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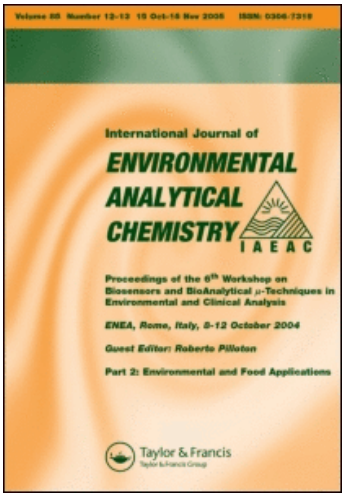

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APPLICATION OF ULTRASOUND TO DISSOLUTION OF ENVIRONMENTAL SAMPLES FOR ELEMENTAL ANALYSIS

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The use of ultrasonic energy to bring biological matrices into solution was studied. Sonication of aqueous suspensions of biological samples in 1% H_2O_2/0.5 M H_2SO_4 mixtures with a commercial 20-kHz probe yielded complete dissolution for a range of materials within 40 min. The physical and chemical processes occurring during sonication were investigated. Analysis of NIST SRM's oyster tissue and pine needles for Cd, Sr, Cu, Zn and Mn by ICP-OES showed good agreement between experimental and certified values. Advantages of the method include shortened dissolution times and lower reagent requirements.

KEY WORDS: Ultrasound dissolution, biological analysis, trace metal determination, ICP-OES, sample dissolution.

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INTRODUCTION

The environmental analysis laboratory of the 1990's is under tremendous pressure to meet the challenges placed on it by the diversity and sheer numbers of samples that have to be processed. To reduce this pressure, methods of analysis need to be improved in terms of economy and speed.[1-3]

Analysis of biological materials for trace elements by atomic spectroscopy[4] requires that the material be first dissolved without loss or contamination[5]. The traditional approach of dissolution in concentrated acids on hot plates is slow and tedious. It also makes dissolution the most error-prone step in the analysis, because contamination is likely to be introduced at this step, especially if large quantities of acids are required to complete the dissolution procedure.

With the exception of microwave techniques,[6-8] methods of sample dissolution have not changed much over the past 4 decades or so. The ultrasound procedure described in this paper was developed with the goal of being faster, less contaminating, and less hazardous than alternative techniques.

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MATERIALS AND METHODS

Ultrasound equipment

A commercial titanium probe, originally designed for biological cell disruption, was used. The probe is powered by a 20 kHz/600 W ultrasonic processor (Ace Glass Inc., NJ, USA), and uses a piezoelectric lead zirconate titanate ceramic transducer to deliver approximately 20 Wcm^{-2} ultrasonic waves. Decompositions were carried out in a flat-bottomed cylindrical borosilicate vessel (11 cm long, 3 cm inner diameter, 80 mL capacity). The vessel was mounted on a laboratory jack, and irradiations were performed inside a steel enclosure lined with sound-deadening styrofoam. The arrangement is shown schematically in Figure 1.

Reagents and solutions

Ultrapure water (18.3 MΩ.cm) was prepared by distillation, followed by passage through a Barnstead D4751 NANOpure® ultrafiltration system (Dubuque, IA, USA). Working metal standards for ICP-OES were prepared by dilution of 1000 µg/mL stock solutions

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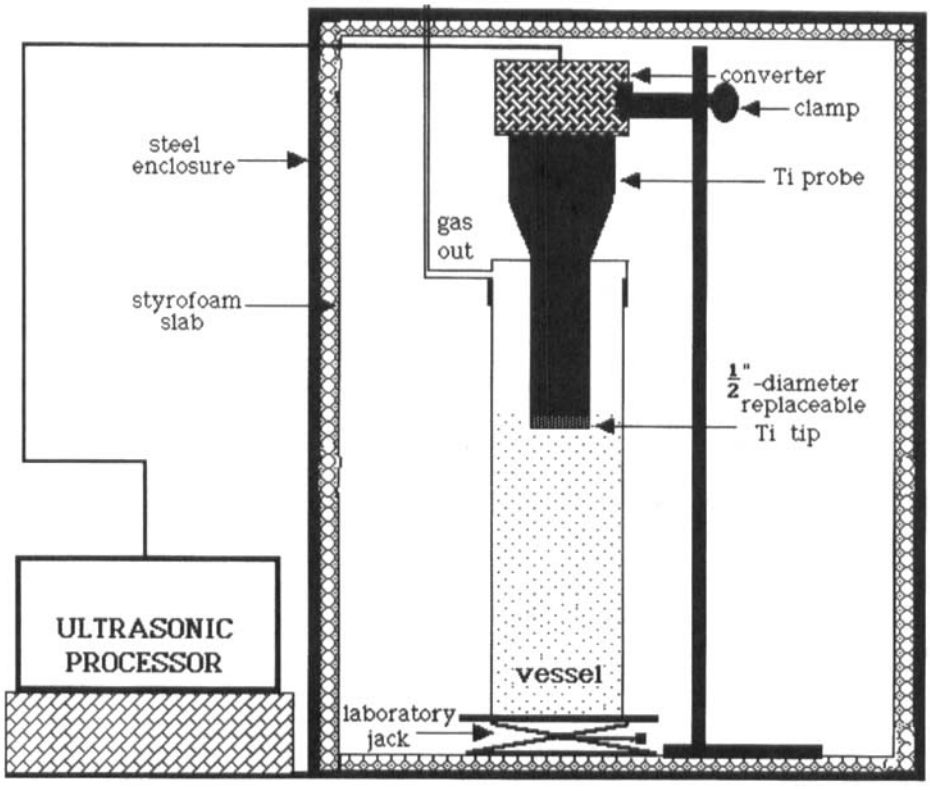

Figure 1 Apparatus used for dissolution of environmental samples.

of Cd, Sr, Cu, Fe, Zn and Mn (Fisher Scientific Co.). KI, H_2SO_4 and H_2O_2 were analytical grade (BDH Chemicals, Toronto, Canada). Reference materials SRM 1566 (Oyster Tissue) and SRM 1575 (Pine Needles) were obtained from National Institute of Standards and Technology (Gaithersburg, MD, USA).

Measurement of H_2O_2

Ultrasound-produced oxidizing species were determined iodimetrically by addition of excess KI and measurement of the I_2 produced with a Hewlett-Packard Model 8451A photodiode array UV-vis spectrometer at λ_{max} = 352 nm.

Sonication procedure for powdered samples

Samples of approximately 100 mg dry material were accurately weighed into the dissolution vessel. Approximately 50 mL of water was added, followed by 2 mL of 30% H_2O_2 and 2 mL concentrated H_2SO_4. A laboratory jack was used to position the vessel so that the tip of the probe was 3 mm below the surface of the solution (about 8 cm above the bottom of the vessel). The timer and power level on the processor were then set to 40 min and "100%" respectively. The blank was prepared by sonicating the same quantities of reagents, minus the sample, at the same power and for the same duration. All sonications were performed in continuous (non-pulsed) mode. At the end of the sonication period, the Ti probe was rinsed, and the solutions were diluted to 100 mL. All analyses were run in quadruplicate.

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Elemental analysis by ICP-OES

Sonicated solutions, blanks and standards were aspirated into a direct reader ICP instrument (ARL 34000, Applied Research, NJ, USA) equipped with a standard pneumatic nebulizer and a dedicated IBM-AT computer for data acquisition and analysis. Aspiration was for 10 sec per solution. Standards were run before and after each set of samples. The ratio of signal intensities for samples and standards was used to determine the concentration of elements in the sample.

RESULTS AND DISCUSSION

Acoustic cavitation

The interaction of ultrasound with matter differs from that of electromagnetic waves. First, ultrasound cannot propagate through a vacuum. Second, at 20 kHz, ultrasound energy passes through an aqueous suspension of biological material at a velocity of approximately 1500 m/sec at a wavelength of about 8 cm. Since these are not molecular dimensions, there is no direct coupling of ultrasound with matter at the molecular level. Yet, when ultrasound of sufficient intensity is passed through water, chemical transformations, including the formation of hydrogen peroxide, are observed[9].

It is now widely accepted that acoustic cavitation is the mechanism by which ultrasound interacts with matter.[10] Cavitation occurs when millions of microscopic

bubbles, which form during the rarefaction phase of the ultrasound wave, are forced to collapse during the compression phase. These bubbles normally form in solution from dissolved atmospheric gases. When a cavitating bubble collapses near the surface of a solid sample particle, microjets of solvent, propagated toward the surface at velocities greater than 100 m/sec, cause pitting and mechanical erosion of the surface.[11] Violent collapse of cavitating bubbles is therefore likely to enhance dissolution of biological materials. When cellulose, a stable structural polymer found in plant tissues, is suspended in water and sonicated for an hour at several hundred watts energy, the fibers are physically fragmented, and the surface area significantly increased (Figure 2). This

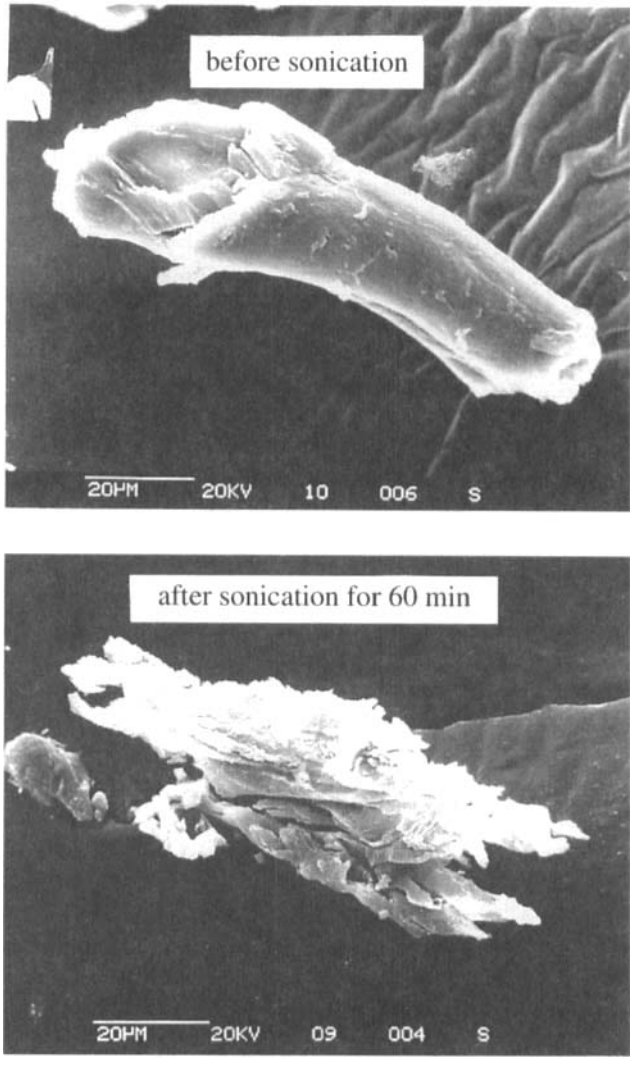

Figure 2 Effect of 600W/20-kHz ultrasound on granular cellulose.

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physical process is important, since the rate of chemical dissolution of solids in a solvent system is proportional to the solvent accessible surface area of the sample.

If cavitating bubbles contain gas, i.e. dissolved air, compression of this gas during the positive pressure phase of the sound wave will result in elevated temperatures inside the bubble. Thermodynamic calculations[12] and experimental studies[13] indicate this temperature to be around 5000 K. These extreme conditions are sufficient to break water molecules apart to generate free radicals[14]

$$H_2O \Rightarrow \cdot OH + \cdot H \quad (1)$$

and since these radicals are short-lived and very reactive, a variety of products are formed, including H_2O_2

$$2 \cdot OH \Rightarrow H_2O_2 \quad (2)$$

Figure 3 shows the quantities of H_2O_2 produced as a function of sonication time. The results show that an increase in cavitating events leads to higher peroxide levels. The figure also shows that peroxide formation is directly related to ultrasound power levels. Bubble collapse is less violent at reduced power, cavitation temperatures are reduced, and peroxide levels are accordingly lowered. The milliwatt levels of power delivered by most commercial ultrasonic baths are typically sufficient for cleaning, degassing of HPLC solvents, extraction of adsorbed metals and organic pollutants from soils and sediments, and so on, but are not adequate for sample dissolution. On the other hand, the several hundred watts of power delivered by ultrasonic probes designed for cell disruption appears to be sufficient. Such probes are now also being used to accelerate or modify a variety of chemical reactions.[15]

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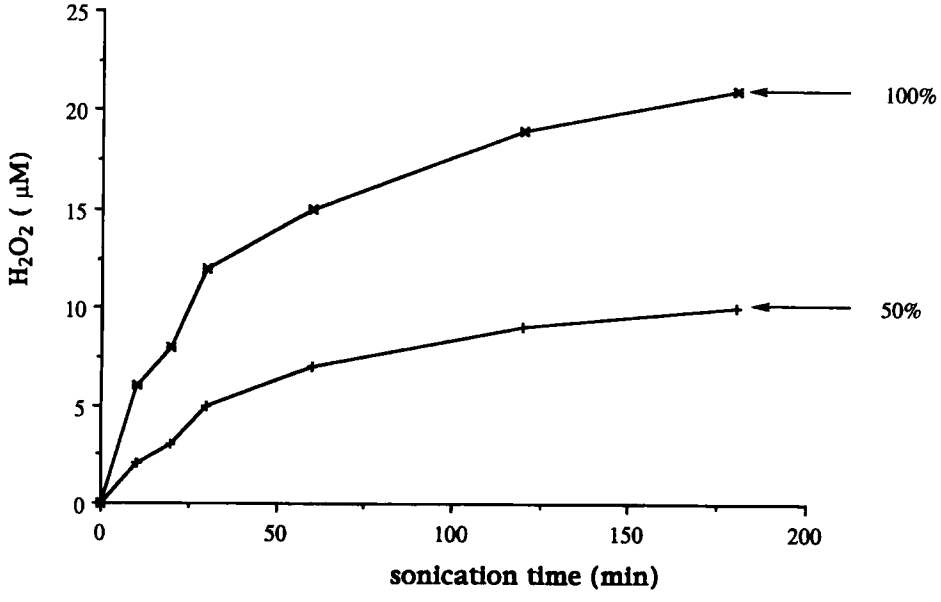

Figure 3 Hydrogen peroxide levels in sonicated water as a function of sonication time and ultrasound power.

Effect of solvent composition

It has recently been reported that ultrasound-produced free radicals and hydrogen peroxide efficiently degrade dissolved organic compounds such as pentachlorophenol in water.[16] Figure 3 summarizes the rate and level of production of oxidants, reported as hydrogen peroxide, over a 3-hr period. The quantity of oxidants produced is clearly sufficient to decompose many organic materials at mg/L levels. On the other hand, we have found that when 100-mg portions of powdered dry bovine liver are sonicated in water, the release of trace metals into solution is only 60% complete in 3 hr, indicating that in-situ generation of oxidizing agents is not adequate to achieve total decomposition of samples of this size. Therefore additional hydrogen peroxide was added to provide more oxidizing capacity. A concentration of 1% (0.3 M) was found optimum. Since the oxidizing power of H_2O_2 is increased at higher acid concentrations, acid was also added to the samples prior to sonication. It was found that neither HNO_3 nor HCl were as effective as H_2SO_4 in increasing dissolution rates. The most effective sulfuric acid concentration at peroxide levels of 1% was 0.5 M; under these conditions total dissolution of a 100-mg sample of bovine liver was achieved after 40 minutes of sonication. This solvent composition was used for all subsequent dissolution studies.

Contamination study

A potential disadvantage associated with the use of an ultrasonic probe to dissolve biological materials prior to elemental analysis is contamination from the probe itself. This is because the most efficient transfer of ultrasound energy to a sample is obtained when the probe horn is directly immersed in the solvent. The forces involved during cavitation when a probe is used are very large. Figure 4 shows the surface of a new titanium probe tip, and the same tip after 15 hr of use. The new surface is featureless and flat; the used tip shows extensive erosion. Since titanium is highly resistant to oxidation, this indicates that the forces involved during cavitation are energetic enough to remove

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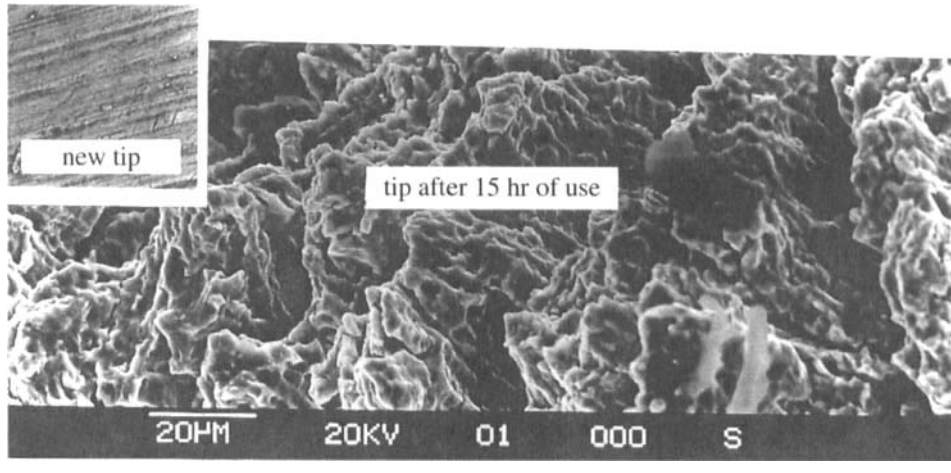

Figure 4 Mechanical erosion at Ti tip.

microscopic portions of metal from the surface of the probe. The presence of Ti in the sample is not generally a concern because it has no known biological activity, and so knowledge of its concentration is not normally of interest. However, impurities in the titanium could be a problem.

Figure 5 shows the results of analyses for Cu, Zn, Cd, Mn, Fe and Sr in blanks as a function of sonication time. Cd, Sr and Mn were not detected, but traces of Cu, Zn and Fe were found. Therefore blank runs were made in all cases, and corrections applied to all analyses.

Applications

Table 1 provides results for the determination of Cd, Mn, Sr, and Cu in 100-mg test portions of the NIST SRM's Oyster Tissue and Pine Needles by ICP-OES following ultrasonic dissolution in 40 mL of 1% H_2O_2/0.5 M H_2SO_4 for 40 min. Agreement between the certified values and the values found experimentally is good, particularly for the elements that have low blanks, such as Cd, Mn and Sr. Agreement is not so good for

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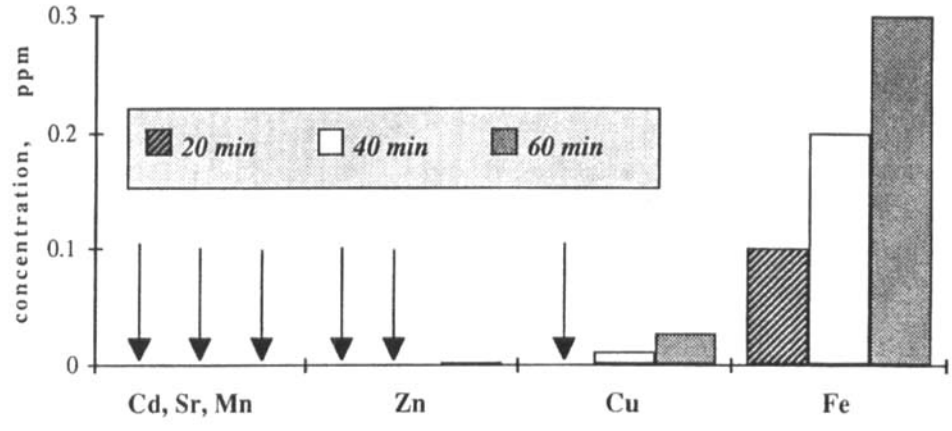

Figure 5 Levels of Cd, Sr, Mn, Zn, Cu and Fe in the blank as a function of sonication time.

Table 1 Elemental Analysis of NIST SRM 1566 (Oyster Tissue) and NIST SRM 1575 (Pine Needles). 100-mg portions (n = 4) were sonicated for 40 min in 0.5 M H_2SO_4/1% H_2O_2 mixtures prior to ICP measurement. nc means not certified; nd means not detected. All quantities are in μg/g.

	Oyster Tissue		*Pine Needles*	
	Found	*Certified*	*Found*	*Certified*
Sr	10 ± 1	10.36 ± 0.56	4.2 ± 0.2	4.8 ± 0.2
Mn	15.8 ± 1.7	17.5 ± 1.2	648 ± 4	675 ± 15
Cd	4 ± 2	3.5 ± 0.4	nd	nc
Zn	830 ± 20	852 ± 14	60 ± 2	67 ± 9
Cu	67 ± 13	63 ± 4	3.7 ± 1.1	3.0 ± 0.3

those elements that have high blanks, such as Zn and Cu. The limits of detection of the ICP method used here are not sufficient for the direct determination of other elements such as Pb and Cr, which are present at sub mg/L levels. Further work on reduction of blank levels is being done by the study of tips fabricated from high purity titanium.

CONCLUSION

It has been shown that ultrasonic energy can be used to dissolve biological materials in the presence of sulfuric acid solutions of dilute (1%) hydrogen peroxide. Some contamination is introduced from metal impurities in the titanium used for the probe tip. The procedure was successfully applied to the determination of Cd, Mn, and Sr in the NIST SRM's Oyster Tissue and Pine Needles.

Acknowledgements

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