



Project Summary

Potential Use of Ultrasound in Chemical Monitoring

Grazyna E. Orzechowska, Edward J. Poziomek, and William H. Engelmann

EPA has been examining the potential of combining sonication with existing measurement technologies for monitoring specific classes of organic pollutants in water. The research specifically addressed using ultrasound (ultrasonic) processors to decompose aqueous organochlorine compounds into ions as a screening method for organochlorine pollutants in water.

The approach in using sonication is applicable to other organic compounds that 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 ion concentrations before and after sonication would be used in monitoring for the pollutants. The organochlorine compounds tested were those usually found as volatile organic compounds (VOCs) at hazardous waste sites. The success with compounds, such as trichloroethylene (C_2HCl_3), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) served as proof-of-principle and forms a rationale for expanding the research to other pollutant classes.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The research described in the full report (based on the Master of Science the-

sis of the first author, G. E. Orzechowska) 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 was present or absent, above or below a predetermined threshold at a given site, or at a concentration within a predetermined range of interest. Screening methods can be used in the field to identify the nature and extent of contamination at individual sites.

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. 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 can be useful to screen samples before confirmatory laboratory analyses. The advantage is in cost savings by limiting the number of samples sent for laboratory analyses.

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 and x-ray fluorescence. One of the clear trends is to miniaturize. Methods that 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 technologies developed as field screening methods are relevant to the monitoring and measurements needs of many U.S. Environmental Protection Agency programs. The need for ground-water monitoring relates to protecting public water supply wells, well fields, springs, and hazardous waste sites as well.

Ground water contains a variety of natural constituents; the various chemical species and concentrations depend on factors such as the specific geochemical environment and the source of the ground water. The major anions that are usually analyzed to indicate general water quality include bicarbonate, chloride, 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 central idea brought forward in this research was to measure the significant parameters such as pH, electrical conductivity, and specific anion concentration before and after sonication of a water sample.

The current research combines sonication with commercially available probes and offers a simple and low-cost approach toward field screening and monitoring.

Description of Ultrasound

Ultrasound is defined as any sound that is of frequency beyond response of the human ear, i.e., generally above 16 kHz. Physical as well as chemical changes are caused by ultrasound and are categorized into two frequency ranges: (1) high frequency or diagnostic ultrasound (2-10 MHz) that causes temporary physical changes in the medium and (2) low frequency or power ultrasound (20-100 kHz) that affects chemical reactivity by cavitation (formation of microbubbles). Average temperatures of 5,000°K and pressures of the order of 1,000 atmospheres are generated by the collapse of cavitation bubbles resulting from the ultrasound power.

Sonochemistry

Sonochemical reactions can be categorized as (1) 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 and (2) secondary reactions involving radicals from primary reactions and other species.

The topics most relevant to this research are homogeneous aqueous sonochemistry

and the sonochemistry of organochlorine compounds.

Principal products from ultrasonic irradiation of water are H_2O_2 and H_2 . The formation of $H\cdot$ and $HO\cdot$ was 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.

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. The sonication of aqueous solutions of organochlorine compounds leads to different products. However, the common product was HCl, as the result of C-Cl bond cleavage, as in $CCl_4 + H_2O \rightarrow Cl_2 + CO + 2 HCl$.

Reviewing the literature on sonochemistry of organochlorine compounds 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 chloride ion, conductivity, and/or pH as a way of monitoring for the presence of the compounds in water.

Research Design Elements

The following materials and equipment were used:

- Four VOC analytes (3-40 ppm) CCl_4 , $CHCl_3$, C_2HCl_3 , C_6H_5-Cl
- One polychlorinated biphenyl (PCB) analyte:
(5-55 ppm in methanol- H_2O with 1% surfactant)
- Ultrasound systems with cup-horn and 1/2-inch diameter horn-probe
- Commercially available probes such as:
ion selective electrodes (ISEs), conductivity cells, and a pH electrode

The following parameters were investigated:

- Sonication times (1-90 minutes)
- Continuous vs. pulsed ultrasonic
- Sample temperatures (constant 30°C)
- Sample volumes (8 - 15 mL)
- Water sources (deionized, tap, well)

Summary and Conclusions

The common denominator in the aqueous sonochemistry of organochlorine com-

pounds is HCl. However, the mechanism and rate of the reaction may differ markedly depending on the conditions under which the sonication was performed. Elucidation of reaction mechanism was not part of the objectives of the present work. However, nothing was encountered that 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 formate ions ($HCOO^-$) were detected as well. However, the formate ions may have originated from the sonochemistry of the methanol solvent. Another possibility might be the oxidation of methanol by secondary sonochemistry reaction products such as chlorine (Cl_2) or hypochlorite ion (OCl^-).

Use of ultrasound in combination with chloride ISE appears more applicable to monitoring nonaromatic organochlorine compounds such as C_2HCl_3 , $CHCl_3$ and CCl_4 . As discussed in the full report, relatively low yields of chloride ion were obtained from chlorobenzene (Ph-Cl) and PCBs. Low yield of chloride ion 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. Such a reaction scheme, though applicable to *decomposition* of Ph-Cl and PCBs, does not lead to the immediate formation of chloride ion.

Sufficient chloride ion was formed under the sonication conditions examined to allow measurement using commercially available chloride ISE. It was apparent that 5 minutes sonication with the cup horn at 60% pulse mode or 1 minute sonication with the 1/2" horn probe resulted in close to 3% or higher yields of chloride ion. This was sufficient to achieve detection with the commercial chloride ISE for 37-40 ppm of C_2HCl_3 , $CHCl_3$ and CCl_4 . Lower concentrations of these compounds should be detectable by increasing the chloride-ion yield.

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 the work that the sonolysis of organochlorine compounds was inhibited at higher pHs. Bicarbonate and carbonate may act as hydroxyl radical scavengers, thus inhibiting the organochlorine compound decomposition. In any event, more research is needed on real-world samples to better understand the implications of pH for monitoring methods development using ultrasound.



Conductivity changes were higher than expected based on measured chloride ion. Ion chromatography of solutions before and after sonication showed that formate ion was produced by the sonication. 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 C_2HCl_3 . Molecular decomposition may have occurred through sonication by other mechanisms but did not result in high yields of chloride ion. The PCB solutions produced no measurable changes in chloride ion, conductivity, or pH under sonication.

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 C_2HCl_3 serve as proof-of-principle and form a base of information that can be used to develop ultrasonic monitoring methods for these compounds.

Grazyna E. Orzechowska is a graduate student at the University of Nevada-LV, Las Vegas, NV 89154-4009 and Edward J. Poziomek is with the Harry Reid Center for Environmental Studies, University of Nevada-LV, Las Vegas, NV 89154-4009. The EPA author, William H. Engelmann, (also the EPA Project Officer, see below), is with the Environmental Monitoring Systems Laboratory, Las Vegas, NV 89193-3478.

The complete report, entitled "Potential Use of Ultrasound in Chemical Monitoring," (Order No. PB94-188190; Cost: \$17.50, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Las Vegas, NV 89193-3478*

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45268

Official Business
Penalty for Private Use \$300

EPA/540/SR-94/502

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35