Figure 5. Using the probe on a potsherd surface.

large volume of water. For these reasons we needed to calculate the *number* of ions in solution and not rely on the *concentration* of ions in solution. The number of ions in solution would necessarily be larger in the wash water than in the 4mL water chamber of the probe because the entire potsherd surface was exposed to water during the desalination, but only a small area of the sherd surface was exposed during the probe reading. Regardless of this difference, these numbers should be proportional if the probe is providing an accurate view of the soluble salt content on the sherds.

The number of ions in solution was calculated by using the equations for the trendlines shown in Figure 4 relating conductivity to concentration. The concentration was then multiplied by the volume of water (4mL for the probe readings, and the volume of the wash water for the desalination readings). The result is the number of moles of ions in solution, and these numbers are shown in Figure 6.

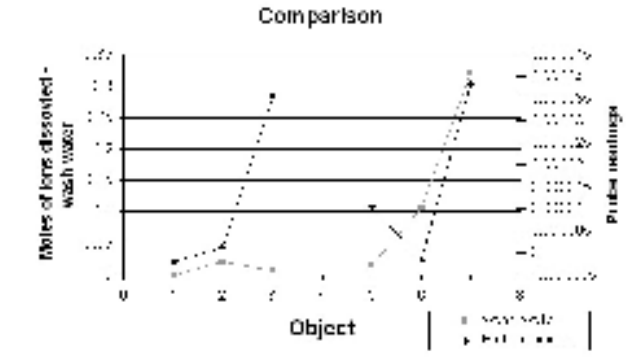



Figure 6. Comparison of conductivity probe readings (on the right) to desalination readings (on the left).

As expected, these ion values are generally proportional. The exceptions to this proportionality are with objects 3 and 6. Object number 6 contained sulfate salts, and we believe that the difference in measurements is largely due to these sulfate compounds. Sulfates tend to have a much lower solubility in water than other salts and the probe was only left on the surface of the pot for about 30 seconds. When submerged in water for desalination, the sulfate salts had much more time to dissolve. This illustrates one very real limitation of the probe: it is difficult to get an accurate reading when dealing with low solubility salts. The disparity for object 3 could be from a non-uniform salt concentration on the surface. We may have tested a salty region on a sherd that overall contained very little salt. Therefore, we must keep in mind that this is only a spot test, and to get accurate results, more than one spot should be tested.

**Conclusions**

The limitations of this probe are (1) that it samples a limited area, and therefore can provide non-representative results, and (2) that it is designed to detect only highly soluble salts. Further tests will be conducted to verify the reliability of the probe measurements. In addition, the potential formation of tidelines is a concern. We have not noticed any tidelines, possibly because all tested objects were subsequently submerged for complete desalination; however there is potential for water sensitive components to become mobile and form tidelines.

Despite these limitations and requirements for future work, the probe has proven to be highly mobile. This allows its use for fieldwork and also in storage areas without moving objects great distances. In general we believe that this is a promising new tool that will aid the conservator or archaeologist in soluble salt detection and measurement.

# Removal of Arsenic and Mercury Contamination from Materials using a Natural, Environmentally Benign Chemical

*by Peggi Cross*

**Forward**

I first became aware of the issue pertaining to the use of pesticides on artifacts in a colloquium presentation at the University of Arizona given by Dr. Timberly Roane of the University of Colorado. I had been independently studying the binding of natural chemicals to arsenic at the time and had found a body of literature suggesting that alpha-lipoic acid would be a very good candidate. My field of study is Materials Science and Engineering with a minor in Environmental Engineering. My focus on the use of natural chemicals that are essential to human existence or chemicals that are manufactured in the human body comes from my belief that in order to maintain a planet that is habitable, we must maintain an equilibrium with our environment. By at least starting with chemicals that have known impacts on human life, we have a chance of not creating unpredictable and devastating effects such as those invoked by the creation of chlorofluorocarbons.

As a returning student with several years of experience in the semiconductor industry, I was also at a point in my life where I was interested in finding a project that would contribute to humanity in a more meaningful way than a project that was just designed to create faster microprocessors, as is the norm in my field. I had just lost a young brother-in-law to cancer from an unknown cause and was most interested in arsenic as it is a carcinogen. I was quickly introduced to Dr. Nancy Odegaard, the leading expert on pesticide use at the Arizona State Museum. Dr. Odegaard embraced my ideas and made time in her busy schedule to help me write my first grant proposal to the National Center for Preservation Training and Technology. And that is how the project was born.

**α-Lipoic acid and its reaction to arsenic and mercury**

α-Lipoic acid is a natural, environmentally benign chemical that is integral to all plants and mammals and is patented as an agent for the cure of many diseases. It has also been demonstrated that α-lipoic acid acts in-vivo for the detoxification of both arsenic and mercury in biochemical studies dating back to the late 1950s (Reiss et al, 1957; Grunert, 1960; and Wagner, 1956). Figure 1 illustrates the structure of α-lipoic acid and the reduced form, dihydrolipoic acid.

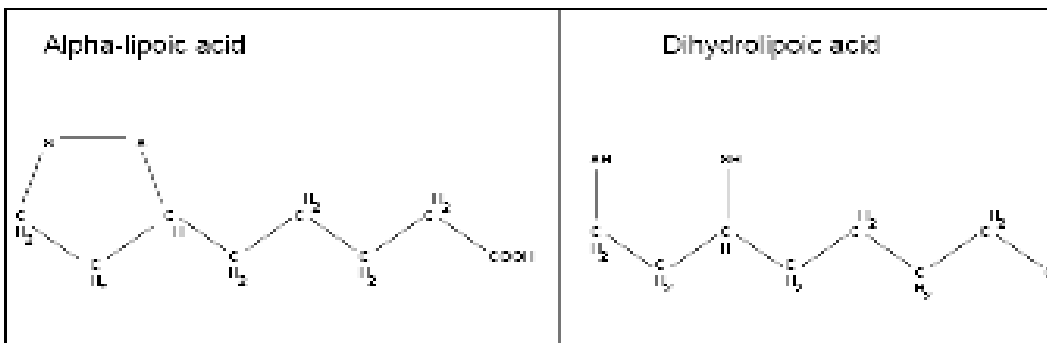
Mercury binds to α-lipoic acid or dihydrolipoic acid at the sulfur sites (Brown, 1968), and it has been demonstrated that arsenic binds to dihydrolipoic acid (Spuches et al, 2005). Literature could not be found that indicated whether or not α-lipoic acid must be reduced in order to bind to arsenic so this became the focus of one of the first experiments.

**Reduction of α-lipoic acid**

Another attribute of the α-lipoic acid is that it can be reduced using the ultraviolet light from sunlight or simple laboratory lamps which conservators are familiar with. Figure 2 shows a typical set-up of solutions in borosilicate test tubes with neoprene stoppers ready for photolytic reduction using an 8 watt UVP UV lamp with a 302 nm (604 $\mu$W/cm$^2$) source. A series of many experiments were run to optimize the solubility, concentration, pH, and photolytic reduction rate using various reagents such as organic solvents, acids, and bases. The reduction of α-lipoic acid to form dihydrolipoic acid (DHLA) was monitored using a UV spectrometer by the disappearance of the 330 nm absorbance peak (Matsugo et al, 1996).

Figure 2. Photograph of the UV lamp and stand with test tubes prepared for a typical exposure run.

Figure 1. The structures of α-lipoic acid and dihydrolipoic acid redrawn from Packer et al (1995).



Once a window was determined for preparation of the α-lipoic acid solutions with a reduction rate that would allow the solutions to be used the same day, testing began on the reaction with arsenic in de-ionized water. The formation of the As-S bond was monitored via the 270 nm absorbance increase with UV spectroscopy (Spuches et al, 2005). As indicated by the graph in Figure 3, the formation of the As-S bond was evident only after alpha-lipoic acid underwent photo-reduction. In addition, reduced lipoic acid does not react with As(V). The arsenic used on museum artifacts was predominately in the form of arsenous acid or sodium arsenite (As(III)) so that will not impact the efficacy of the treatments for this application.

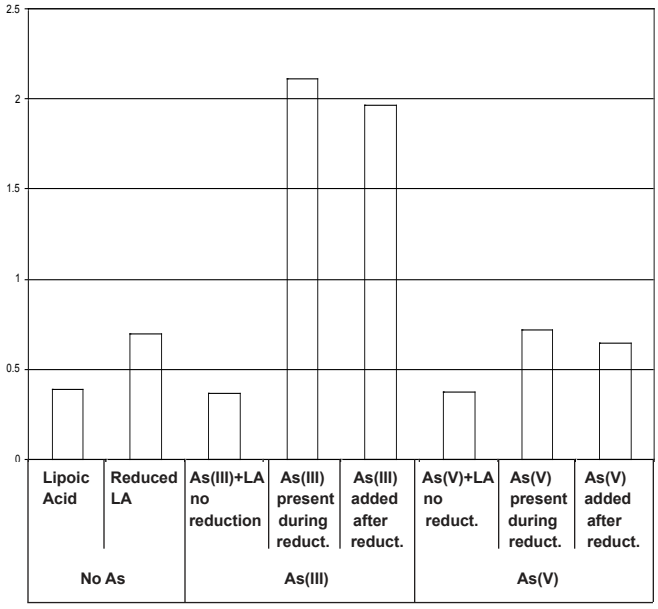



Figure 3. As-S Formation from As(III) and As(V) with lipoic acid before and after reduction and with the arsenic present during photochemical reduction of lipoic acid or added afterwards (180 min exposure to 302nm UV Source).

### Contamination of materials

Solutions of sodium arsenite or mercuric chloride were dispensed onto 550 mm diameter filter paper (Whatman No.1), wool or cotton fabric test pieces, or feathers (free range Quail) and then allowed to dry prior to measurement of the levels of contamination, using a Niton handheld X-ray Fluorescence instrument. Feather pieces were approximately 3/4 inch square and were measured for contamination prior to testing to insure that there were no detectable levels of arsenic or mercury. Even dispersions were obtained using a pumped spray bottle.

### Process sequence and techniques

The process sequence found to be most effective was a three step process including: 1) pre-wetting the material to be decontaminated, 2) treating the material with the reduced lipoic acid solution and 3) rinsing the material by placing it at an angle and rinsing in a serpentine pattern from top to bottom with a wash squeeze bottle. Various pre-wetting and rinse solutions were tested in order to enhance wettablity and penetration into the dense fibers but surfactants were avoided in order to avoid the need for vigorous rinsing in order to remove them.

The methodology used to optimize the treatment solution and process sequence included a series of full factorial experiments analyzed using an Analysis of Variance (ANOVA). For instance Figure 4 shows the average arsenic levels measured using XRF after treatment of filter paper with an average initial arsenic level of 307 μg/cm$^2$. The variables tested were: 1) using carbonated water vs. de-ionized water as the pre-wetting agent, 2) using reduced lipic acid vs. no treatment solution and 3) using carbonated water vs. deionized water as the rinse reagent. The lipoic acid clean step was shown to have a significant effect (p=0.0005) on the reduction of the arsenic contamination.

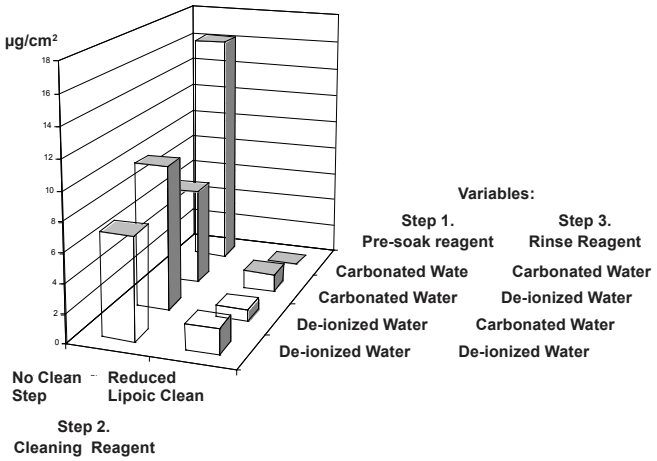



Figure 4. Average residual Arsenic(III) ($\mu$g/cm$^2$) on filter paper after different cleaning sequences. (Original contamination : 307 $\mu$g/cm$^2$ Arsenic as $NaAsO_2$.)

Tests of this nature continued with increasing levels of arsenic and mercury until a process was developed for removing approximately 1500 μg/cm$^2$ of arsenic or mercury to very low levels. In general, lower levels of residues could be achieved on non-sulfur containing materials, and mercury could not be removed from the sulfur containing materials such as wool and feathers using the treatment developed.

### On-going work

Work is ongoing to look at the effect of the arsenic and mercury salts on the materials before and after contamination and treatment using ATR-FTIR. There are very promising results that show that the increased crystallinity of cellulose

material due to sodium arsenite treatment can be reversed with the reduced lipoic acid treatment. This indicates that the solutions may to be effective at treating cellulose-containing materials such as wood.

*Acknowledgements*

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