Detecting and Identifying Salts during the Desalination Process with Spot Test Papers

Desalination is a relatively common conservation treatment used to remove soluble salts and prevent ongoing damage on objects including ceramics, metals, stone, and textiles. As part of the desalination treatment process for an extensive collection of Native American ceramic vessels, Arizona State Museum conservators sought to find an inexpensive, efficient, and accurate method for soluble salts identification. This paper describes a study of EM Quant test strips which were found to meet these criteria, providing semi-quantitative determination of chloride, nitrate, and sulfate ions in desalination bath solutions in the mg/l range without additional preparation of the samples.

A number of methods have been used over the years for the determination of salt concentrations. Rathgen (1905) and Plenderleith (1971) describe some of the methods employed in the last century. Many protocols have been developed based on the direct relationship between the salinity of a solution and the conductivity of a solution (Lal Gauri 1986, Holbrow 1995, Costa Pessoa 1996, Ling 1996, Paterakis 1996, Beaubien 1999, Unruh 2001, Selwyn 2006, White 2010).

Conductivity bridges were used in conservation labs in the twentieth century and portable meters came into common use in the 1990s (Zimmt 1993). Readings through these instruments are extremely useful for the interpretation of soluble salt quantities based on the measure of current carried by salts in bath solutions but they can not be used to calculate exact amounts. Nor do they indicate the types of salts present.

Previously, the identification of specific salts has been possible through several methods. Chemical spot tests, particularly the silver nitrate test, have been used by conservators for many years to test for halides in solution but it requires the use of silver nitrate reagent and is fairly difficult to use for gathering quantitative data. Ion meters with combination electrodes for specific ions became available and remain useful for providing concentrations in parts per million (Semczak 1977). However, when testing desalination water, the meter must be calibrated and multiple electrodes must be used to identify multiple components.

Other analytical instruments used for identification of salts have included XRD, FTIR, Ion chromatography, and Microscopy. At the Arizona State Museum, the cost in equipment, time, and labor in doing FTIR, specific ion electrode meter readings, microscopy, and microchemistry in the ASM lab could not be justified for all of the hundreds of ceramic pots treated by desalination. XRD, Ion chromatography, and other instrumentation available at the UA are particularly expensive due to laboratory and technician charges.

Spot test papers for materials characterization have great utility in conservation labs, and sulfate and nitrate test papers have been discussed previously (Odegaard 2005). The EM Quant test strips which we investigated and used allow time-saving, semi-quantitative determination of important ions and compounds in the mg/l range without additional preparation of the samples, thus saving time and labor. When very large numbers of pots are to be treated, this becomes a consideration.

The procedure for proper use of the strips is:

> the reaction zones are wetted with the solution being tested by simple dipping;
>
> the excess liquid is then shaken off;
>
> after the given reaction time has elapsed - a maximum of two minutes - the coloring of the reaction zone is compared with the color scale on the package to determine the concentration.

Evaluation of the EM Quant test strips involved several steps. Dr. Patricia Hill, a chemistry professor from Millersville University in Pennsylvania, was a visiting scholar at the Arizona State Museum in 2009 and agreed to make up six concentrations for each of the chloride (Cl), nitrate (NO_2), and sulfate (SO_4) salt solution concentrations for testing the EM Quant strips. The EM Test Strips provided consistent and accurate readings for the six test concentrations of each type of salt solution, and these solutions were retained for reference and training purposes.

It was also important to examine possible diffuculties that might arise from differences in an operator/tester's interpretation of the results. Desalination water samples were retained from the ASM Pottery Project desalination treatments. Over 160 samples were evaluated using the EM Test Strips during two separate reading sessions. 150 were selected for further evaluation taking into account the microsiemens (μS) conductivity level, the pottery pre-treatment condition, and the presence of pre-treatment fills.

Samples with significant reading discrepancy were run again and judged by Odegaard and Zimmt. An Excel spread sheet of the readings from the sessions indicates that there was a significant discrepancy between testers' interpretation of the test strip reaction. The operator of session 2 had much less experience then the one from session 1. This testing demonstrated that experience, patience, and diligence in protocol procedure are required in order to obtain reliable results.

Sulfate testing
    30 discrepancies (@20%) including
    3 errors in session 1
    30 errors in session 2

Nitrate testing
    30 discrepancies (@20%) including
    10 errors in session 1
    30 errors in session 2

Chloride testing
    11 discrepancies (@ 8%) including
    4 errors in session 1
    7 errors in session 2

by Nancy Odegaard, Patricia Hill, Brunella Santarelli, and Werner Zimmt

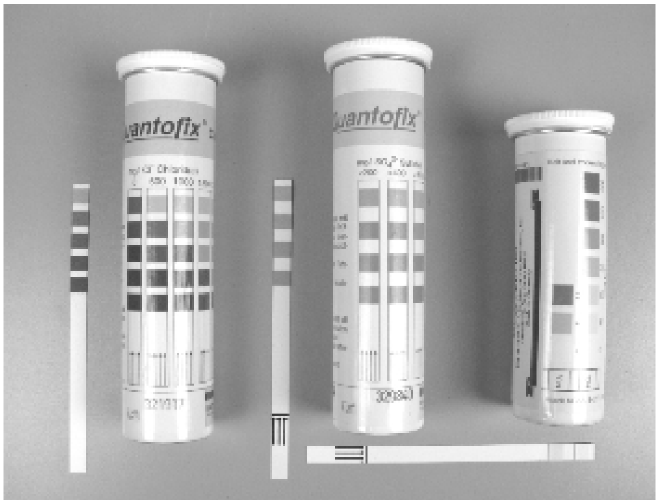
Numerous desalination water samples were prepared for Fourier Transform Infrared Spectroscopy (FTIR). Selections were based on particularly high levels of sulfate, nitrate, or chloride salts detected by the EM Test Strips or because the conductivity levels were high yet these salts did not reveal high levels on the test strips. Brunella Santarelli, a graduate student in the Heritage Conservation Science program in the Department of Materials Science at the University of Arizona and research assistant at the Arizona State Museum, performed the analyses.

Small samples of water were taken from their vials, dried on glass slides, and a scalpel was used to transfer the dry crystals to the ATR platform. The FTIR was run then compared to several libraries for identification.

The EM Quant papers utilize different chemical reactions and are measured in different increments but they do follow the same procedures for use. The chemical reactions take place on paper squares affixed to a plastic strip and are indicated by color changes. We also found that the test strips for the different salts have different detection levels and categorized them at the following levels.

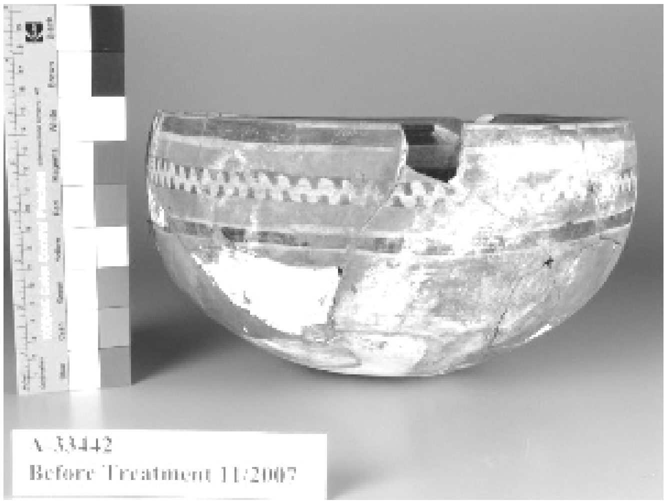
	Chloride	Nitrate	Sulfate
Low	<500 mg/l	25 mg/l	<200 mg/l
Medium	>1000 mg/l	100 mg/l	>400 mg/l
High	>2000 mg/l	250 mg/l	>1200 mg/l

Chloride, Sulfate, Nitrate Quantofix test strips from EM Quant as they appear before use.



The Sulfate Test Papers have test zones on the strips that contain varying amounts of the red-colored thorin-barium complex. In the presence of the equivalent amount of sulfate ions the color changes to that of the yellow thorin (*o*-[3,6-disulfo-2-hydroxy-1-naphtyl-azo]-benxenearsonic acid). The color reaction is red - yellow, and the detection gradations are : <200 · >400 · >800 · >1200 · >1600 mg/l SO_4^{2-}. High sulfate levels in several samples were also analyzed and confirmed with FTIR using a Thermo Nicollet Avatar 360 instrument and found to correlate to the extensive use of old plaster-of-Paris fills used in the pottery.

Salado bowl:	500 mg/l Cl
	250 mg/l NO_2
	1660 mg/l SO_4
	1000 μS conductivity
	2.6 days for desalination



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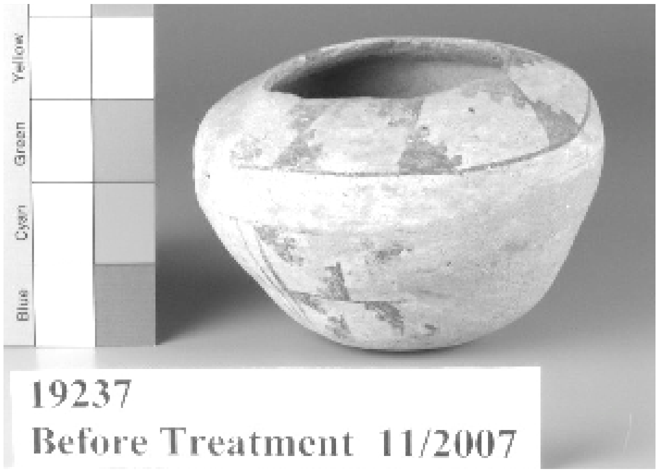
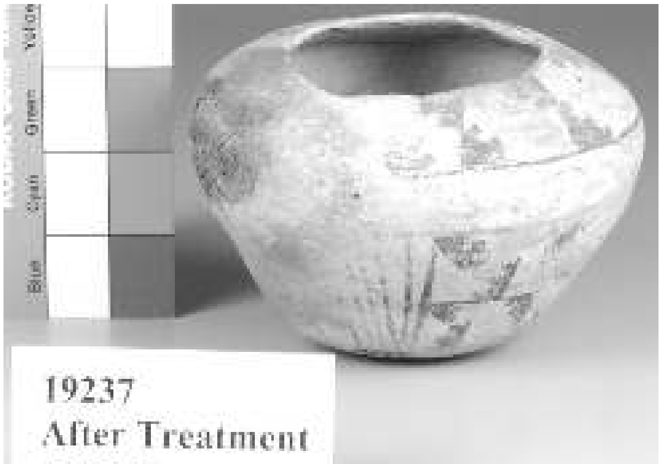
The Nitrate Test Papers have test zones on the strips that form a red-violet color when nitrate is reduced and converted to nitrous acid which diazotizes an aromatic amine, this coupled with N-(1-naphthyl)-ethylenediamine to form a red-violet azo dye. The color reaction is white - red-violet, and the detection gradations are: 0 · 10 · 25 · 50 · 100 · 250 · 500 mg/l NO^{3-}. High nitrate levels in several samples were also analyzed and confirmed with FTIR and found to correlate to possible contamination from agricultural fertilizers used on the soils where the pottery was excavated.

Salado bowl: 500 mg/l Cl
250 mg/l NO$_2$
200 mg/l SO$_4$
640 μS conductivity
1.6 days for desalination

The Chloride Test Papers have test zones on the strips that contain varying amounts of silver ions. In the presence of the equivalent amount of chloride ions there is a decolorizing as silver chromate is converted to silver chloride. The concentration of chloride is measured semi-quantitatively by visual comparison with the color scale. The color reaction is brown - yellow, and the detection gradations are: 0 · 500 · 1000 · 1500 · 2000 · ≥ 3000 mg/l Cl^{-}. High chloride levels in several samples were also analyzed with FTIR; however, the characteristic wavelength region for chloride is outside the instrument' s range. We suspect that many of the pots with high chloride levels were treated with hydrochloric acid to remove calcium carbonate deposits obscuring the decorations. When used for this purpose, HCl converts the insoluble calcium carbonate to the soluble calcium chloride leaving soluble chloride salts.

Anasazi jar: **2000 mg/l Cl**
0 mg/l NO2
200 mg/l SO4
1810 μS conductivity
3.0 days for desalination





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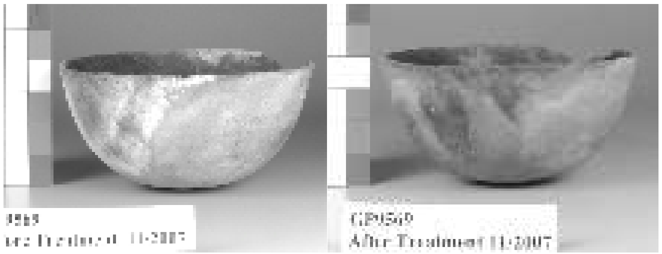
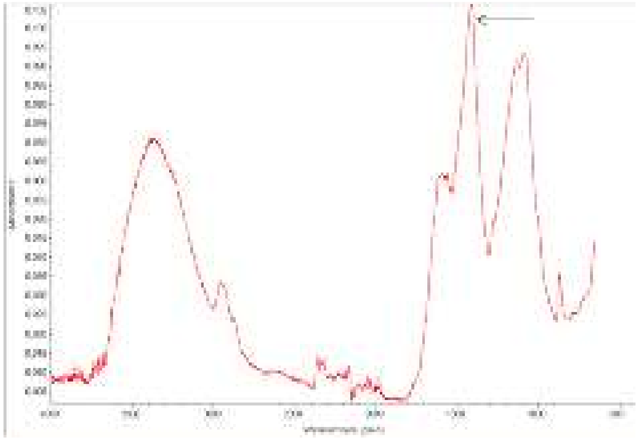
Pottery examples that had very visible soluble salt efflorescence in pre-treatment and high micro-siemen conductivity reading during desalination but low sulfate, nitrate, and chloride test strip levels during desalination bath water testing were also analyzed with FTIR. Calcium carbonate was the most commonly identified semi-soluble salt identified. Polysilicates were also found. These soluble silicates, especially sodium, potassium and lithium silicates, are generally not distinct stoichiometric chemical substances (with a specific chemical formula and molecular weight), but rather aqueous solutions of glasses, resulting from combinations of alkali metal oxide and silica in varying proportions.

Hohokam bowl:

500 mg/l Cl	1210 μS conductivity
100 mg/l NO2	4.8 days desalination
200 mg/l SO4	



FTIR spectra indicated high peak for calcite (calcium carbonate)



In Conclusion, EM Test Strips offer inexpensive, time-saving, and semi-quantitative determination of chloride, nitrate, and sulfate ions held in desalination bath solutions without additional preparation of the samples.

They can suggest possible explanations for salt efflorescence on pottery such as: (a) the use of hydrochloric acid for the removal of insoluble salts (calcite) without dilution or rinsing, (b) a burial deposition associated with fertilized fields, (c) the generous use of plaster of Paris in restoration fills, and (d) the probable presence of other salts including carbonates, phosphates, and silicates. They can also be cut into smaller strips, can be carried/used anywhere, and do not require special disposal restrictions. Different test strips can also be efficiently used together. These test strips are a useful analytical tool for conservation labs of any size or budget.

Acknowledgements

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Supplies and Equipment

Merck Chemical Company. merck-chemicals.com/industrial-laboratory-chemicals

MACHEREY-NAGEL Inc. 2850 Emrick Blvd. Bethlehem, PA 18020, USA. 1-888-321-6224. sales-us@mn-net.com.

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