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Potential Use of Ultrasound in Chemical Monitoring

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POTENTIAL USE OF ULTRASOUND
IN CHEMICAL MONITORING

by

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NOTICE

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), partially funded and managed the extramural research described here. It has been peer reviewed by the Agency and approved as an EPA publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

EPA has been examining the potential of combining sonication with other technologies for monitoring specific classes of organic pollutants in water. The research specifically addressed using ultrasonic processors to decompose organochlorine compounds into ions which could be detected using a specific ion electrode as a screening method for organochlorine pollutants. Changes in chloride, conductivity, and pH were measured using commercially available equipment before and after sonication in order to detect the presence of the organochlorine pollutant. The results obtained are very promising. Chloride ion could be detected in aqueous solutions of low ppm concentrations of carbon tetrachloride, chloroform, and trichloroethylene after one minute sonication. The increases of chloride ion were accompanied by increases in conductivity and decreases of pH. Ion chromatography of solutions before and after sonication showed that formate ion was also formed. Aromatic and polyaromatic chloro compounds represented by chlorobenzene and polychlorobiphenyls, respectively, did not form chloride ion as readily as did carbon tetrachloride, chloroform, and trichloroethylene. The potential of combining sonication with commercially available measurement technologies for monitoring specific pollutants in water is judged to be high. The results achieved with the organochlorine compounds tested serve as proof-of-principle and form a base of information which can be used to develop ultrasound monitoring methods for these compounds.

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CHAPTER 1

INTRODUCTION

The U.S. Environmental Protection Agency has been examining the potential of combining sonication with other technologies for monitoring specific classes of organic pollutants in water. The research described in this report relates to a search for new concepts for field screening methods applicable to hazardous waste sites with emphasis on *in situ* groundwater monitoring.

Field screening involves the use of rapid, low-cost test methods to determine whether a parameter of interest is present or absent, above or below a predetermined threshold at a given site, or at a concentration within a predetermined range of interest (1). Screening methods can be used in the field to identify the nature and extent of contamination at individual sites. Although they may not be as accurate or precise as laboratory methods, some are very accurate and precise as well as sensitive. Field screening methods:

- allow rapid identification of contaminants present and their relative levels;
- allow priorities to be set at a site and identification to be made of hot spots;
- help to either quickly establish a more comprehensive monitoring program for a given site, or prioritize the site relative to other sites;
- have the potential to accelerate site clean-up and to reduce cost; and
- are needed to support on-site monitoring and characterization activities.

The technologies developed as field screening methods are relevant to the monitoring and measurements needs of many U.S. Environmental Protection Agency (EPA) programs which may use field screening data to support a variety of go/no-go environmental management decisions. The overall challenge of field screening involves dealing with numerous compounds within many classes (organic, inorganic, biomarker, and radionuclide), across various media, and in complex mixtures.

Desirable characteristics of field screening devices are that they be: sensitive, specific, user-friendly, real-time, able to handle a broad range of samples, rugged, small in size, lightweight, low in cost, and reliable. A proper blend of these characteristics is chosen to meet specific needs.

A few field screening methods are available now, and more are being developed. The most mature are judged to be those based on gas chromatography, x-ray fluorescence, and infrared spectroscopy. One of the clear trends is to miniaturize. Various hand-held vapor sensors can be purchased which are applicable to field screening needs. These are based on, for example, tin oxide catalytic oxidation, ion mobility spectrometry, and photoionization detection. Hand-held colorimeters are also available. A recent overview of the state of the art of field screening and analysis technologies was performed by Koglin and Poziomek (1).

Methods which are still in various stages of development include the use of fiber optic sensors and chemical microsensors, such as piezoelectric quartz microbalances and surface acoustic wave (SAW) probes. The fiber optic technology typically involves the measurement of a chemical or biochemical reaction and is relevant to *in situ* monitoring. The use of a fiber optic system could also

1

involve measurements of spectroscopic properties of the pollutant molecules using any one of several techniques such as luminescence (including laser-induced fluorescence), UV-visible, near and mid infrared absorption, spectrochemical emission, and surface-enhanced Raman. The piezoelectric and SAW microsensors require chemical/biological reactions or molecular association effects involving the pollutant being measured. These techniques are still emerging. They have the potential for achieving sensitivities at the part-per-billion (ppb) level, and many are amenable to remote sensing and *in situ* modes. However, considerable research is still required, especially in developing sensor recognition coatings for the devices.

The need for ground-water monitoring has been discussed by Makeig (2). A comprehensive review highlighting potential wellhead protection field technologies is also available (3). This relates to protecting public water supply wells, well fields, and springs from contamination. The technologies reviewed apply to ground-water monitoring at hazardous waste sites as well. Methods are presented which may be especially useful for field screening.

The detection limits of field methods are not always as low as laboratory methods, and the accuracy of field methods is not always as reliable as laboratory methods. This is especially critical, for example, if the detection limit of the field method does not meet water quality criteria or regulatory requirements. Nevertheless, less accurate methods might be useful to screen samples prior to confirmatory laboratory analyses. The advantage is in cost savings by limiting the number of samples sent for laboratory analyses.

Groundwater contains a variety of natural constituents, with the various species and concentrations depending on factors such as the specific geochemical environment and the source of the groundwater (4). The major anions that are usually analyzed to indicate general water quality include bicarbonate, chloride (Cl^-), nitrate, and sulfate. Other general indicators of water quality include electrical conductivity, temperature, pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), oxidation reduction (redox) potential, total suspended solids (TSS), total dissolved solids (TDS), and turbidity. *The idea being brought forward in this research is to measure several of these general parameters such as pH, electrical conductivity, and specific anion concentration before and after sonication of a water sample.* An increase of Cl^- concentration after sonication, for example, could be an indicator that the water was polluted with organochlorine compounds. Commercially available Cl^- electrodes have a sensitivity limit at the low parts-per-million (ppm) level. This is the sensitivity to be expected, therefore, for organochlorine compound detection by combining sonication with ion selective electrode (ISE) technology.

This research complements approaches already being taken for characterizing hazardous sites. The Resource Conservation and Recovery Act (RCRA) interim status regulations, for example, identified four indicator parameters for use in monitoring ground-water contamination in the detection phase: specific conductance, pH, total organic carbon, and total organic halides (5). Organic halide monitoring, however, is difficult and not readily amenable to *in situ* use. *In situ* ground-water monitoring has been identified as one of the major technology needs in field screening (1). The present research combines sonication with commercially available probes and offers a simple approach toward field screening and monitoring.

Success in this monitoring approach requires destruction of neutral organochlorine pollutants and formation of Cl^-. Formation of H^+ and other ions may be utilized or exploited as well. A later section describes the known sonochemistry of water and organochlorine compounds.

The classical use of sonication with environmental samples has been to assist in the extraction of semivolatile organic contaminants from soil (6). Interest has also emerged recently in the possibility of using sonication to remediate groundwater (7). Sulfate, nitrite, nitrate, p-nitrophenol, phosphate, and oxalate were identified as products of parathion sonolysis (7). *No reports have been published on use of ultrasound in monitoring.*

CHAPTER 2

OBJECTIVE

The objective of this study was to examine the potential of combining sonication with existing measurement technologies for monitoring specific classes of organic pollutants in water. The research specifically addressed using ultrasound processors to decompose organochlorine compounds into ions as a screening method for organochlorine pollutants in water.

The approach in using sonication is obviously applicable to other organic compounds which contain other halides, phosphorus, nitrogen, and sulfur that, when released, could be easily quantified. Anions specific to the inorganic components would be produced in sonication. Changes in anion concentrations before and after sonication would be used in monitoring for the pollutants. The selection of organochlorine compounds was made because these compounds are the most common pollutants found at hazardous waste sites. Success with compounds such as trichloroethylene (TCE), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) will serve as proof-of-principle and form a base for expanding the research to other pollutant classes.

CHAPTER 3

DESCRIPTION OF ULTRASOUND

There are two compilations which give an excellent summary of the fundamentals of ultrasound (8,9).

Ultrasound Definition

Ultrasound is defined as any sound which is of frequency beyond that to which the human ear can respond, i.e., above 16 KHz. In the terms of frequency ranges, and physical as well as chemical changes caused by ultrasound, there are two categories:

- high frequency or diagnostic ultrasound (2-10 MHz); such irradiation causes temporary physical changes in the medium; and
- low frequency or power ultrasound (20-100 kHz); this affects chemical reactivity.

A whistle constructed by F. Galton (10) 100 years ago was the first device generating ultrasound. It is an example of a transducer which can change one form of energy (gas motion) into another (sound). The whistle had an adjustable resonance cavity capable of generating sounds of known frequencies. Galton used the device to determine the threshold hearing frequencies of people and animals.

Cavitation

The term cavitation was first used by Sir John Thornycraft and Sidney Barby (11) at the turn of the 19th century during their observation of propeller inefficiency in destroyers. They observed that water was "torn apart," producing tiny bubbles due to a tremendous reduction in pressure on the trailing faces of the blades. It is the energy generated on the collapse of these bubbles which is the underlying reason for the erosion damage of propellers. The same cavitation bubbles can be produced by the irradiation of a liquid with power ultrasound. The energy generated on the collapse of these bubbles is given as the underlying reason for chemical enhancements and transformations which can be achieved in sonochemistry (9).

Sound is transmitted through any liquid as waves consisting of alternating compression and rarefaction cycles. If the rarefaction wave is sufficiently powerful, it can develop a negative pressure large enough to overcome the intermolecular forces of bonds in fluids. In this situation, the molecules will be torn apart from each other to form tiny microbubbles throughout the medium. In ultrasonic cavitation, the compression cycle follows rarefaction. This can cause the microbubbles to collapse almost instantaneously with the release of a large amount of energy.

Transient cavitation bubbles are voids or vapor-filled bubbles produced by ultrasonic intensities in excess of 10 W cm^{-2}. They exist for one, or at most a few, acoustic cycles, expanding to the radius of at least twice their initial size, before collapsing violently in the compression phase. On their collapse, they may be a source of nuclei for further cavitation by disintegration into smaller

bubbles. Bubbles which oscillate in the acoustic field with a much longer lifetime give stable cavitation.

Temperature and Pressure Phenomena

The high temperatures and pressures created during transient cavitation are difficult to calculate and measure experimentally. Some models predict maximum temperature and pressure as high as 10,000 K and 10,000 atmospheres, respectively. More realistic estimates from increasingly sophisticated hydrodynamic models yield estimates of approximately 5,000 K and 1,000 bars with effective times of > 100 ns (8, p.130).

Equations have been developed in the early 1950's for estimating the maximum temperature and pressure developed within the bubble at the moment of collapse (9, p.11):

$$T_{max} = T_o[\frac{P_m(h-1)}{P}]$$

(1)

$$P_{max} = P[\frac{P_m(h-1)}{P}]^{\frac{h}{h-1}}$$

(2)

where:

T_{max} = the maximum temperature
P_{max} = the maximum pressure
T_o = the ambient (experimental) temperature
h = the ratio of specific heats of the gas (or gas/vapor) mixture
P = the pressure in the bubble at its maximum size and is usually assumed to be equal the vapor pressure of the liquid
P_m = liquid pressure at collapse.

Calculations using these equations suggest that for water at 25°C, the average temperatures of 5,000 K and pressures of the order of 1,000 atmospheres are generated by the collapse of cavitation bubbles due to power ultrasound.

Determination of the temperatures reached in a cavitating bubble has remained a challenging problem. Flint and Suslick (12) briefly reviewed various approaches including a laborious comparative rate analysis of the decomposition of metal carbonyls involving a substantial extrapolation of kinetic parameters (13). The same authors reported the use of sonoluminescence as more convenient and desired determination of the effective temperature of cavitation bubbles collapse. The methodology was adapted from plasma techniques based on rotational and vibrational diatomic emission spectra. Sonoluminescence spectra from silicone oil were determined and analyzed. The observed emission was compared to synthetic spectra as a function of rotational and vibrational temperatures. The effective cavitation temperature was found to be 5075 ± 156 K based on this comparison.

Regardless of the details of the theoretical and experimental studies, it is clear that cavitational collapse generates hot spots with effective temperatures of several thousand degrees.

Practical Applications of Power Ultrasound

An overview of practical applications of power ultrasound shows many uses in automotive, electronic, optical, semiconductor, biomedical, and other industries (14). The widest application in liquids is cleaning. The widest application in solids is plastic welding. Less established areas in

liquids include: soldering, cell disruption, inhalation therapy, degassing, and medical surgery. There is also some industrial use for deburring, erosion testing, extraction, emulsification, solids dispersion, fuel atomization, and crystal growth. Experimental use of ultrasound in liquids involves sterilization, filtration, drying of textiles, and metal grain refinement.

Other applications in solids include metal welding, metal forming, impact grinding, rotary abrasive machining, metal cutting, fatigue testing, trimming of composites, and dental descaling. Airborne applications include particle agglomeration, defoaming, and drying.

CHAPTER 4

SONOCHEMISTRY

The first account of the chemical effect of ultrasonic waves was published in 1927 by Richards and Loomis (15). A number of phenomena were noted including acceleration of the explosion rate of nitrogen triiodide, hydrolysis rate of methyl sulfate, and reduction rate of iodate by sulfite. Recent updates of homogeneous and heterogeneous sonochemistry were provided by Suslick (16) and Boudjouk (17). Sonochemical reaction can be categorized as:

- primary reactions involving thermal decomposition of solvent, solute or gases present in solution as a result of high temperatures and pressures attained upon bubble collapse
- secondary reactions involving radicals from primary reactions and other species.

The topics most relevant to the present research are homogeneous aqueous sonochemistry and the sonochemistry of organochlorine compounds. These are discussed in the next sections.

Water

The principal products from ultrasonic irradiation of water are H_2O_2 and H_2. Various data support the presence of hydroxyl radicals and hydrogen atoms as intermediates (8, p.138). The sonolysis of water to produce hydrogen peroxide was first reported by Smith *et al.* (18):

$$H_2O \rightarrow HO\cdot + H\cdot \rightarrow H_2O_2 + H_2 \tag{3}$$
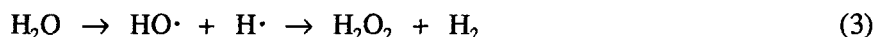
The formation of H· and HO· is attributed to the thermal dissociation of water vapor present in the cavities during the compression phase. The wide range of oxidations and reductions that occur with aqueous sonochemistry is often a consequence of secondary reactions of these high energy intermediates.

Examples of reactions that appear to be involved in water sonolysis in the presence of gases: Ar, O_2, N_2, and air (19, p.26) follow:

1)   under Ar:

$$H_2O \rightarrow H\cdot + HO\cdot \tag{4}$$
$$HO\cdot + H\cdot \rightarrow H_2O \tag{5}$$
$$2\ HO\cdot \rightleftharpoons O\cdot + H_2O \tag{6}$$
$$2\ HO\cdot \rightarrow H_2O_2 \tag{7}$$

$$2\ H\cdot \rightarrow H_2 \tag{8}$$
$$2\ O\cdot \rightarrow O_2 \tag{9}$$
$$O_2 + H\cdot \rightarrow HO_2\cdot \tag{10}$$
$$HO_2\cdot + H\cdot \rightarrow H_2O + O\cdot \tag{11}$$

2)   under O_2:

$$O_2 \rightarrow 2\ O\cdot \tag{12}$$
$$O_2 + H\cdot \rightarrow HO_2\cdot \tag{13}$$

$$2\ HO_2\cdot \rightarrow H_2O_2 + O_2 \tag{14}$$

8

3)   under N_2:

$$N_2 + HO\cdot \rightarrow N_2O + H\cdot \qquad (15)$$
$$N_2 + O\cdot \rightleftharpoons N_2O \qquad (16)$$
$$N_2 + O\cdot \rightleftharpoons NO + N\cdot \qquad (17)$$

$$N_2O + O\cdot \rightarrow N_2 + O_2 \qquad (18)$$
$$NO + H\cdot \rightarrow N\cdot + HO\cdot \qquad (19)$$
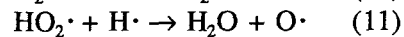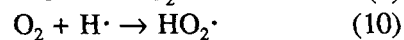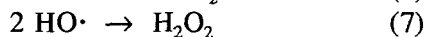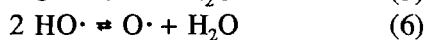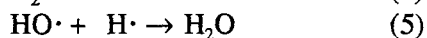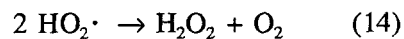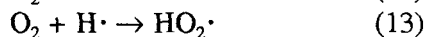
4)   under air:
        as in 2 and 3 plus $N_2 + O_2 \rightarrow 2\ NO$ $\qquad\qquad$ (20)
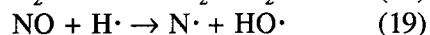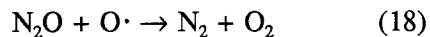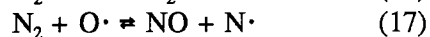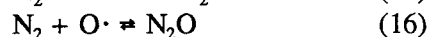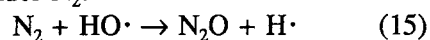
These reactions have been proposed to be analogous to combustion and shock tube chemistry. In the absence of HO· scavengers (e.g., N_2), the main product of the sonolysis of water is H_2O_2.

Organochlorine Compounds

Various organochlorine compounds have been sonicated either as aqueous solutions, as dispersions, or in nonaqueous solutions with the formation of a wide range of highly degraded products.

Early investigations of the effects of ultrasonic irradiation on aqueous solutions of organochlorine compounds and KI were made in 1929 by Smith et al. (18). At the end of one minute of sonication of an aqueous solution of CCl_4 in the presence of starch and KI, the solution became opaque a blue color formed which became much more intense than that obtained by three minutes sonication of KI and starch alone. This was cited as evidence of C-Cl bond cleavage causing the acceleration of iodine formation due to presence of Cl_2.

In the early 1950's, Weissler et al. (20) carried out more detailed studies on ultrasonic oxidation of KI by CCl_4 as an effect of C-Cl bond cleavage. It was also concluded that the main reaction was between water and dissolved carbon tetrachloride to give chlorine which then oxidized iodide:

$$CCl_4 + H_2O \rightarrow Cl_2 + CO + 2\ HCl \qquad (21)$$

$$3\ I^- + Cl_2 \rightarrow I_3^- + 2\ Cl^- \qquad (22)$$
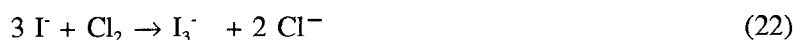
The oxidation of KI solution proceeded only about one-fifteenth as rapidly in the absence of CCl_4 as in its presence.

A number of investigators have studied the sonochemistry of organochlorine compounds. Examples of the principal products found in aqueous and nonaqueous solutions are given in Tables 1 and 2, respectively.

The sonication of aqueous solutions of organochlorine compounds leads to different products. However, in each of the reported studies (Table 1), the common product is HCl. Sonication of organochlorine compounds, either neat or in nonaqueous solution, should be expected to yield HCl as well. This would not be true for compounds such as CCl_4, in which no hydrogen is available (Table 2).

Cheung and coworkers (23) reported preliminary results on the use of ultrasound to destroy organochlorine compounds at the 100-1000 ppmv range in aqueous solution. Quantitative data with 120 ppm CH_2Cl_2 in water yielded a first-order rate constant of $3.93 \times 10^{-2} \pm 2.7 \times 10^{-3}$ min^{-1} under the particular sonication experimental conditions. No organochlorine species (other than CH_2Cl_2) were identified using GC/MS to follow the sonochemistry. Decreases in pH were noted as the CH_2Cl_2 was destroyed. It was concluded that sonochemical destruction of organochlorine compounds appears to be a potentially powerful method of remediation, which may compete with or serve as an adjunct to other advanced oxidation processes. Personal communication established that Cheung was not considering the potential use of ultrasound in chemical monitoring (31).

Table 1.   Principal Products from Sonication of Organochlorine Compounds in Water.

Organochlorine compound	Product(s)	Reference
CCl_4	Cl_2 CO_2 HCl C_2Cl_6 HOCl	18, 19, 20, 21, 22, 23
R_2CHCl	R_2CHOH HCl	24, 25
$Cl_3CCH(OH)_2$	HCl	26
CH_2Cl_2	HCl	23
Cl_3CCH_3	HOCl HCl Cl_2 CO_2 C_2Cl_6	22, 23, 27, 28
Cl_2CCHCl (TCE)	HCl	23

Table 2.   Principal Products from Sonication of Organochlorine Compounds in Nonaqueous Solvents.

Organochlorine compound	Product(s)	Reference
$CHCl_3$	HCl CCl_4 CH_2Cl_2 Cl_3CCHCl_2 Cl_2CCCl_2 Cl_3CCCl_3 Cl_2CCHCl (TCE)	(8, p. 147; 29)
CCl_4	Cl_2 Cl_3CCCl_3	(30)

Toy and coworkers (27) have considered the use of sonolysis to decompose Cl_3CCH_3 in water at 1-10 ppm levels. The interest was in defining process conditions. It was found that as the volume of the same concentration of Cl_3CCH_3 was increased, the sonolysis digestion efficiency decreased. Solution volumes were varied from 500 to 56,775 mL. The sonolysis digestion was followed using GC analysis (for decreasing Cl_3CCH_3), and ion chromatography (for increasing Cl^-).

Petrier and coworkers (32) examined the potential applications of sonochemical treatment as a way to treat toxic wastes containing sodium pentachlorophenate (PCP). The main feature was rapid cleavage of the C-Cl bond giving Cl^-.

Reviewing the literature on sonochemistry of organochlorine compounds as summarized above did not lead to any reports on the use of ultrasound for chemical monitoring. However, the reported sonochemistry of organochlorine compounds in water gave much support for using sonication in combination with changes in Cl^-, conductivity and/or pH as a way of monitoring for the presence of the compounds in water.

CHAPTER 5

EXPERIMENTAL

Sample Preparation

High purity (99%) chemicals were used for sample solution preparations. Methanol (MeOH), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), and chlorobenzene (Ph-Cl) were purchased from Burdick and Jackson Laboratories Inc. Trichlorethylene (TCE) was purchased from Baker Reagents. 3,3'-Dichlorobiphenyl (PCB) and 4,4'-dichlorobiphenyl (PCB) were obtained from Chem Service. Triton X-100™ and technical grade humic acid, sodium salt, were purchased from Aldrich Chemical Company, Inc. Potassium chloride (KCl) solution (1000 ppm Cl^-) was obtained from Orion.

The stock solutions of analytes were prepared in MeOH. Aliquots of stock solutions were taken for preparation of aqueous samples (1:100 dilution). PCB samples, a 1:1 combination of the 3,3'- and 4,4'- isomers, were diluted in 1% aqueous solution of Triton X-100. Dilution of analyte solutions was made to obtain roughly the same concentrations (ppm) of organic chlorine among samples, except for those of PCBs, which were somewhat lower due to limited availability of reagents.

The following deionized water solution samples were used in the experiments:

TCE   3.7 ppm (3.0 ppm Cl) and 37 ppm (30 ppm Cl)
CCl_4 4.0 ppm (3.7 ppm Cl) and 40 ppm (37 ppm Cl)
$CHCl_3$ 3.7 ppm (3.3 ppm Cl) and 37 ppm (33 ppm Cl)
Ph-Cl 9.4 ppm (3.0 ppm Cl) and 94 ppm (30 ppm Cl)
PCB   5.5 ppm (1.7 ppm Cl) and 55 ppm (17 ppm Cl)

Deionized water was used for the blanks.

Tap water solutions of analytes, i.e., TCE (36.6 ppm), CCl_4 (39.7 ppm), $CHCl_3$ (37.1 ppm), and Ph-Cl (94.1 ppm), were prepared from the same stock solutions in MeOH. Tap water was used for the blanks. Aqueous solutions of analytes were freshly prepared before analysis.

Two well-water samples, Brad Ford (Ash Meadow, Nevada, sampled 4/16/93) and Hawaii (Grand Canyon, Arizona, sampled 4/23/93), were stored at 4°C in screw-cap glass bottles after they had been used in another study in May 1993. They were used in the present study (August 1993) without dilution or further processing.

Equipment

A Branson Ultrasonic Corporation Sonifer Model 450 was used for sonication of samples. The unit was equipped with a power supply, a soundproof box, a converter, a cup horn, and 1/2" horn probe. Figure 1 shows the cup horn and the 1/2" horn probe. Sonication was performed in glass screw-cap reaction tubes (Figure 2). The tubes were modified from commercially available screw-cap vials by rounding their bottoms and adding glass supporting rings. The design of the tubes allowed them to be placed into the sonicator cup-horn at the same depth.
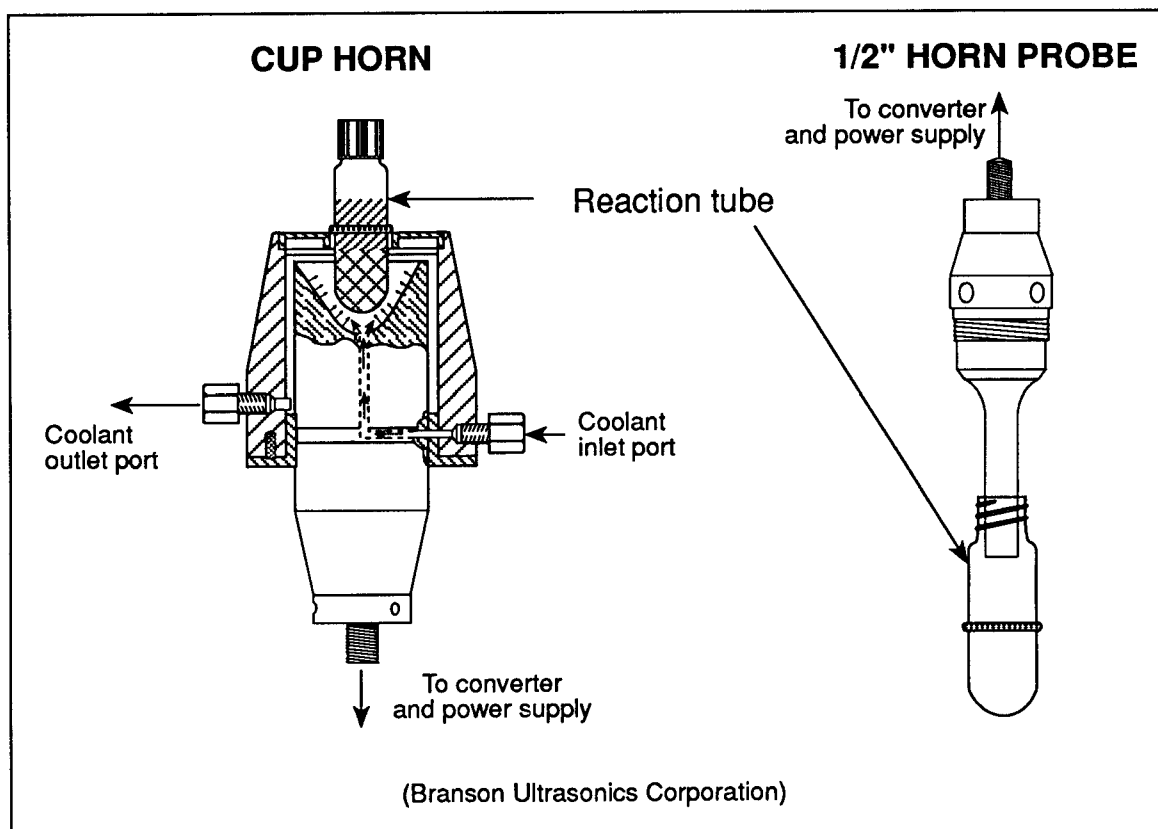
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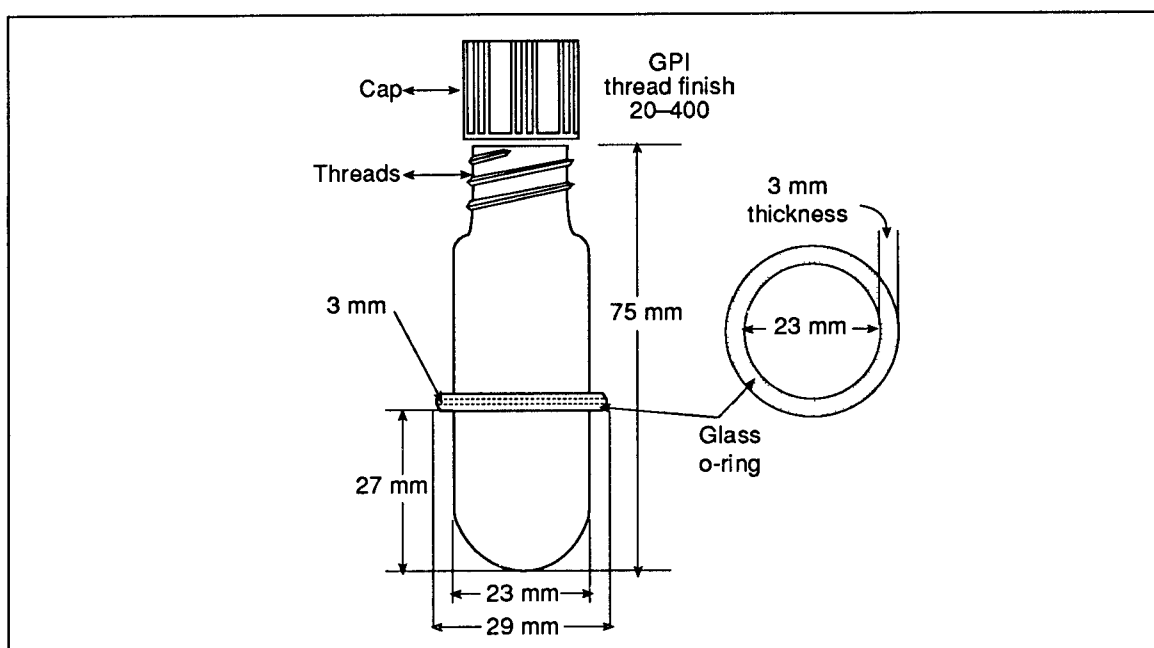**Figure 1.** Sketches of the cup horn and the 1/2" horn probe used in sonication experiments.

Figure 2. Sonication reaction tube.

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A constant temperature circulator (Model 1160 of VWR Scientific Company) was used as a cooling bath. The cooled liquid (commercial anti-freeze, polyethylene glycol) was pumped through the cup-horn system with a peristaltic pump (Cole Parmer Instrument No.7520-25) equipped with an easy-load pump head (Cole Parmer Instrument, Model 7518).

The following measurement equipment was used:

- Conductivity Meter, Orion Model 180 C™, Orion Cell No. 018010, temperature compensator, Orion No. 018870;
- pH/Ion Selective Electrode Meter (ISE), Orion Model EA 940™, temperature compensator Orion No. 91700;
- Electrodes: Cl^-, Orion Solid State Combination™ (Cl^- ISE), No. 9617, and pH, Orion Ross™ Combination, No. 8103.
- Ion chromatograph Dionex - Quick, IonPac AG4A Guard Column, IonPac AS4A Analytical Column, suppress conductivity detector.

Sonication Procedures and Measurements

Sonication of samples and blanks was performed using two ultrasound systems: a cup-horn and a 1/2" horn probe. Both the cup horn and the 1/2" horn probe were placed in the soundproof box. Sample solutions were pipetted into reaction tubes. Each individual sample tube was closed and then placed in the cup horn system for sonication. In the case of the 1/2" horn probe system, the horn was directly immersed in the sample tube. The tube was placed into the cup horn which also served as a cooling bath. The coolant (polyethylene glycol) was pumped through the cup horn using a constant temperature circulator. The temperature of the circulator was set at -10°C. The cup horn and the 1/2" horn probe operated at the maximum output control setting i.e., 10, during experiments.

The following experimental parameters were investigated:

- continuous vs. pulse sonics (pulse mode 10%-90%)
- time of sonication (1-90 min)
- sample volume (8-15 ml)
- different concentrations of analytes
- temperature of samples after sonication
- different water sources (deionized, tap, well)

At least two series of three replicates of a sample and a blank were sonicated and measured. The conductivity and pH/ISE meters were calibrated daily for each series of experiments. The limit of detection for the Cl^- ISE electrode was 1.8 ppm. The conductivity meter and Cl^- ISE electrode were calibrated in concentration units, i.e., mg/L (ppm) using Cl^- standard solutions. Calibration curve equations obtained with regression analysis had correlation coefficients of 0.998-0.999. Standard solutions used for calibrating the Cl^- ISE were in a range 1-15 ppm Cl^- for deionized water and 50-250 ppm Cl^- for tap and well water. Though one of the points (1 ppm) was below the sensitivity limit of the Cl^- ISE, excellent correlation coefficients were obtained. This allowed estimates down to 0.5 ppm Cl^-. Calibrations of the conductivity meter were made with standard solutions of 1-25 ppm Cl^- for deionized water, and 100-1000 ppm Cl^- for tap and well water. Measurements of conductivity, Cl^-, and pH were made in samples before and after sonication. The effects of sonication were noted as changes in these parameters.

Relative errors of conductivity and Cl⁻ measurements ranged from 1% to 10% and were concentration-related, i.e., higher errors were found at lower concentrations. The errors were 1% or less in pH measurements.

Examples of levels of ion concentrations and pH in deionized water and tap water used for sample preparations are presented in Table 3. These represent blanks.

Table 3.   Average Levels of Ion Concentrations and pH in Samples of Deionized Water and Tap Water Before Sonication.

Water	Conductivity [ppm]	Cl⁻ [ppm]	pH
Deionized	(6)ᵃ 0.00 ± 0.00	(6) 0.40 ± 0.05ᵇ	(6) 6.50 ± 0.01
Tap	(6) 330 ± 4	(6) 98.3 ± 1.1	(6) 8.37 ± 0.02

ᵃ Number of samples.
ᵇ Results below the limit of quantitation (Ref. 33)

There were no changes in ion concentrations and pH after sonication of the deionized and tap water blanks. However, there were some variations among *different* samples of tap water. These variations were of no consequence since measurements were always performed before and after sonication.

The sample volume used with the cup horn system was 8 mL. That corresponded to the minimum volume needed for measurements with the conductivity cell. The optimum sample volume for use with the 1/2" horn probe was 15 mL. That allowed proper immersion of the probe.

Continuous and pulse modes were utilized. In the pulse mode, ultrasonic vibrations are transmitted to a solution at a rate of one pulse per second. The pulse duration can be adjusted from 10% to 90%, enabling a solution to be processed at full ultrasonic intensity while limiting temperature build-up.

Changes in ion concentration and pH were not evident upon sonication at low concentration of organochlorine compounds, i.e., 3.7 ppm TCE, 4.0 ppm CCl₄, 3.7 ppm CHCl₃, 9.4 ppm Ph-Cl, and 5.5 ppm PCB for the sonication times examined.

Optimization of conditions with the cup-horn system

Changes in conductivity, Cl⁻ content, and pH of TCE solutions with the cup horn at various pulse modes are shown in Figure 3. The sonication time was 10 minutes. The greatest increase of ion concentrations and the greatest decrease of pH were observed at the 60% pulse mode. Much lower changes were noticed at the constant mode (100%), which may be explained by losses of power output during sonication. The same pattern of changes was found as the result of 5 and 20 minutes sonication. The longer the sonication time, the greater the observed changes.

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Sonication time - dependent changes with the cup horn system at the 60% pulse mode in TCE solution are shown in Figure 4. The greatest changes in ion concentration were observed at the 60-minute sonication time; however, the 5-minute sonication time was sufficient to allow increases of conductivity and Cl^- as well as decreases of pH in the sample to be noted. Sonication times greater than 60 minutes were not examined.
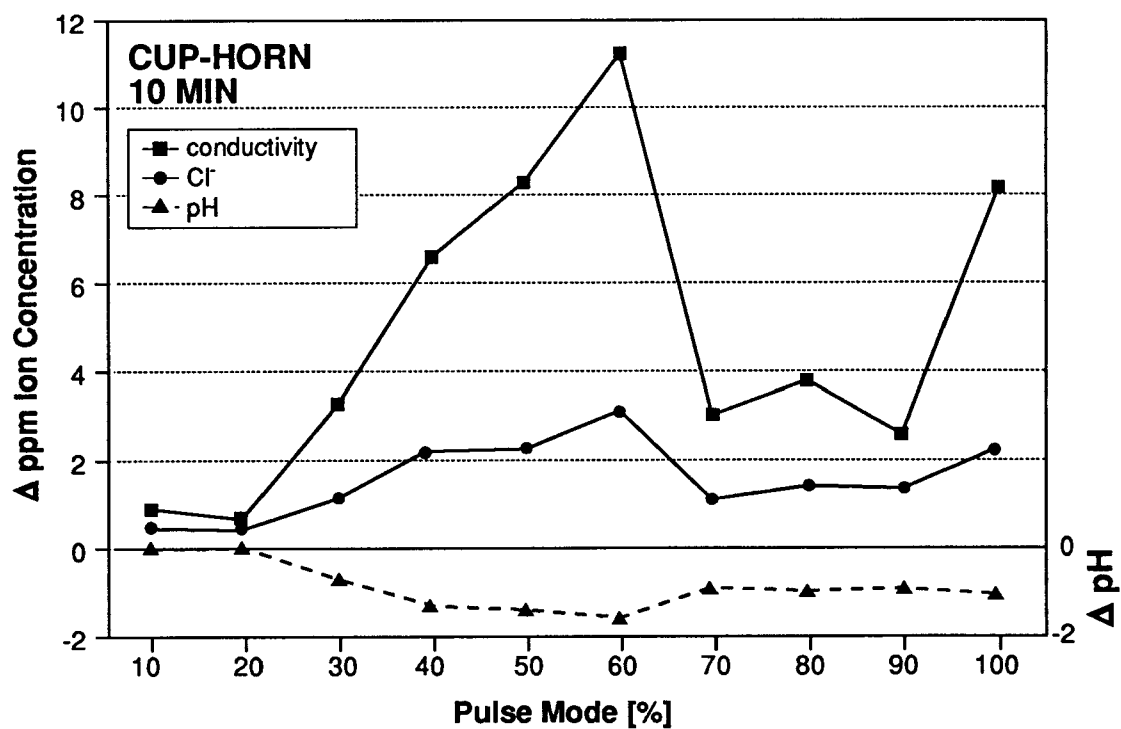
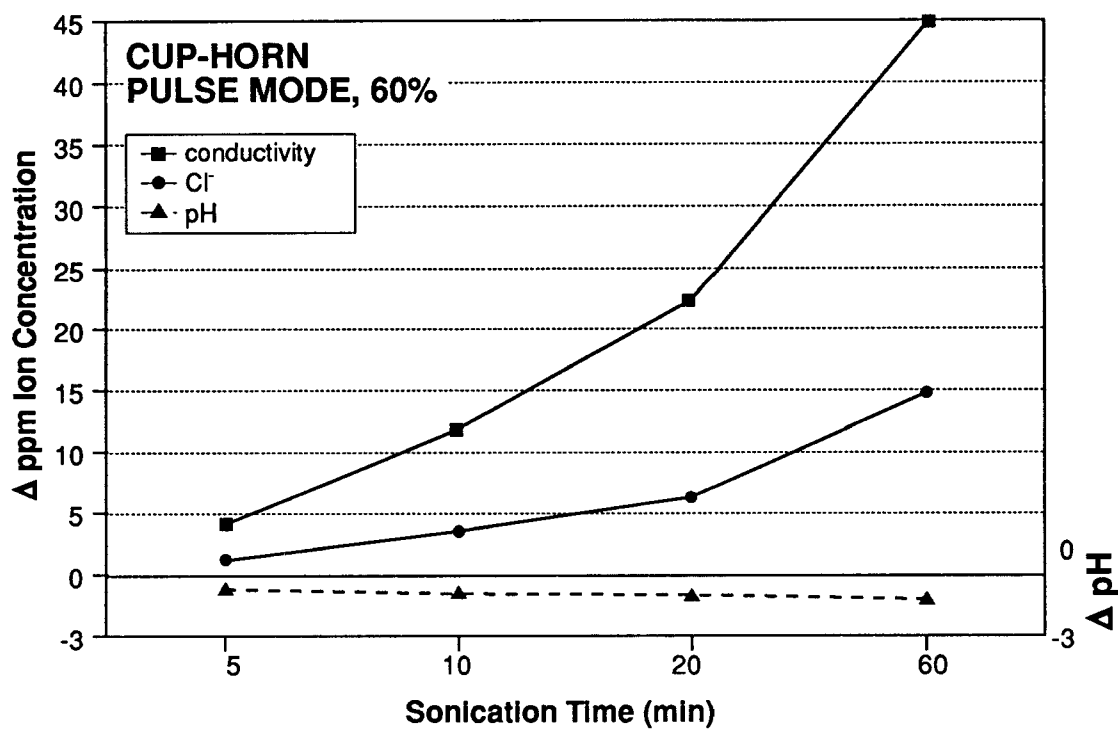**Figure 3.** Changes upon sonication of 37 ppm TCE vs. pulse mode.

Figure 4. Changes upon sonication of 37 ppm TCE vs. time.

CHAPTER 6

RESULTS AND DISCUSSION

Ion Chromatography Analysis

Increases in Cl^- in a sample after sonication were used as evidence that C-Cl bond cleavage occurred. Organic chlorine became measurable as chloride ion. The increases in conductivity were due to the formation of Cl^- and other ionic products. Ion chromatography was used to identify products resulting from cup horn sonication experiments at the 60% pulse mode and 10 minutes sonication time. Four sample solutions of each analyte were examined including a 1% aqueous solution of Triton X-100 that served as the blank for PCB solutions. One sample solution from each set was analyzed by ion chromatography, and the remaining three were analyzed according to the procedure described previously. Ion chromatograms before and after sonication are presented in Figures 5-10 for solutions of TCE, $CHCl_3$, CCl_4, Ph-Cl, PCB, and Triton X-100. Data of Cl^- concentrations in samples after sonication obtained from ion chromatography and Cl^- ISE measurements are presented in Table 4.

The data show very good agreement for Cl^- between the two methods. This confirmed credibility of Cl^- ISE measurements in the present work.

Five standard solutions of Cl^- (1-15 ppm) were used to prepare a calibration curve for the ion chromatography experiments. Heights of peaks were used in the regression analysis. The correlation coefficient was 0.996. Chromatograms for the standard solutions are shown in Figure 11.

Chloride ion was not detected by either method in the deionized water used for these experiments. Ion chromatograms of the deionized water blanks before and after sonication are shown in Figure 12. No changes are evident.

Table 4.   Concentration of Cl^- Obtained from Ion Chromatography and Cl^- ISE Measurements.
(Samples sonicated in the cup horn at 60% pulse mode at 10 minutes.)

Sample	Method	
	Ion Chromatography [a] Cl^- [ppm]	ISE [b] Cl^- [ppm]
TCE (37 ppm)	2.80	2.67 ± 0.18
CCl_4 (40 ppm)	3.74	3.81 ± 0.50
$CHCl_3$ (37 ppm)	4.55	4.37 ± 0.25
Ph-Cl (94 ppm)	0.50	0.40 ± 0.05
PCB (55 ppm)[*]	0.30	0.20 ± 0.08[**]
1% aq.sol.Triton X-100	0.30	0.20 ± 0.02[**]

[a] 1 sample per compound   [*] PCB solution in 1% aqueous solution Triton X-100.
[b] 3 samples per compound   [**] Results below limit of quantitation. (Ref. 33)

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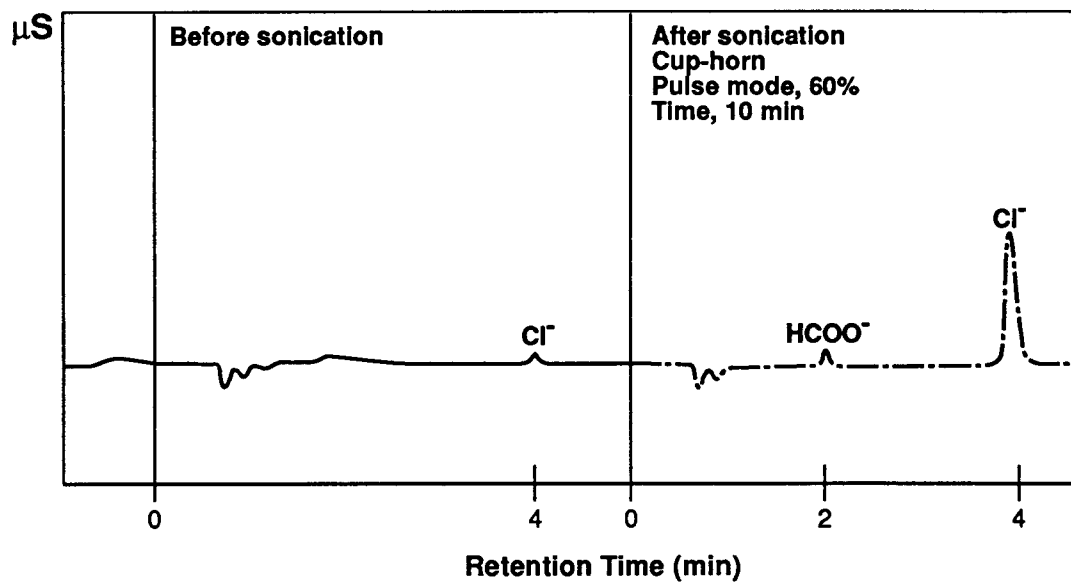
Figure 5. Ion chromatograms of 37 ppm TCE.
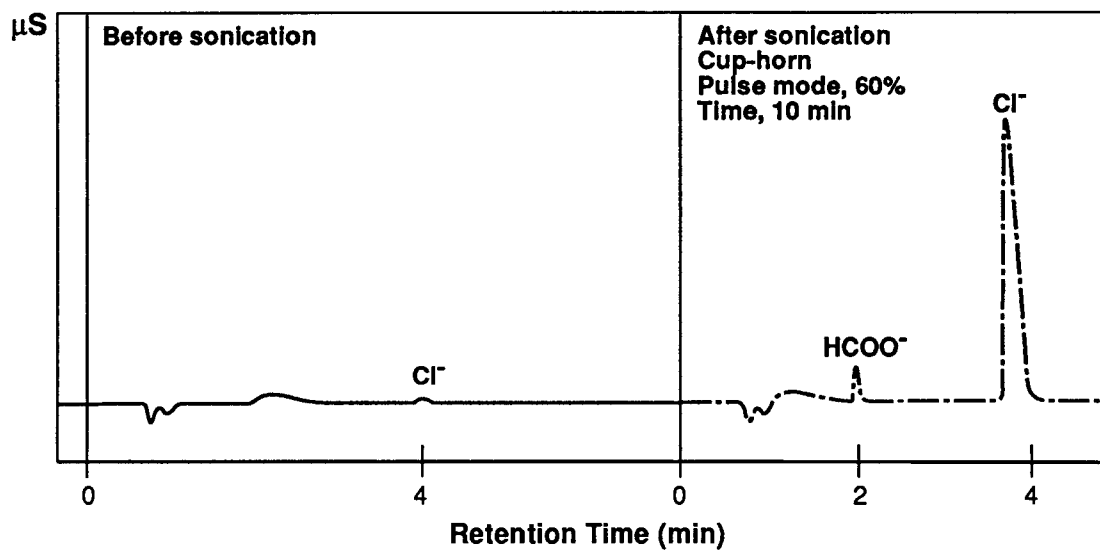
Figure 6. Ion chromatograms of 37 ppm CHCl₃.

| μS | Before sonication | After sonication
Cup-horn
Pulse mode, 60%
Time, 10 min | Cl⁻ |

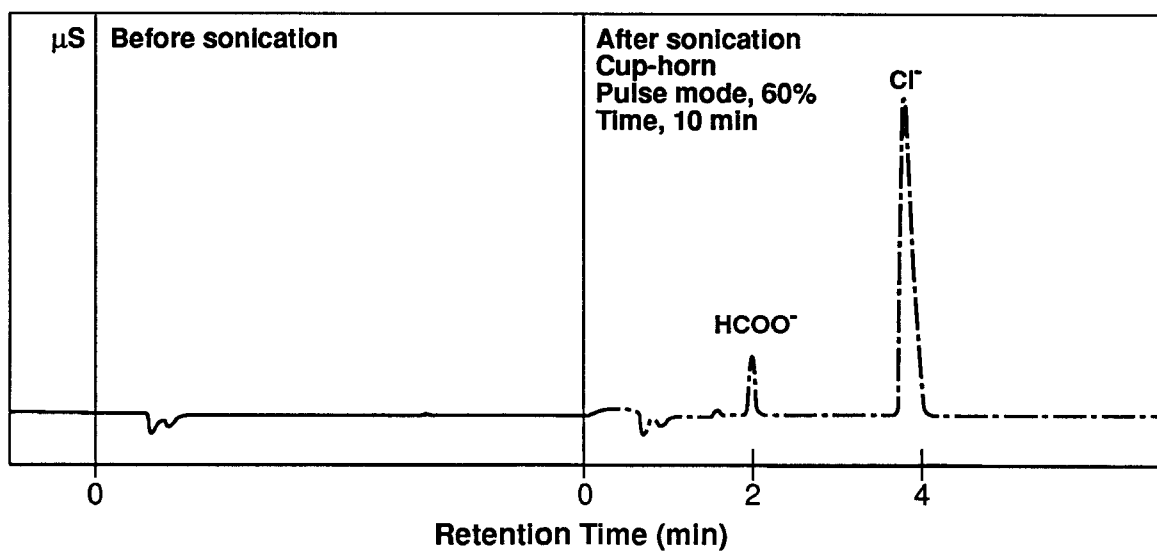**Figure 7.** Ion chromatograms of 40 ppm CCl4.
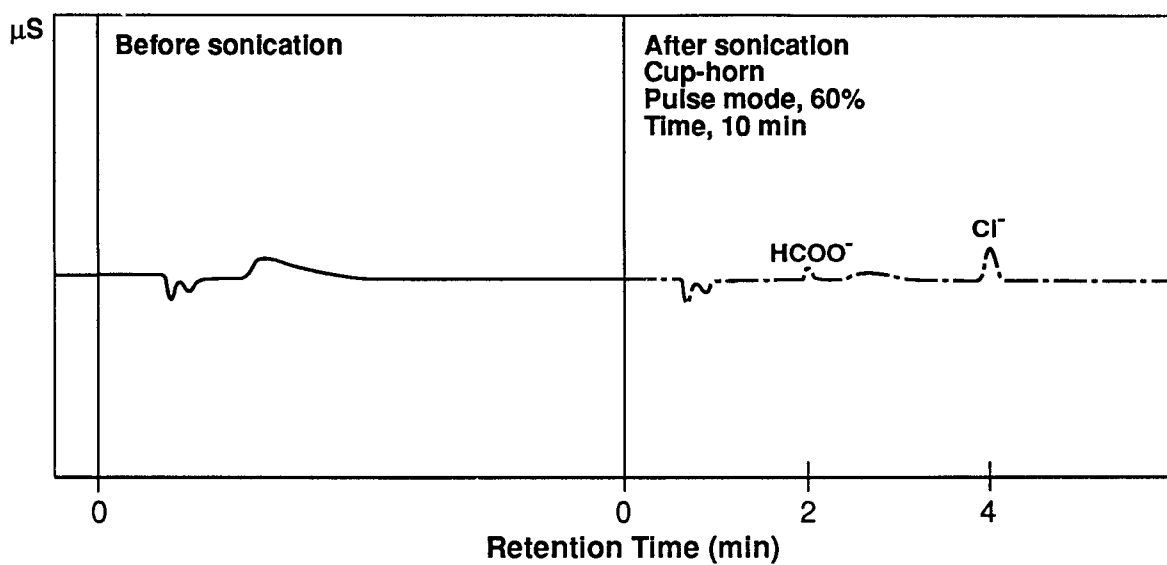

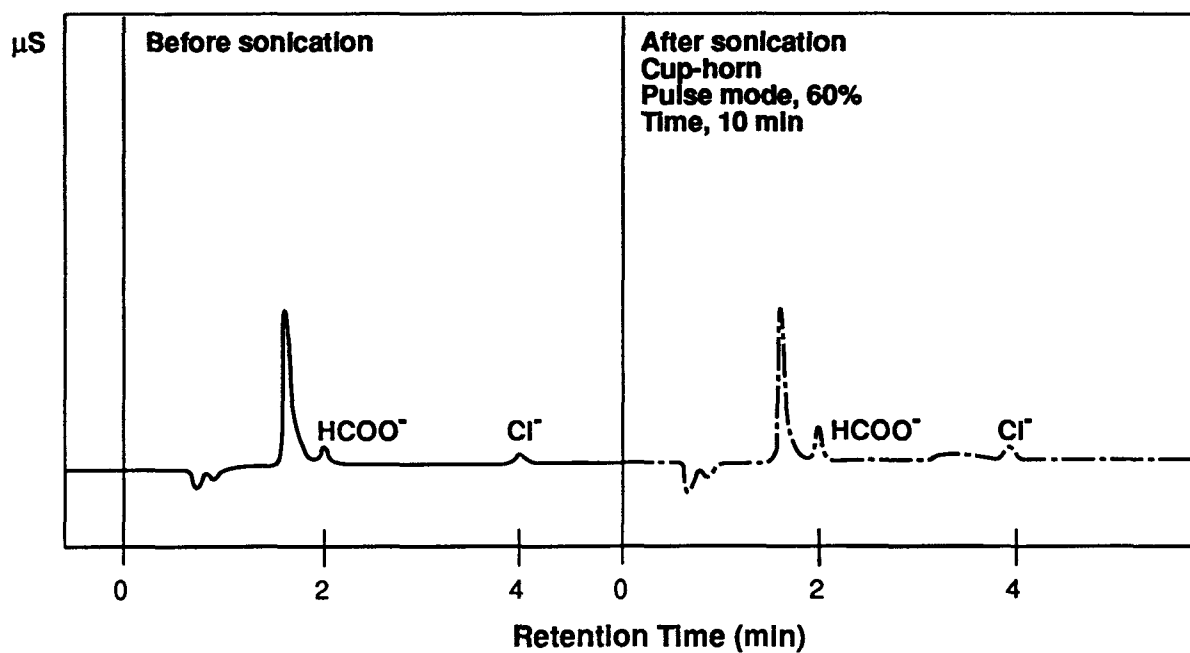**Figure 8.** Ion chromatograms of 94 ppm Ph-Cl.

20

Figure 9. Ion chromatograms of 55 ppm PCB in 1% Triton-X-100.
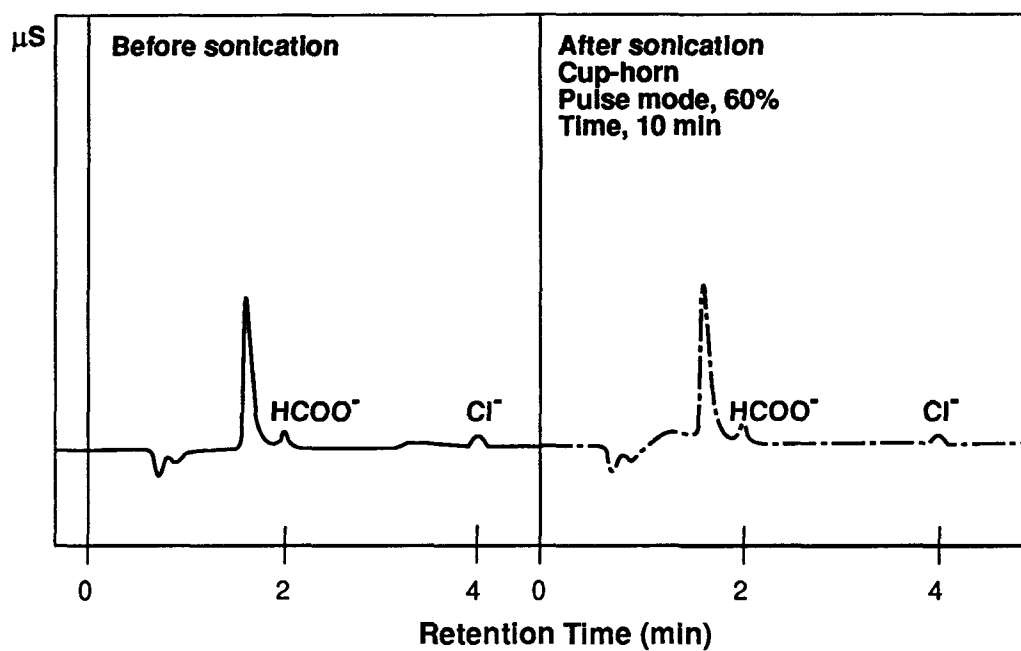

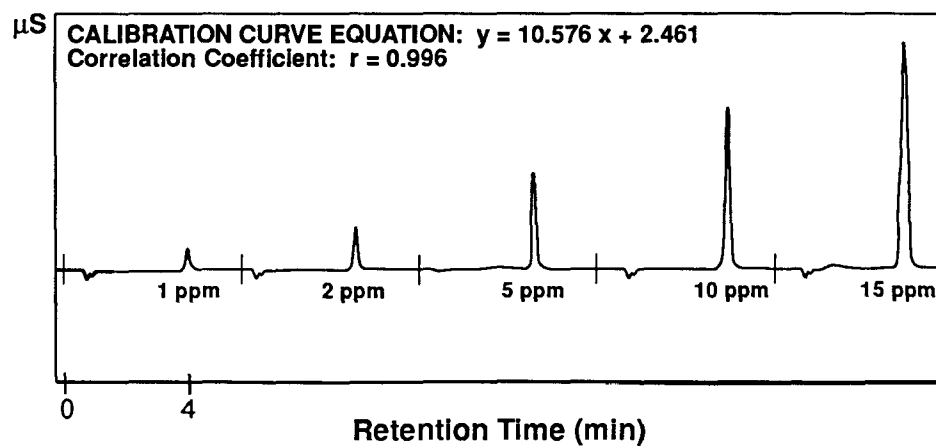**Figure 10.** Ion chromatograms of 1% Triton-X-100.

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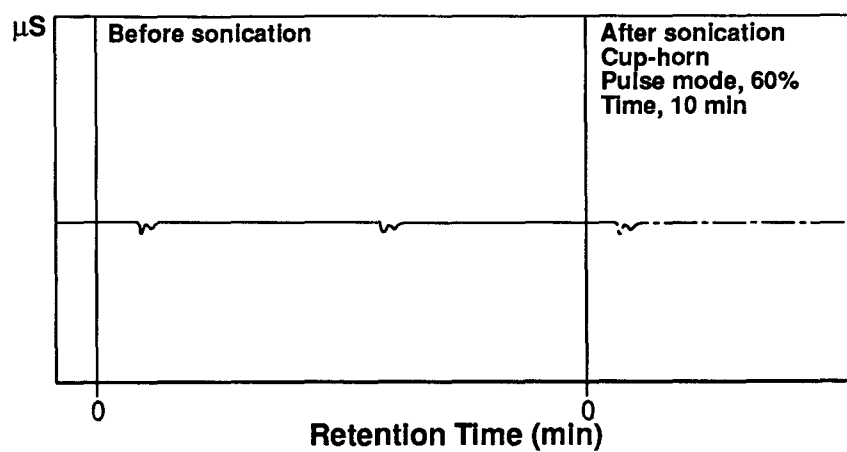**Figure 11.** Ion chromatograms of Cl⁻ standard solutions.

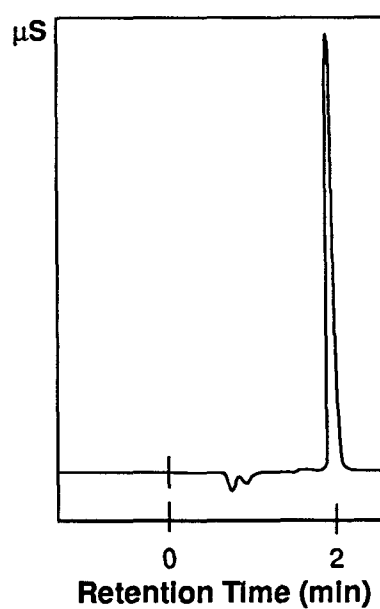**Figure 12.** Ion chromatograms of deionized water.

Figure 13. Ion chromatogram of 10 ppm $HCOO^-$.

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Formate ion (HCOO⁻) was not detected in samples before sonication except for PCB and Triton X-100. Formate ion was detected in all samples after sonication. See Figures 5-10. No other major sonication products were noted in the ion chromatograms.

A 10 ppm standard solution of HCOO⁻ was run in the ion chromatography system (Figure 13). The height of the peak was used in calculating HCOO⁻ concentration insample solutions. Formate ion concentrations after sonication were estimated to be: 0.29 ppm (TCE sample), 0.88 ppm (CCl₄ sample), 0.69 ppm (CHCl₃ sample), and 0.20 ppm (Ph-Cl sample). These results are semiquantitative at best but give an appreciation of the HCOO⁻ levels. For the PCB and Triton X-100 samples, the concentration of HCOO⁻ was the same before and after sonication and was estimated to be 0.39 ppm. Clearly, the Triton X-100 solution contained ionic impurities including Cl⁻, HCOO⁻, and another substance which were evident in the ion chromatograms in a relatively high concentration but not identified.

The concentration ratios of HCOO⁻/Cl⁻ using the ion chromatography results were calculated as follows: 0.10 (0.29/2.80) (TCE), 0.23 (0.88/3.74) (CCl₄), 0.15 (0.69/4.55) (CHCl₃), and 0.40 (0.20/0.50) (Ph-Cl). The highest ratio was for Ph-Cl, a compound which did not give a high Cl⁻ yield. Differences in sonication mechanisms might be reflected by the ratio variations; however, time did not allow a detailed study of this phenomenon. A source of formate ion could also be through the sonochemistry of methanol which was used to prepare solutions of anlaytes.

Changes in Conductivity

A. Cup-horn system, 60% pulse mode.

Changes in conductivity with sonication time using the cup horn system at 60% pulse mode are shown in Figure 14. The greatest changes of ion concentration were observed at 20 minutes, the lowest at 5 minutes. Changes in conductivity for Ph-Cl solutions were noted only after 10 and 20 minutes sonication. The changes, however, were very small (1 ppm to 2.5 ppm). PCB solutions were sonicated for 10 minutes; no changes in conductivity were noted. The greatest changes of ion concentration were observed with solutions of CHCl₃ and CCl₄. The average output power for the cup-horn system was 160 Watts. Temperatures of samples after sonication ranged from 27°C to 30°C.

B. 1/2" Horn probe system.

Sonication with the 1/2" horn probe was performed at 2 minutes in constant and 60% pulse modes, and at 1 minute in constant and 80% pulse modes. The changes in conductivity of sample solutions are shown in Figure 15. In contrast to the cup horn system, it was noted that the constant mode is more effective than the 60% pulse mode. The changes of ion concentration at 2 minutes sonication at the 60% pulse mode were at least half those observed at the constant mode. There were no significant differences noted in conductivity changes between 1 minute sonication at the constant and 80% pulse modes; they were higher, however, than those found after 2 minutes sonication at the 60% pulse mode. In the 1/2" horn probe system, effectiveness of sonication seemed greater at the constant mode in comparison to the cup horn. For both systems, effectiveness increased with sonication time.

The greatest changes of ion concentration with the horn probe were noted with solutions of CCl₄, i.e., 21 ppm at 2 minutes, and 8.5 ppm at 1 minute at constant mode. In contrast, the greatest changes with the cup horn were observed for CHCl₃ solutions. This was surprising, but the results were found to be repeatable.
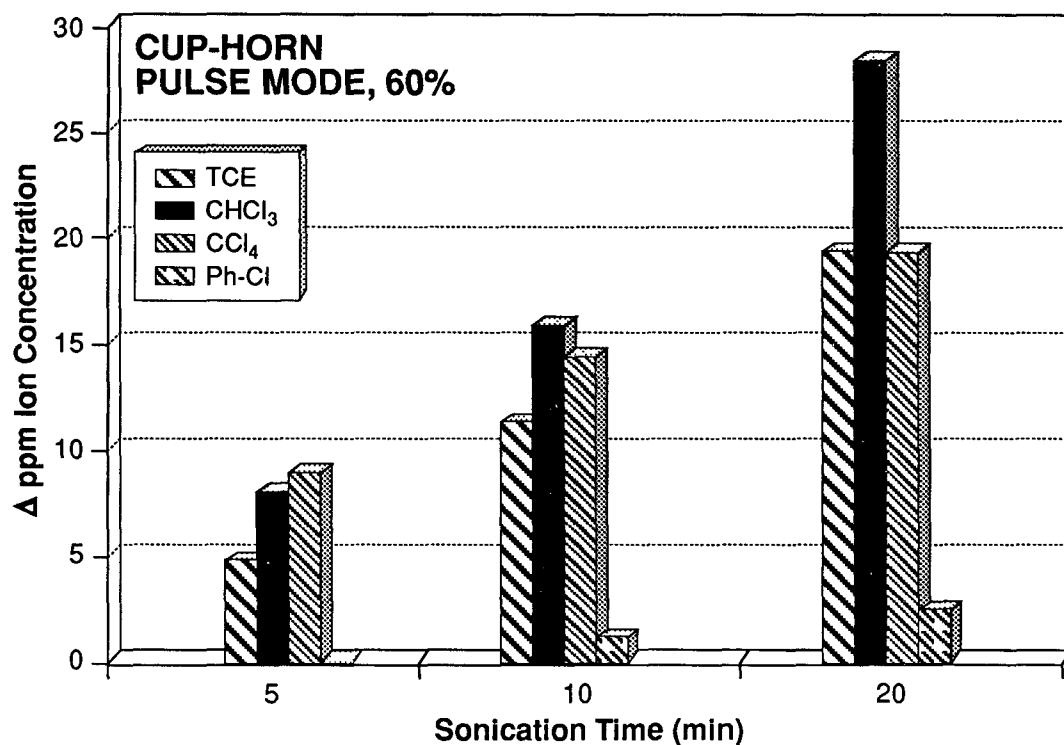
23

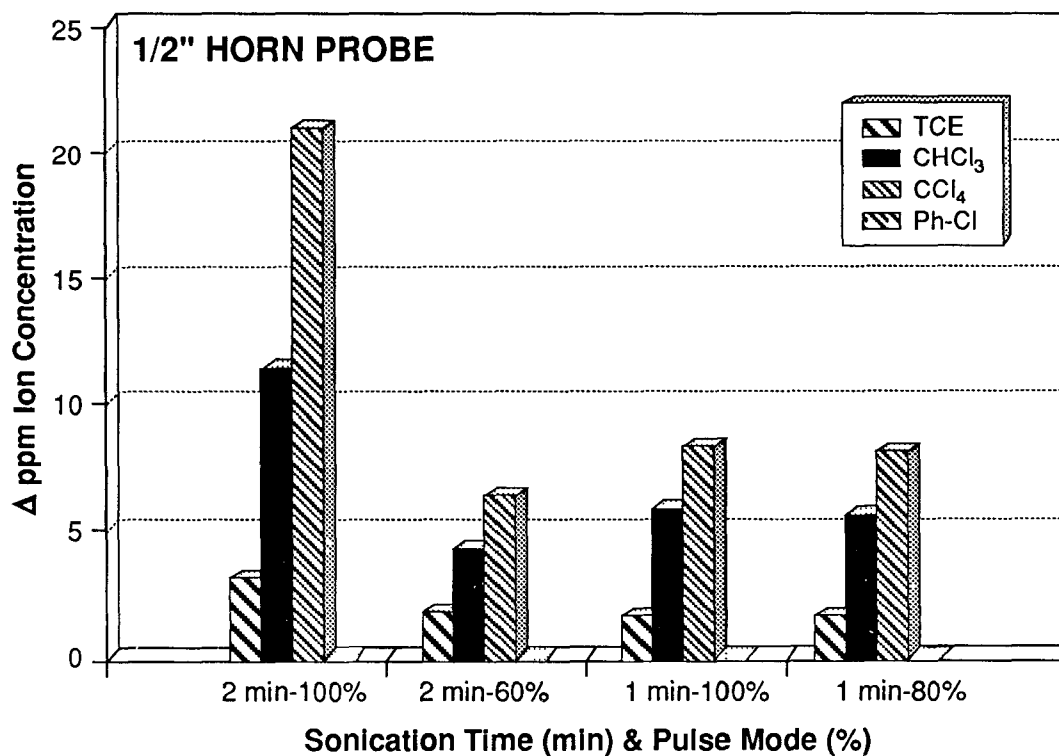**Figure 14.** Changes in conductivity upon sonication vs. time.

Figure 15. Changes in conductivity upon sonication vs. time and pulse mode.

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Increases in ion concentrations were observed for TCE solutions with the horn probe, but there were no measurable changes for Ph-Cl solutions.

The average output power in the 1/2" horn probe was 220 watts. The temperature of a sample after sonication was 30-35°C.

Changes in Cl⁻ Concentrations

A. Cup-horn system, 60% pulse mode.

Changes in Cl^- concentration versus sonication time in the cup horn system at 60% pulse mode are shown in Figure 16. The greatest relative increases of Cl^- were observed with $CHCl_3$ solutions at each sonication time. The longer the sonication time, the greater were the increases for all analyte solutions. There was measurable but low Cl^- (less than 0.40 ppm) in Ph-Cl solution after 10 and 20 minutes sonication. Changes in Cl^- concentration in PCB solutions were not noted after sonication for ten minutes.

B. 1/2" Horn-probe system.

Changes in Cl^- concentration for sample solutions after sonication in the 1/2" horn probe system are presented in Figure 17. The greatest increase of Cl^- was noted for CCl_4; smaller changes of Cl^- were observed for $CHCl_3$ and TCE. This parallels conductivity changes (Figure 15). There were measurable but very small increases of Cl^- concentration for Ph-Cl solutions (estimated lower than 0.3 ppm) after 2 minutes sonication at the constant mode.

Changes in pH

A. Cup-horn system, 60% pulse mode.

Changes of pH in sample solutions upon sonication in the cup horn at 60% pulse mode versus sonication time are shown in Figure 18. The changes were greater with longer sonication times. At 20 minutes the pH decreased by 2.3 units for CCl_4 solutions. The smallest relative changes of pH were with solutions of Ph-Cl at sonication time of 10 and 20 minutes. These changes, however, were much larger than would have been predicted based on Cl^- or conductivity results. The implication is that Ph-Cl is reacting but Cl^- is not a major product. Hydroxylation may be occuring at an open position of the aromatic ring. pH changes were measurable but small with solutions of PCB, and are not illustrated in Figure 18. This parallel the lack of changes in Cl^- and conductivity for PCB solutions mentioned earlier.

B. 1/2" Horn-probe system.

Changes in pH upon sonication versus time and pulse mode in the 1/2" horn probe are presented in Figure 19. As noted with the cup horn, pH changes were larger with longer sonication times. Smaller changes were noted at the 60% pulse mode in comparison to the constant mode for the same sonication time (2 minutes). There were no differences in pH changes between the constant and 80% pulse modes at 1 minute sonication. The changes in pH at 1 minute sonication in the horn-probe were comparable with those using the cup horn for 10 minutes of sonication. The greatest changes of pH were observed in CCl_4 solutions at 2 minutes of sonication. The change was a decrease in 3.8 units of pH using the constant mode. There were measurable changes in pH of the Ph-Cl solution after sonication. It was interesting to find that the pH changes with Ph-Cl, though small (0.3 units),
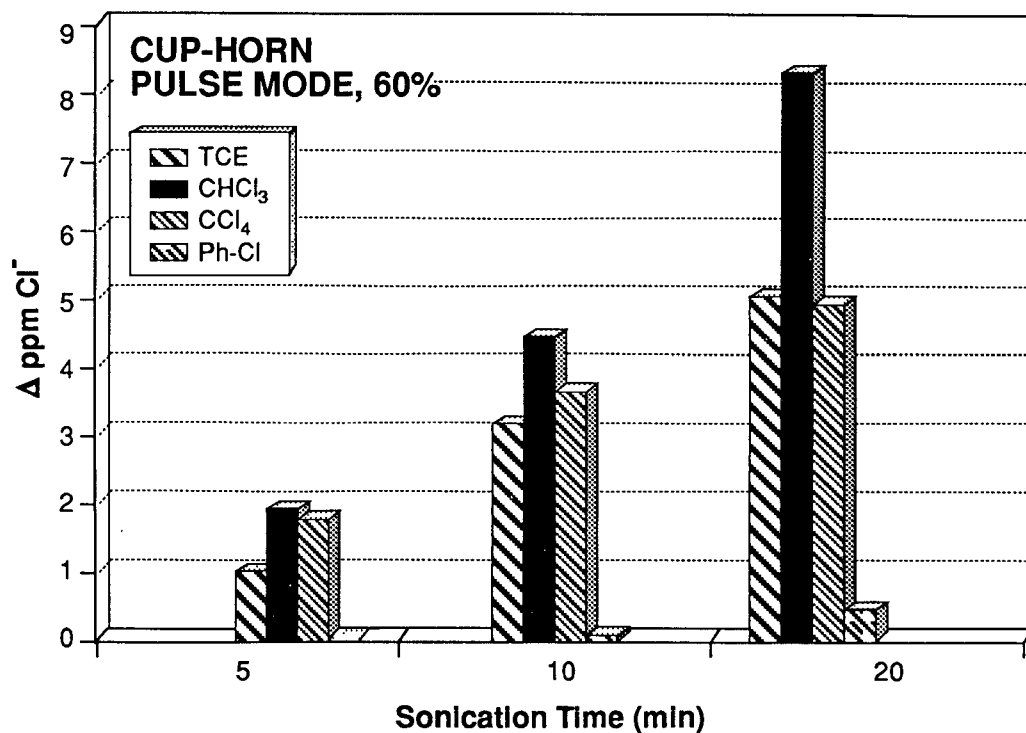
25

Figure 16. Changes in Cl⁻ concentration upon sonication vs. time.
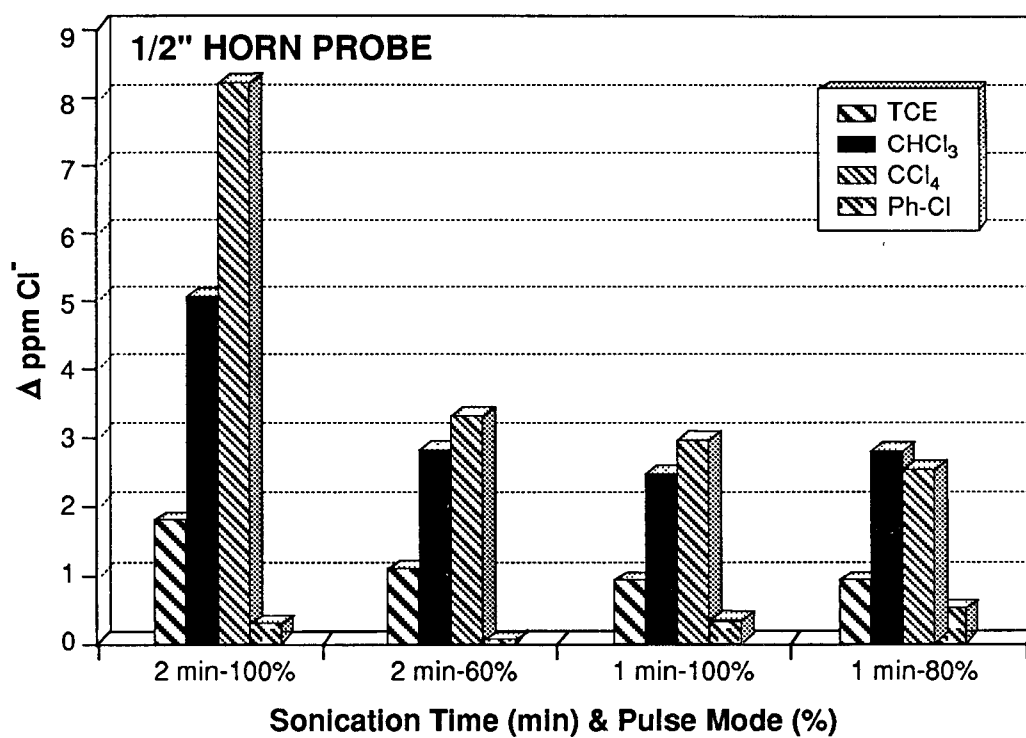

Figure 17. Changes in Cl⁻ concentration upon sonication vs. time and pulse mode.
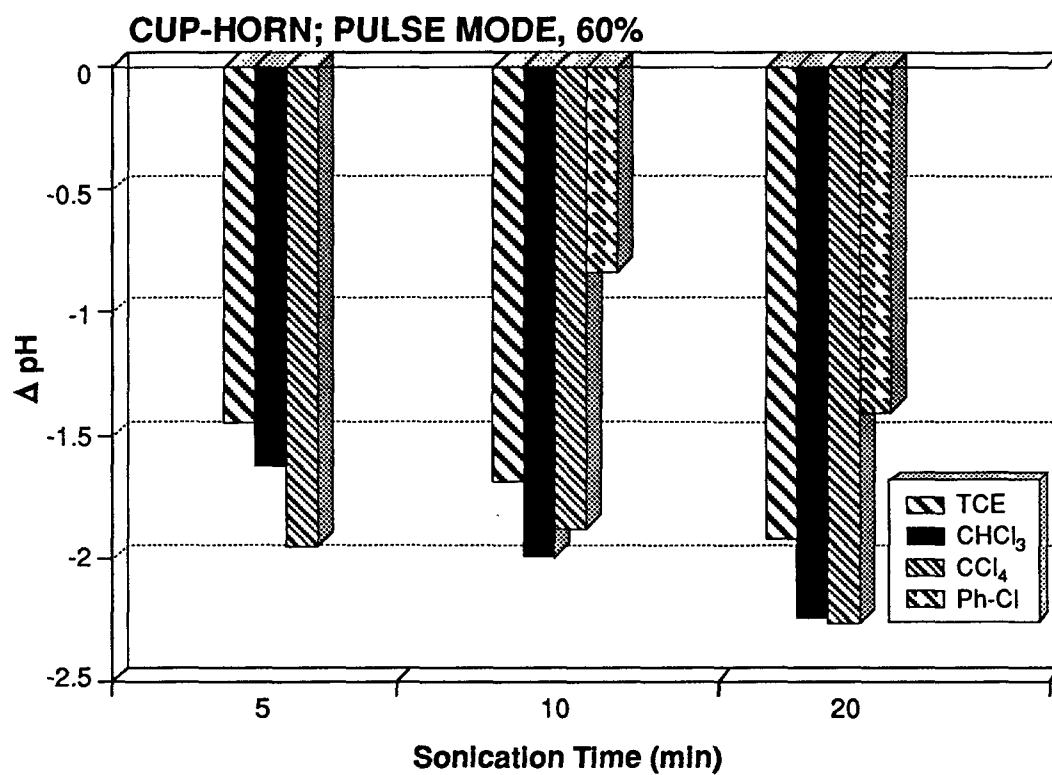
Figure 18. Changes in pH upon sonication vs. time.
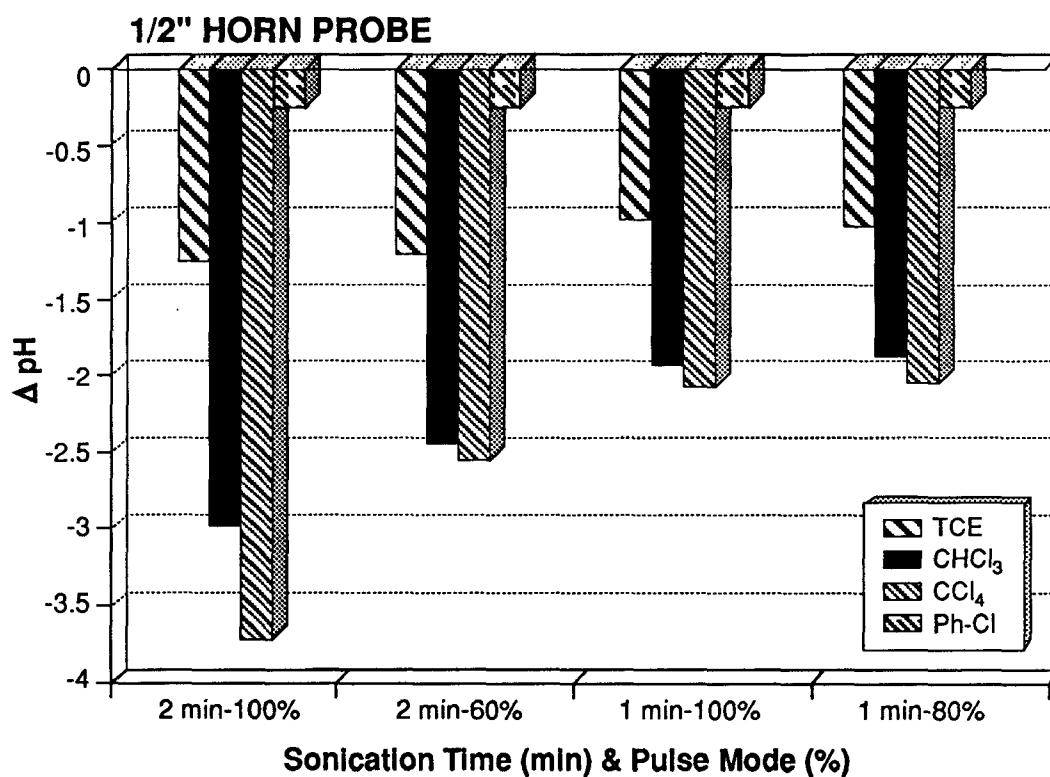

Figure 19. Changes in pH upon sonication vs. time and pulse mode.

were significant but much smaller than the pH changes for Ph-Cl solutions in the cup horn. No explanation can be offered at the present time.

Tap Water Samples

Solutions of TCE (37 ppm), CCl_4 (40 ppm), $CHCl_3$ (37 ppm), and Ph-Cl (94 ppm) were prepared in tap water. Sonication was performed in the cup horn system at 60% pulse mode at 10 minutes, and in the 1/2" horn probe at 80% pulse mode at 1 minute. Using tap water solutions, changes in conductivity and pH were observed to be far lower than those in deionized water. This may be explained by the initial pH. As mentioned earlier, the tap water pH was on the average 8.4, whereas the deionized water pH was 6.5. It is known that the rate of organochloro compound sonolysis increases with lower pH (23). Also, any bicarbonates and carbonates which are present may act as buffering agents. Furthermore, bicarbonate and carbonate may serve as hydroxyl radical scavengers (19), thus possibly inhibiting sonochemistry processes involving such radicals. Figure 20 shows the differences in sonication of 37 ppm $CHCl_3$ in tap and deionized water.

The changes observed with the horn probe were lower than those from the cup horn comparing either tap or deionized water. This was expected from previous experiments under similar condition.

Well Water Samples

Two well-water samples were sonicated in the cup horn system at 60% pulse mode at 10 minutes. Measurement data of conductivity, Cl^- concentrations, and pH, before and after sonication, are presented in Table 5. No changes were noted as a result of the sonication within experimental errors. Gas chromatography/mass spectrometry results showed the presence of $CHCl_3$ at 0.6 ppm in the Hawaii well water sample. This concentration would not be detectable using sonication in combination with changes in Cl^-, conductivity, and/or pH with the measurement equipment used in this research. However, it was judged important to check real-world samples in the event there were any unknown factors which might influence changes of the parameters being measured in the absence of 1 ppm levels or higher of organochlorine compounds. Ion chromatographs of the real-world samples showed the presence of low ppm F^-, Br^-, and NO_3^-, and high ppm (94 and 176) of SO_4^{-2} in addition to Cl^-. As shown in Table 5, their presence had no impact on Cl^-, conductivity, and pH as a result of sonication.

No organic anions (such as formate and acetate) were shown to be present within the sensitivity limits of the ion chromatograph.

The results in Table 5 show how reproducible the measurements were with the same sample and how well the Cl^- results with the ISE corresponded to those obtained with the ion chromatograph.

The real world samples numbered only two. Additional ones will have to be examined in the development of an ultrasound method. Samples of well water from soil areas rich with humus would be especially important; however, none were available for the present proof-of-concept study.

Reaction Mechanism

The common denominator in the aqueous sonochemistry of organochlorine compounds is HCl. All reports indicate it to be among the principal products (Table 1). However, the mechanism and rate of the reaction may differ markedly depending on the conditions. As shown in Table 2, there may be a variety of products.

**CUP-HORN
PULSE MODE, 60%
TIME, 10 MIN**

**1/2" HORN PROBE
PULSE MODE, 80%
SONICATION TIME, 1 MIN**

Δ ppm Ion Concentration

conductivity
Cl⁻
pH

16
14
12
10
8
6
4
2
0

0
-2
-4 Δ pH

Tap Water   Deionized Water   Tap Water   Deionized Water
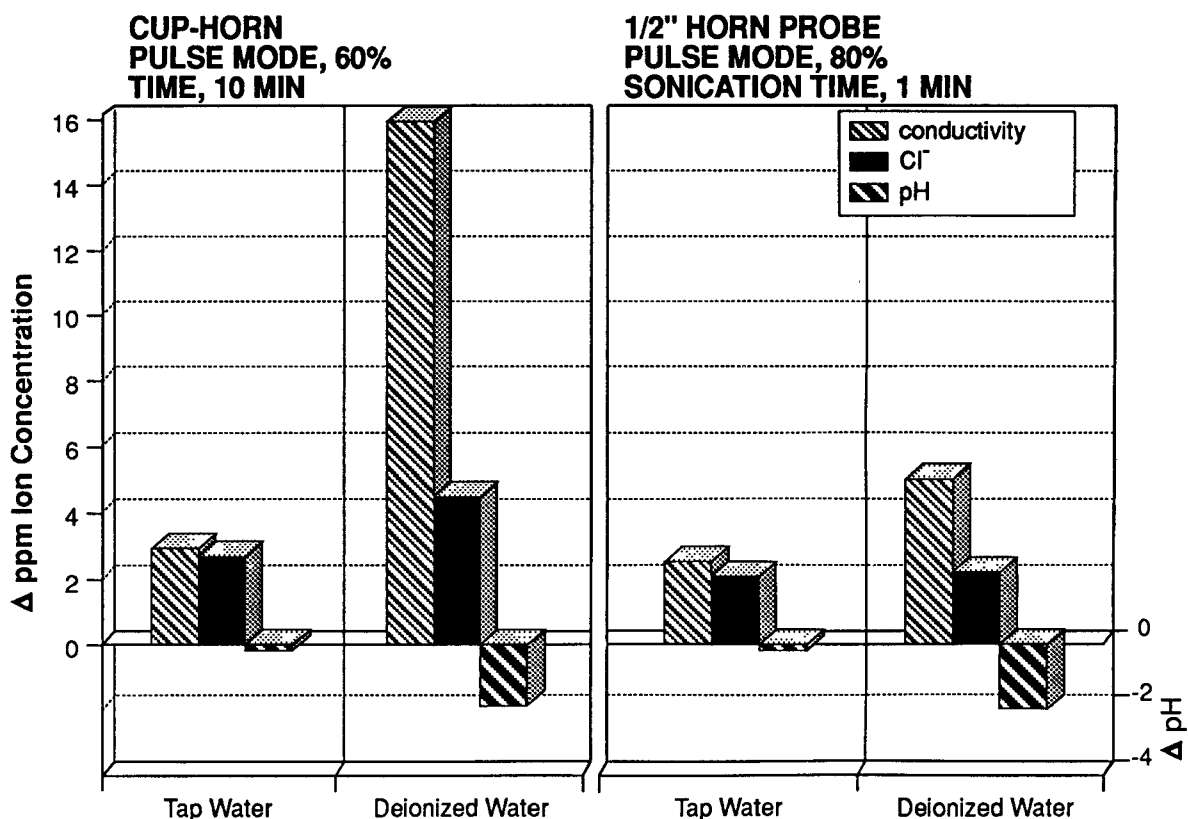
Figure 20. Changes upon sonication of 37 ppm $CHCl_3$ in tap and deionized water.

Elucidation of reaction mechanism was not part of the objectives of the present work. However, nothing was encountered which would counter the expectation that the major mechanism involves hydrogen and hydroxyl radical reactions with the pollutants. Under the conditions of the present experiments, HCl was the major *ionic product*. Small amounts of $HCOO^-$ were detected as well. However, the formate may have originated from the sonochemistry of methanol solvent. Another possibility might be the oxidation of methanol by secondary sonochemistry reaction products such as Cl_2or HOCl.

Use of ultrasound in combination with Cl^- ISE appears more applicable to monitoring nonaromatic organochlorine compounds such as TCE, $CHCl_3$ and CCl_4. As discussed earlier, relatively low yields of Cl^- were obtained from Ph-Cl and PCBs. Low yield of Cl^- does not necessarily mean that the aromatic compounds did not react. A logical explanation is that hydroxyl radicals oxidized Ph-Cl and the PCB mixture without dehalogenation. Sedlak and Andren (34) examined the oxidation of PCBs by hydroxyl radicals generated with Fenton's reagent. (This is a buffered solution of H_2O_2 and Fe^{2+}.) It was found through GC/MS that the halogenated sites were unreactive but that hydroxyl attacked one of the PCB nonhalogenated sites. Such a reaction scheme, though applicable to *decomposition* of Ph-Cl and PCBs, does not lead to the immediate formation Cl^-.

Table 5. Measurement data of conductivity, Cl⁻, and pH in well water samples. (Samples were sonicated in the cup horn system at 60% pulse mode, at 10 minutes).

Sample	Before Sonication			After Sonication		
	Conductivity ppm	Cl⁻ ppm	pH	Conductivity ppm	Cl⁻ ppm	pH
Brad Ford Ash Meadow Nevada 4/16/93[a]	308 309 308 305 308 _[b] -	41.1 40.4 40.9 39.2 44.2 38.6 40.1	8.64 8.60 8.63 8.66 8.58 8.68 8.76	305 305 308	41.3 41.6 42.2	8.60 8.64 8.39
Average±STD IC[c]	308±2	40.6±1.8 40.1±0.3	8.65±0.06	306±2	41.7±0.5	8.54±0.13
Hawaii Grand Canyon Arizona 4/23/93	180 175	19.6 20.5	8.37 8.32	173 178	19.6 20.2	8.35 8.36
Average IC	178	20.1 21.2±0.1	8.34	177	19.9	8.35

[a] Sampling date
[b] Volume of a sample not sufficient to measure conductivity.
[c] Ion chromatography data obtained from the Analytical Lab at HRC-UNLV.[1]

Essentially no Cl⁻ was detected with the PCB sample. However, Cl⁻ in relatively low yields was detected with Ph-Cl. This may be due to its volatility. Kotronarou and coworkers (35) reviewed the nature of sonochemical reactions and pointed out that they are characterized by the simultaneous occurrence of pyrolysis and free radical reactions. *Volatile* solutes will participate in pyrolysis reactions because of their presence inside the bubbles during the collapse of the cavities. In the solvent layer surrounding the hot bubble, both pyrolysis and free radical reactions are possible. Pyrolysis in the interfacial region is predominant at high solute concentrations. Free radical reactions are likely to predominate at low solute concentrations. The latter mechanism is more likely for the low ppm concentrations of pollutants used in the present research. The relatively low yields of Cl⁻ from Ph-Cl and PCB are not unexpected.

It is interesting to note that photocatalytic oxidation (use of TiO_2) of pentachloro-phenol through hydroxyl radical attack proceeds through the para position of the aromatic ring to form chloride (36). Formate and acetate were formed during the latter stages of photooxidation. Useful information may be gained in predicting the outcome of sonochemical reactions by examining the literature on hydroxyl radical oxidation.

Possible mechanisms in the sonochemistry of organochlorine compounds in water are illustrated in Figure 21.

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[1] Ion chromatograph Dionex DX-300, conductivity detector. Analytical method of EPA-300.0

ENHANCED HYDROLYSIS

$$-\overset{|}{\underset{|}{C}}Cl \xrightarrow[H_2O]{)))} -\overset{|}{\underset{|}{C}}OH + HCl$$

REACTION WITH HO·

$$H_2O \xrightarrow{)))} H\cdot + HO\cdot$$

$$-\overset{|}{\underset{|}{C}}\text{-Cl} + HO\cdot \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + HOCl$$
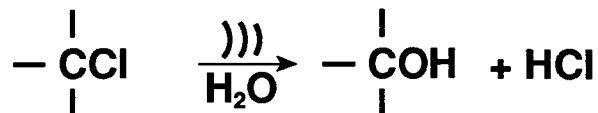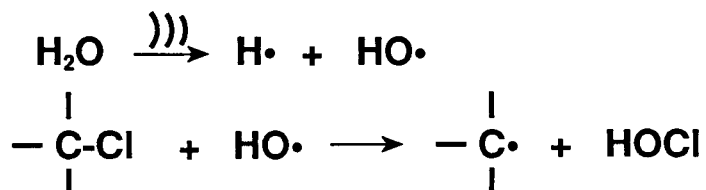
SECONDARY REACTIONS SUCH AS WITH H_2O_2

$$2HO\cdot \longrightarrow H_2O_2$$

$$2 -\overset{|}{\underset{|}{C}}\text{-Cl} + H_2O_2 \longrightarrow 2 -\overset{|}{\underset{|}{C}}\cdot + 2\,HOCl$$

C-Cl BOND CLEAVAGE

$$-\overset{|}{\underset{|}{C}}\text{-Cl} \xrightarrow[H_2O]{)))} -\overset{|}{\underset{|}{C}}\cdot + Cl\cdot$$

__EXAMPLE__

$$CCl_4 + H_2O \xrightarrow{)))} Cl_2 + CO + 2\,HCl$$

$$2\,CCl_4 \xrightarrow[\text{No } H_2O]{)))} C_2Cl_6 + Cl_2$$

REACTION WITH H·

$$H_2O \xrightarrow{)))} H\cdot + HO\cdot$$

$$-\overset{|}{\underset{|}{C}}\text{-Cl} + H\cdot \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + HCl$$
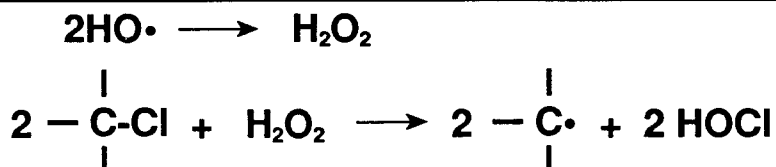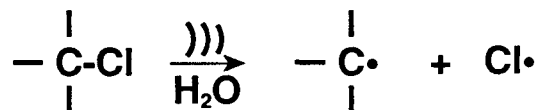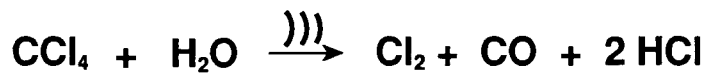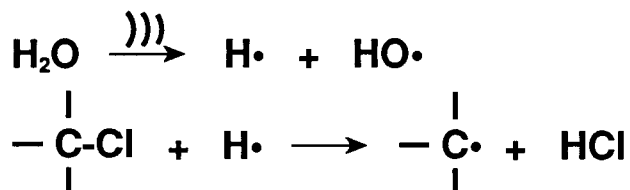
Figure 21. Possible mechanisms in the sonochemistry of organochlorine compounds in water.

The use of sonication in combination with measuring changes in Cl^-, conductivity, and pH in real time is a very simple approach in monitoring organochlorine compounds in water. However, there are many parameters that may affect the rate of Cl^- production. One may not necessarily be able to provide controls in a field situation to optimize the course of sonochemical reactions. For field screening, in situations in which the potential contaminants are known and in which the water system characteristics are understood, optimization may not be needed. Sonication experiments with water from a particular location using potential pollutants of interest should allow an understanding of what to expect in monitoring the well water and what the data obtained from that well water means.

Design of the ultrasound system and choice of equipment options are very important. Such choices impact on the sonochemistry. For example, in the present work, greater changes in Cl^- and ionic conductivity occurred with $CHCl_3$ solutions using the *cup horn*. However, with the *horn probe*, greater changes were observed with CCl_4. This remains unexplained and could not have been predicted without performing the experiments.

The ultimate goal for field measurements is to design an ultrasound system which would allow a probe to be placed into 2" and 4" diameter monitoring wells. Preliminary engineering designs were not considered under the scope of this work, but the possibility of miniaturized ultrasound systems appears feasible. For example, tapered microtip horns are commercially available with diameters of 3.2 mm. These can be used for volumes ranging from 1-2 mL. The design of a cell system compatible for both sonolysis and reaction product measurements present technical challenges, but these do not appear insurmountable.

The work by Toy (27), which showed that as the volume capacity of the same concentration of Cl_3CCH_3 increases, the sonolysis efficiency decreases, has important implications for *in situ* sonolysis cell design. A system is needed with the smallest possible volume allowing solution residence time to be maximized and products to be measured. Special cells would not be needed for situations in which water samples were brought to ultrasound systems emplaced in the back of a field truck or contained in field laboratories. Rapid screening of many samples under such situations is judged to be feasible.

Perhaps the most important chemical parameter which needs to be taken into account in developing ultrasound monitoring methods is pH. Cheung and coworkers (23) recorded pH data in destroying organochlorine compounds in water. The pH decreased rapidly in all cases. In experiments with CH_2Cl_2, the rate of HCl formation seemed to peak at approximately pH 4. It was speculated that pH may be useful in driving the reaction toward HCl as the final product. Results from the present research confirmed the pH decreases. It also appears from our work that the sonolysis of organochlorine compounds is inhibited at higher pHs. As mentioned earlier, bicarbonate and carbonate may act as hydroxyl radical scavengers, thus inhibiting the organochlorine compound decomposition (see the discussion on tap water and reference 19). In any event, more research is needed on real-world samples to better understand the implications of pH for monitoring methods development using ultrasound.

It does not appear that chemical additives need to be considered to achieve organochlorine compound degradation rates for monitoring applications. Sufficient Cl^- was formed under the sonication conditions examined to allow measurement using commercially available Cl^- ISEs. Table 6 contains a summary of Cl^- yields under various sonication conditions for the experiments discussed previously. It is apparent that 5 minutes sonication with the cup horn at 60% pulse mode or 1 minute sonication with the ½" horn probe resulted in close to 3% or higher yields of Cl^-. This

was sufficient to achieve detection with the commercial Cl^- ISE for 37-40 ppm of TCE $CHCl_3$ and CCl_4. Lower concentrations of these compounds should be detectable by increasing the Cl^- yield. The simplest way would be to increase sonication time. Twenty minutes sonication of the $CHCl_3$ solution raised the yield to 25.3%. Optimization of yield was not part of the current research and was not pursued further.

Destruction of hazardous substances, including organochlorine compounds, using ultrasound has been proposed. References were cited earlier. In such cases high reaction yields are important. The application examined in the present research does not require high yields. This should be of advantage in designing ultrasound systems for monitoring purposes that are smaller and require less energy. The presence of some ions such as bicarbonate and carbonate might be expected to inhibit the desired sonochemistry. On the other hand, other ions may increase the rate. For example, I^- was found to accelerate both H_2S oxidation and CCl_4 degradation (7).

Another important question for sonolysis experiments in the real world for monitoring applications relates to the effect of suspended particles. Kotronarou (19) studied the effect of large sand particles (500 μm average) and fine particles (7 nm average) on the sonication rate of sulfide oxidation. Large particles might be expected to *decrease* the rate because of sound attenuation. The fine particles might *enhance* the rate by providing additional nuclei for bubble formation. The effects of sand particles at the sizes and concentrations studied were *insignificant*. This implies that no problems should be encountered in chemical monitoring scenarios.

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Table 6.　　　Summary of Cl^- Yields [%] Under Various Sonication Conditions.

Compound (ppm)	Cup Horn			½" Horn Probe			
	Deionized Water Solutions						
	Sonication time, min & pulse mode (%)						
	5 (60)	10 (60)	20 (60)	2 (const)	2 (60)	1 (Const)	1 (80)
TCE (37)	3.1	10.3	16.8	5.8	3.4	2.7	2.6
$CHCl_3$ (37)	5.6	13.3	25.3	15.2	8.2	7.5	8.2
CCl_4 (40)	4.6	9.7	13.1	22.4	8.9	8.0	6.6
Ph-Cl (94)	-	0.2	1.8	1.3	0.6	1.3	1.8
Tap Water Solutions							
TCE (37)	-	6.7	-	-	-	-	3.0
$CHCl_3$ (37)	-	8.1	-	-	-	-	6.1
CCl_4 (40)	-	10.1	-	-	-	-	6.8
Ph-Cl (94)	-	0.2	-	-	-	-	-

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CHAPTER 7

SUMMARY AND CONCLUSIONS

The objective of this study was to examine the potential of combining sonication with other technologies for monitoring specific classes of organic pollutants in water. The research specifically addressed using ultrasonic processors to decompose organochlorine compounds into ions as a screening method for organochloro pollutants. Changes in Cl^-, conductivity, and pH were measured using commercially available equipment before and after sonication.

The results obtained are very promising. Chloride ion could be detected in aqueous solutions of low ppm CCl_4, $CHCl_3$, and TCE after one minute sonication. The increases of Cl^- were accompanied by increases in conductivity and decreases of pH. The conductivity changes were higher than expected based on measured Cl^-. Ion chromatography of solutions before and after sonication showed that formate ion was also formed. Other ions may have formed as well, but the concentrations were too low to allow their detection relative to formate and chloride. Aromatic and polyaromatic chloro compounds represented by Ph-Cl and PCBs, respectively, did not form chloride ion as readily as did CCl_4, $CHCl_3$, and TCE. Molecular decomposition may have occurred through sonication by other mechanisms but not resulting in high yields of Cl^-. The PCB solutions gave no measurable changes in either Cl^-, conductivity, or pH.

The potential of combining sonication with commercially available measurement technologies for monitoring specific pollutants in water is judged to be high. The results achieved with the organochlorine compounds CCl_4, $CHCl_3$, and TCE serve as proof-of-principle and form a base of information which can be used to develop ultrasound monitoring methods for these compounds. The probability of success of similar approaches in developing ultrasound monitoring methods for other classes of pollutants is judged to be high.

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