ANALYSIS OF DISINFECTION BY PRODUCTS IN DRINKING WATER BY SOLID PHASE EXTRACTION

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(ABSTRACT)

The objectives of this research were to develop a broad spectrum method for the extraction, concentration, and analysis of drinking water disinfection by products using solid phase extraction (SPE), and to determine if this method had lower detection limits and less variability than the proposed liquid-liquid extraction method, EPA Method 551. The disinfection by products investigated were halogenated nitriles, ketones, and aldehydes. The SPE method extracted and concentrated samples using the C-18 Empore Extraction Disks, and desorbed the analytes with methyl-tert-butyl ether (MTBE) as a solvent. The results showed that with the SPE method the recoveries were low (0-50%) for most compounds, and the limit of detection (LOD) values were in the range of 0.2 to 50 ug/L, which were much higher than those for EPA Method 551. The variability was also higher than for EPA Method 551. The SPE method also appeared to be concentration dependent; the recoveries decreased as analyte concentration increased. Highly saline conditions (250 g/L NaCl) resulted in low recoveries and concentration dependencies for some compounds. Even though the SPE method was easier and faster, the lower method detection limit (MDL) values and lower variability made Method 551 more preferable. Further analysis of the SPE method using a new cyclohexyl disk was also recommended.

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I. INTRODUCTION

This research focuses on halo-organic compounds that are produced as a result of the disinfection of public water supplies. These chemicals fall under the heading "disinfection by-products" and are potentially toxic compounds identified in drinking waters (Hodgeson _et al._, 1988; Orme and Ohanian, 1988). These by-products are formed by the reaction of chlorine with organic materials in the water, and they are being considered for regulation by the United States Environmental Protection Agency (USEPA). In accordance with the Safe Drinking Water Act of 1974, the USEPA is required to protect public drinking water supplies from any contaminants that are potentially harmful to humans.

The present method for the extraction, concentration, and analysis of the disinfection by-products is EPA Method 551, which is a liquid-liquid extraction procedure for halogenated neutral organics that uses methyl-tert-butyl ether (MTBE) as a solvent. This thesis proposes an alternate method that uses solid phase extraction with the C-18 (octadecyl) Empore Extraction Disks with MTBE as a solvent. The reason for replacing liquid-liquid extraction with solid phase extraction was to develop a method that was more accurate, easier to perform, and less variable than Method 551. The compounds analyzed in this research were as follows:

Bromochloroacetonitrile	1,2-Dibromoethane
2-Chlorobenzaldehyde	1,1-Dichloroacetone
Chloropicrin	1,1,1-Trichloroacetone
Dibromoacetonitrile	Trichloroacetonitrile
1,2-Dibromo-3-chloropropane	Trichloroethylene

The objectives of this research project were:

1. To develop a broad spectrum method that could replace liquid-liquid extraction with solid phase extraction that uses the C-18 Empore Extraction Disks.

2. To determine if this method had lower detection limits and less variability than EPA Method 551.

II. LITERATURE REVIEW

A. FORMATION OF HALOGENATED ACETONITRILES, KETONES, AND ALDEHYDES

In this section the reactions which produce most of the disinfection by products will be discussed. According to Kopfler et al. (1985), "disinfection of drinking water with chlorine is known to produce a variety of chlorinated derivatives by reaction of the chlorine with the organic substances found in the source water." Concern has also been raised about the formation of mutagenic products in vivo by reacting ingested residual chlorine with organic materials (Kopfler et al., 1985).

The dihaloacetonitriles, which include bromochloroacetonitrile and dibromoacetonitrile, are one group of compounds that result from the chlorination of drinking water. The formation of haloacetonitriles and some trihalomethanes (THMs) is due to the halogenation of certain amino acids, such as aspartic acid, tryptophan, kynurenine, kynurenic acid, and tyrosine, associated with humic substances in natural waters. Brominated by products are formed due to small amounts of bromide ion present in natural waters. This ion is converted to BrCl or Br_2 by chlorine, and chlorination and bromination become competing reactions with bromination being the stronger reaction (Bieber and Trehy, 1983).

In the study performed by Kopfler et al. (1985), several compounds, including trichloroacetonitrile, 1,1-dichloroacetone, 1,1,1-trichloroacetone, were identified when humic materials were chlorinated. These three compounds have been identified in drinking water. This study also discussed the potential for in vivo production of mutagenic by products, which is a concern since dihaloacetonitriles are formed when chlorine reacts with amino acids.

B. HEALTH EFFECTS AND CHEMICAL PROPERTIES OF DISINFECTION BY PRODUCTS

The following section discusses the known health effects of the disinfection by-products selected for this study. There are limited data on human health effects for most of the compounds, thus the available data on the effects on animals are presented.

1,1-Dichloroacetone (DCA) and 1,1,1-Trichloroacetone (TCA): There were very limited data found on the health effects of these two compounds. Both compounds are relatively weak mutagens compared to their corresponding 1,3-derivatives, and their carcinogenicity has not become evident (Bull and Robinson, 1985). According to Orme and Ohanian (1988), "1,1-Dichloroacetone has been shown to produce liver toxicity in mice receiving a single dose of 325 mg/kg but not at 130 mg/kg." No toxicity data were found on TCA.

2-Chlorobenzaldehyde (CBA): There is very little information on the health effects of 2-chlorobenzaldehyde, which in this study is a representative aromatic aldehyde not actually being considered for regulation. According to Lewis (1991), 2-chlorobenzaldehyde is a "poison by intraperitoneal and intravenous routes. When heated to decomposition it emits toxic fumes of Cl^-."

Dibromoacetonitrile (DBAN), Bromochloroacetonitrile (BCAN), and Trichloroacetonitrile (TCAN): The health effects observed in rat studies using these compounds included decreased organ-to-body weight ratios, fetotoxicity, decreased maternal weight gain, decreased birth weight of pups for all three compounds, and decreased pup survival with TCAN only (Orme and Ohanian, 1988). In a study using female A/J mice, both TCAN and BCAN significantly increased lung tumors while the increase in tumors with DBAN was not significant. Data were not available on the health effects in humans (NRC, 1987).

Chloropicrin (CP): This compound was used during World War I as a toxic antipersonnel agent, and a level of 4 ppm in the air incapacitated soldiers. Effects of inhalation include pulmonary irritation and edema, respiratory irritation, frequent coughing, nausea, and increase in pulse rate. Concentrations of 0.3 ppm have been reported to cause lacrimation, and concentrations of 119 ppm with 30 minutes of exposure or 298 ppm with 10 minutes of exposure were reported to be lethal (NRC, 1987). Research is in progress to study the long-term effects of chloropicrin exposure (Orme and Ohanian, 1988).

Trichloroethylene (TCE): Trichloroethylene is used as a dry-cleaning agent, as a solvent in vapor degreasing, and as a decaffinating agent in coffee. Its presence in the air may cause irritation to the eyes, ears, nose, and throat, and skin contact causes irritation. It has been determined to be a carcinogen, and acute exposure depresses the central nervous system and causes symptoms such as nausea, vomiting, headache, dizziness, and fatigue. Trichloroethylene has been reported to cause unconsciousness and death as well as addiction and peripheral neuropathy (Sittig, 1981).

1,2-Dibromoethane (EDB): This compound, also known as ethylene bromide or ethylene dibromide (EDB), is used as a constituent in ethyl gasoline and as a fumigant for ground pest control. Skin contact may cause erythema, blistering, and skin ulcers, and it is irritating to the eyes and to the respiratory tract. Inhalation may cause injury to the respiratory tract, and it has caused injury to the liver and kidneys in animals. EDB may also cause depression in the central nervous system and vomiting (Sittig, 1981).

1,2-Dibromo-3-chloropropane (DBCP): DBCP has principally been used as a pesticide in agriculture, but as of November 1977 EPA suspended all registrations for pesticide uses due to health risks. Possible effects of chronic exposure to DBCP are sterility, diminished renal function, and degeneration and cirrhosis of the liver. In experiments with mice and rats, gastric and mammary cancers resulted with the ingestion of DBCP, and there is a concern for a cancer risk for humans (Sittig, 1981).

Table II-1 presents a summary of physical/chemical properties of some of the compounds being investigated. Data for some of the compounds were not available. This table will be referred to in later chapters.

C. REGULATIONS OF DISINFECTION BY-PRODUCTS

At the time this research was initiated, the USEPA was in the process of developing new regulations to require monitoring for the disinfection by-products listed above. The Safe Drinking Water Act (SDWA) amendments of 1986 required maximum contaminant levels (MCLs) to be established for compounds listed in the Advanced Notice for Proposed Rulemakings (1983); this list included trichloroethylene and

TABLE II-1: PHYSICAL/CHEMICAL PROPERTIES OF ANALYTES

Analyte	Boiling Point	Vapor Pressure	Solubility
Trichloroacetonitrile	84.6 C[1]		
Trichloroethylene	86.7 C[2]	58mm @ 20 C[2]	1100 mg/L @ 25 C[1]
1,1-Dichloroacetone	120.0 C[1]		
Chloropicrin	112.0 C[1]	16.9mm @ 20 C[3]	2000 mg/L[1]
1,2-Dibromoethane	131.6 C[1]	11mm @ 20 C[3]	4.31 mg/L @ 30 C[1]
1,1,1-Trichloroacetone	134.0 C[2]		
1,2-Dibromo-3-Chloropropane	196.0 C[3]	0.8mm @ 21 C[3]	1000 mg/L @ 25 C[1]
2-Chlorobenzaldehyde	211.9 C[1]		

1 Handbook of Environmental Data on Organic Chemicals, 1983
2 Taken from MSDS of Aldrich Chemical Co.
3 Taken from MSDS of Chem Services

dibromochloropropane. The amendments also called for the development of a drinking water priority list of contaminants that may be present in the drinking water supply. MCLs would be established for these compounds, and the list would be updated every three years. The original list was finalized in January, 1988 and included bromochloroacetonitrile, chloropicrin, dibromoacetonitrile, trichloroacetonitrile, and halogenated acids, alcohols, aldehydes, ketones, and other nitriles. The proposed rule for the disinfection by-products was scheduled to be completed in late 1991, and the final rule was scheduled for 1993 (Pontius, 1990).

The June 1991 status report on the development of the regulations, which has not undergone formal USEPA review, updated the list of compounds likely to be regulated. It stated that the haloacetonitriles, chloropicrin, and others had been removed from the list because they did not seem to be a significant health risk at levels that occurred in drinking water and that there was little data on the stability of these compounds in water. The setting of MCLs for these compounds was not anticipated at this time, but they may be regulated in the future (Regli, 1991).

D. EPA METHOD 551

1. Overview of Method

EPA has developed a method for analyzing disinfection by-products using liquid-liquid extraction (LLE) to concentrate the aqueous analytes, followed by capillary column gas chromatography with an electron capture detector (ECD). This method uses methyl-tert-butyl ether (MTBE) as a solvent, employs ionic strength adjustment, and includes dechlorination/preservation with ammonium chloride.

Liquid-liquid extraction, as used in EPA Method 551, involves "the transfer of a component(s) from one liquid to another in order to attain a separation" (Blumberg, 1988). The solvents for the extraction must be chosen on the basis of the characteristics they have in common with the compounds to be separated. The solvents may be very similar or different in their physico-chemical properties; however, they must be "different enough to provide two different separate phases, i.e. not to be homogeneously miscible in the region of interest" (Blumberg, 1988). MTBE, the extracting solvent, is poorly soluble in water and sufficiently nonpolar to dissolve the target disinfection by products.

The procedure for sample preparation, extraction, and analysis for Method 551 is as follows. Five mL of sample is poured into a 40 mL vial and weighed. The internal standard is added along with 8 g of NaCl, which aids in increasing recoveries. The vial is then shaken to dissolve the NaCl. In order to extract the sample, 2 mL of MTBE is added to the vial, and the vial is shaken for about one minute. While the vial is inverted, the water and MTBE phases are allowed to separate; this takes approximately two minutes. Using a Pasteur pipet, the organic solvent phase is transferred to an autosampler vial, making certain that a dual phase is not present. The remaining sample is discarded, and the empty vial is weighed in order to calculate the net weight of the sample. The extract in the autosampler vial is then analyzed using the GC/ECD, injecting 1-2 uL and recording the area of the peaks. In order to identify the peaks, the retention times are compared to those on a reference chromatogram. The method detection limits for this method are shown in Table II-2 (Hodgeson and Cohen, 1990).

2. Gas Chromatography

According to Moore et al. (1982), chromatography is defined as "a general method of separation in which a mixture is partitioned between two separate phases that are in close contact, one of them moving relative to the other." One of these phases is mobile, which can be a liquid or a vapor, and one is stationary, which can be a solid or a liquid coated on a solid. In the case of gas chromatography, the mobile phase is a vapor of an inert gas and the stationary phase is a liquid film coated on a solid. The sample is injected into a vaporization chamber, it enters the gas stream, and as it flows over the stationary phase the compounds in the sample equilibrate to the phase for which it has the most affinity. The more a compound has an affinity for the mobile gas phase, the faster it will move through the column. Eventually, the compounds are separated into bands and they move past a detector, which sends a signal to a recorder. Each of the compounds has a different time in which it passed the detector; this is the retention time (Moore et al., 1982).

The conditions for chromatography in Method 551 were as follows. The primary column used was a DB-1 column with 1.0 um film thickness. Linear velocity of the helium carrier was 23 cm/sec at 35°C, injector temperature was 200°C, and detector temperature was 290°C. The oven temperature program was: 35°C held for 9 minutes, increased to 40°C at a rate of 1°C/minute and held for 3 minutes, increased to 120°C at a

TABLE II-2: METHOD DETECTION LIMITS FOR EPA METHOD 551

Analyte	Fortified Conc. ug/L	Mean Meas Conc. ug/L	Std. Dev. ug/L	Method Detection Limit ug/L
Bromochloroacetonitrile	.029	.027	.0030	.011
Chloropicrin	.029	.030	.0033	.012
Dibromoacetonitrile	.080	.072	.0097	.034
1,2-Dibromoethane	.028	.028	.0017	.006
1,2-Dibromo-3-chloropropane	.043	.041	.0027	.009
1,1-Dichloropropanone-2 (DCA)	.021	.020	.0013	.005
Trichloroacetonitrile	.143	.135	.0307	.092
Trichloroethylene	.018	.023	.00076	.002
1,1,1-Trichloropropanone (TCA)	.043	.044	.0033	.012

rate of 6°C/minute until all compounds have eluted. The temperature was then held at 150°C for 5 minutes (Hodgeson and Cohen, 1990).

The secondary column was a DB-210 with 0.5 um film thickness. Linear velocity of the helium carrier was 27 cm/sec, injector temperature was 200°C, and detector temperature was 290°C. The oven temperature program was: 30°C held for 11 minutes, increased to 120°C at a rate of 10°C/minute and held at this temperature until all compounds have eluted. The temperature was then held at 150°C for 5 minutes. This column was used as a confirmatory column for the primary column (Hodgeson and Cohen, 1990).

3. Dechlorination and sample preservation

Dechlorination and sample preservation are both necessary in order to bind and remove the free chlorine in samples and to keep the components in samples from degrading until they can be analyzed. In Method 551, ammonium chloride was used for both dechlorination and preservation of the sample. Ammonium chloride was preferred because other common dechlorination agents, such as sodium sulfite, thiosulfate, and ascorbic acid, promote decomposition of the dihaloacetonitriles and chloropicrin (Hodgeson and Cohen, 1990). In Method 551, ammonium chloride was added to the sample vial prior to sample collection, and the concentration used was 0.1 g/L, which was adequate to bind the free chlorine and to preserve most of the analytes. An exception was trichloroacetonitrile, which was very unstable; samples must be analyzed for this compound immediately. In general, ammonium chloride was a good choice for dechlorination and preservation with a maximum safe holding time of seven days (Hodgeson et al., 1988).

E. SOLID PHASE EXTRACTION

1. Definition and research

Solid phase extraction (SPE), or liquid solid extraction, is another method of isolating compounds from samples undergoing environmental analysis. According to Hagen et al. (1990), SPE "normally utilizes short, packed columns or cartridges containing sorbent particles which effectively replace the solvent partitioning approach in the extraction process." The cartridge usually consists of a polypropylene plastic tube or a glass tube with porous metal or plastic frits on both ends and the stationary sorbent particles in the middle (Markell et al., 1990). Typically, the procedure for SPE involves washing the column with the eluting solvent and allowing it to dry using air pulled through by a vacuum, passing the sample through and allowing the column to dry again, and eluting the compounds adsorbed to the column by gravity flow of the eluting solvent. There is a wide range of sample sizes, flow rates, cartridge sizes, and volumes of eluting solvent; these vary depending on the type of compounds being analyzed and the percentage of recoveries (Junk and Richard, 1988).

There have been many studies done using SPE in a wide variety of applications. Junk and Richard (1988) performed research on using SPE for removing organic compounds in water, including pesticides and polycyclic organic materials. Hagen et al. (1990) investigated extracting pesticides, polychlorinated biphenyls and phthalates from ground, surface and tap waters. The determination of chlorophenols in water using SPE was an application investigated by Janda and van Langenhove (1989). The USEPA recently developed a method for analyzing organic compounds in drinking water using SPE--Method 525 (Eichelberger et al., 1988). The most popular of the solid supports for SPE was octadecyl (C-18) bonded porous silica (Junk and Richard, 1988), which most of the above mentioned researchers used.

In some cases, using SPE is more advantageous than using LLE. Generally, SPE is faster and less labor intensive than LLE. It also uses less solvents, which is more cost effective and reduces the amount of waste produced during analysis (Hagen et al., 1990). However, there are disadvantages of using cartridges for SPE. One problem is that interferences are encountered in sample extracts due to the ability of the eluting solvent to extract certain compounds from the plastic tube of the cartridge (Junk et al., 1988). Markell et al. (1990) also discusses three other potential problems:

> 1. ...the [SPE] columns' somewhat narrow internal diameter limits usable flow rates to a range (1-10 mL/min) that necessitates long trace-enrichment times for large sample volumes...
>
> 2. ...a too-rapid flow through an SPE cartridge can cause kinetic effects in the bed of 40-um particles that in turn prevent the recovery of certain analytes.
>
> 3. ...relatively dirty samples...can rapidly plug the small cross-sectional area of a typical cartridge, and the increasingly slower volumetric flows can increase extraction times.

The next section discusses a potential solution to these problems.

2. Empore Extraction Disks

A new technology has been developed for SPE that may solve many of the problems encountered with the cartridge. The Empore Extraction Disks, manufactured by 3M and distributed by Analytichem International, are membrane systems which contain 90 weight-percent octyl (C-8)- or octadecyl (C-18)-bonded silica particles and 10 weight-percent fibrilated PTFE. They are available in two sizes, 47-mm and 25-mm diameter, and they are 0.5 mm thick. The disks are comparable to the SPE cartridge device but have smaller sized particles with a high surface area, and they are used in a conventional filtration system (Hagen et al., 1990). The procedure for using the disks is basically the same as for the cartridges and will be discussed in detail in a later chapter.

Using the extraction disks in place of the cartridges has several advantages. Kraut-Vass and Thoma (1991) state that "the speed of liquid-solid extraction...can be dramatically increased by substituting extraction disks in place of extraction cartridges." The results they presented showed that a 1 L sample took 20 minutes to extract using the disks compared to 2-3 hours for the cartridges. The reliability of the disks and cartridges was about the same, but use of the disk for very low concentrations needed further study (Kraut-Vass and Thoma, 1991).

The other difficulties in using the SPE cartridges are eliminated or lessened by using the extraction disk. The wider bed of the disk decreases plugging and the disk format improves mass transfer (Markell et al., 1990). Also, the problem involving interference compounds that were being extracted from the plastic tube of the cartridge into the sample extract does not exist with the extraction disk (Hagen et al., 1990).

III. METHODS AND MATERIALS

In this chapter, details will be given on the methods of extraction and analysis of drinking and reagent water samples containing the ten disinfection by-products previously listed. Specific details of the data analysis procedures will also be presented.

A. REAGENTS

The following certified, ACS-grade chemicals were purchased from Chem Services (West Chester, PA): trichloroacetonitrile (CAS 545-06-2), trichloroethylene (99%) (CAS 79-01-6), 1,2-dibromo-3-chloropropane (98%) (CAS 96-12-8), and 1,2-dibromoethane (99%) (CAS 106-93-4). Chloropicrin (CAS 76-06-2) and bromochloroacetonitrile (96%) were purchased from Columbia Organic Chemical Company, Inc. (Camden, SC). The following chemicals were purchased from Aldrich Chemical Company, Inc.: dibromoacetonitrile (97%), 1,1,1-trichloroacetone (97%) (CAS 918-00-3), 2-chlorobenzaldehyde (99%) (CAS 89-98-5), 1,1-dichloroacetone (98%) (CAS 513-88-2), 1-bromobutane (98%) (CAS 109-65-9), 1-bromohexane (98%) (CAS 111-25-1), and 1-bromodecane (98%) (CAS 112-29-8). HPLC grade methyl-tert-butyl ether and methanol were obtained from Fisher Scientific (Pittsburgh, PA). Reagent water consisted of distilled water that was processed through a Milli-Q water purification unit (Millipore Corporation, Milford, MA). The Empore Extraction Disks were purchased from Analytichem International (Harbor City, CA) or J. T. Baker, Inc. (Philipsburg, NJ).

Drinking water used for preparation of laboratory solutions was obtained from a conventional water treatment plant that treated river water. The treatment process consisted of prechlorination, lime addition, fluoridation, coagulation by polyaluminum chloride, flocculation, sedimentation through rapid sand filters, and then post chlorination with a target concentration of 1 mg/L chlorine.

B. GLASSWARE

All glassware and sample vials were washed in dish detergent and rinsed thoroughly with both drinking water and distilled water.

C. DETERMINATION OF GAS CHROMATOGRAPHIC CONDITIONS

1. Column conditions

The GC used in this research was the Hewlett Packard 5890 with an electron capture detector (ECD), which is sensitive to halogenated compounds. The column used was a DB-624, which was 30m x 0.32mm ID and had a 1.8 um film thickness. This polysiloxane column is composed mostly of methyl substituents with a few percent cyanopropylphenyl. Helium was the carrier gas, and nitrogen was the detector makeup gas. The injector temperature was 200°C and the detector temperature was 300°C. A splitless injection was employed, and the injector purge was activated after 0.50 minutes at a flow of 50 mL/min. The injection volume was approximately 1 uL. The oven temperature program was as follows: 40°C held for 11 minutes, increased to 240°C at a rate of 10°/min.

2. Retention times

In order to be able to quantitate each compound, the retention times of each compound must be determined on the GC. The solvent used to make the standards was methyl-tert-butyl ether (MTBE), and each standard was made at a concentration of 100 mg/L. Methanol and methylene chloride were tried as solvents, but they did not work as well as MTBE because recoveries were poor when methanol was used and because a very large solvent peak occured when methylene chloride was used. Each compound was injected into the GC separately, and the retention time was noted. A mixture of the ten compounds, each having a concentration of 10 mg/L, was then made and injected into the GC to determine if there was any compound interference and to see if the retention times remained the same.

D. CALIBRATION

1. Internal standards

Three internal standards were selected from the bromoalkane series. Bromoalkanes are halogenated compounds not usually found in drinking water. The standards were chosen on the basis of their retention times and proximity in the chromatogram to the compounds being investigated. The retention times of the standards were close to those of the by products with no interferences. An internal standard was chosen with an early, middle, and late retention time in order to bracket the entire range of compounds. These standards were prepared in MTBE at a concentration of 100 mg/L.

2. Response factors

In order to calculate response factors (RF) for each compound, this procedure was followed: three samples, which contained the ten compounds and the three internal standards, were prepared in MTBE. Each of the samples contained 2ug/5mL of the internal standards, but the concentrations of the ten analytes were varied; one contained 5ug/5mL, another contained 2ug/5mL, and the third contained 0.2ug/5mL. The concentration of 2ug/5mL was selected on the basis of an average concentration of 10 ug/L for by-products in drinking water (data cited in Method 551) and assuming a 0.2 L sample volume for SPE and a SPE elution volume of 5 mL. The following equation illustrates this calculation:

$$(10 \text{ ug/L} \times 0.2 \text{ L})/5 \text{ mL} = 2\text{ug/5mL} \qquad [1]$$

The other concentrations were selected as ratios to this concentration (5ug/5mL = 2.5:1, 0.2ug/5mL = 0.1:1).

Each of the three samples was injected seven times into the GC under the conditions previously described. The peak area of each analyte was obtained, and the RF value for each compound was calculated using Equation 2.

$$RF = [(A_x)(C_{is})]/[(A_{is})(C_x)] \qquad [2]$$

where:

A_x = peak area of the analyte (arbitrary area units)
A_{is} = peak area of the internal standard (arbitrary area units)
C_x = concentration of the analyte (ug/5mL)
C_{is} = concentration of the internal standard (ug/5mL)

The RF values over the range should be constant with a relative standard deviation of less than 10% if the values will be used to calculate concentrations in drinking and reagent water samples. Since the RF values were not constant, as will be shown in the results chapter, linear regressions were performed on these values in order to calculate the RF based on each sample's response.

E. METHOD OF SOLID PHASE EXTRACTION AND ANALYSIS

1. Sample preparation

In a typical solid phase extraction experiment, 250 g of NaCl (to increase ionic strength) and 100 mg of ammonium chloride (NH_4Cl) (for dechlorination) were added to 1 L water. The water was shaken vigorously to dissolve the salts. A known concentration of the ten analytes (in methanol) and 5 mL of methanol were then added with gentle mixing (the methanol aids in increasing the flow rate of the sample through the SPE apparatus).

2. Sample extraction

The SPE apparatus consisted of a vacuum pump with a gauge, a 500 mL suction flask, a disk base, a graduated filter funnel, a clamp, and a 25 mL graduated test tube. The clamp held together the disk base and the filter funnel, and they were attached to the suction funnel by a rubber stopper on the disk base. The suction funnel and the vacuum pump were connected to a three-pronged manifold using Tygon tubing. The graduated test tube was placed inside of the suction funnel to collect the extract. Figure III-1 (Analytichem International, no date) shows a diagram of this apparatus.

A 25 mm Empore Extraction Disk was placed on the SPE apparatus and prewashed with 10-20 mL of MTBE. A vacuum of approximately 20mm Hg was

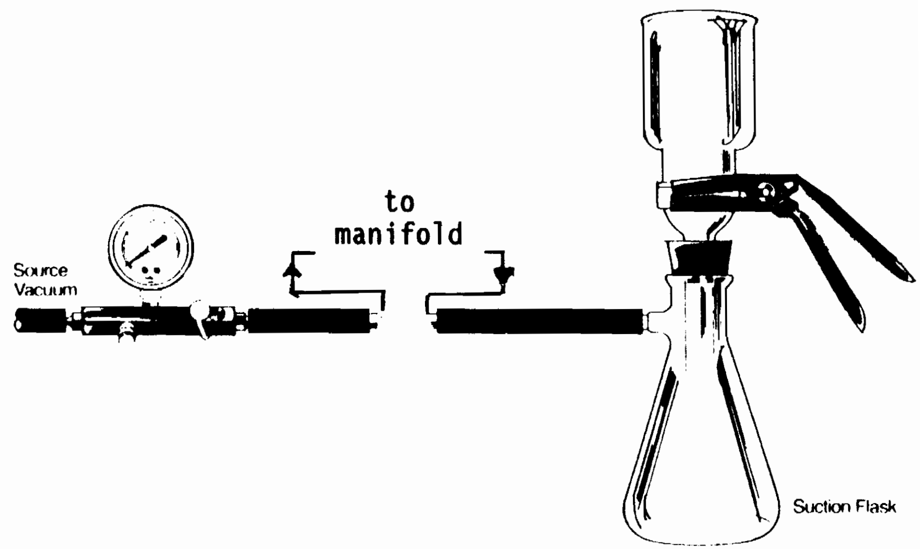


FIGURE III-1: DIAGRAM OF SPE APPARATUS

applied to pull the solvent through, and this vacuum was maintained for five minutes to pull air through the disk. A volume of 10-20 mL of methanol was added and the vacuum applied to allow most of the methanol to be pulled through. At this point, the disk was not allowed to become dry until the extraction had been completed. The previous step was then repeated with 10-20 mL of reagent water. A 200 mL sample was poured into the apparatus and the vacuum adjusted to yield a flow rate of approximately 22 mL/min.

After the sample was processed, air was pulled through the disk for approximately 30 seconds to remove water from the disk. The waste water in the suction flask was disposed, and a graduated test tube was placed under the tip of the filter base inside of the suction flask. A volume of 5 mL of MTBE was added to the filtering flask. Half of the solvent was pulled through and the other half was allowed to remain for approximately one minute and then pulled through. This extract was collected in the graduated test tube, and the volume was brought up to 5 mL with MTBE. The extract was then transferred to a glass sample vial and refrigerated until analysis.

3. Sample analysis

Before the sample extract was injected into the GC, the internal standards were added at the following concentrations: 2ug/5mL of 1-bromobutane, 2ug/5mL of 1-bromohexane, and 5ug/5mL of 1-bromodecane. For some of the samples 1-bromohexane was increased to 5ug/5mL. The reason for having different concentrations of the internal standards was to attempt to have similar peak areas for standards and analytes. The sample extract was mixed and 1 uL injected into the GC under conditions previously described. The data obtained were then analyzed as described in the next section.

F. METHODS OF DATA ANALYSIS

1. Percent recovery

Equation 3 was used to calculate the concentration of each analyte, as follows:

$$C_x = [(A_x)/(A_{is} \times RF)] \times C_{is} \qquad [3]$$

where:

C_x = concentration of the analyte (ug/L)
C_{is} = concentration of the internal standard (ug/L)
A_x = peak area of the analyte (arbitrary area units)
A_{is} = peak area of the internal standard (arbitrary area units)
RF = response factor

This concentration can be converted to percent recovery by dividing C_x by the original concentration of analyte added into the sample and multiplying by 100. Percent recovery was useful in determining the amount of the original concentration that was actually detected by the method, and for a broad spectrum method a recovery of 50 percent for each compound was acceptable.

2. Limit of detection and limit of quantitation

The limit of detection (LOD) is defined as "the lowest concentration level that can be determined to be statistically different from a blank" (Keith et al., 1983). Two methods were used to determine the LOD values. One was the recommended EPA method (Longbottom and Lichenberg, 1982), and the other was the Low Level Standard method, both which are described as follows:

Two samples were prepared, one with only reagent water and NaCl and the other with 0.5 ug/L of analytes added. Seven 200 mL samples for each of the above were processed through SPE and analyzed on the GC. The seven blank samples were processed first, followed by the other seven samples. Once these data were collected, the LOD values were calculated using the EPA recommended method and Equation 4.

$$LOD = t_{(n-1,\ 1-a\ =\ .99)}(SD) \qquad [4]$$

where:

$t_{(n-1,\ 1-a\ =\ .99)}$ = the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

SD = standard deviation of the replicate analyses.

The same data were used to calculate the LOD values by the Low Level Standard method, which added the average concentration of the blank (ug/L) to three standard deviations of the 0.5 ug/L standard.

The limit of quantitation (LOQ) is defined as "the level above which quantitative results may be obtained with a specified degree of confidence" (Keith <u>et al.</u>, 1983). The LOQ was used to define "the lower limit of the useful range of measurement methodology" (Keith <u>et al.</u>, 1983). Two methods were also used to calculate the LOQ: the Low Level Standard method, which added the average concentration of the blank (ug/L) to ten standard deviations of the 0.5 ug/L standard, and the Keith <u>et al.</u> method, which added the average concentration of the blank (ug/L) to ten standard deviations of the blank.

G. EXPERIMENTS TO EVALUATE SPE PERFORMANCE

1. Drying time experiment

One of the experiments performed involved the determination of the best drying time for the extraction disk after the sample had been processed. The instructions for the Empore Extraction Disk recommended that air should be pulled through by the vacuum for 5-30 minutes (Analytichem International, no date). Since long suction times could result in losses of volatile compounds, a shorter time period was also investigated. In this experiment, six samples containing 10 ug/L of each of the ten compounds were prepared. Three of the samples were processed with a drying time of ten minutes afterwards, and the other three samples had a drying time of 30 seconds after processing.

2. Comparison of recoveries

The next set of experiments determined whether or not the addition of NaCl and NH_4Cl noticeably affected the sample recoveries. Three conditions were used for each set of samples: one set contained neither NaCl nor NH_4Cl, one set had only NaCl added, and the third set contained both. Six samples were in each set; of these, two were of each concentration (0.5 ug/L, 1.0 ug/L, and 10.0 ug/L). Each of the samples was processed through SPE and analyzed on the GC.

3. Standard addition experiment

The final experiment involved the determination of sample concentrations by the standard addition method. This method was used in order to check the concentrations obtained by the internal standard method. In the first part of the experiment, the following samples were prepared:

A: Reagent water with NaCl
B: Reagent water with NaCl and 0.5 ug/L compounds
C: Reagent water with NaCl and 1.0 ug/L compounds
D: Reagent water with NaCl and 5.0 ug/L compounds
E: Reagent water with NaCl and 10.0 ug/L compounds
F: Reagent water with NaCl and NH_4Cl
G: Drinking water with NaCl and NH_4Cl

Seven 200 mL samples for each of the above were processed through SPE and analyzed on the GC. Once these data were collected, the concentrations of the disinfection by products in sample G were calculated using the internal standards and then used to determine the concentrations for standard addition. A low, medium, and high concentration of each compound was selected for the standard addition and are listed in Table III-1. The following samples were then prepared:

H: Drinking water with NaCl and NH_4Cl
I: Drinking water with NaCl, NH_4Cl, and low concentration compounds
J: Drinking water with NaCl, NH_4Cl, and medium concentration compounds
K: Drinking water with NaCl, NH_4Cl, and high concentration compounds

Five 200 mL samples of each of the above were processed through SPE and analyzed on the GC. After these data were collected, graphs of measured concentration versus amount of standard added were plotted for each compound. The concentrations of the compounds were determined by extrapolating a straight line down to the x-intercept and then using Equation 5.

$$\text{concentration} = \frac{\text{x-intercept}}{\text{slope}} \qquad [5]$$

TABLE III-1: STANDARD ADDITION CONCENTRATIONS FOR DRINKING WATER SAMPLES

Analyte	Low (ug/L)	Medium (ug/L)	High (ug/L)
Trichloroacetonitrile	0.5	1.0	2.5
Trichloroethylene	4.0	7.0	10.0
1,1-Dichloroacetone	0.5	1.0	2.5
Chloropicrin	0.5	1.0	2.5
1,2-Dibromoethane	0.5	1.0	2.5
1,1,1-Trichloroacetone	10.0	17.0	25.0
Bromochloroacetonitrile	2.0	4.0	8.0
Dibromoacetonitrile	2.0	4.0	8.0
1,2-Dibromo-3-chloropropane	0.5	1.0	2.5
2-Chlorobenzaldehyde	0.5	1.0	2.5

IV. RESULTS

In this section, laboratory data are presented that illustrate how the solid phase extraction process with Empore Extraction Disks was optimized. Detection limits for the optimized SPE procedure are compared with those from EPA Method 551.

A. OPTIMIZATION OF SOLID PHASE EXTRACTION PROCEDURE

1. Order of elution and retention times

Table IV-1 presents the elution order of the ten disinfection by products and the typical retention time of each. These retention times typically varied $\pm$ 0.2 minutes over a four month period. The internal standards and their approximate retention times were: 1-bromobutane (12.4 minutes), 1-bromohexane (20.0 minutes), and 1-bromodecane (27.9 minutes). The internal standard for TCAN, TCE, DCA, and CP was 1-bromobutane; 1-bromohexane was the internal standard for EDB, TCA, BCAN, and DBAN; 1-bromodecane was the internal standard for DBCP and CBA.

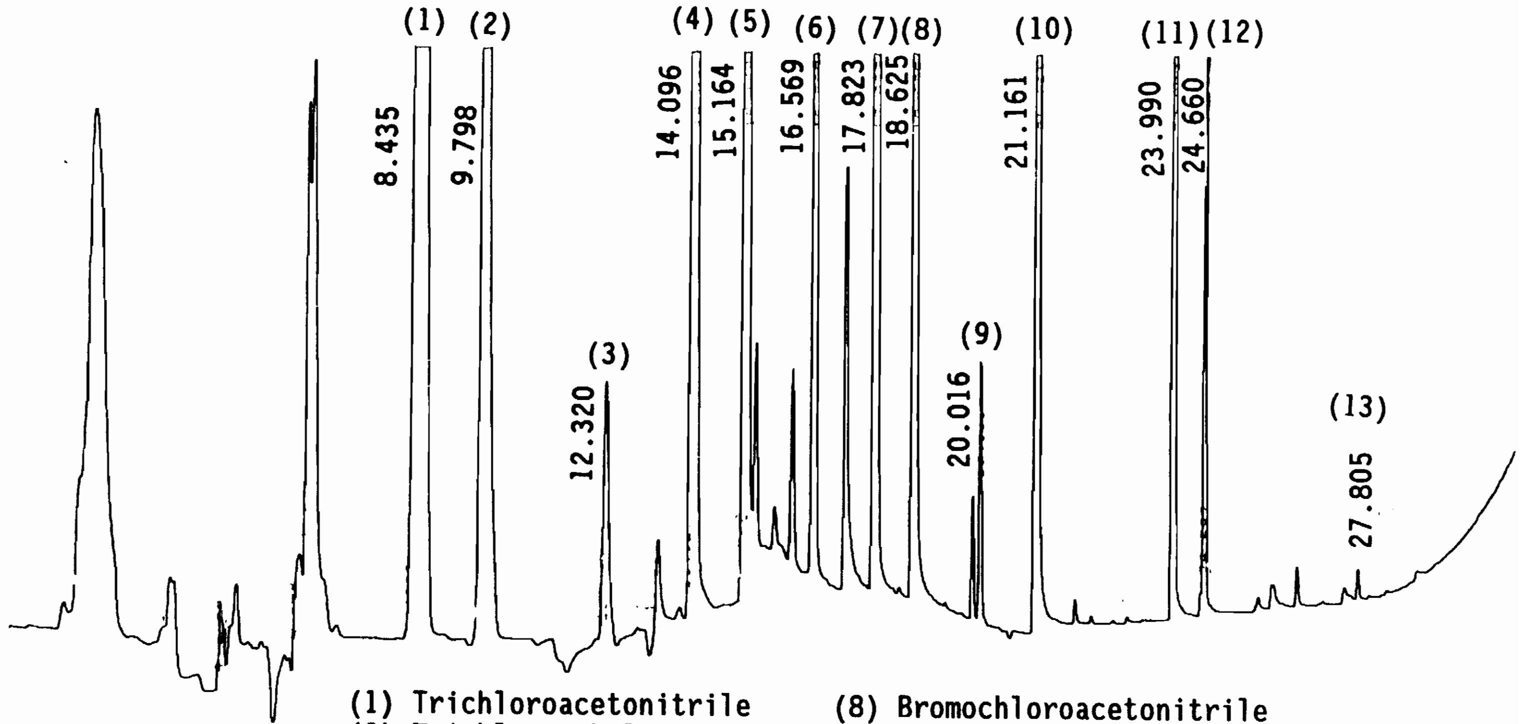
An example of a chromatogram of the ten analytes and internal standards is presented in Figure IV-1. This chromatogram was of a sample used to determine RF values, and the concentration of both the analytes and internal standards was 2ug/5mL. Figure IV-2 shows a chromatogram of a typical tap water sample (sample number H1) containing the internal standards at concentrations of 2ug/5mL, 5ug/5mL, and 5ug/5mL, respectively and with the disinfection by-products labelled.

A regression analysis was performed comparing retention time and

TABLE IV-1: ORDER OF ELUTION AND RETENTION TIMES

Analyte	Typical Retention Time (min)*
Trichloroacetonitrile	8.4
Trichloroethylene	9.8
Dichloroacetone	14.1
Chloropicrin	15.2
1,2-Dibromoethane	16.6
1,1,1-Trichloroacetone	17.8
Bromochloroacetonitrile	18.6
Dibromoacetonitrile	21.2
1,2-Dibromo-3-chloropropane	24.0
2-Chlorobenzaldehyde	24.6

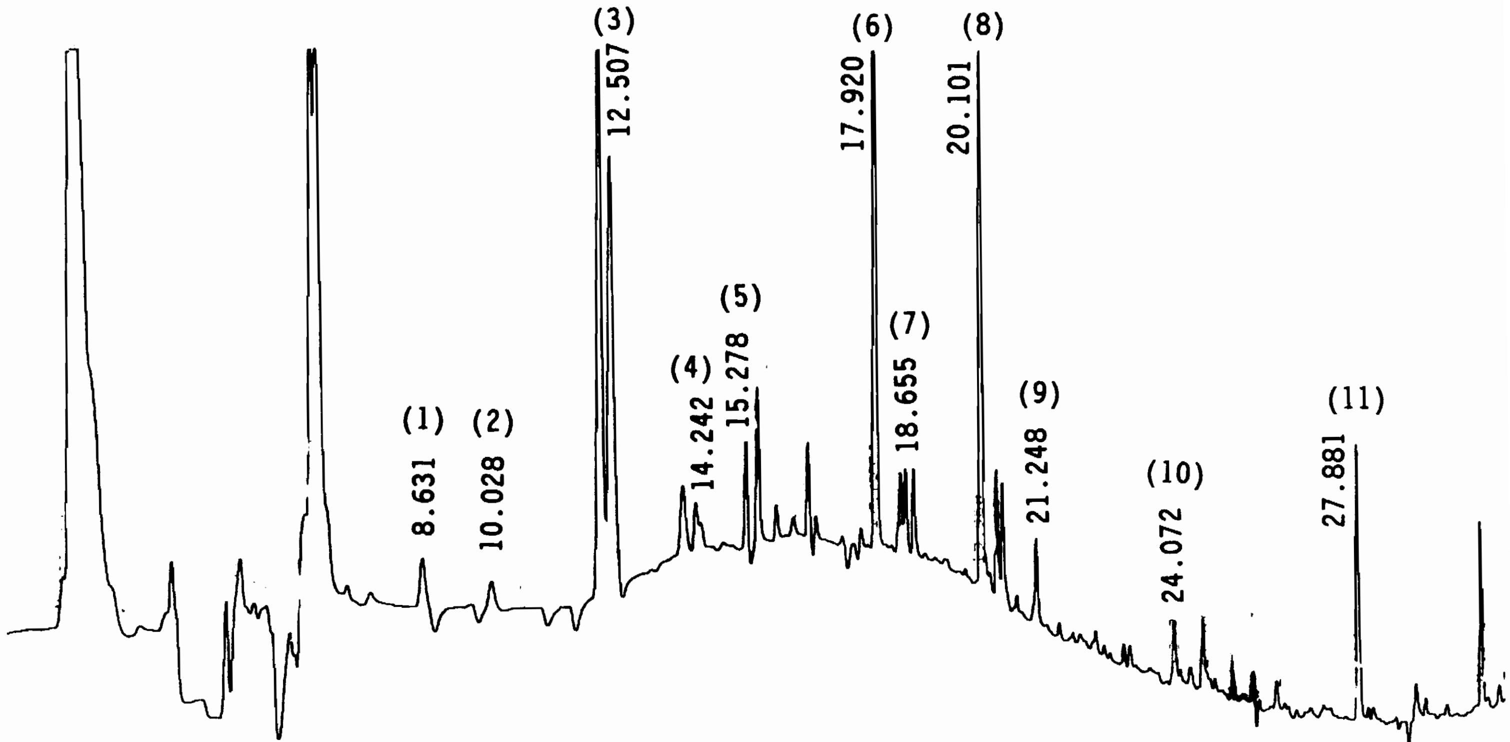
*Retention times typically varied ± 0.2 minutes over a four month period.



(1) Trichloroacetonitrile
(2) Trichloroethylene
(3) 1-Bromobutane
(4) 1,1-Dichloroacetone
(5) Chloropicrin
(6) 1,2-Dibromoethane
(7) 1,1,1-Trichloroacetone
(8) Bromochloroacetonitrile
(9) 1-Bromohexane
(10) Dibromoacetonitrile
(11) 1,2-Dibromo-3-chloropropane
(12) 2-Chlorobenzaldehyde
(13) 1-Bromodecane

Conditions: Injector temp = 200°C, Detector temp = 300°C, 40°C (held 11 minutes) to 240°C at 10°/min, purge on 0.50 min, split 50:1

FIGURE IV-1: CHROMATOGRAM OF TEN ANALYTES AT 10 mg/L WITH THREE INTERNAL STANDARDS AT 400 mg/L



(1) Trichloroacetonitrile
(2) Trichloroethylene
(3) 1-Bromobutane (2ug/5mL)
(4) 1,1-Dichloroacetone
(5) Chloropicrin
(6) 1,1,1-Trichloroacetone
(7) Bromochloroacetonitrile
(8) 1-Bromohexane (5ug/5mL)
(9) Dibromoacetonitrile
(10) 1,2-Dibromo-3-chloropropane
(11) 1-Bromodecane (5ug/5mL)

Conditions: Injector temp = 200°C, Detector temp = 300°C, 40°C (held 11 minutes) to 240°C at 10°/min, purge on 0.50 min, split 50:1

FIGURE IV-2: CHROMATOGRAM OF TYPICAL TAP WATER SAMPLE AND INTERNAL STANDARDS boiling points (see Table II-1); the R-square value was 0.96, which indicated a high degree of correlation between these two terms. Retention time is generally proportional to boiling point for GC columns that are composed principally of methyl silicones; the DB-624 is greater than 90 percent methyl silicone according to the manufacturer (J & W). Another regression analysis was performed comparing retention time and vapor pressure (see Table II-1); the R-square value was 0.80, which also indicated a high degree of correlation between these two terms as well.

2. Drying time

The data from the drying time experiment are presented in Table IV-2. These data compare the percent change in peak area of each compound rather than percent recoveries since the internal standard data necessary to calculate the recoveries had not yet been evaluated. For most of the compounds, the decrease in drying time from ten minutes to 30 seconds resulted in an increase in peak area.

A Wilcoxon paired-sample test (Zar, 1984) was performed on the drying time data to determine if the difference between the two drying times was significant. According to this test, the difference between the two drying times was significant at a 95 percent confidence level.

3. Response factors

The calculated RF values are presented in Table IV-3. As shown in this table, the RF values varied with the concentration of the analytes when the concentration of the internal standard was constant. This result was not unexpected for an electron capture detector (McNair and Bonelli, 1968). Due to these results, RF values were calculated using linear regressions to vary the values depending on the analyte/internal

TABLE IV-2: RESULTS FROM DRYING TIME EXPERIMENT

Analyte	Average Area*		Percent
	10 Minutes	30 Seconds	Change in Area
Trichloroacetonitrile	0	8815	100%
Trichloroethylene	5173	15798	67%
1,1-Dichloroacetone	76148	167148	54%
Chloropicrin	49748	47318	-5%
1,2-Dibromoethane	27022	55733	52%
1,1,1-Trichloroacetone	46790	56454	17%
Bromochloroacetonitrile	9405	28966	68%
Dibromoacetonitrile	10464	29225	64%
1,2-Dibromo-3-chloropropane	150630	241135	38%
2-Chlorobenzaldehyde	43786	24517	-79%

*NOTE: Averge of three measurements

TABLE IV-3: AVERAGE RF VALUES*

Analyte	Concentration 0.2ug/5mL	Concentration 2ug/5mL	Concentration 5ug/5mL
Trichloroacetonitrile	56.68 ± 2.76	49.45 ± 5.39	40.30 ± 0.57
Trichloroethylene	13.84 ± 0.80	9.86 ± 1.02	7.44 ± 0.08
1,1-Dichloroacetone	27.65 ± 1.73	20.00 ± 2.14	15.00 ± 0.16
Chloropicrin	19.82 ± 0.62	20.97 ± 2.70	0.64 ± 0.39
1,2-Dibromoethane	28.51 ± 1.64	19.74 ± 0.40	14.84 ± 0.15
1,1,1-Trichloroacetone	113.74 ± 7.60	78.01 ± 1.56	58.02 ± 1.38
Bromochloroacetonitrile	71.63 ± 3.75	55.97 ± 1.11	46.15 ± 0.95
Dibromoacetonitrile	62.09 ± 3.13	51.70 ± 1.03	43.12 ± 0.94
1,2-Dibromo-3-chloropropane	158.83 ± 4.72	120.81 ± 6.49	74.24 ± 0.77
2-Chlorobenzaldehyde	19.04 ± 0.53	14.67 ± 0.67	10.37 ± 3.02

*NOTE: Concentrations of internal standards were 2ug/5mL (400 mg/L) standard peak area ratios. This method was used throughout the remainder of the sample analysis.

4. Comparison of recoveries

Figures IV-3, IV-4, IV-5, IV-6, IV-7, and IV-8 are graphs of percent recovery data that compare three types of samples: those with neither NaCl nor NH_4Cl added, those with only NaCl added, and those with both salts added. Graphs for three different concentrations of the ten analytes are presented--10 ug/L, 1 ug/L, and 0.5 ug/L. Each data set was divided into two graphs due to the wide range in values; note that the range on the y-axis varies from graph to graph. The raw data used to graph these figures are provided in Appendix A.

In general, salt addition and compound elution time appeared to be correlated; the early eluting compounds (e.g., TCE, DCA, CP) exhibited decreased recoveries with salt addition, and the late eluting compounds (e.g., DBCP, CBA) showed improved recoveries. Those compounds that eluted in between the early and late eluting compounds (e.g., TCA, BCAN, DBAN) were not affected by salt addition. Generally, TCAN was not recovered under any of the conditions tested.

As can be seen from the graphs for the compounds at 10 ug/L, the addition of NaCl generally improved recoveries, but the addition of NH_4Cl slightly decreased recoveries. BCAN and DBAN recoveries were not affected by the presence of either NaCl or NH_4Cl. At the 1 ug/L concentration, the presence of NaCl decreased recoveries of TCE, DCA, and CP, and the addition of NH_4Cl further decreased the recoveries of these compounds. Recoveries for EDB, DBCP, and CBA were improved with the addition of NaCl, and NH_4Cl had little effect. The recoveries of

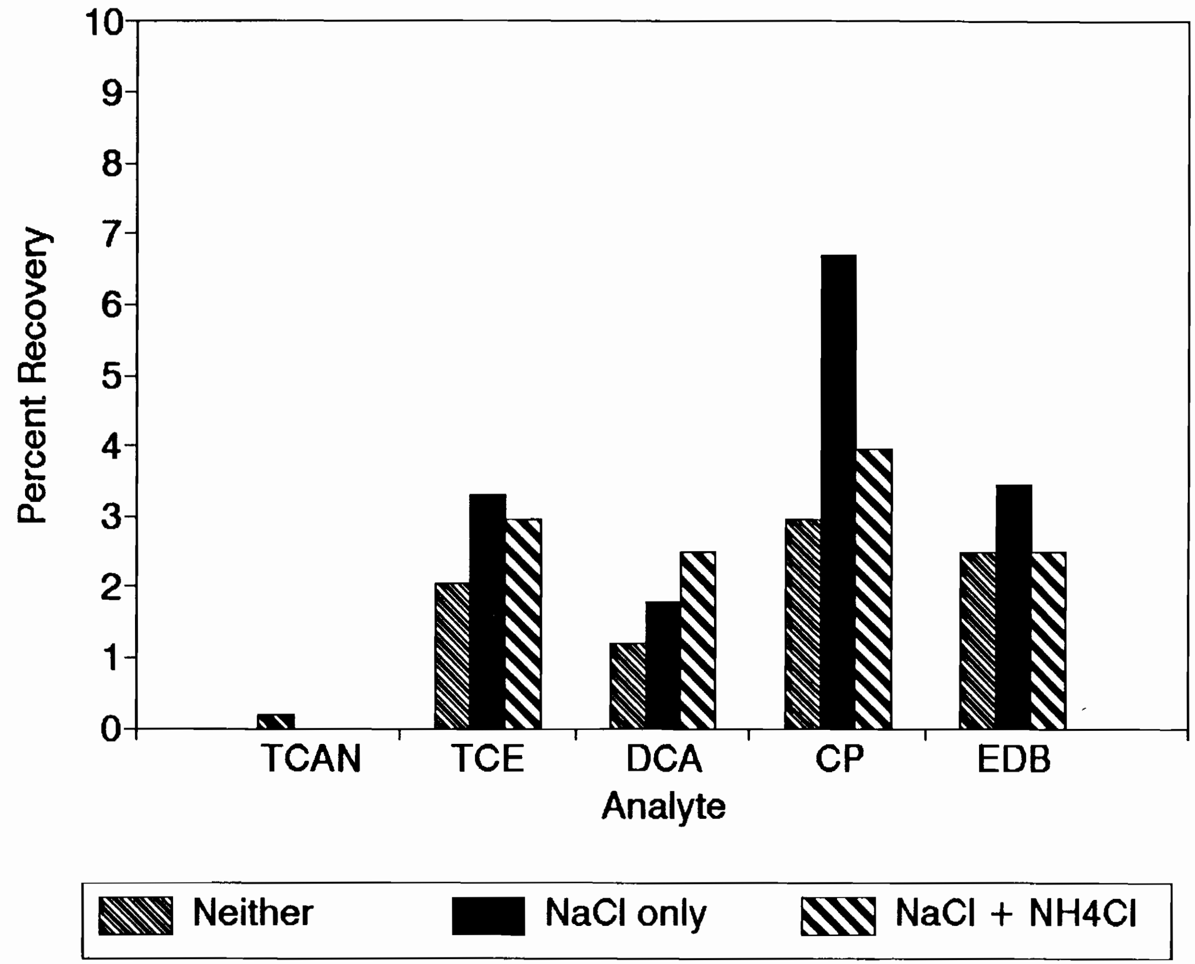


FIGURE IV-3: PERCENT RECOVERY VERSUS ANALYTE WHEN ANALYTE CONCENTRATION WAS 10 ug/L IN REAGENT WATER

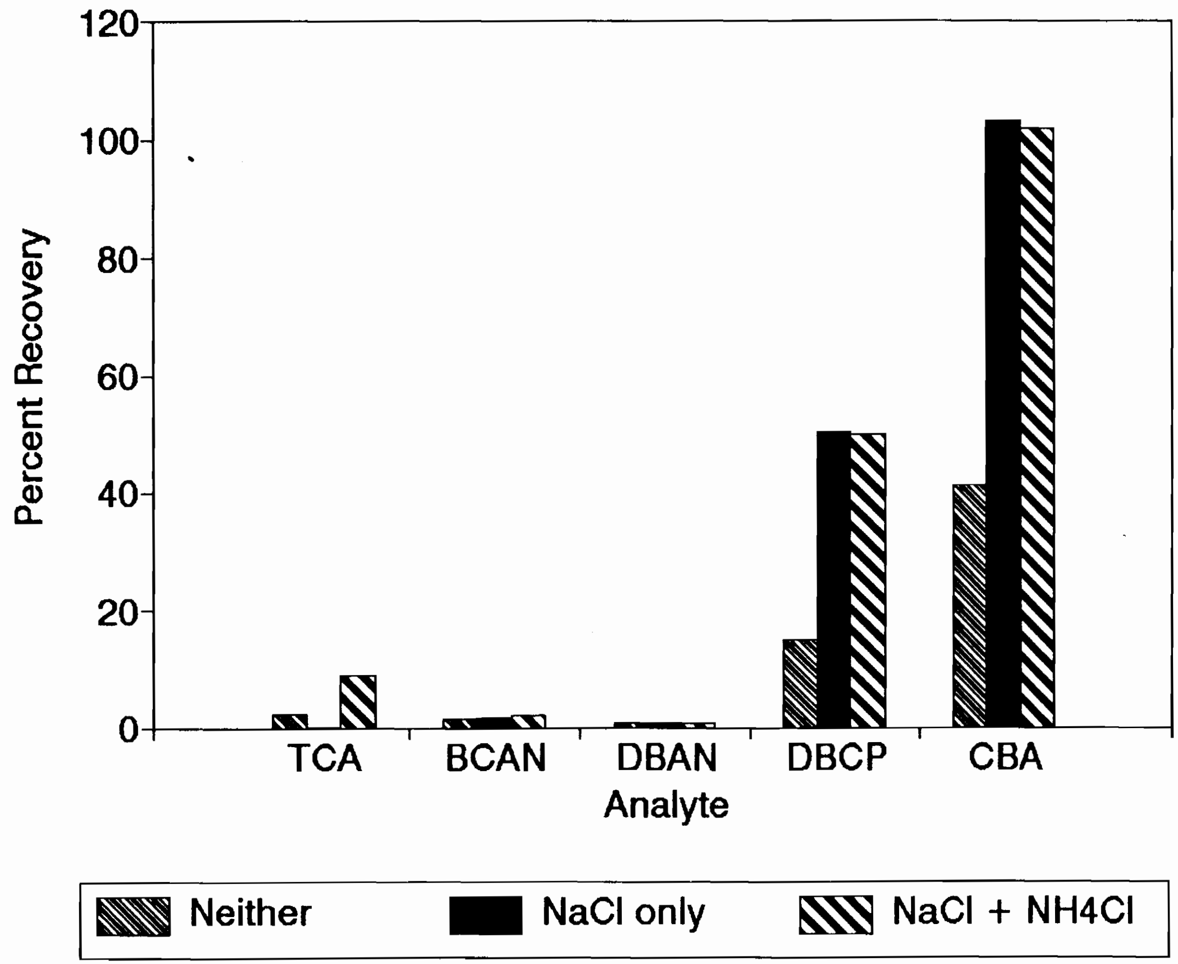


FIGURE IV-4: PERCENT RECOVERY VERSUS ANALYTE WHEN ANALYTE CONCENTRATION WAS 10 ug/L IN REAGENT WATER

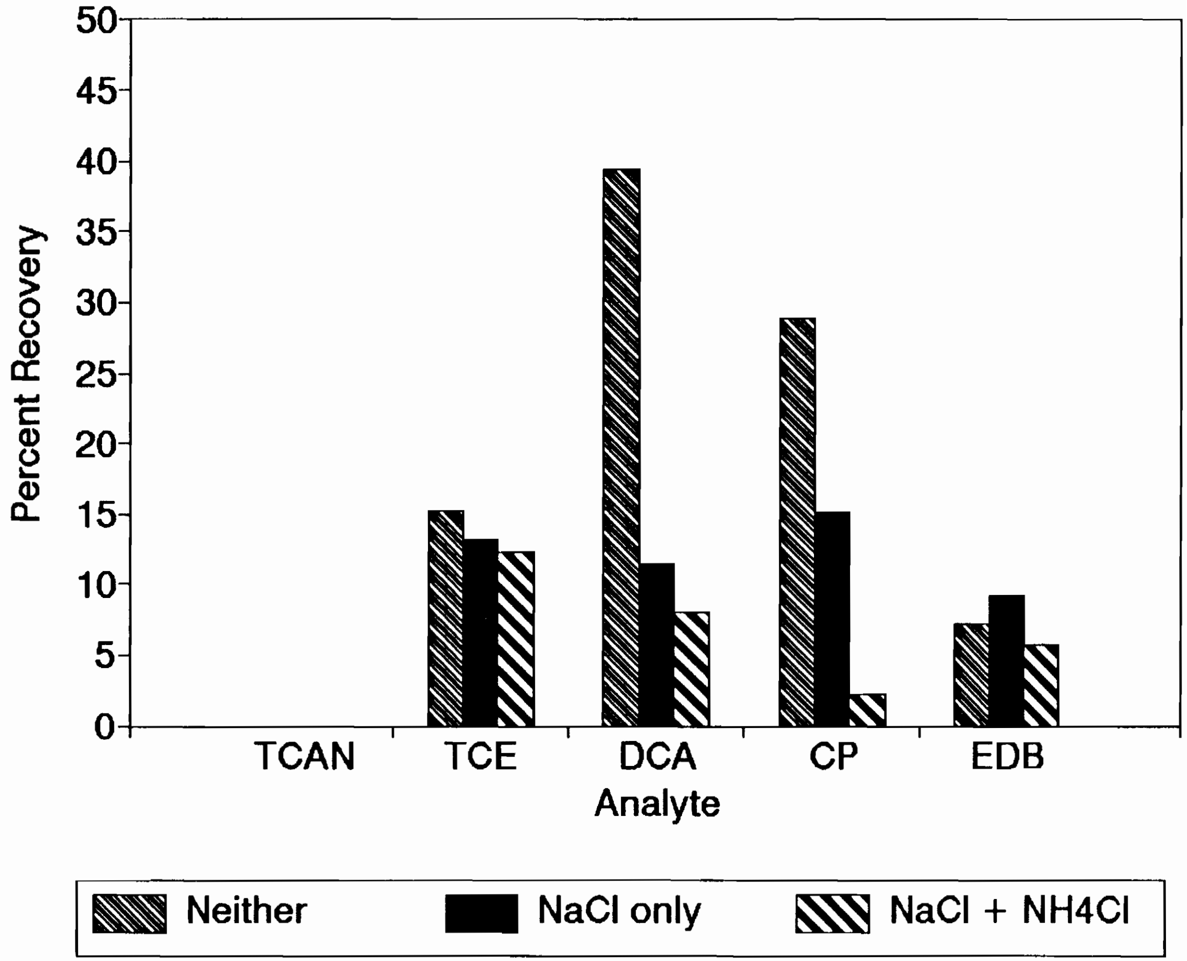


FIGURE IV-5: PERCENT RECOVERY VERSUS ANALYTE WHEN ANALYTE CONCENTRATION WAS 1 ug/L IN REAGENT WATER

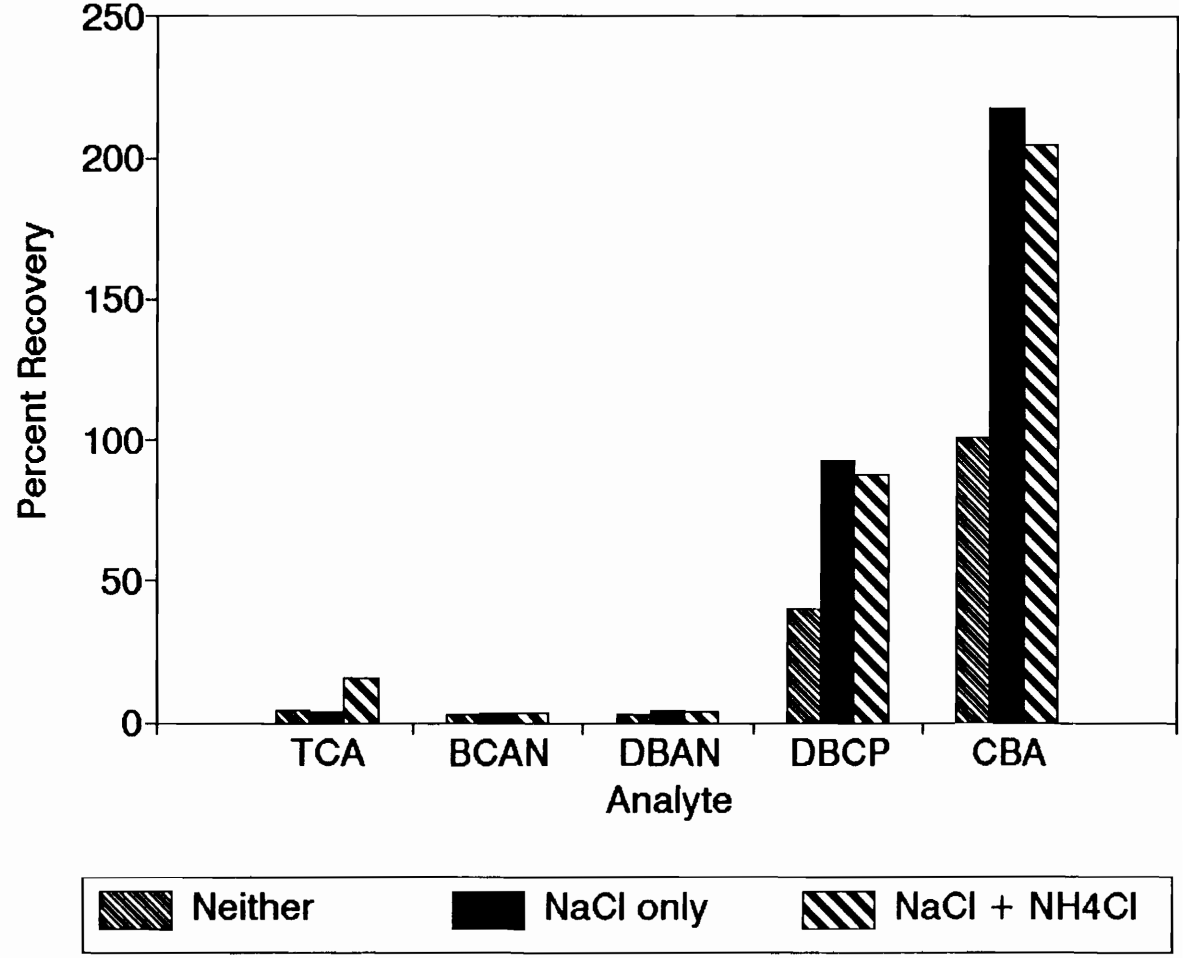


FIGURE IV-6: PERCENT RECOVERY VERSUS ANALYTE WHEN ANALYTE CONCENTRATION WAS 1 ug/L IN REAGENT WATER

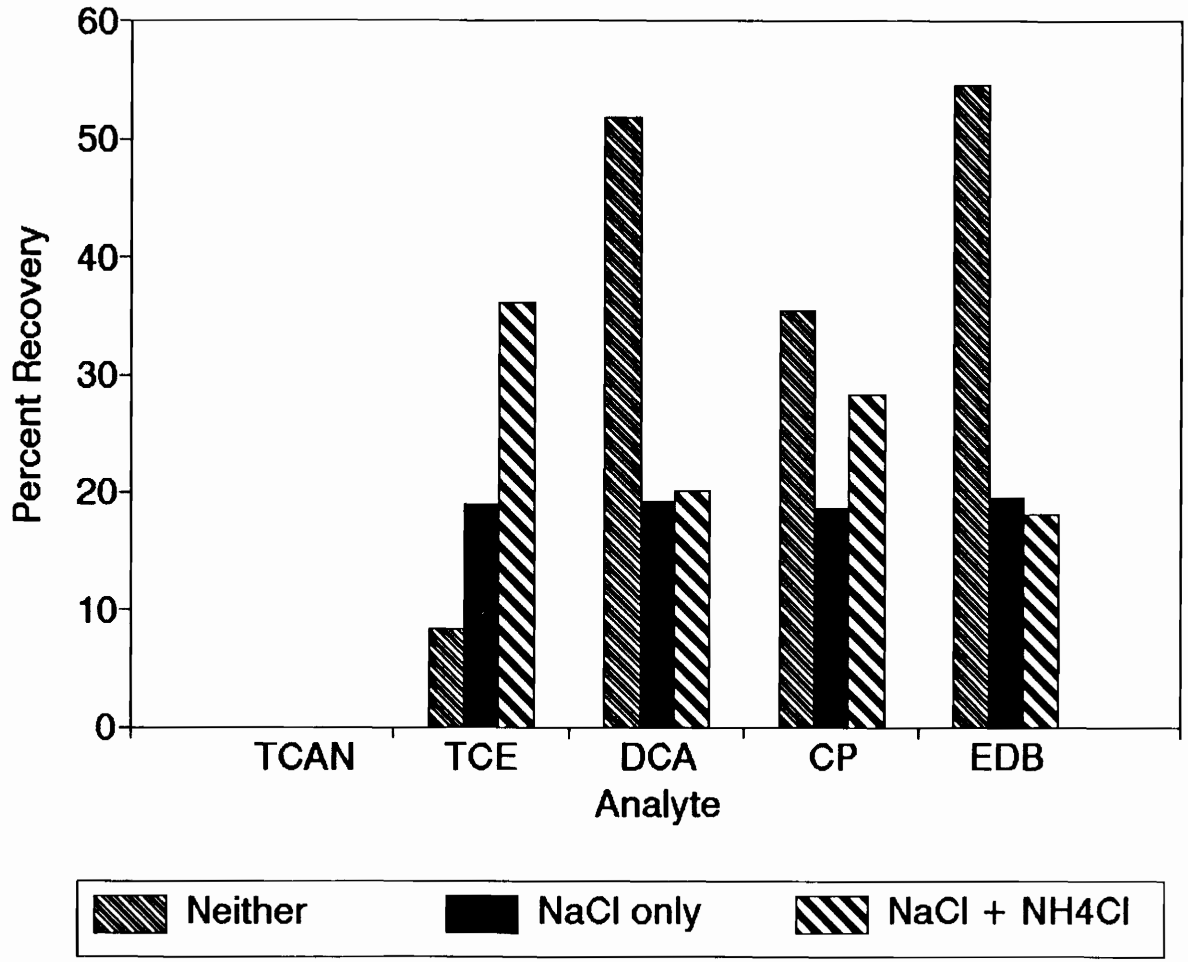


FIGURE IV-7: PERCENT RECOVERY VERSUS ANALYTE WHEN ANALYTE CONCENTRATION WAS 0.5 ug/L IN REAGENT WATER

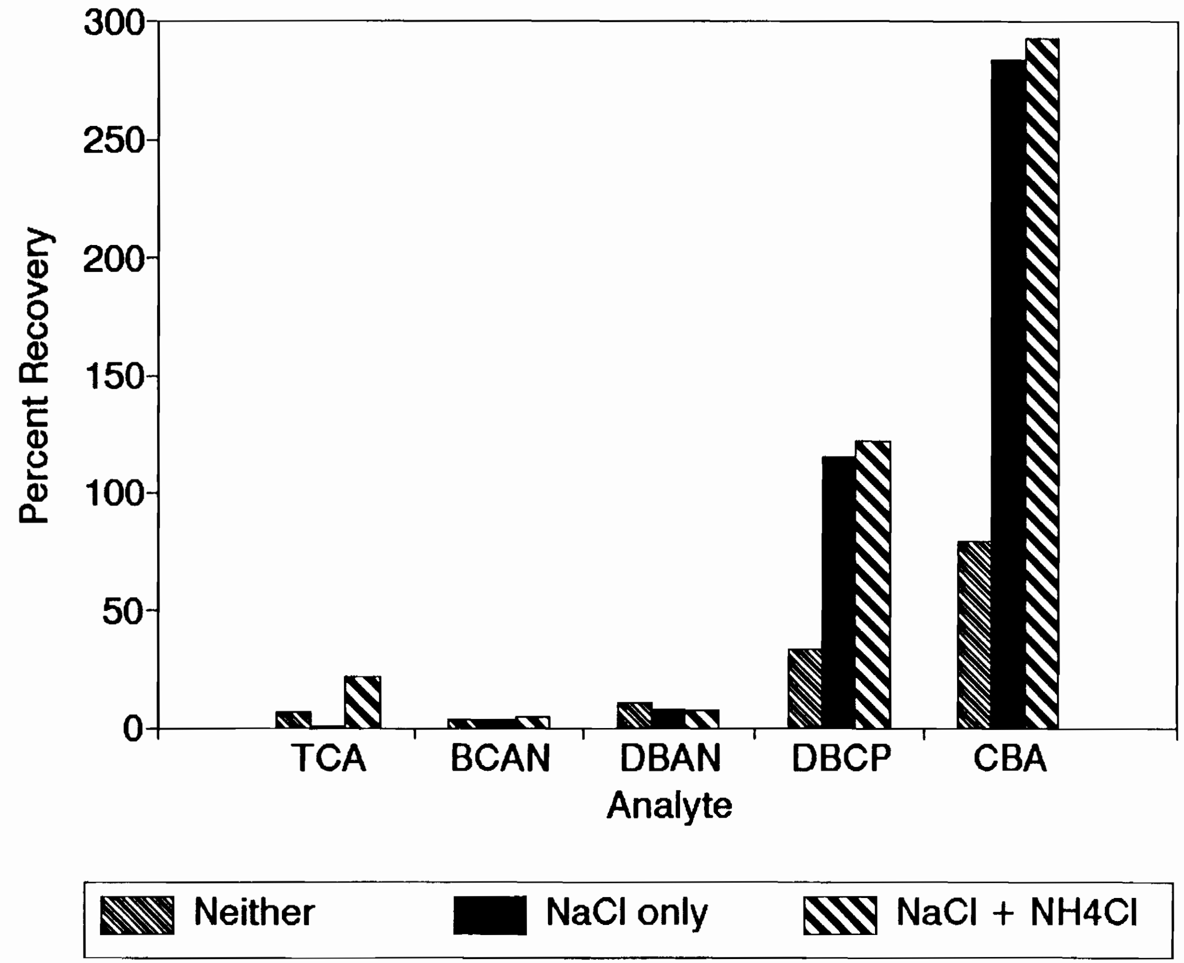


FIGURE IV-8: PERCENT RECOVERY VERSUS ANALYTE WHEN ANALYTE CONCENTRATION WAS 0.5 ug/L IN REAGENT WATER

TCA, BCAN, and DBAN were not affected by the addition of either salt. Finally, for the compounds at 0.5 ug/L, the recoveries of DCA, CP, EDB,and TCA decreased when NaCl was added and were little affected when NH_4Cl was added. Both NaCl and NH_4Cl increased recoveries of TCE. The addition of NaCl and NH_4Cl had relatively no effect of the recoveries of BCAN and DBAN, and the addition of NaCl increased the recoveries of DBCP and CBA with NH_4Cl having minor effects.

The graphs also showed that some of the recoveries for DBCP and CBA were considerably above 100 percent with some recoveries close to 300 percent. The reason for this is not known; however, contamination of samples or additional sources of the disinfection by-products could be a cause. Other studies have experienced the same situation; EPA Method 625 stated that the average percent recovery for bis (2-ethylhexyl) phthalate was 129 percent, and the average percent recovery for 3,3'-dichlorobenzidine was 184 percent. No explanation was given (Longbottom and Lichtenberg, 1982).

An analysis of variance was performed on the above data using Minitab Data Analysis Software (Minitab, Inc., release 7.2, 1989) in order to compare the three treatments--compound, type of salt addition, and concentration--and to determine which treatment or combination of treatments had the most significant effect on the recoveries. Table IV-4 shows the results of this test; the interaction of all three treatments could not be calculated because this would cause the degree of freedom for the error to be zero. The hypothesis (H_0) for the analysis was that each treatment did not have a significant effect on the recoveries, and H_0 was rejected when the probability value (P) was

TABLE IV-4: ANALYSIS OF VARIANCE FOR RECOVERY

Source	DF	SS	MS	F	P
Compound[1]	9	194798.9	21644.3	83.11	<0.001
Salt[2]	2	4619.7	2309.8	8.87	0.001
Concentration[3]	2	13854.8	6927.4	26.60	<0.001
Compound*Salt	18	35714.3	1984.1	7.62	<0.001
Compound*Concentration	18	23554.7	1308.6	5.02	<0.001
Salt*Concentration	4	913.4	228.3	0.88	0.487
Error	36	9376.0	260.4		
Total	89	282831.7			

1 Compound = ten individual analytes
2 Salt = type of salt addition (neither, NaCl only, or both NaCl and NH_4Cl)
3 Concentration = concentration of analyte (0.5, 1.0, or 10 ug/L)

DF = degrees of freedom SS = sum of squares MS = mean square
F = F-ratio ($MS_{treatment}/MS_{error}$) P = probability value

less than 0.05. Therefore, the treatments that had a significant effect were compound, salt addition, concentration, the interaction betweencompound and salt addition, and the interaction between compound and concentration. The treatment with the highest level of significance was the compound.

B. COMPARISON TO EPA METHOD 551

Table IV-5 presents the data that compare limits of detection calculated by the EPA recommended method and the Low Level Standard method. This table also compares the calculated LOD values with the MDL values obtained from EPA Method 551. For all of the compounds except EDB and DBCP, the LOD values calculated by the Low Level Standard method are higher than those calculated by the EPA recommended method. All of the calculated LOD values are higher than the MDL values from EPA Method 551.

A Wilcoxon paired-sample test (Zar, 1984) was performed on the limit of detection data to determine if the difference between the EPA Method 551 values and the EPA recommended method values was significant. According to this test, the difference between the two sets of values was significant at a 95 percent confidence level.

Table IV-6 presents the data that compare limits of quantitation calculated by the Low Level Standard method and the Keith et al. (1983) method. For all of the compounds except EDB, DBCP, and CBA, the LOQ values determined by the Low Level Standard method are lower than those determined by the Keith et al. (1983) method.

TABLE IV-5: COMPARISON OF LOD VALUES

Analyte	Limit of Detection, ug/L EPA 551[1]	SPE (EPA Method)[2]	SPE (Low Level)[3]
Trichloroacetonitrile	0.092	N/D[4]	0.648
Trichloroethylene	0.002	4.757	10.335
1,1-Dichloroacetone	0.005	2.002	6.878
Chloropicrin	0.012	N/D	N/D
1,2-Dibromoethane	0.006	16.884	13.934
1,1,1-Trichloroacetone	0.012	0.939	1.168
Bromochloroacetonitrile	0.011	0.724	1.022
Dibromoacetonitrile	0.034	0.260	3.672
1,2-Dibromo-3-chloropropane	0.009	7.485	3.180
2-Chlorobenzaldehyde	N/A[5]	26.676	45.018

1 **EPA 551 MDL Values** = method detection limits reported in EPA Method 551 and calculated by the EPA method described below.

2 **EPA Method** = EPA recommended limit of detection calculated by measuring the average response of a standard, subtracting an average blank value from each response, and multiplying this value by the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

3 **Low Level Standard Method** = limit of detection calculated by measuring the average response of a blank and then adding three times the standard deviation

4 **N/D** = Not detected; this compound was not detected using the Empore Extraction Disk procedure, thus a detection limit could not be calculated.

5 **N/A** = Data not available.

TABLE IV-6: COMPARISON OF LOQ VALUES

Analyte	Low Level Standard Method[1] (ug/L)	Keith et al. (1983) Method[2] (ug/L)
Trichloroacetonitrile	0.078	1.978
Trichloroethylene	22.370	24.639
1,1-Dichloroacetone	9.743	17.744
Chloropicrin	N/D[3]	N/D[3]
1,2-Dibromoethane	65.062	40.928
1,1,1-Trichloroacetone	3.876	4.942
Bromochloroacetonitrile	2.339	3.121
Dibromoacetonitrile	1.993	9.338
1,2-Dibromo-3-chloropropane	23.044	8.534
2-Chlorobenzaldehyde	101.760	99.452

1 **Low Level Standard Method** = limit of quantitation calculated by measuring the average response of a blank and then adding ten times the standard deviation of the response of a low level standard.

2 **Keith _et al._ (1983) Method** = limit of quantitation calculated by measuring the average response of a blank and then adding ten times the standard deviation of the response of the blank.

3 **N/D** = Not detected; compound was not recovered using the Empore Extraction Disk procedure, thus a quantitation limit could not be calculated.

C. STANDARD ADDITION RESULTS

The raw data from the standard addition experiment are presented in Appendix B. Table IV-7 presents the standard addition results for the reagent water samples, and Table IV-8 presents the standard addition results for the drinking water samples. Figure IV-9 shows an example of a good standard addition graph (R-square = 0.97), and Figure IV-10 shows an example of a poor standard addition graph (R-square = 0.34). Regressions were performed for the measured concentrations versus the known concentration added, and the values for the slope, R-square value, and negative x-intercepts (which were equal to the actual concentrations) were determined for each compound. The actual concentrations were also compared to the concentrations determined by the internal standard method.

The results for the reagent water samples showed that only 60 percent of the R-square values were above the recommended 0.80. Also, few of the concentrations calculated by the internal standard method were similar to those determined by standard addition. For the drinking water samples, the results showed that 90 percent of the R-square values were above 0.80, and the concentrations from the internal standard method were more similar to those from the standard addition method.

Wilcoxon paired-sample tests (Zar, 1984) were performed on both the reagent water data and the drinking water data to determine if the difference between the standard addition method results and the internal standard method results was significant. According to these tests, the difference between the two sets of values was not significant at a 95 percent confidence level for both reagent and drinking water samples.

TABLE IV-7: COMPARISON OF STANDARD ADDITION AND INTERNAL STANDARD RESULTS FOR DETERMINATION OF ANALYTE CONCENTRATION IN REAGENT WATER

Analyte	Slope	R Square Value	Concentration (ug/L)	
			-Intercept	Int. Std. Method
Trichloroacetonitrile	0.21	0.83	0.34	0.08
Trichloroethylene	2.58	0.34	3.45	4.20
1,1-Dichloroacetone	1.01	0.95	2.84	2.22
Chloropicrin	7.86	0.85	0.17	0
1,2-Dibromoethane	N/C*	N/C*	N/C*	2.37
1,1,1-Trichloroacetone	0.09	0.88	4.39	0.19
Bromochloroacetonitrile	0.04	0.30	13.31	0.12
Dibromoacetonitrile	N/C*	N/C*	N/C*	1.22
1,2-Dibromo-3-chloropropane	34.77	1.00	-0.10	0.89
2-Chlorobenzaldehyde	54.93	0.99	0.37	21.69

***N/C** = Not calculated; measured concentration was nearly independent of added concentration.

TABLE IV-8: COMPARISON OF STANDARD ADDITION AND INTERNAL STANDARD RESULTS FOR DETERMINATION OF ANALYTE CONCENTRATION IN DRINKING WATER

Analyte	Slope	R Square Value	Concentration (ug/L) -Intercept	Concentration (ug/L) Int. Std. Method
Trichloroacetonitrile	2.86	0.83	0.49	1.37
Trichloroethylene	2.93	0.56	2.76	3.14
1,1-Dichloroacetone	1.82	0.95	0.50	0.53
Chloropicrin	4.42	0.95	0.64	2.50
1,2-Dibromoethane	3.40	0.97	0.20	0
1,1,1-Trichloroacetone	3.49	0.90	4.66	10.15
Bromochloroacetonitrile	0.84	0.99	1.51	1.03
Dibromoacetonitrile	1.20	1.00	1.00	0.95
1,2-Dibromo-3-chloropropane	13.77	1.00	0.05	0.27
2-Chlorobenzaldehyde	26.90	0.95	0.14	0

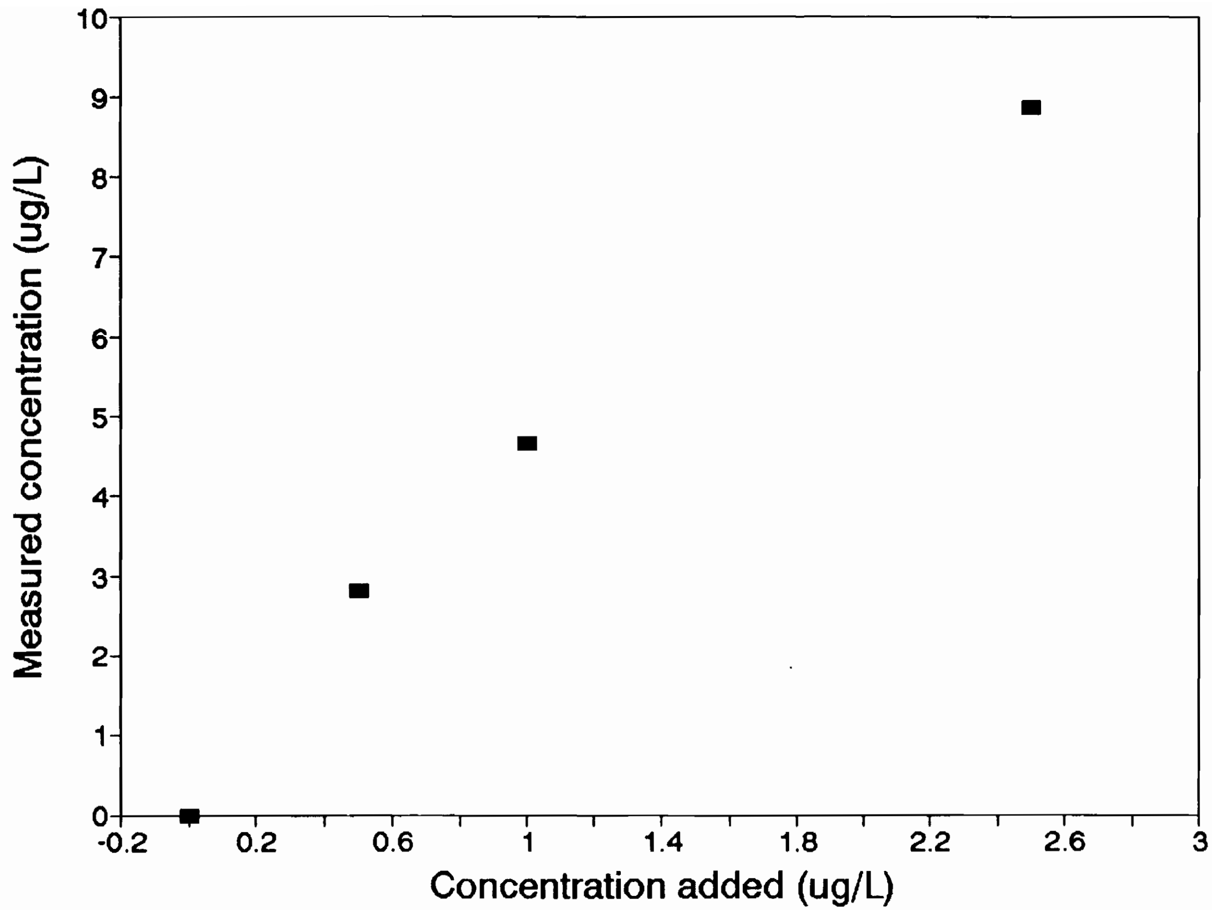


FIGURE IV-9: SAMPLE GRAPH OF STANDARD ADDITION FOR 1,2-DIBROMOETHANE IN DRINKING WATER

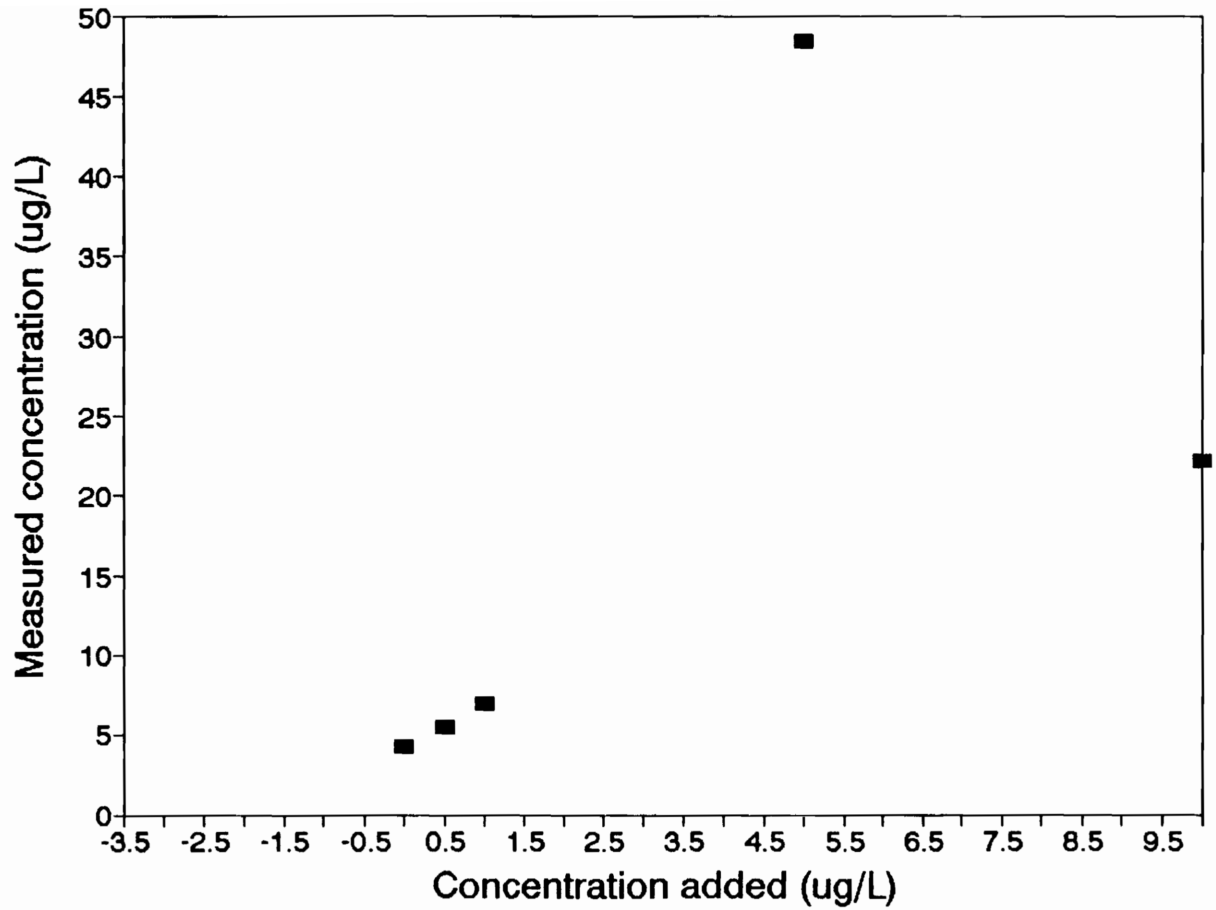


FIGURE IV-10: SAMPLE GRAPH OF STANDARD ADDITION FOR TRICHLOROETHYLENE IN REAGENT WATER

Additional regressions were calculated to determine if the physical/chemical properties and the recoveries were correlated. Regressions were calculated for the recoveries of compounds spiked at 1 ug/L and 5 ug/L when they were correlated with vapor pressure and solubility. The results are given in Table IV-9. Since all of the R-square values were considerably low and less than 0.20, no correlations between vapor pressure and recovery or solubility and recovery were evident.

TABLE IV-9: RESULTS FROM REGRESSION ANALYSIS OF PERCENT RECOVERY AND PHYSICAL/CHEMICAL PROPERTIES

Regression	R Square	Slope
1 ug/L vs. Vapor Pressure	0.133	-0.327
1 ug/L vs. Solubility	0.0004	-0.0005
5 ug/L vs. Vapor Pressure	0.171	-0.621
5 ug/L vs. Solubility	0.102	0.0147

V. DISCUSSION

A. OPTIMIZATION OF SOLID PHASE EXTRACTION PROCEDURE

1. Order of elution and retention times

After the elution order of the analytes was determined, the physical/chemical properties of the analytes were examined to determine possible reasons for this order. The trend was that the early eluting compounds had lower boiling points and higher vapor pressures than the late eluting compounds. Lower boiling points and higher vapor pressures tend toward more volatility, and this assumption was confirmed by the regressions performed on retention time versus boiling point (R-square = 0.96) and retention time versus vapor pressure (R-square = 0.80). The more volatile compounds, therefore, eluted first with the less volatile eluting later.

2. Drying time experiment

The purpose of the drying time experiment was to determine the best length of time to dry the Empore Extraction Disk by air suction after samples were processed. In the experiment performed by Hagen et al. (1990), air was drawn through the extraction disk for "several minutes" after the sample was processed. This followed the directions included with the Empore Extraction Disks, which stated that the length of time the air should be pulled through was 5-30 minutes. However, Kraut-Vass and Thoma (1991) dried the disk for one minute and stated that "prolonged air suction may result in losses." That statement proved to be correct in this research, for, as stated in the results chapter, when the length of time air was drawn through the extraction disk was decreased from ten minutes to 30 seconds, there was an increase in percent change in peak area for most compounds; therefore, a drying time of less than one minute is recommended.

3. Comparison of recoveries

One of the purposes of the recovery comparison experiment was to determine if recoveries of the analytes could be increased by adding NaCl. As the results of this experiment showed, salt addition and compound elution time were highly correlated. The addition of salt decreased the recoveries of the more volatile compounds but increased the recoveries of the less volatile, higher boiling compounds; recoveries of the compounds that eluted in the middle were unaffected by salt addition. This could be because the C-18 disk did not perform well under highly saline conditions. According to Rachel Grace (personal communication), a technical assistant with Analytichem International, research in mid 1991 showed that salt increased the hydrophobic nature of the C-18 disk. The C-18 polymerized and completely covered the surface of the silica, which prevented the surface from being available for the retention of compounds. As a result of this research, a new cyclohexyl disk was developed that stayed conditioned in highly saline environments. This disk had more silanol activity, which allowed water and methanol to keep the bonded phase conditioned and allowed the surface to be available for retention. The cyclohexyl disk was not available at the time the disinfection by-products were investigated (Grace, 1992).

Another possible explanation for the correlation between salt addition and compound elution time was that SPE may not work well for volatile compounds. These compounds may not adsorb to the disk, or they may not be readily desorbed by water through the disk. Since increasing the salt concentration generally decreases water solubility, salt addition should increase the affinity of analytes for the nonpolar C-18 SPE disk. Indeed, the percent recoveries of the less volatile compounds improved upon the addition of salt. For more volatile compounds, the decrease in water solubility appears to have increased volatilization.

Another reason for the observed results was that some volatilization occurred before and during analysis and that the SPE method was sensitive to holding time. Attempts were made to minimize the volatilization of the ten compounds during analysis; these included storing samples with minimum headspace, avoiding agitation of samples, analyzing samples soon after preparation, and adding the compounds to solutions in which the salts were already dissolved. Hodgeson et al. (1988) stated that TCAN is unstable and must be analyzed for immediately. Some losses of the earlier eluters could have occurred since several days usually passed between sample elution and GC analysis, even though the extracted samples were refrigerated and NH_4Cl was used to dechlorinate and preserve the samples. The results may have been improved if sample analysis had been performed immediately. Also, some losses could have occurred during analysis when the sample was poured repeatedly and as a result of the analysis itself being performed in a fume hood.

A trend that was observed was that the recoveries appeared to be concentration dependent; the recoveries increased as the concentration of the compounds decreased. This could be due to the previously discussed problem of the C-18 disk not performing well under saline conditions. Since there was limited retention of the compounds, there would be a lower percentage recovered as the concentration of the compounds increased.

Another purpose of the recovery comparison experiment was to determine if the addition of NH_4Cl as a dechlorination agent had any effect on recoveries. As stated earlier, EPA Method 551 recommended the use of NH_4Cl as a dechlorination agent, and Hodgeson et al. (1988) gave a maximum of seven days as a safe sample holding time when using NH_4Cl. In general, the addition of NH_4Cl had little or no effect on the recoveries of the analytes tested in this research. When NH_4Cl did have a minor effect, the recoveries decreased for some compounds and increased for others without a particular trend.

B. COMPARISON TO EPA METHOD 551

The objectives of this experiment were to determine the LOD and LOQ values for the SPE method, compare the ways these values were calculated, and compare the LOD values to the MDL values presented in EPA Method 551. Of the two methods used to calculate the LOD values, the EPA recommended method produced lower values than the Low Level Standard method. This was because the EPA recommended method required subtraction of the blank concentration from the standard's concentration before the standard deviation calculation was done and then required multiplication by the t value (3.14), where the Low Level Standard Method required the addition of three standard deviations of the standard to the average concentration of the blank. Therefore, the major difference between the two methods was that one method subtracted the blank concentration and the other added to the blank concentration. In either case, the LOD values for the SPE method were noticeably higher than those in EPA Method 551. This was due to higher variability in the detected concentrations of the compounds for replicate samples.

Of the two methods used to calculate the LOQ values, the Low Level Standard method produced lower values than the Keith et al. (1983) method for six of the compounds. The Low Level Standard method required addition of three standard deviations of the standard to the average concentration of the blank, where the Keith et al. (1983) method required addition three standard deviations of the blank to the average concentration of the blank. Therefore, the only difference between the two methods was the standard deviation that was used, and the higher LOQ value occurred when the standard deviation was higher. As with the LOD values, the variability in the concentrations of the compounds for replicate samples was large.

C. STANDARD ADDITION RESULTS

The purpose of the standard addition experiment was to compare the quantitation of the ten compounds by two independent methods: 1) the internal standard method, and 2) the standard addition method. The results of the Wilcoxon paired-sample tests performed on these data showed that the differences between the standard addition method values and the internal standard method values were not significant. These results were due to the standard addition values not being consistently higher or lower than the internal standard values. When the reagent water results from the standard addition method were compared with those from the internal standard method, very few of the concentrations were close to each other. For the drinking water samples, the two methods produced more similar results although there still were some noticeable differences. The reagent water standard addition results were less similar to the internal standard results and had lower R-square values than the drinking water standard addition results. The reason for the difference was not apparent since the experiments were performed similarly. A reason for the differences in the results obtained by the two methods was that the recoveries appeared to be concentration dependent, which would affect the standard addition results. Therefore, the use of standard addition is not recommended because it was concentration dependent and it did not improve the results.

VI. SUMMARY AND CONCLUSIONS

The focus of this research was on compounds called "disinfection by-products," which have been identified in drinking water supplies. These halo-organic chemicals are potentially toxic compounds, and the USEPA has proposed to regulate them in drinking water. The objectives of this research were to develop a broad spectrum method for the extraction, concentration, and analysis of certain drinking water disinfection by-products (haloacetonitriles, haloketones, and haloaldehydes) by solid phase extraction (SPE) and to determine if this method had lower detection limits and less variability than the proposed liquid-liquid extraction method, EPA Method 551. The SPE method extracted and concentrated samples with the C-18 Empore Extraction Disks, and desorbed the analytes with methyl-tert-butyl ether (MTBE) as a solvent. The compounds investigated were: bromochloro- acetonitrile (BCAN), 2-chlorobenzaldehyde (CBA), chloropicrin (CP), dibromoacetonitrile (DBAN), 1,2-dibromo-3-chloropropane (DBCP), 1,2-dibromoethane (EDB), 1,1-dichloroacetone (DCA), 1,1,1-trichloro-acetone (TCA), trichloroacetonitrile (TCAN), and trichloroethylene (TCE).

The results from the experiments performed showed that a drying time for the extraction disk after the sample was processed should be less than one minute. For the ten compounds investigated, vapor pressure and boiling point were correlated with retention time, and the more volatile, lower boiling point compounds eluted first. The results also showed that there was a correlation between salt addition and retention time; as retention time increased, the recoveries increased. The recoveries also appeared to be concentration dependent, with higher concentrations being more poorly recovered. The low recoveries and the appearance of concentration dependency could be due to the fact that the C-18 disk did not perform well under highly saline conditions. The recoveries for DBCP and CBA were the only ones which were consistently above 50 percent. The limit of detection (LOD) values for this method were higher than those of Method 551, and the limit of quantitation (LOQ) values appeared to be high for the SPE method as well. Finally, when standard addition method results and internal standard method results were compared, the methods gave similar results for only a few of the compounds.

From the results of the research described in this thesis, the following conclusions were derived:

1. Although the SPE method improved the recoveries of DBCP and CBA, it was not successful for recovery of the other eight compounds. This could be due to the C-18 disk performance under saline conditions.

2. The limit of detection values for the SPE method were higher than those for EPA Method 551. Generally, the SPE method's LOD values were 10-1000 times higher than those reported in EPA Method 551.

3. There was more variability in the results for the SPE method than for EPA Method 551 (see Table II-2).

4. The SPE method appeared to be concentration dependent due to the problem with the C-18 disk, with lower concentrations (i.e., $\leq$ 1 ug/L) being recovered to a greater extent than higher concentrations (i.e., $\geq$ 10 ug/L).

In the future, it is recommended that EPA Method 551 be used instead of the SPE method for these compounds. Even though the SPE method was easier and faster, the lower MDL values and low variability make Method 551 more preferable at this time. It is also recommended that the cyclohexyl disks be investigated for use in the SPE method.

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APPENDIX A: DATA FROM SALT ADDITION EXPERIMENT

The following gives an explanation of each sample number and of what each sample consists. All samples were prepared in reagent water.

Sample no.	Concentration	Description
25 and 26	10 ug/L	Neither salt added
27 and 28	1 ug/L	Neither salt added
29 and 30	0.5 ug/L	Neither salt added
37 and 38	10 ug/L	NaCl added only
39 and 40	1 ug/L	NaCl added only
41 and 42	0.5 ug/L	NaCl added only
45 and 46	10 ug/L	NaCl & NH_4Cl added
47 and 48	1 ug/L	NaCl & NH_4Cl added
49 and 50	0.5 ug/L	NaCl & NH_4Cl added

APPENDIX A: DATA FROM SALT ADDITION EXPERIMENT

sample no	DBPName	RF	Conc	Percent rec
25	TCAN	57.34	0.809	0.202
25	TCE	13.85	9.315	2.329
25	DCA	27.84	5.137	1.284
25	CP	20.00	11.954	2.988
25	EDB	28.65	10.086	2.522
25	TCA	114.72	7.914	1.978
25	BCAN	71.45	5.154	1.289
25	DBAN	62.42	2.267	0.567
25	DBCP	164.93	59.156	14.789
25	CBA	16.46	172.300	43.075
26	TCAN	57.34	0.650	0.162
26	TCE	13.88	7.146	1.787
26	DCA	27.87	4.250	1.063
26	CP	20.00	11.751	2.938
26	EDB	28.66	9.826	2.456
26	TCA	114.73	7.789	1.947
26	BCAN	71.46	4.892	1.223
26	DBAN	62.44	1.805	0.451
26	DBCP	164.99	58.324	14.581
26	CBA	16.49	158.107	39.527
27	TCAN	57.36	0.000	0.000
27	TCE	13.93	3.551	8.876
27	DCA	27.47	20.525	51.312
27	CP	20.00	5.552	13.879
27	EDB	28.84	3.440	8.599
27	TCA	115.45	1.779	4.448
27	BCAN	71.64	1.354	3.384
27	DBAN	62.47	0.697	1.742
27	DBCP	168.22	17.337	43.342
27	CBA	16.81	45.669	114.174
28	TCAN	57.36	0.000	0.000
28	TCE	13.86	8.665	21.663
28	DCA	27.70	10.993	27.483
28	CP	20.01	17.470	43.675
28	EDB	28.87	2.353	5.883
28	TCA	115.47	1.614	4.034
28	BCAN	71.67	0.791	1.977
28	DBAN	62.45	1.363	3.408
28	DBCP	168.42	14.855	37.138
28	CBA	16.84	35.192	87.979
29	TCAN	57.36	0.000	0.000
29	TCE	13.96	1.167	5.833
29	DCA	27.81	6.676	33.380
29	CP	20.00	8.667	43.337
29	EDB	28.47	16.505	82.525
29	TCA	115.44	1.879	9.397
29	BCAN	71.66	0.961	4.804
29	DBAN	62.45	1.314	6.570
29	DBCP	169.07	6.816	34.078
29	CBA	16.89	17.391	86.956
30	TCAN	57.36	0.000	0.000
30	TCE	13.94	2.174	10.871
30	DCA	27.63	14.054	70.271
30	CP	20.00	5.514	27.571
30	EDB	28.79	5.319	26.596
30	TCA	115.58	0.681	3.407
30	BCAN	71.69	0.351	1.756
30	DBAN	62.40	3.016	15.080
30	DBCP	169.08	6.659	33.294
30	CBA	16.90	14.290	71.448
37	TCAN	57.36	0.000	0.000
37	TCE	13.81	13.223	3.306
37	DCA	27.77	8.284	2.071
37	CP	20.02	27.856	6.964
37	EDB	28.57	13.158	3.289
37	TCA	115.52	1.191	0.298
37	BCAN	71.43	5.600	1.400

APPENDIX A (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
37	DBAN	62.43	1.994	0.498
37	DBCP	155.17	193.702	48.425
37	CBA	15.87	396.665	99.166
38	TCAN	57.36	0.000	0.000
38	TCE	13.80	13.393	3.348
38	DCA	27.82	5.999	1.500
38	CP	20.02	25.756	6.439
38	EDB	28.54	14.206	3.551
38	TCA	115.59	0.617	0.154
38	BCAN	71.42	5.861	1.465
38	DBAN	62.43	2.247	0.562
38	DBCP	154.08	209.812	52.453
38	CBA	15.79	428.057	107.014
39	TCAN	57.36	0.000	0.000
39	TCE	13.88	7.276	18.190
39	DCA	27.84	5.229	13.071
39	CP	20.00	8.669	21.674
39	EDB	28.81	4.496	11.240
39	TCA	115.44	1.877	4.693
39	BCAN	71.64	1.434	3.584
39	DBAN	62.45	1.539	3.848
39	DBCP	166.62	37.506	93.764
39	CBA	16.69	87.124	217.810
40	TCAN	57.36	0.000	0.000
40	TCE	13.93	3.323	8.308
40	DCA	27.87	3.925	9.813
40	CP	19.99	3.448	8.620
40	EDB	28.86	2.962	7.406
40	TCA	115.53	1.123	2.808
40	BCAN	71.65	1.206	3.014
40	DBAN	62.43	1.935	4.839
40	DBCP	166.67	36.867	92.168
40	CBA	16.69	87.130	217.826
41	TCAN	57.36	0.000	0.000
41	TCE	13.93	3.579	17.894
41	DCA	27.89	3.315	16.574
41	CP	19.99	3.070	15.349
41	EDB	28.87	2.534	12.672
41	TCA	115.63	0.274	1.368
41	BCAN	71.68	0.619	3.093
41	DBAN	62.45	1.510	7.548
41	DBCP	167.91	21.134	105.669
41	CBA	16.79	52.177	260.883
42	TCAN	57.36	0.000	0.000
42	TCE	13.92	3.983	19.915
42	DCA	27.86	4.327	21.633
42	CP	19.99	4.355	21.775
42	EDB	28.79	5.234	26.170
42	TCA	115.64	0.163	0.816
42	BCAN	71.68	0.682	3.408
42	DBAN	62.44	1.679	8.397
42	DBCP	167.61	24.936	124.681
42	CBA	16.76	61.344	306.721
45	TCAN	57.36	0.000	0.000
45	TCE	13.82	12.254	3.063
45	DCA	27.74	9.320	2.330
45	CP	20.01	19.262	4.816
45	EDB	28.62	11.165	2.791
45	TCA	111.50	35.956	8.989
45	BCAN	71.30	8.122	2.030
45	DBAN	62.42	2.287	0.572
45	DBCP	153.46	219.040	54.760
45	CBA	15.74	445.393	111.348
46	TCAN	57.36	0.000	0.000
46	TCE	13.83	11.283	2.821
46	DCA	27.71	10.778	2.694
46	CP	20.00	12.216	3.054

APPENDIX A (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
46	EDB	28.69	8.733	2.183
46	TCA	111.53	35.736	8.934
46	BCAN	71.28	8.526	2.132
46	DBAN	62.42	2.327	0.582
46	DBCP	156.14	179.503	44.876
46	CBA	15.94	368.528	92.132
47	TCAN	57.36	0.000	0.000
47	TCE	13.90	5.591	13.978
47	DCA	27.92	2.186	5.464
47	CP	19.99	1.737	4.343
47	EDB	28.87	2.597	6.493
47	TCA	114.86	6.686	16.715
47	BCAN	71.64	1.362	3.406
47	DBAN	62.45	1.343	3.357
47	DBCP	166.86	34.440	86.100
47	CBA	16.71	80.069	200.172
48	TCAN	57.36	0.000	0.000
48	TCE	13.92	4.219	10.547
48	DCA	27.87	4.209	10.521
48	CP	19.99	0.000	0.000
48	EDB	28.88	2.049	5.122
48	TCA	114.94	6.082	15.204
48	BCAN	71.65	1.235	3.089
48	DBAN	62.45	1.551	3.878
48	DBCP	166.78	35.449	88.623
48	CBA	16.70	83.556	208.890
49	TCAN	57.36	0.000	0.000
49	TCE	13.84	10.701	53.503
49	DCA	27.87	3.919	19.596
49	CP	20.00	11.257	56.283
49	EDB	28.86	2.632	13.161
49	TCA	115.13	4.451	22.255
49	BCAN	71.67	0.889	4.443
49	DBAN	62.45	1.453	7.265
49	DBCP	167.73	23.475	117.375
49	CBA	16.78	56.687	283.434
50	TCAN	57.36	0.000	0.000
50	TCE	13.92	3.730	18.649
50	DCA	27.87	4.120	20.602
50	CP	19.99	0.000	0.000
50	EDB	28.81	4.571	22.856
50	TCA	115.16	4.171	20.855
50	BCAN	71.67	0.838	4.192
50	DBAN	62.45	1.337	6.684
50	DBCP	167.58	25.262	126.308
50	CBA	16.77	60.481	302.407

APPENDIX B: DATA FROM STANDARD ADDITION EXPERIMENT

The following gives an explanation of each sample number and of what each sample consists. The number beside each sample letter is the replicate number.

Sample	Description
A	Reagent water with NaCl
B	Reagent water with NaCl and 0.5 ug/L compounds
C	Reagent water with NaCl and 1 ug/L compounds
D	Reagent water with NaCl and 5 ug/L compounds
E	Reagent water with NaCl and 10 ug/L compounds
F	Reagent water with NaCl and NH_4Cl
G	Drinking water with NaCl and NH_4Cl
H	Drinking water with NaCl and NH_4Cl
I	Drinking water with NaCl, NH_4Cl, and low concentration compounds
J	Drinking water with NaCl, NH_4Cl, and medium concentration compounds
K	Drinking water with NaCl, NH_4Cl, and high concentration compounds

APPENDIX B: DATA FROM STANDARD ADDITION EXPERIMENT

sample no	DBPName	RF	Conc	Percent rec
A 1	TCAN	57.35	0.543	0.000
A 1	TCE	13.92	4.050	0.000
A 1	DCA	27.87	4.132	0.000
A 1	CP	19.99	0.000	0.000
A 1	EDB	28.65	10.038	0.000
A 1	TCA	115.50	1.357	0.000
A 1	BCAN	71.67	0.857	0.000
A 1	DBAN	62.45	1.292	0.000
A 1	DBCP	169.41	2.564	0.000
A 1	CBA	16.87	23.117	0.000
A 2	TCAN	57.36	0.000	0.000
A 2	TCE	13.89	6.079	0.000
A 2	DCA	27.89	3.125	0.000
A 2	CP	19.99	0.000	0.000
A 2	EDB	28.94	0.000	0.000
A 2	TCA	115.66	0.000	0.000
A 2	BCAN	71.71	0.000	0.000
A 2	DBAN	62.45	1.415	0.000
A 2	DBCP	169.53	1.084	0.000
A 2	CBA	16.88	19.103	0.000
A 3	TCAN	57.36	0.000	0.000
A 3	TCE	13.93	3.381	0.000
A 3	DCA	27.90	2.849	0.000
A 3	CP	19.99	0.000	0.000
A 3	EDB	28.94	0.000	0.000
A 3	TCA	115.66	0.000	0.000
A 3	BCAN	71.71	0.000	0.000
A 3	DBAN	62.47	0.868	0.000
A 3	DBCP	169.53	1.156	0.000
A 3	CBA	16.90	14.945	0.000
A 4	TCAN	57.36	0.000	0.000
A 4	TCE	13.89	6.725	0.000
A 4	DCA	27.88	3.626	0.000
A 4	CP	19.99	0.000	0.000
A 4	EDB	28.94	0.000	0.000
A 4	TCA	115.66	0.000	0.000
A 4	BCAN	71.71	0.000	0.000
A 4	DBAN	62.40	3.068	0.000
A 4	DBCP	169.59	0.398	0.000
A 4	CBA	16.85	32.736	0.000
A 5	TCAN	57.36	0.000	0.000
A 5	TCE	13.93	2.877	0.000
A 5	DCA	27.93	1.818	0.000
A 5	CP	19.99	0.000	0.000
A 5	EDB	28.94	0.000	0.000
A 5	TCA	115.66	0.000	0.000
A 5	BCAN	71.71	0.000	0.000
A 5	DBAN	62.48	0.451	0.000
A 5	DBCP	169.60	0.287	0.000
A 5	CBA	16.85	32.200	0.000
A 6	TCAN	57.36	0.000	0.000
A 6	TCE	13.96	0.448	0.000
A 6	DCA	27.97	0.000	0.000
A 6	CP	19.99	0.000	0.000
A 6	EDB	28.75	6.519	0.000
A 6	TCA	115.66	0.000	0.000
A 6	BCAN	71.71	0.000	0.000
A 6	DBAN	62.47	0.817	0.000
A 6	DBCP	169.60	0.293	0.000
A 6	CBA	16.91	10.206	0.000
A 7	TCAN	57.36	0.000	0.000
A 7	TCE	13.90	5.874	0.000
A 7	DCA	27.97	0.000	0.000
A 7	CP	19.99	0.000	0.000
A 7	EDB	28.94	0.000	0.000
A 7	TCA	115.66	0.000	0.000
A 7	BCAN	71.71	0.000	0.000

APPENDIX B (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
A 7	DBAN	62.47	0.644	0.000
A 7	DBCP	169.59	0.419	0.000
A 7	CBA	16.88	19.520	0.000
B 1	TCAN	57.36	0.000	0.000
B 1	TCE	13.90	5.283	26.416
B 1	DCA	27.86	4.331	21.656
B 1	CP	19.99	0.000	0.000
B 1	EDB	28.52	14.856	74.281
B 1	TCA	115.59	0.625	3.127
B 1	BCAN	71.69	0.436	2.180
B 1	DBAN	62.46	1.113	5.566
B 1	DBCP	168.72	11.088	55.441
B 1	CBA	16.84	34.638	173.188
B 2	TCAN	57.36	0.000	0.000
B 2	TCE	13.90	5.534	27.668
B 2	DCA	27.87	4.161	20.806
B 2	CP	19.99	0.000	0.000
B 2	EDB	28.50	15.521	77.607
B 2	TCA	115.61	0.425	2.126
B 2	BCAN	71.69	0.491	2.455
B 2	DBAN	62.46	1.168	5.839
B 2	DBCP	168.44	14.514	72.572
B 2	CBA	16.84	34.007	170.036
B 3	TCAN	57.36	0.000	0.000
B 3	TCE	13.91	5.157	25.787
B 3	DCA	27.85	4.778	23.892
B 3	CP	19.99	0.000	0.000
B 3	EDB	28.30	22.763	113.816
B 3	TCA	115.54	1.006	5.032
B 3	BCAN	71.68	0.666	3.332
B 3	DBAN	62.46	1.143	5.715
B 3	DBCP	168.46	14.307	71.534
B 3	CBA	16.81	44.595	222.975
B 4	TCAN	57.36	0.000	0.000
B 4	TCE	13.92	3.934	19.669
B 4	DCA	27.90	2.858	14.288
B 4	CP	19.99	0.000	0.000
B 4	EDB	28.74	6.859	34.294
B 4	TCA	115.63	0.222	1.108
B 4	BCAN	71.69	0.361	1.805
B 4	DBAN	62.46	0.918	4.590
B 4	DBCP	168.95	8.278	41.389
B 4	CBA	16.87	23.121	115.606
B 5	TCAN	57.36	0.000	0.000
B 5	TCE	13.86	8.523	42.617
B 5	DCA	27.86	4.409	22.046
B 5	CP	19.99	0.000	0.000
B 5	EDB	28.73	7.484	37.421
B 5	TCA	115.54	1.029	5.146
B 5	BCAN	71.66	0.995	4.976
B 5	DBAN	62.46	1.119	5.597
B 5	DBCP	168.42	14.853	74.263
B 5	CBA	16.80	48.342	241.710
B 6	TCAN	57.36	0.000	0.000
B 6	TCE	13.88	7.307	36.537
B 6	DCA	27.88	3.523	17.615
B 6	CP	19.99	0.000	0.000
B 6	EDB	28.60	11.956	59.779
B 6	TCA	115.56	0.857	4.287
B 6	BCAN	71.66	0.899	4.497
B 6	DBAN	62.46	1.054	5.269
B 6	DBCP	168.49	13.940	69.700
B 6	CBA	16.81	43.832	219.162
B 7	TCAN	57.36	0.000	0.000
B 7	TCE	13.94	2.658	13.288
B 7	DCA	27.90	2.678	13.391
B 7	CP	19.99	0.000	0.000

APPENDIX B (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
B 7	EDB	28.87	2.344	11.722
B 7	TCA	115.66	0.000	0.000
B 7	BCAN	71.67	0.740	3.701
B 7	DBAN	62.46	1.061	5.305
B 7	DBCP	168.63	12.266	61.328
B 7	CBA	16.82	42.374	211.871
C 1	TCAN	57.35	0.513	1.284
C 1	TCE	13.90	5.738	14.344
C 1	DCA	27.90	2.710	6.775
C 1	CP	19.99	2.056	5.141
C 1	EDB	28.86	2.624	6.561
C 1	TCA	115.51	1.266	3.164
C 1	BCAN	71.68	0.655	1.637
C 1	DBAN	62.46	1.090	2.726
C 1	DBCP	167.59	25.166	62.915
C 1	CBA	16.74	68.604	171.511
C 2	TCAN	57.36	0.000	0.000
C 2	TCE	13.91	4.965	12.414
C 2	DCA	27.88	3.693	9.232
C 2	CP	19.99	2.890	7.226
C 2	EDB	28.85	3.072	7.681
C 2	TCA	115.56	0.812	2.029
C 2	BCAN	71.68	0.591	1.478
C 2	DBAN	62.46	0.875	2.187
C 2	DBCP	167.75	23.195	57.989
C 2	CBA	16.77	61.075	152.687
C 3	TCAN	57.36	0.000	0.000
C 3	TCE	13.83	10.968	27.421
C 3	DCA	27.87	4.079	10.197
C 3	CP	19.99	3.661	9.152
C 3	EDB	28.85	3.273	8.182
C 3	TCA	115.57	0.716	1.791
C 3	BCAN	71.68	0.587	1.468
C 3	DBAN	62.45	1.238	3.094
C 3	DBCP	167.93	20.963	52.406
C 3	CBA	16.77	60.681	151.702
C 4	TCAN	57.36	0.000	0.000
C 4	TCE	13.91	5.168	12.919
C 4	DCA	27.90	2.813	7.033
C 4	CP	19.99	1.774	4.436
C 4	EDB	28.87	2.449	6.122
C 4	TCA	115.61	0.390	0.974
C 4	BCAN	71.68	0.582	1.456
C 4	DBAN	62.46	0.916	2.290
C 4	DBCP	167.69	23.985	59.963
C 4	CBA	16.76	64.573	161.431
C 5	TCAN	57.36	0.000	0.000
C 5	TCE	13.88	7.557	18.892
C 5	DCA	27.89	3.446	8.614
C 5	CP	19.99	2.606	6.515
C 5	EDB	28.85	3.097	7.742
C 5	TCA	115.60	0.499	1.247
C 5	BCAN	71.68	0.623	1.558
C 5	DBAN	62.45	1.274	3.184
C 5	DBCP	167.91	21.172	52.931
C 5	CBA	16.78	56.718	141.795
C 6	TCAN	57.36	0.000	0.000
C 6	TCE	13.84	10.028	25.070
C 6	DCA	27.88	3.643	9.108
C 6	CP	19.99	3.853	9.633
C 6	EDB	28.84	3.547	8.868
C 6	TCA	115.64	0.128	0.321
C 6	BCAN	71.68	0.630	1.575
C 6	DBAN	62.46	1.081	2.703
C 6	DBCP	168.23	17.130	42.824
C 6	CBA	16.81	46.048	115.120
C 7	TCAN	57.36	0.000	0.000

APPENDIX B (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
C 7	TCE	13.92	4.296	10.741
C 7	DCA	27.89	3.148	7.869
C 7	CP	19.99	2.200	5.499
C 7	EDB	28.87	2.559	6.398
C 7	TCA	115.62	0.342	0.855
C 7	BCAN	71.68	0.540	1.351
C 7	DBAN	62.45	1.298	3.244
C 7	DBCP	167.90	21.348	53.370
C 7	CBA	16.77	60.149	150.373
D 1	TCAN	57.15	8.924	4.462
D 1	TCE	13.05	77.831	38.915
D 1	DCA	27.63	14.094	7.047
D 1	CP	20.10	105.096	52.548
D 1	EDB	28.83	3.765	1.882
D 1	TCA	115.38	2.365	1.182
D 1	BCAN	71.65	1.147	0.573
D 1	DBAN	62.45	1.319	0.660
D 1	DBCP	154.10	209.468	104.734
D 1	CBA	15.91	378.034	189.017
D 2	TCAN	57.32	1.519	0.760
D 2	TCE	13.18	66.543	33.272
D 2	DCA	27.73	9.896	4.948
D 2	CP	20.08	88.263	44.132
D 2	EDB	28.83	3.672	1.836
D 2	TCA	115.48	1.532	0.766
D 2	BCAN	71.66	1.004	0.502
D 2	DBAN	62.46	1.213	0.607
D 2	DBCP	155.98	181.833	90.916
D 2	CBA	16.02	337.295	168.648
D 3	TCAN	57.30	2.372	1.186
D 3	TCE	13.06	77.130	38.565
D 3	DCA	27.72	10.059	5.030
D 3	CP	20.07	80.009	40.004
D 3	EDB	28.83	3.756	1.878
D 3	TCA	115.54	0.963	0.482
D 3	BCAN	71.66	0.946	0.473
D 3	DBAN	62.46	1.096	0.548
D 3	DBCP	157.52	159.787	79.893
D 3	CBA	16.12	299.545	149.772
D 4	TCAN	57.36	0.000	0.000
D 4	TCE	13.03	79.464	39.732
D 4	DCA	27.72	10.194	5.097
D 4	CP	20.09	95.269	47.635
D 4	EDB	28.84	3.386	1.693
D 4	TCA	115.63	0.257	0.129
D 4	BCAN	71.67	0.759	0.379
D 4	DBAN	62.46	0.959	0.480
D 4	DBCP	155.63	186.926	93.463
D 4	CBA	15.99	349.560	174.780
D 5	TCAN	57.36	0.000	0.000
D 5	TCE	13.75	17.445	8.723
D 5	DCA	27.80	6.981	3.491
D 5	CP	20.03	40.848	20.424
D 5	EDB	28.87	2.398	1.199
D 5	TCA	115.64	0.189	0.095
D 5	BCAN	71.68	0.691	0.345
D 5	DBAN	62.46	0.922	0.461
D 5	DBCP	157.75	156.431	78.215
D 5	CBA	16.13	293.038	146.519
D 6	TCAN	57.36	0.000	0.000
D 6	TCE	13.82	12.367	6.183
D 6	DCA	27.78	7.788	3.894
D 6	CP	20.02	32.710	16.355
D 6	EDB	28.87	2.355	1.177
D 6	TCA	115.64	0.169	0.085
D 6	BCAN	71.67	0.737	0.369
D 6	DBAN	62.46	0.990	0.495

sample no	DBPName	RF	Conc	Percent rec
D 6	DBCP	156.14	179.492	89.746
D 6	CBA	16.02	336.538	168.269
D 7	TCAN	57.36	0.000	0.000
D 7	TCE	13.87	7.973	3.987
D 7	DCA	27.80	6.744	3.372
D 7	CP	20.00	11.842	5.921
D 7	EDB	28.90	1.336	0.668
D 7	TCA	115.65	0.113	0.057
D 7	BCAN	71.68	0.603	0.302
D 7	DBAN	62.47	0.861	0.431
D 7	DBCP	155.55	188.136	94.068
D 7	CBA	15.96	359.416	179.708
E 1	TCAN	57.24	5.091	1.273
E 1	TCE	13.65	25.979	6.495
E 1	DCA	27.65	12.923	3.231
E 1	CP	20.06	68.266	17.066
E 1	EDB	28.87	2.474	0.619
E 1	TCA	115.30	3.051	0.763
E 1	BCAN	71.66	0.905	0.226
E 1	DBAN	62.46	1.040	0.260
E 1	DBCP	145.00	353.076	88.269
E 1	CBA	15.44	570.287	142.572
E 2	TCAN	57.29	3.155	0.789
E 2	TCE	13.73	19.625	4.906
E 2	DCA	27.65	13.078	3.270
E 2	CP	20.06	72.793	18.198
E 2	EDB	28.88	2.104	0.526
E 2	TCA	115.42	1.987	0.497
E 2	BCAN	71.67	0.771	0.193
E 2	DBAN	62.46	0.891	0.223
E 2	DBCP	143.70	375.237	93.809
E 2	CBA	15.36	603.421	150.855
E 3	TCAN	57.33	1.287	0.322
E 3	TCE	13.73	19.522	4.881
E 3	DCA	27.67	12.106	3.027
E 3	CP	20.05	59.648	14.912
E 3	EDB	28.89	1.737	0.434
E 3	TCA	115.50	1.347	0.337
E 3	BCAN	71.68	0.653	0.163
E 3	DBAN	62.47	0.758	0.190
E 3	DBCP	144.35	364.100	91.025
E 3	CBA	15.39	588.662	147.166
E 4	TCAN	57.29	2.921	0.730
E 4	TCE	13.64	26.637	6.659
E 4	DCA	27.66	12.677	3.169
E 4	CP	20.06	73.314	18.329
E 4	EDB	28.89	1.846	0.461
E 4	TCA	115.54	1.015	0.254
E 4	BCAN	71.68	0.654	0.164
E 4	DBAN	62.47	0.777	0.194
E 4	DBCP	143.55	377.688	94.422
E 4	CBA	15.37	600.219	150.055
E 5	TCAN	57.35	0.388	0.097
E 5	TCE	13.71	20.915	5.229
E 5	DCA	27.67	12.335	3.084
E 5	CP	20.06	73.309	18.327
E 5	EDB	28.89	1.819	0.455
E 5	TCA	115.57	0.752	0.188
E 5	BCAN	71.68	0.628	0.157
E 5	DBAN	62.47	0.744	0.186
E 5	DBCP	147.35	314.399	78.600
E 5	CBA	15.59	505.296	126.324
E 6	TCAN	57.35	0.241	0.060
E 6	TCE	13.70	21.578	5.394
E 6	DCA	27.69	11.345	2.836
E 6	CP	20.06	69.017	17.254
E 6	EDB	28.89	1.871	0.468

sample no	DBPName	RF	Conc	Percent rec
E 6	TCA	115.59	0.606	0.151
E 6	BCAN	71.68	0.647	0.162
E 6	DBAN	62.47	0.807	0.202
E 6	DBCP	149.11	286.063	71.516
E 6	CBA	15.67	474.170	118.542
E 7	TCAN	57.36	0.000	0.000
E 7	TCE	13.71	20.925	5.231
E 7	DCA	27.68	11.769	2.942
E 7	CP	20.05	64.348	16.087
E 7	EDB	28.88	1.966	0.491
E 7	TCA	115.60	0.484	0.121
E 7	BCAN	71.68	0.673	0.168
E 7	DBAN	62.47	0.818	0.204
E 7	DBCP	147.62	310.012	77.503
E 7	CBA	15.58	512.628	128.157
F 1	TCAN	57.36	0.000	0.000
F 1	TCE	13.95	1.585	0.000
F 1	DCA	27.91	2.581	0.000
F 1	CP	19.99	0.000	0.000
F 1	EDB	28.64	10.627	0.000
F 1	TCA	115.65	0.123	0.000
F 1	BCAN	71.70	0.173	0.000
F 1	DBAN	62.47	0.662	0.000
F 1	DBCP	169.25	4.605	0.000
F 1	CBA	16.88	20.105	0.000
F 2	TCAN	57.36	0.000	0.000
F 2	TCE	13.89	6.468	0.000
F 2	DCA	27.97	0.000	0.000
F 2	CP	19.99	0.000	0.000
F 2	EDB	28.25	24.438	0.000
F 2	TCA	115.66	0.000	0.000
F 2	BCAN	71.71	0.000	0.000
F 2	DBAN	62.46	1.150	0.000
F 2	DBCP	169.52	1.276	0.000
F 2	CBA	16.94	0.000	0.000
F 3	TCAN	57.36	0.000	0.000
F 3	TCE	13.88	6.828	0.000
F 3	DCA	27.97	0.000	0.000
F 3	CP	19.99	0.000	0.000
F 3	EDB	28.44	17.849	0.000
F 3	TCA	115.36	2.503	0.000
F 3	BCAN	71.71	0.000	0.000
F 3	DBAN	62.47	0.701	0.000
F 3	DBCP	169.51	1.371	0.000
F 3	CBA	16.94	0.000	0.000
F 4	TCAN	57.36	0.000	0.000
F 4	TCE	13.95	1.423	0.000
F 4	DCA	27.97	0.100	0.000
F 4	CP	19.99	0.000	0.000
F 4	EDB	28.94	0.000	0.000
F 4	TCA	115.53	1.066	0.000
F 4	BCAN	71.71	0.000	0.000
F 4	DBAN	62.46	0.996	0.000
F 4	DBCP	169.55	0.880	0.000
F 4	CBA	16.94	0.000	0.000
F 5	TCAN	57.36	0.000	0.000
F 5	TCE	13.96	0.934	0.000
F 5	DCA	27.97	0.000	0.000
F 5	CP	19.99	0.000	0.000
F 5	EDB	28.40	19.074	0.000
F 5	TCA	115.51	1.263	0.000
F 5	BCAN	71.71	0.000	0.000
F 5	DBAN	62.46	0.893	0.000
F 5	DBCP	169.58	0.536	0.000
F 5	CBA	16.94	0.000	0.000
F 6	TCAN	57.36	0.000	0.000
F 6	TCE	13.93	2.972	0.000

APPENDIX B (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
F 6	DCA	27.92	1.906	0.000
F 6	CP	19.99	0.000	0.000
F 6	EDB	28.64	10.600	0.000
F 6	TCA	115.65	0.071	0.000
F 6	BCAN	71.71	0.000	0.000
F 6	DBAN	62.47	0.659	0.000
F 6	DBCP	169.56	0.677	0.000
F 6	CBA	16.94	0.000	0.000
F 7	TCAN	57.36	0.000	0.000
F 7	TCE	13.93	2.952	0.000
F 7	DCA	27.97	0.000	0.000
F 7	CP	19.99	0.000	0.000
F 7	EDB	28.50	15.449	0.000
F 7	TCA	115.63	0.274	0.000
F 7	BCAN	71.71	0.000	0.000
F 7	DBAN	62.47	0.595	0.000
F 7	DBCP	169.55	0.841	0.000
F 7	CBA	16.94	0.000	0.000
G 1	TCAN	57.29	2.790	0.000
G 1	TCE	13.86	8.872	0.000
G 1	DCA	27.97	0.000	0.000
G 1	CP	19.99	0.000	0.000
G 1	EDB	28.94	0.000	0.000
G 1	TCA	114.01	13.983	0.000
G 1	BCAN	71.63	1.541	0.000
G 1	DBAN	62.39	3.458	0.000
G 1	DBCP	169.62	0.000	0.000
G 1	CBA	16.94	0.000	0.000
G 2	TCAN	57.35	0.484	0.000
G 2	TCE	13.95	1.836	0.000
G 2	DCA	27.97	0.000	0.000
G 2	CP	19.99	0.000	0.000
G 2	EDB	28.94	0.000	0.000
G 2	TCA	114.31	11.360	0.000
G 2	BCAN	71.67	0.706	0.000
G 2	DBAN	62.45	1.300	0.000
G 2	DBCP	169.62	0.000	0.000
G 2	CBA	16.94	0.000	0.000
G 3	TCAN	57.35	0.483	0.000
G 3	TCE	13.94	2.550	0.000
G 3	DCA	27.97	0.000	0.000
G 3	CP	19.99	0.000	0.000
G 3	EDB	28.94	0.000	0.000
G 3	TCA	114.03	13.754	0.000
G 3	BCAN	71.60	2.229	0.000
G 3	DBAN	62.44	1.647	0.000
G 3	DBCP	169.62	0.000	0.000
G 3	CBA	16.94	0.000	0.000
G 4	TCAN	57.35	0.443	0.000
G 4	TCE	13.93	3.120	0.000
G 4	DCA	27.97	0.000	0.000
G 4	CP	19.99	0.000	0.000
G 4	EDB	28.94	0.000	0.000
G 4	TCA	114.31	11.437	0.000
G 4	BCAN	71.62	1.833	0.000
G 4	DBAN	62.45	1.465	0.000
G 4	DBCP	169.62	0.000	0.000
G 4	CBA	16.94	0.000	0.000
G 5	TCAN	57.30	2.754	0.000
G 5	TCE	13.86	8.632	0.000
G 5	DCA	27.97	0.000	0.000
G 5	CP	19.99	0.000	0.000
G 5	EDB	28.94	0.000	0.000
G 5	TCA	114.12	13.040	0.000
G 5	BCAN	71.60	2.256	0.000
G 5	DBAN	62.47	0.706	0.000
G 5	DBCP	169.62	0.000	0.000

APPENDIX B (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
G 5	CBA	16.94	0.000	0.000
G 6	TCAN	57.29	3.035	0.000
G 6	TCE	13.87	8.132	0.000
G 6	DCA	27.97	0.000	0.000
G 6	CP	19.99	0.000	0.000
G 6	EDB	28.94	0.000	0.000
G 6	TCA	114.34	11.153	0.000
G 6	BCAN	71.61	1.949	0.000
G 6	DBAN	62.44	1.691	0.000
G 6	DBCP	169.62	0.000	0.000
G 6	CBA	16.94	0.000	0.000
G 7	TCAN	57.35	0.443	0.000
G 7	TCE	13.92	4.370	0.000
G 7	DCA	27.97	0.000	0.000
G 7	CP	19.99	0.000	0.000
G 7	EDB	28.94	0.000	0.000
G 7	TCA	114.55	9.369	0.000
G 7	BCAN	71.63	1.517	0.000
G 7	DBAN	62.44	1.566	0.000
G 7	DBCP	169.62	0.000	0.000
G 7	CBA	16.94	0.000	0.000
H 1	TCAN	57.33	1.082	0.000
H 1	TCE	13.92	3.959	0.000
H 1	DCA	27.92	2.113	0.000
H 1	CP	19.99	3.235	0.000
H 1	EDB	28.94	0.000	0.000
H 1	TCA	115.12	11.324	0.000
H 1	BCAN	71.68	1.660	0.000
H 1	DBAN	62.46	2.476	0.000
H 1	DBCP	169.49	1.602	0.000
H 1	CBA	16.94	0.000	0.000
H 2	TCAN	57.31	2.218	0.000
H 2	TCE	13.93	3.186	0.000
H 2	DCA	27.94	1.057	0.000
H 2	CP	19.99	3.412	0.000
H 2	EDB	28.94	0.000	0.000
H 2	TCA	115.04	12.913	0.000
H 2	BCAN	71.69	1.040	0.000
H 2	DBAN	62.48	0.887	0.000
H 2	DBCP	169.62	0.000	0.000
H 2	CBA	16.94	0.000	0.000
H 3	TCAN	57.31	2.073	0.000
H 3	TCE	13.92	3.898	0.000
H 3	DCA	27.97	0.000	0.000
H 3	CP	19.99	2.246	0.000
H 3	EDB	28.94	0.000	0.000
H 3	TCA	115.23	9.074	0.000
H 3	BCAN	71.69	0.988	0.000
H 3	DBAN	62.48	0.826	0.000
H 3	DBCP	169.62	0.000	0.000
H 3	CBA	16.94	0.000	0.000
H 4	TCAN	57.35	0.458	0.000
H 4	TCE	13.91	4.463	0.000
H 4	DCA	27.97	0.000	0.000
H 4	CP	19.99	2.888	0.000
H 4	EDB	28.94	0.000	0.000
H 4	TCA	115.08	12.245	0.000
H 4	BCAN	71.68	1.268	0.000
H 4	DBAN	62.48	0.760	0.000
H 4	DBCP	169.62	0.000	0.000
H 4	CBA	16.94	0.000	0.000
H 5	TCAN	57.30	2.367	0.000
H 5	TCE	13.93	3.334	0.000
H 5	DCA	27.97	0.000	0.000
H 5	CP	19.99	3.246	0.000
H 5	EDB	28.94	0.000	0.000
H 5	TCA	114.93	15.356	0.000

APPENDIX B (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
H 5	BCAN	71.69	1.237	0.000
H 5	DBAN	62.48	0.734	0.000
H 5	DBCP	169.62	0.000	0.000
H 5	CBA	16.94	0.000	0.000
I 1	TCAN	57.24	5.292	0.000
I 1	TCE	13.48	40.256	0.000
I 1	DCA	27.93	1.817	0.000
I 1	CP	20.00	6.742	0.000
I 1	EDB	28.91	2.881	0.000
I 1	TCA	112.56	66.409	0.000
I 1	BCAN	71.65	2.978	0.000
I 1	DBAN	62.44	4.605	0.000
I 1	DBCP	169.00	7.677	0.000
I 1	CBA	16.87	25.454	0.000
I 2	TCAN	57.28	3.450	0.000
I 2	TCE	13.50	38.350	0.000
I 2	DCA	27.92	1.868	0.000
I 2	CP	20.00	7.413	0.000
I 2	EDB	28.90	3.137	0.000
I 2	TCA	112.32	71.829	0.000
I 2	BCAN	71.64	3.274	0.000
I 2	DBAN	62.44	4.753	0.000
I 2	DBCP	168.95	8.194	0.000
I 2	CBA	16.87	25.279	0.000
I 3	TCAN	57.29	3.162	0.000
I 3	TCE	13.58	31.677	0.000
I 3	DCA	27.84	5.280	0.000
I 3	CP	20.00	7.834	0.000
I 3	EDB	28.90	3.164	0.000
I 3	TCA	112.11	76.307	0.000
I 3	BCAN	71.64	3.658	0.000
I 3	DBAN	62.48	0.745	0.000
I 3	DBCP	168.89	9.022	0.000
I 3	CBA	16.86	28.021	0.000
I 4	TCAN	57.23	5.684	0.000
I 4	TCE	13.43	44.414	0.000
I 4	DCA	27.93	1.625	0.000
I 4	CP	20.00	8.137	0.000
I 4	EDB	28.90	3.062	0.000
I 4	TCA	112.09	76.782	0.000
I 4	BCAN	71.63	4.184	0.000
I 4	DBAN	62.42	5.725	0.000
I 4	DBCP	168.84	9.614	0.000
I 4	CBA	16.86	28.280	0.000
I 5	TCAN	57.26	4.048	0.000
I 5	TCE	13.79	14.630	0.000
I 5	DCA	27.93	1.548	0.000
I 5	CP	19.99	1.644	0.000
I 5	EDB	28.92	1.853	0.000
I 5	TCA	113.51	45.648	0.000
I 5	BCAN	71.67	2.211	0.000
I 5	DBAN	62.44	4.229	0.000
I 5	DBCP	169.09	6.514	0.000
I 5	CBA	16.87	22.889	0.000
J 1	TCAN	57.28	3.451	0.000
J 1	TCE	13.73	19.716	0.000
J 1	DCA	27.85	4.854	0.000
J 1	CP	20.00	7.511	0.000
J 1	EDB	28.87	6.348	0.000
J 1	TCA	112.15	75.431	0.000
J 1	BCAN	71.58	6.310	0.000
J 1	DBAN	62.40	7.833	0.000
J 1	DBCP	167.98	20.351	0.000
J 1	CBA	16.85	32.927	0.000
J 2	TCAN	57.33	1.348	0.000
J 2	TCE	13.73	19.604	0.000
J 2	DCA	27.92	2.111	0.000

APPENDIX B (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
J 2	CP	20.00	6.584	0.000
J 2	EDB	28.88	4.928	0.000
J 2	TCA	112.58	66.095	0.000
J 2	BCAN	71.61	4.790	0.000
J 2	DBAN	62.43	5.447	0.000
J 2	DBCP	168.32	16.062	0.000
J 2	CBA	16.87	25.517	0.000
J 3	TCAN	57.35	0.573	0.000
J 3	TCE	13.90	5.907	0.000
J 3	DCA	27.92	2.211	0.000
J 3	CP	19.99	3.113	0.000
J 3	EDB	28.90	3.663	0.000
J 3	TCA	113.16	53.336	0.000
J 3	BCAN	71.63	3.764	0.000
J 3	DBAN	62.44	4.488	0.000
J 3	DBCP	169.07	6.818	0.000
J 3	CBA	16.90	14.948	0.000
J 4	TCAN	57.28	3.505	0.000
J 4	TCE	13.69	22.900	0.000
J 4	DCA	27.92	1.940	0.000
J 4	CP	19.99	4.661	0.000
J 4	EDB	28.89	4.459	0.000
J 4	TCA	112.85	60.129	0.000
J 4	BCAN	71.63	3.975	0.000
J 4	DBAN	62.43	5.242	0.000
J 4	DBCP	168.44	14.626	0.000
J 4	CBA	16.86	26.466	0.000
J 5	TCAN	57.29	2.981	0.000
J 5	TCE	13.76	16.723	0.000
J 5	DCA	27.93	1.557	0.000
J 5	CP	20.00	8.521	0.000
J 5	EDB	28.90	3.884	0.000
J 5	TCA	112.61	65.332	0.000
J 5	BCAN	71.62	4.644	0.000
J 5	DBAN	62.42	6.407	0.000
J 5	DBCP	168.43	14.711	0.000
J 5	CBA	16.87	25.338	0.000
K 1	TCAN	57.17	7.969	0.000
K 1	TCE	13.51	38.055	0.000
K 1	DCA	27.84	5.314	0.000
K 1	CP	20.00	14.395	0.000
K 1	EDB	28.84	8.838	0.000
K 1	TCA	110.95	102.476	0.000
K 1	BCAN	71.56	7.394	0.000
K 1	DBAN	62.37	10.582	0.000
K 1	DBCP	166.91	33.827	0.000
K 1	CBA	16.74	71.042	0.000
K 2	TCAN	57.14	9.196	0.000
K 2	TCE	13.53	35.826	0.000
K 2	DCA	27.83	5.720	0.000
K 2	CP	20.00	14.358	0.000
K 2	EDB	28.84	8.559	0.000
K 2	TCA	110.76	106.730	0.000
K 2	BCAN	71.55	8.183	0.000
K 2	DBAN	62.37	10.649	0.000
K 2	DBCP	166.88	34.109	0.000
K 2	CBA	16.73	72.899	0.000
K 3	TCAN	57.14	9.371	0.000
K 3	TCE	13.47	40.787	0.000
K 3	DCA	27.84	5.174	0.000
K 3	CP	20.00	12.763	0.000
K 3	EDB	28.84	8.417	0.000
K 3	TCA	111.04	100.315	0.000
K 3	BCAN	71.56	7.204	0.000
K 3	DBAN	62.38	9.729	0.000
K 3	DBCP	167.00	32.628	0.000
K 3	CBA	16.75	67.624	0.000

APPENDIX B (CON'T.)

sample no	DBPName	RF	Conc	Percent rec
K 4	TCAN	57.17	8.010	0.000
K 4	TCE	13.50	38.642	0.000
K 4	DCA	27.84	5.331	0.000
K 4	CP	20.00	14.298	0.000
K 4	EDB	28.83	9.321	0.000
K 4	TCA	110.76	106.651	0.000
K 4	BCAN	71.54	8.583	0.000
K 4	DBAN	62.36	11.522	0.000
K 4	DBCP	166.48	39.248	0.000
K 4	CBA	16.74	69.891	0.000
K 5	TCAN	57.11	10.639	0.000
K 5	TCE	13.41	46.355	0.000
K 5	DCA	27.83	5.541	0.000
K 5	CP	20.00	14.722	0.000
K 5	EDB	28.83	9.247	0.000
K 5	TCA	110.74	107.220	0.000
K 5	BCAN	71.54	8.379	0.000
K 5	DBAN	62.36	11.205	0.000
K 5	DBCP	166.78	35.375	0.000
K 5	CBA	16.72	75.654	0.000

VITA

Diane Lynne Sexton (nee Southall) was born on April 22, 1968 in Richmond, VA. She graduated Summa Cum Laude from Prince Edward Academy in 1986, and she received a B.S. degree in Biochemistry from Virginia Tech in 1990. While completing her undergraduate degree, she was employed by the Water Quality Lab of the Agricultural Engineering Department, and she was one of the recipients of the Outstanding Extension Team Award from Epsilon Sigma Phi for her contribution to water quality education for rural households. After obtaining a M.S. degree in Environmental Chemistry from Virginia Tech, Mrs. Sexton hopes to obtain a position in the environmental chemistry field in the Wilmington, DE area, where she is now residing.

Diane L. Sexton