, since the first should have shown evidence during subsequent runs. llowever, in either case it is apparent that the purge efficiency of a compound is likely to vary from lab to lab, since reproducibility would require duplication of conditions. Purge efficiencies seem to have more use as approximations, giving as idea of the expected purge amount rather than the actual amount. Assuming that standards are treated the same as samples, and assuming that the sample matrix has no large effect upon the purge efficiency, the actual value of the purge efficiency is not of major importance and affects only the sensitivity of the analytical method. Therefore it is important to verify purge efficiencies if conclusions are to be based upon their values. Overall, the lower values found here had no apparent effect on the usefulness of the technique used.

Kaw Reservoir Sample

The following compounds appeared to be formed during chlorination of the Kaw sample: chloroform, carbon tetrachloride, bromodichloromethane, dibromochloromethane, dichloroiodomethane, and bromoform. This agrees with the findings of the National Organics Reconnaissance Survey (32) and subsequent studies: most or all water supplies involving chlorination contain at least traces of these and other compounds. It would not be reasonable to think that Stillwater would be different; indeed, the findings of Slimak (43) showed that several of these compounds are present in Stillwater's current water supply. Furthermore, it is unlikely that these compounds were picked up as impurities from the lab, since chloroform, carbon tetrachloride, and bromoform were the only ones ever present in this lab.

Based on ion current values and assuming similar response by the compounds, the total trihalomethane content of the treated Kaw water appears to equal or exceed 100 ppb, which is the maximum allowable concentration set by the Environmental Protection Agency in early 1978 (60) for cities with populations over 75,000. Although Stillwater's population is not that large, there are three reasons for the relevance of this regulation. First, it is not reasonable to think that only people living in cities with populations over 75,000 will be affected by these compounds, if indeed they are harmful. Second, one of the reasons for building the Kaw pipeline is to allow the city to grow by increasing its water supply. Thus Stillwater will probably exceed 75,000 in the future. Third, the EPA plans to phase smaller communities into the regulation and to lower the limit as soon as it is feasible (61). Therefore, while it cannot be said definitely that the Kaw water is safe or unsafe for use a drinking water, it is clear that more work needs to be done to determine the levels of organics and their fluctuations throughout the year. A study by Smith et al. (62) found large temporal variations in levels of trihalomethanes, and concluded that single-sample/singletime assays are futile. So many factors beyond man's control can vary the levels of precursors in the raw water that constant monitoring will probably be necessary to ensure consistently low trihalomethane levels in treated water.

As of this writing, other samples of the Kaw reservoir have been analyzed by several laboratories. Their results were basically the same as those reported here; levels of trihalomethanes ranging from 161 to 256 ppb were found (63). As with this study, however, these results are preliminary and more tests are required to draw any definite conclusions. But these results indicate the potential for trihalomethane levels higher than those allowed by the EPA.

Finally, of related interest is a study done here at OSU (64); this study found evidence of several pesticides at low levels in the Kaw reservoir. Among the compounds tentatively identified were aldrin, DDT, chlordane, and toxaphene, at levels ranging from 16 to 160 ng/L (parts per trillion). Again, more work needs to be done to determine levels and variations of these pesticides.

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