

# FINAL REPORT

U.S. Department of Energy

## **The Sonophysics and Sonochemistry of Liquid Waste Quantification and Remediation**

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### 3. Executive Summary

The objective of this proposal was to study the physics and chemistry of acoustic cavitation--that is, the formation, growth, and violent collapse of bubbles--for its eventual application as both an analytical tool for toxic waste identification and monitoring, as well as a cost-effective technique for liquid-waste-contaminant remediation. We proposed an in-depth and comprehensive study, involving some of the leading sonophysics/sonochemistry research groups in the country, to study and to optimize the parameters associated with acoustic cavitation as applied to environmental applications. Our specific aims and accomplishments were:

- *To design and to undertake a series of experiments to elucidate the fundamental physics of sonochemical reactions.* Knowledge of the mechanism for sonochemical reactions is important in order to optimize sonochemical processes. Sonochemical activity appears to be confined to the bubble interior, and to a small region surrounding the bubble. Thermal mechanisms (heating, as opposed to electrical, etc.) appear to be the most important mechanism for sonochemical degradation.
- *To undertake a broad theoretical study of the fundamentals of acoustic cavitation and nonlinear bubble dynamics that would both support the experimental research and lead to models that would permit inductive examination of new techniques.* In association with colleagues worldwide, chemical reactions have been incorporated into theoretical models.

- *To examine the potential for the use of sonoluminescence (light emission associated with acoustic cavitation) to quantify and to monitor the presence of alkali metals and other elements in waste liquids.* Sonoluminescence has been used to quantify alkali metals in laboratory settings.
- *To determine the optimal acoustical parameters in the use of sonochemistry for liquid-waste-contaminant identification and remediation.* We have found that optimization depends on the particular systems design. However, we note that parameters such as hydraulic pressure spikes dramatically influence sonoluminescence activity.
- *To design and to evaluate more effective sonochemical reactors.* Typical reactors use large and bulky ultrasonic horns in batch reactor designs. We have found a small, efficient system that operates at 230 kHz, which appears to generate much more sonoluminescence than a wasteful horn system.
- *To evaluate the efficacy of sonochemistry for liquid waste quantification and/or remediation by undertaking a series of experiments at a ‘test bed’.* Unfortunately, chemical degradation of mercury, our primary interest, did not develop to a point that validated test bed measurements.

The goals of this broad-based program focussed on understanding some basic physics and chemistry associated with intense cavitation, focusing on environmental remediation efforts. Our accomplishments include designing a scaled-down, but efficient version of ultrasonic horn systems, quantifying alkali metal contaminants in laboratory settings, and finding novel optimization parameters for increasing quantifiable parameters. Perhaps the most important

accomplishments of our program involved the training of several graduate students in environmental remediation science.

#### **4. Research Objectives**

A variety of investigators have demonstrated the utility of the sonochemical reactor; for example, the natural half-life of parathion, a pesticide of widespread use, is 108 days. Under ultrasonic irradiation at 20 kHz in deionized water, all of the initial parathion is degraded in less than two hours; ultrasonic irradiation in an aqueous solution containing the highly toxic pentachlorophenate (PCP) results in the almost complete degradation of PCP in about 100 minutes; researchers have also found that acoustic irradiation of chlorinated C1 and C2 volatile organic compounds (VOCs) resulted in a VOC destruction of up to 99.9% in less than an hour.

Although sonochemistry holds such high promise for use in waste contaminant remediation, the principal mechanism that leads to chemical degradation, acoustic cavitation, is a complex and difficult to understand phenomenon. Chemists who are performing experiments in sonochemistry know little of acoustic cavitation and how to use it in an optimal way; physicists who know something about cavitation bubble dynamics don't understand the chemistry. Indeed, the President of the European Society of Sonochemistry has deemed this field a "black art", whose progress is mainly empirical, and which will lack credibility as a mature science until multidisciplinary teams involving both physicists and chemists examine the problem from a fundamental viewpoint. We proposed a systematic study of the phenomenon of acoustic cavitation as it applies to sonochemistry, and especially as it applies to waste contaminant remediation.

We established a multidisciplinary team involving internationally recognized experts in the field of acoustic cavitation from the Applied Physics Laboratory and the Center for Process Analytic Chemistry, at the University of Washington; We were joined by experts in cavitation and sonochemistry from Melbourne, Australia, in a collaboration in which a scientist from the University of Melbourne spent several weeks in our lab performing experiments and then continued the research back in his home university. We were also joined by researchers in Brussels, Belgium. A graduate student there spent three months (at their expense) in our lab, performing sonochemical measurements. He will graduate in January, 2001.

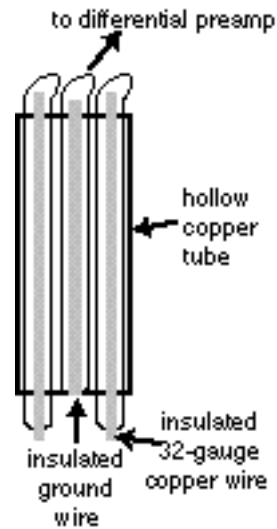
## **5. Methods and Results**

*Electrical signals from cavitation:* The first project to be described involves an experiment to determine the basic mechanism for cavitation-chemistry, or sonochemistry, in particular the light-emission process: What is the fundamental mechanism for light emission from cavitating bubbles? There are many theories, but most fall into one of two camps. The first is that during the bubble collapse, the interior heats up quazi-adiabatically, and light emission is a result of an incandescence. The second camp claims that the light-emission process is electrical. During the bubble collapse, there is an electrical discharge that results in light emission. Chemical degradation optimization depends greatly on which mechanism is dominant. We proposed to look for an electrical signal that would be generated if discharges were involved.

We designed and built two cavitation systems to explore the electrical pulse hypothesis. In addition, we designed and built several probes to detect an electrical pulse. The probes were differential probes, since a single probe acts as an antenna. We hoped to remove a majority of the

common mode signals using the differential probe. A schematic of the probe is illustrated below. Each probe consisted of a set of insulated 32-gauge copper wire surrounded by a 1-mm hollow copper tube that was grounded to the rest of the system. The probe tips were separated by approximately 0.5 mm. The probes were connected to a commercial high speed differential amplifier with a gain of 10. The output was then sent to an oscilloscope for recording the data.

*Fig. 1. A schematic of the differential probe used to look for electrical signals from a cavitation field. The probe consists of two insulated 32-gauge wires connected to a differential amplifier (INA106KP-ND). A third wire, connected to a hollow copper tube surrounding the probe tips, was used as a common signal ground. The output of the  $\times 10$  differential amp was sent to an oscilloscope for recording and analyzing the signal. The diameter of the system was approximately 1 mm. Silver paint was used to coat the tips, except at the extreme edges, to decrease the noise level.*

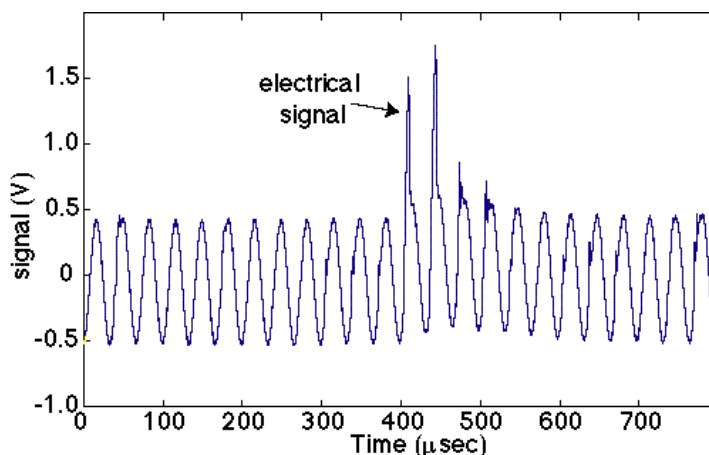


A similar probe was constructed to observe an electrical signal (if any) from a single cavitating bubble; however, in order to position the probe close to the bubble, the probe tips were oriented such that the tips faced each other, with a separation of approximately 1 mm.

Our experiments showed that one does get an electrical signal from a cavitation field; however the probe *must* be in contact with the field in order to detect the signal. Figure 2 illustrates the electrical pulse we receive from a probe that comes in contact with a well-defined cavitation field consisting of about a hundred bubbles. The sinusoidal signal is direct electrical coupling with the driving transducer (operating at about 30 kHz). The large spikes that occur around 400  $\mu$ s are the result of the probe coming in contact with the cavitation field. Note that these spikes

are positive; we can also obtain negative spikes (not shown here). We believe that these signals are directly a result of a bubble coming in contact with the probe.

*Fig. 2. A differential probe is placed near a well-defined cavitation zone. Electrical coupling with the driving transducer gives rise to the observed sinusoidal variations, and correspond to the driving frequency. If the probe comes in contact with the cavitation zone, we observe electrical spikes superimposed on the sinusoidal signal.*



One possible mechanism for the observed spikes is that the collapsing bubble actually pushes against one of the probe tips, causing a change in capacitance between the differential probe tips. If the tips move closer together, one gets a unipolar, say, positive pulse. If the probe tips are pushed apart, the unipolar pulse becomes negative. We do not expect, nor have we observed, an electrical pulse from a single cavitating bubble, unless the bubble comes in direct contact with the probe tip. This evidence suggests that if there is an electrical pulse emanating from bubbles, it is weak. Another possibility is that charges from the bubble are being conducted to the probe tip during contact (it is known that bubble possess a negative charge).

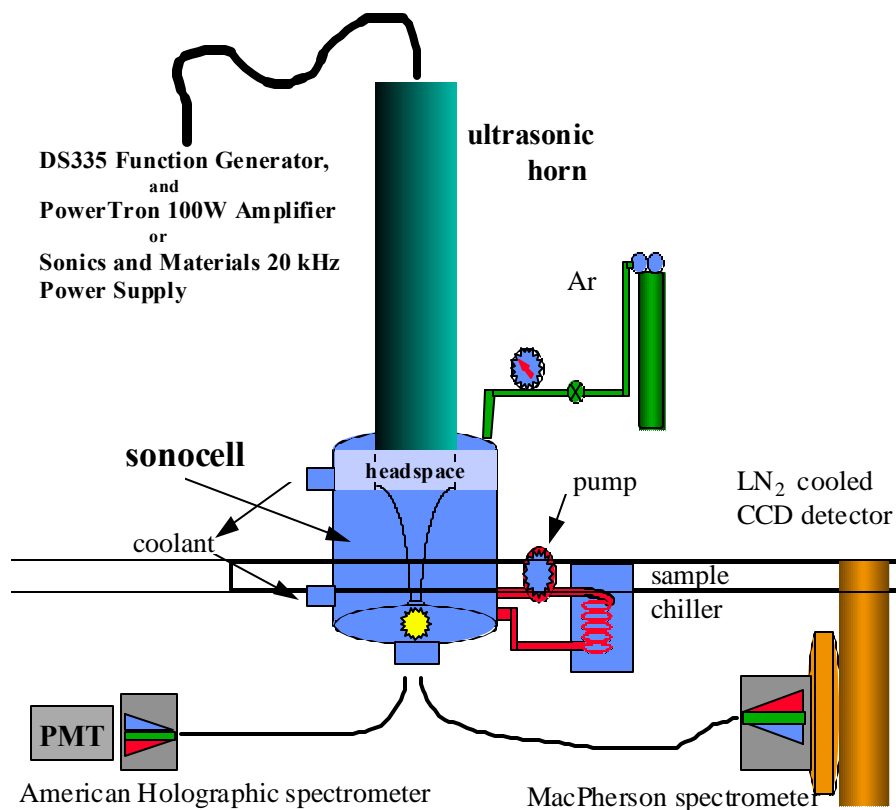
Near-IR spectroscopy: A second project involved performing near IR spectroscopy. Two cells were designed for multiple bubble sonoluminescence (MBSL) spectroscopy experiments. The first cell is designed around a 20 kHz acoustic horn with replaceable titanium tips from Sonics & Materials (Fig. 3). The horn is squeezed into a stainless steel cell via O-rings and a compression ring, to seal the cell up to 100 psi for pressure experiments. The cell is thermostated by



circulating coolant in a jacket, as well as flowing the cell fluid (at 4L/min.) through a temperature control bath. Several ports are located on the cell for gas ports (one for headspace, another for bubbling), a pressure transducer, a thermocouple, a needle hydrophone, and a septum port for addition or withdrawal of samples. The total volume is approximately 80 mL with a 10 mL headspace. Directly opposite the horn tip is a 2 cm quartz window against which a fiber optic bundle is placed. Light collected through the fiber optic is imaged onto one of several detection systems, including a liquid nitrogen cooled Princeton CCD array, directly onto a room temperature PMT, or through an ISA double monochromator onto the PMT. This arrangement allows for great versatility and expandability.

The second cell is more useful for high frequency (from 100 kHz to 1 MHz ) experiments. The transducer is located at the bottom of 1.5 inch diameter teflon cylinder, and isolated from the sample matrix by a thin teflon sheet. Opposite the transducer is a 2 cm window in a stainless steel lid through which light is collected in the same manner as the above cell.

## 20 kHz MBSL Instrument Layout

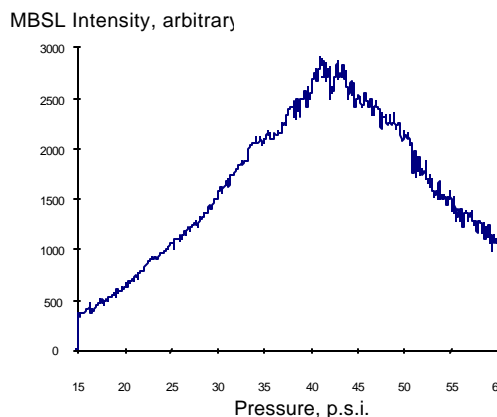


*Fig. 3. Experimental apparatus for spectroscopy studies. This system allows us to change gas, liquid, and static (or hydraulic) pressure, at a constant temperature.*

An important factor in achieving good spectral results and efficient sonochemistry for MBSL is efficient cavitation with strong light output. Much of our progress in this area to date involves increasing the sonoluminescence output from our systems. Several techniques have been designed with this in mind. First, it has been observed that an increase of up to two orders of magnitude may be achieved by simply increasing the static pressure over the cavitating solution (see Fig. 4). With aqueous solutions a bimodal increase in light emission occurs with a local maximum at 30 psi. and a global maximum at 50 psi. With organic systems (such as heptane) a single maximum is observed at approximately 40 psi. which is 100 times brighter than at atmospheric pressure. The maximum in intensity is not well understood, since it is well known that increasing the ambient pressure should make cavitation more difficult, and thereby decrease

the overall intensity from MBSL. We note that the decreasing intensity that we observe above 50 psi is probably due to the difficulty in generating cavitation at high static pressures.

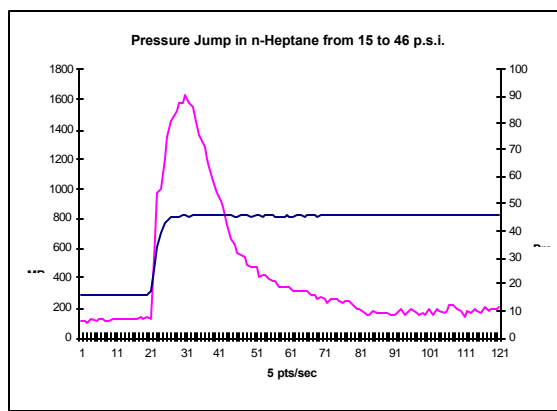
*Fig. 4. In this figure we show how the light intensity from MBSL varies as the static pressure is quazi-statically changed from ambient conditions of 1 atm (15 psi) to 4 atm (60 psi). We are able to achieve large increases in the total light output from many systems, in this particular case, heptane. The peak in intensity is not well understood, since it is well known that increasing the ambient pressure should make cavitation more difficult, and thereby decrease the overall intensity from MBSL.*



Another one to two orders of magnitude in intensity may be achieved by something that has come to be known in our labs as pressure jumping. In a typical experiment the pressure is quickly increased from atmospheric pressure to somewhere between 1.5 and 3 atmospheres. The jump occurs in approximately 1 second and is limited by the equilibrium time of flow from a 3 liter gas reservoir between the argon tank and the cell. The result of such an experiment is an immediate increase in sonoluminescence intensity, followed by a period of unstable, yet comparable intensity, ending with a return of the light level to the baseline level for that given pressure (see Fig. 5). This period of enhanced cavitation may last from 10 seconds to several minutes, depending on the solution, analytes, temperature, and final pressure. Similar results have been observed with frequency scanning and jumping, and remains to be further explored. So far, we have performed experiments in aqueous solutions of salts, with low concentrations of organics, organic solutions with low concentrations of water, and with pure organic systems. Each system has a unique set of physical properties that must be incorporated into a model for

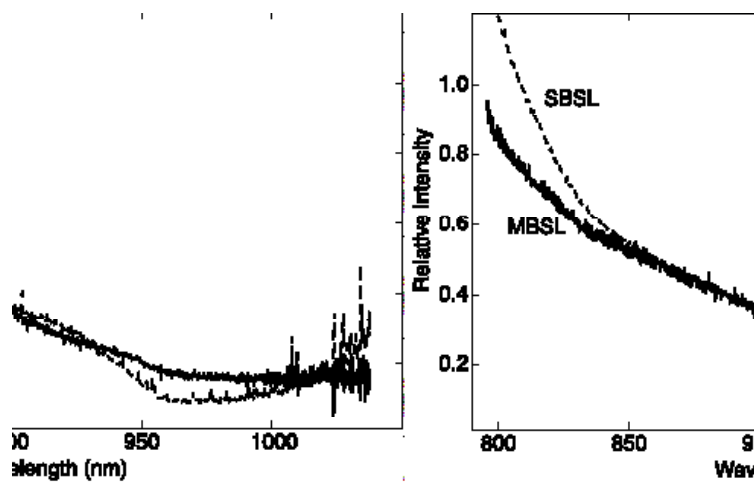
maximizing sonoluminescence output. From these experiments a paper has been published in Physical Review E titled "Cooperative Effects in Sonoluminescence." We feel that these results are very promising for generating more intense cavitation for liquid waste remediation. Although we have yet to fully understand the results, our coordinating work with a single-bubble cavitation system may shed light onto this matter. At present, we do not observe a similar behavior from single-bubble systems.

*Fig. 5. An abrupt pressure jump (from 15-46 psi) is initiated in n-heptane. The total SL intensity increases by a factor of 16 in this case. We added trace amounts of thiophene, a heterocyclic, since it is well known to be very difficult to destroy with high intensity ultrasound. By increasing the cavitation intensity, here monitored as light production, we may be able to help degrade cyclic hydrocarbons in a more efficient manner.*

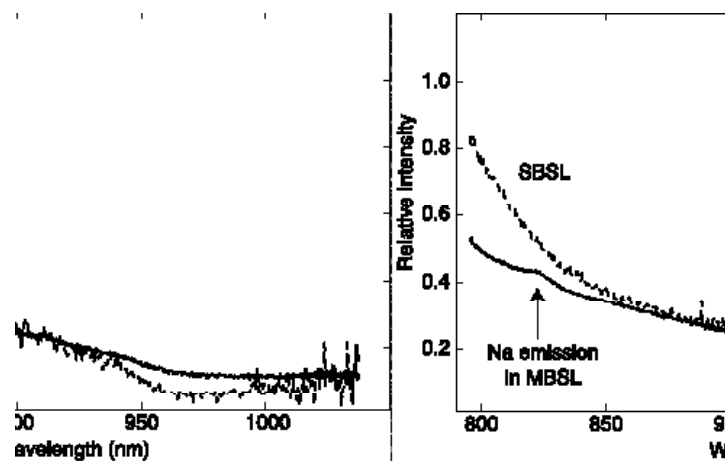


The results of our near-IR experiments is shown in Figs. 6 and 7. In Fig. 6, we show that near-IR spectra can be obtained from both MBSL and SBSL. In Fig. 7 we show how a small presence of NaCl can affect the spectra of MBSL. Importantly, we observe the sodium emission originating from the 3d-3p transition near 819 nm. As far as we know, these are the first known results for sonoluminescence emission in the near-IR.

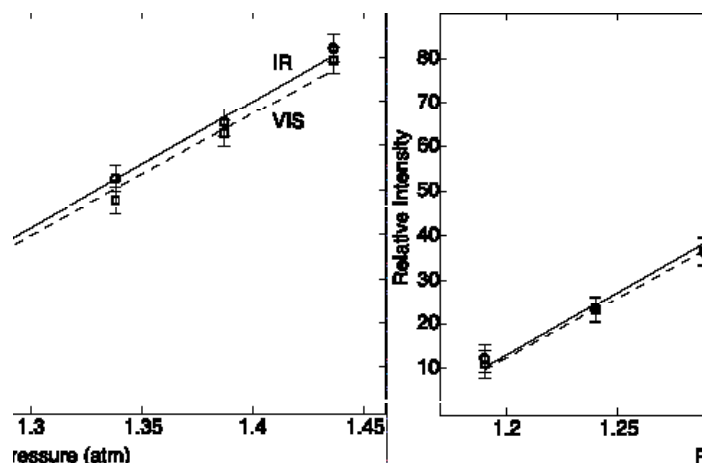
In Fig. 8, we show how the integrated light intensity varies for both the visible and near-IR. As expected, the light intensity varies linearly with pressure.



**Figure 6.** Near-IR spectra collected for SBSL (dashed line) and MBSL (solid line).

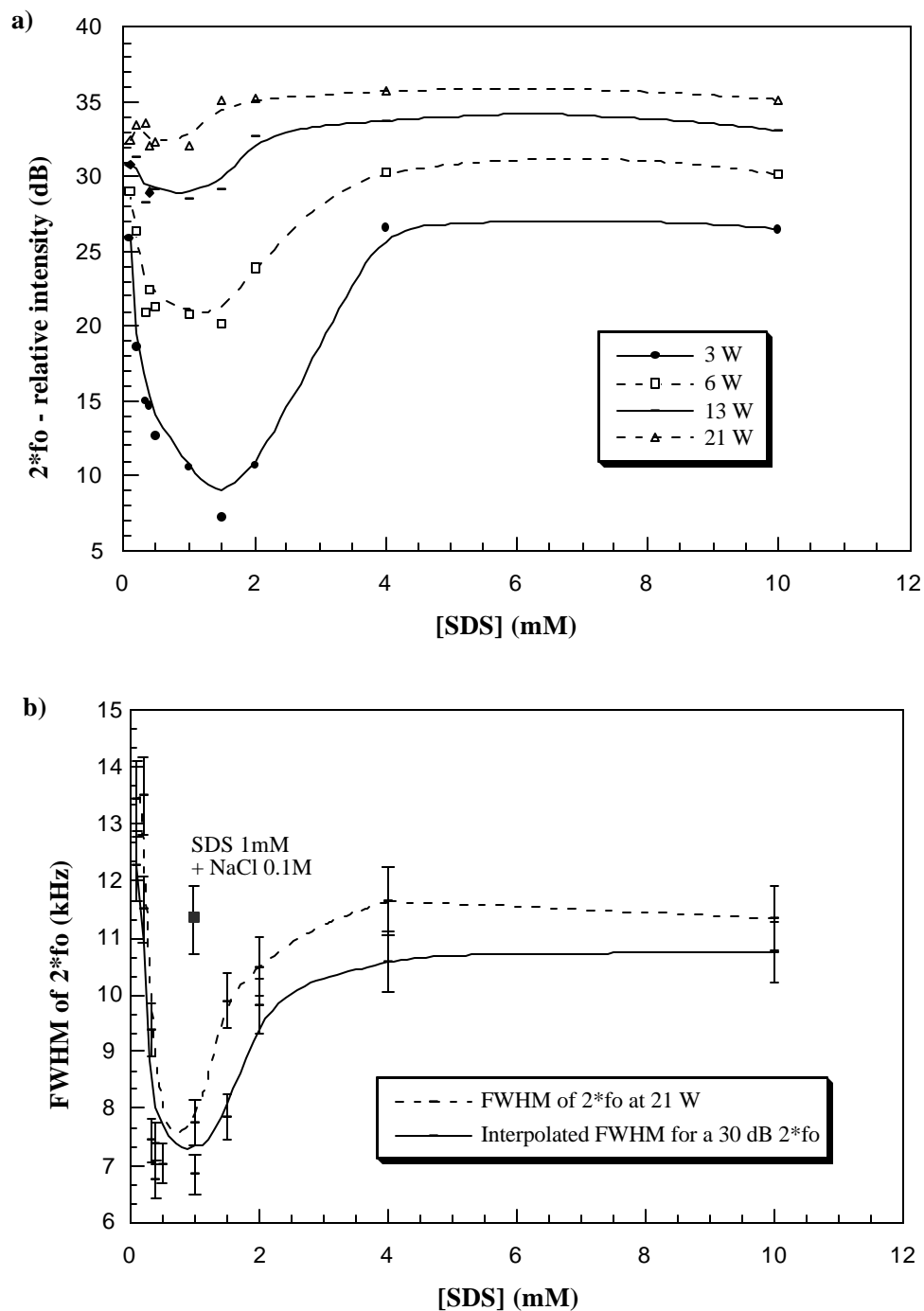


**Figure 7.** Near-IR spectra in 0.1 M NaCl of SBSL (dashed line) and MBSL (solid line).

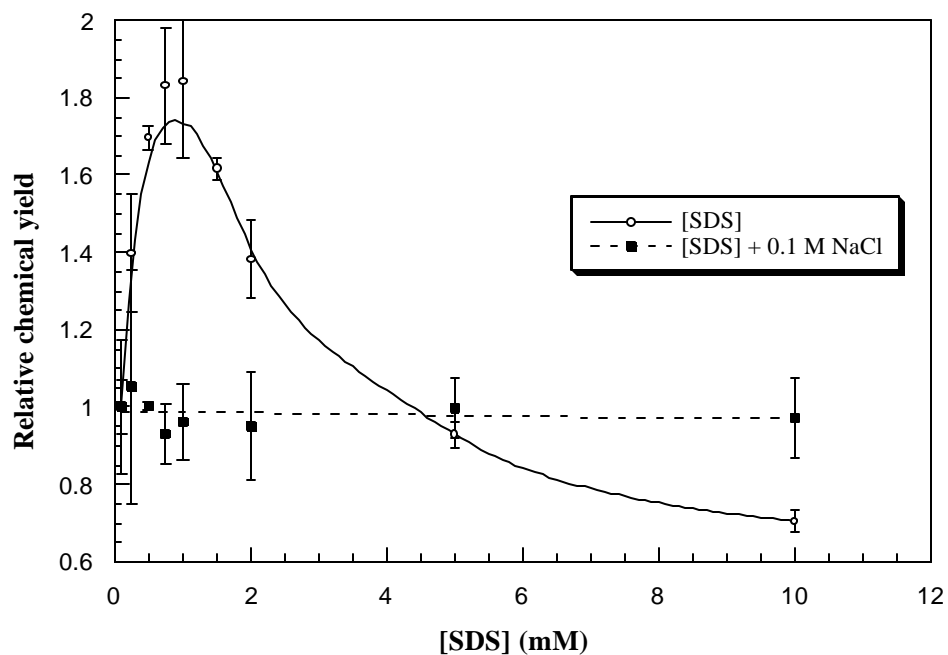


**Figure 8.** The integrated light intensity in the near-IR (solid line) and UV-visible intensity (dashed line) are shown as a function of drive pressure. The lines are a linear least squares fit to the actual data points shown. Near-IR data shown as circles, UV-visible data shown as squares. The near-equal slopes are a coincidence, and depend on the gain for each receiver.

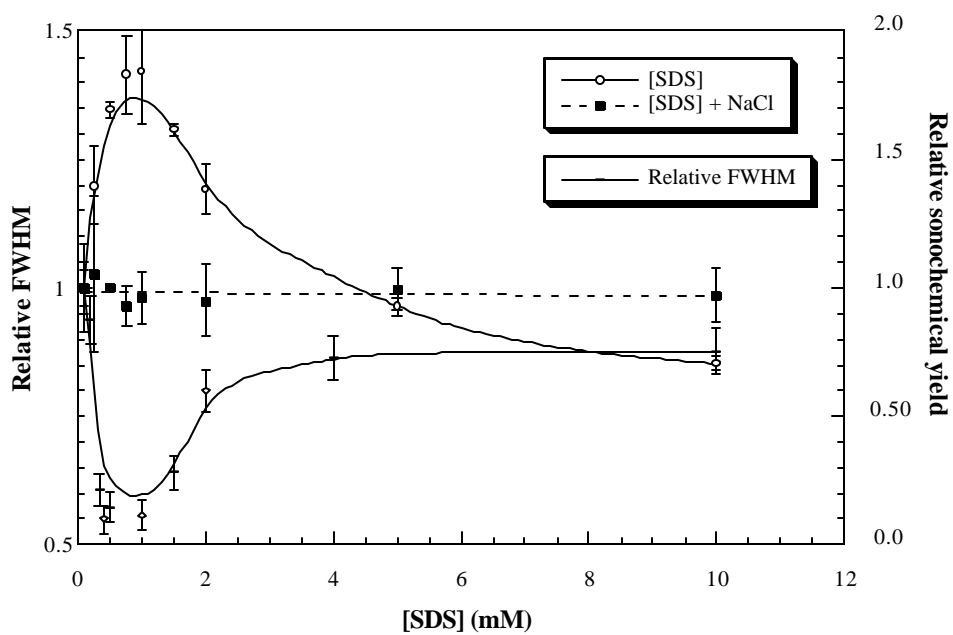
Correlation between cavitation noise and light/chemical activity: Monitoring sonochemical activity is difficult, since not all activity can be correlated with acoustic noise emissions or light emissions. However, we have found that we can manipulate the cavitation field by adding a small amount of sodiumdodecylsulfate (SDS). Upon addition of this surfactant, the cavitation field apparently becomes very homogeneous and more light is emitted and sonochemical and acoustic emissions can be correlated. The results of these studies are shown in Figs 9-11. We believe that the SDS coats the bubbles with a negative charge, preventing coalescence, and thus enhancing sonochemical activity.



**Figure 9.** (a) The FWHM of the second harmonic of the acoustic spectrum for various power levels. (b) Interpolated values take into account variations due to power levels.



**Figure 10.** Sonochemical yield with SDS, and with NaCl.

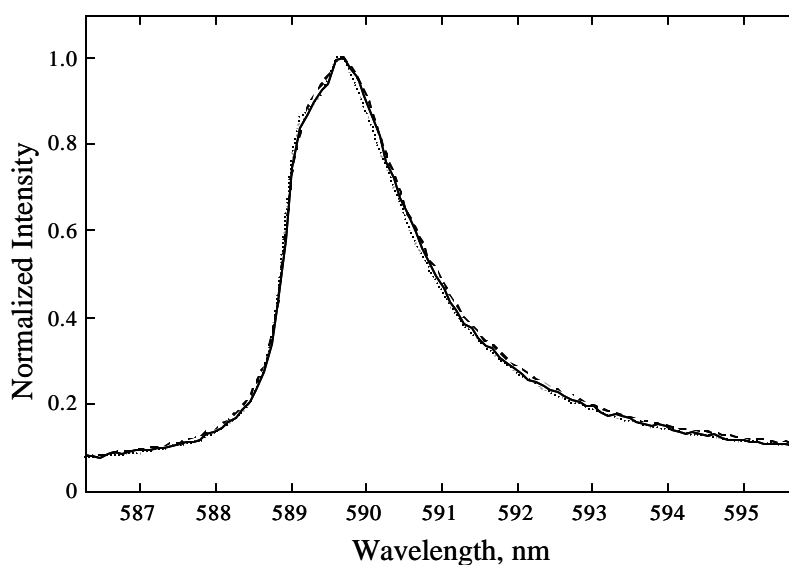


**Figure 11.** Sonochemical yield correlated with acoustic FWHM data.



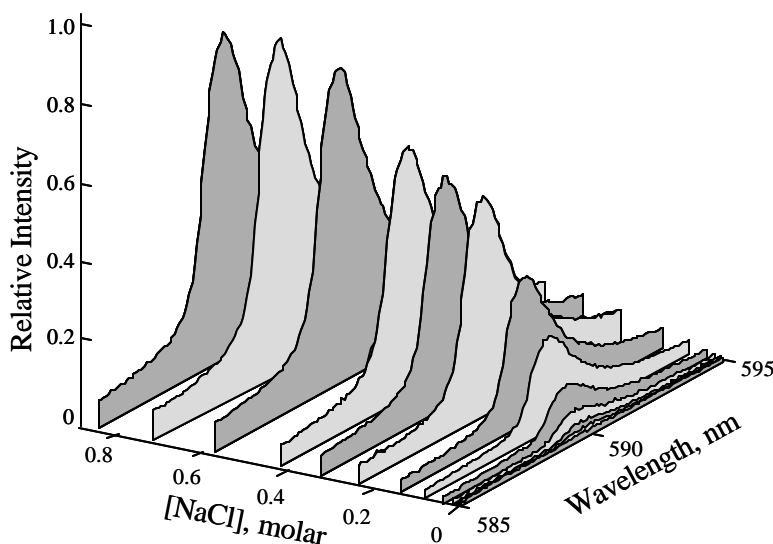
*Quantification of alkali metals using sonoluminescence:* The goal of the research, detailed in the dissertation attached as Appendix A, was to develop a technique using sonoluminescence to simultaneously quantify sodium and calcium in a flowing stream format. The specific aims were to:

- Characterize sonoluminescence emission from model chemical systems containing concentrations of sodium and calcium relevant to chlor-alkali and calcium chloride production processes. An important aspect of this research was to determine if the sonoluminescence intensity was repeatable for a given system, even when the optical probes were removed and replaced several times (as might happen in a remediation environment). Figure 12 shows that sonoluminescence can be very repeatable.



**Figure. 12.** Spectra of 1.0 M NaCl are shown from three different solutions on different days. The optical train had been moved and reassembled between each run (as a consequence of sharing equipment), and the spectra have been normalized to equal intensity to account for differing integration times.

When alkali and alkaline earth salts are present with a noble gas in a sonoluminescing solution, the cations are reduced to neutral species, which then emit atomic spectral lines. The shape and intensity are determined by the concentrations of the salts, as well as other controllable parameters. Data is presented demonstrating that MBSL from alkali salt solutions can be modeled over a broad range of concentrations and used for quantitative analysis. Information from changes in shape and intensity of the emission lines over a wide range of salt concentrations can be used to construct Partial Least Squares (PLS) models. These models can be used to determine salt concentration from as low as parts per billion through saturation. An example of alkali metal emissions is shown in Fig. 13. Further experimental details can be found in Appendix A.



**Figure 13.** Sodium Doublet Emission Below 1 Molar. The general peak shapes of sodium change little with concentration below 1 molar. The intensity increases logarithmically.

- Develop and build a prototype cavitation flow cell with integrated cavitation transducer and light collection capabilities in an on-line process stream format. Such a device is needed for

in situ analysis of DOE contaminants. Details regarding novel flow-through cells are provided in Appendix A.

## **6. Relevance, Impact and Technology Transfer**

*a. How does this new scientific knowledge focus on critical DOE environmental management problems?* The focus of this project was to better understand the basic physics and chemistry of high of high-intensity ultrasound for chemical waste remediation.

*b. How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks and meet DOE compliance requirements?* We have discovered several factors that can be used to optimize remediation processes using high-intensity ultrasound. Specifically, pressure-spiking and surfactant additives can greatly enhance sonoluminescence, and may also enhance waste remediation efficiency.

*c. To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide-ranging applications and the timeliness to meet needs-driven applied technology development?* Our efforts have focussed on understanding the physics and chemistry of ultrasound remediation efforts, and thus optimization and the efficiency of this new technology can be enhanced.

*d. What is the project's impact on individuals, laboratories, departments, and institutions? Will results be used? If so, how will they be used, by whom, and when?* Our results are in the process of being published, and may be used by others. However, since our funded effort was not continued, the application of our findings may or may not be continued by others.

*e. Are larger scale trials warranted? What difference has the project made? Now that the project is complete, what new capacity, equipment, or expertise has been developed?* We have learned that individual sonochemical reactor systems have specific optimization parameters. If large scale systems are developed, they can (and should!) be optimized for their individual use. We have the expertise to optimize such systems, if developed.

*f. How have the scientific capabilities of collaborating scientists been improved?* Due to our collaborative efforts, we have significantly improved the capabilities of each collaborator. The individual expertise and equipment from each lab can combine to form outstanding technical expertise that can be used in development of waste remediation systems.

*g. How has this research advanced our understanding in the area?* One of the most important findings from our study is that cavitation bubbles can be optimized for sonochemical activity, and that surface effects are important for this optimization.

*h. What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?* Scientifically, the hurdles involve optimization and efficiency of power usage. Programmatically, the hurdle of vertical integration from basic research to advanced development must be overcome.

*i. Have any other government agencies or private enterprises expressed interest in the project?*

*Please provide contact information.* None, so far.

## **7. Project Productivity**

The project was very productive. Our goals were very ambitious, yet we managed to complete almost every task.

## **8. Personnel Supported**

To some extent, the following personnel were supported by this grant: T. J. Matula, L. A. Crum, C. Frensley, A. Robinson, M. Ashokkumar, W. MacNamara, and L. Burgess.

## **9. Publications**

T. J. Matula, et al., ARLO, **1**, 13-17 (2000).

T. J. Matula and L. A. Crum, Sonochemistry and Sonoluminescence, ed. L. A. Crum (Kluwer Academic Publishers 1999) 145-158.

T. J. Matula, Phil. Trans. R. Soc. Lond. A. **357** 225-249 (1999).

T. J. Matula and L. A. Crum, Phys Rev. Lett. **80**, 865-868 (1998).

D. Kuhns, A. Brodsky, and L. Burgess, Phys. Rev. E, **57**, 1702-1704 (1998).

A. Brodsky, J. Mathematical Physics, **38**, 5127-5142 (1997).

## **10. Interactions**

Our collaborators include K. Suslick, U. I., Champaign-Urbana, W. Moss, LLNL, and F. Greiser, U. Melbourne, AU.

## **11. Transitions**

None that we are familiar with.

## **12. Patents**

none

## **13. Future Work**

Much work needs to be done to optimize specific usage systems, however, we have been unsuccessful in obtaining funding for this research.