Conductivity Probe Prototype: Measuring Soluble Salt Content on Ancient Ceramics

The presence of soluble salts on pottery is a concern for conservators as it often influences decisions regarding treatment, handling, and display of objects. The deleterious effects of soluble salts are well known and a source of concern for object stability. Identifying the damage caused by soluble salts is easily done visually. However, identifying the presence of soluble salts on objects that do not yet exhibit early signs of pitting or spalling can be more difficult.

Spot tests have proven useful in determining the presence and type of salts on surfaces. However, some of these tests are not quantitative, and the job of prioritizing treatments, especially in large collections, becomes a frustrating guessing game. Our goal in developing a conductivity probe was to create a portable, non-destructive, quantitative tool for comparing the soluble salt content on ceramics.

Design

The idea for the probe and the first model were developed by Werner Zimmt and Nancy Odegaard at the Arizona State Museum Conservation Lab. This prototype is shown in Figure 1 and was designed as an attachment to a LabLine Lectro Mho Meter. The original apparatus included a wax probe holding two platinum (Pt) wires. A rigid plastic cylinder and a foam gasket were held against a pot's surface, and filled with deionized (DI) water. The wax probe was placed in the water to measure the water conductivity – a measurement of the salt dissolved from the pot's surface.

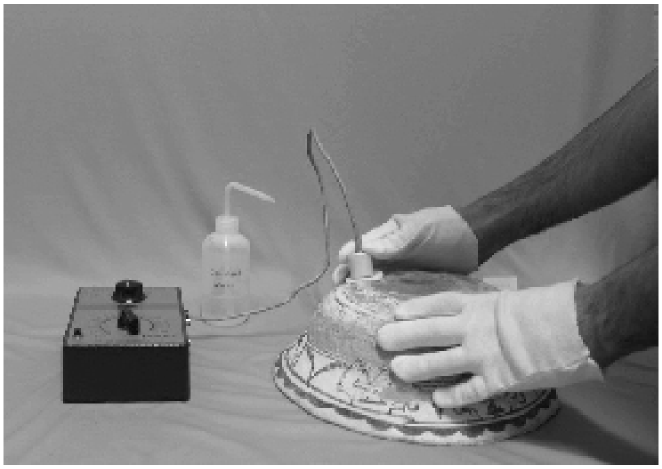


Figure 1. Mock up of first conductivity probe prototype.

This design confirmed the general principles of the technique but proved to be inherently problematic. It was difficult simultaneously to hold the probe in contact with the pot's surface, read/adjust the meter, and prevent water from leaking onto the vessel. The water volume could not be held constant, and it was difficult to achieve reliable conductivity readings. For these reasons, Nancy and Werner encouraged us to refine the probe to be more user-friendly and accurate.

The new design for the conductivity probe is a single apparatus that contains a water chamber with fixed volume, Pt wires, a flexible silicone gasket to make contact with pot surfaces, and a syringe to remove water from the chamber to minimize the amount of water left on the vessel. In addition, this new probe has been designed to work with the Oaklon EC Testr conductivity meter, which can be worn in an armband or placed in a wall-mount for increased maneuverability.

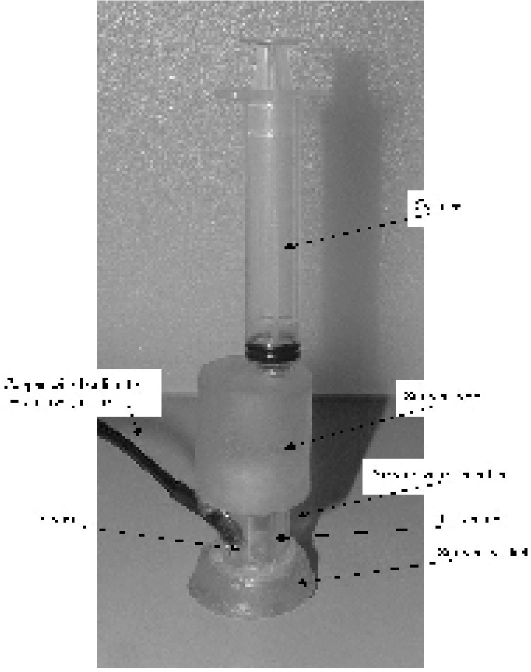


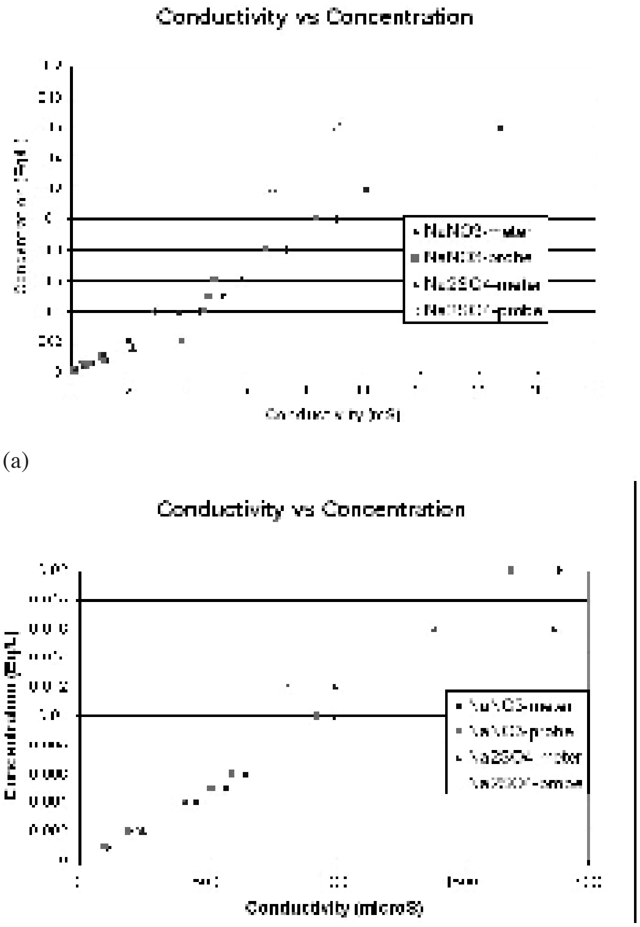
Figure 2. Refined conductivity probe design.

To fill the water chamber, one must first draw DI water into the syringe. This water is then injected into the chamber through a Teflon tube while the probe is held against a ceramic surface. The silicone gasket minimizes leakage of water onto the ceramic surface. As soluble salts are dissolved the conductivity of the water in the chamber increases and is measured with the Pt wires. After the conductivity value has stabilized, the water is drawn out of the chamber with the syringe. It is necessary to rinse the syringe and chamber with DI water between each measurement, but this can be done quickly by plunging DI water in the syringe from a beaker until the reading on the conductivity meter returns to 0μS.

Calibration

To determine the reliability of this new probe design, a variety of salt solutions at different concentrations and ion species were measured. These measurements were taken using the Oaklon EC Testr conductivity meter alone as well as with the probe attachment. For the probe measurements, the salt solutions were drawn into the syringe and then deposited into the chamber as it was held in contact with a glass dish. Between each measurement, the probe was rinsed with DI water until a zero reading was obtained.

The conductivity measurements were plotted against ion concentration to create a calibration curve. Because we are interested in the ions in solution, we decided to measure concentration in equivalents per liter (essentially the molarity of an ion of interest rather than the molarity of the compound as a whole). In Figure 3, you can see concentration vs. conductivity for both the high conductivity meter (0-19.90mS) and the low conductivity meter (0-1990μS).

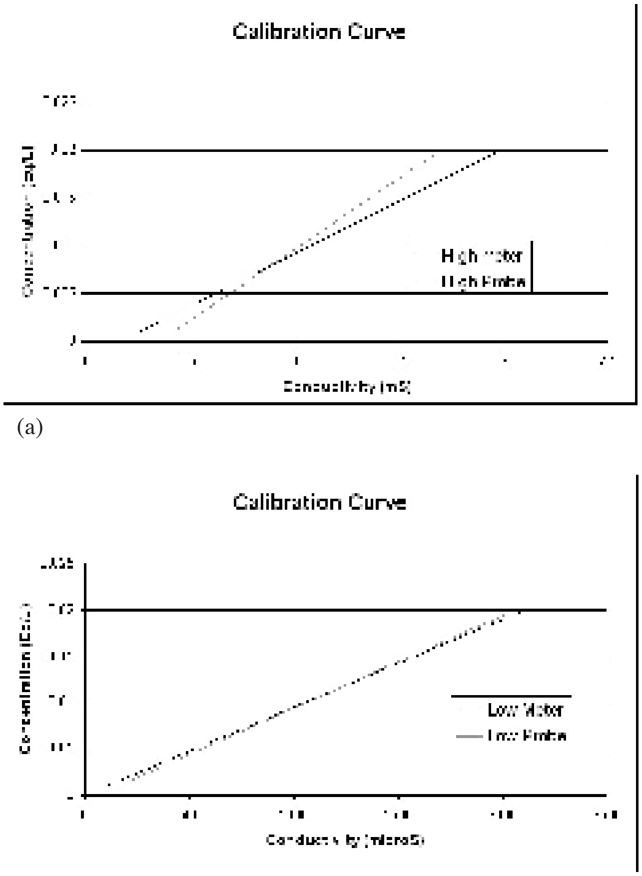


(a)

(b)

Figure 3. Conductivity vs. salt concentration for the probe and conductivity meter alone (a) using the high conductivity meter and (b) using the low conductivity meter.

As shown by these graphs, there is good agreement between the measurements made on the same solutions with the probe and with the meters alone. There is also good agreement between different salt types at the same concentration. This allows us to establish a general curve relating measured conductivity to the concentration of salt in solution. Figure 4 shows the general calibration curves established by averaging the trendlines from the different salt solutions. Using these, a conductivity measurement will provide a good idea of ion concentration.



(a)

(b)

Figure 4. Calibration curves for (a) the high conductivity meter, and (b) the low conductivity meter.

Testing

After using the probe with prepared salt solutions of known concentration, the next step was to try it on modern potsherds that were spiked with various salt compounds and compare the readings to those from the water used to desalinate the sherds. Each sherd or vessel was weighed, and the surface salt content was tested with the probe (Figure 5). These test pieces were then submerged in known amounts of water to begin desalination. The conductivity of the water was measured periodically until values stabilized after approximately 3 days. The measurements from the water were then compared to the initial probe readings.

It is important to note that the conductivity measurements provide information about the concentration of ions in solution; however, it was necessary to use different volumes of water for the desalination process due to the larger size of some vessels. The result was that the concentrations in the wash water did not necessarily reflect the concentration of salt on a potsherd; that is to say, even a very salty object can yield a low concentration of ions when placed in a very

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.

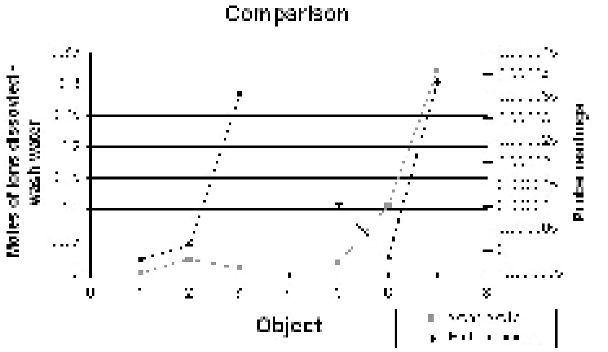


Figure 6. Comparison of conductivity probe readings (on the right) to desalination readings (on the left).

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.