

# On-site Elemental Analysis of Art and Artifacts

*Archaeological Site Survey, Art Conservation, and Archaeometric Studies with the Handheld Thermo Scientific NITON® XL3t and XL3p XRF Analyzer – Simply Superior XRF*



## Introduction

With new advancements in technology, archaeometry – or the collection of quantitative data from archaeological samples and works of art – is quickly becoming one of the most trusted methods in archaeological and museum studies. Whether the task is reconnaissance survey, site mapping for excavation, conservation, or establishing provenance, quantitative chemical data has grown to be the method most often sought out to accomplish these project goals. The ability to obtain quantitative elemental data in the field, in real time, is invaluable to any archaeologist or conservator. Handheld Thermo Scientific NITON XL3 Series x-ray fluorescence (XRF) analyzers are the perfect tools for the job.

## The Thermo Scientific NITON Solution

As the longtime industry leader in handheld XRF analysis, we are uniquely capable of providing handheld nondestructive testing solutions for art and artifacts in the field, in the lab, or on the museum wall. XL3 Series analyzers combine the most powerful – 50 kV – miniaturized x-ray tubes ever used in handheld XRF instruments with multiple primary filters for optimal sample excitation.

These essential tools have been engineered to take routine laboratory measurements into the field and change the fundamental way in which this field does research. With the ability to identify and quantify virtually any element from magnesium through uranium in any sample, our analyzer is the ideal option for portable archaeometric analysis.

## From the Field to the Museum Wall

NITON XL3 Series analyzers can be used in the field as reconnaissance survey tools. By performing in-situ soil analysis at a site of suspected prehistoric or historic human activity, the user can identify areas such as sub-surface architectural features, hearth areas and fire

pits, burial grounds, and much more based on trend analysis of the elemental composition of the soil.<sup>1</sup> Pairing a systematic sampling grid with a



Figure 1: Eye feature on a painted object through the lens of the NITON analyzer CCD camera.

## Archaeometric Studies

### NITON XL3 Benefits At-a-Glance

- Optional integrated color CCD camera and sample imaging system to visually identify, locate, specify, and save the image of the analysis area together with XRF results (see Figure 1)
- Lowest limits of detection – better trace element identification and quantification for better materials characterization, sourcing, and comparative studies
- Helium purge for light elements (Mg, Al, Si, P, and S) in alloys, lithic samples, and soils for the best characterization
- Numeric on-screen results with spectra for guidance in the field – spectra on screen and on PC (see Figure 2)
- Automatic parameter optimization – voltage and current adjust automatically based on sample and range of elements of interest for most accurate, repeatable results every time
- Integrated Bluetooth™ and USB communications for direct data file transfer to user's PC or networked storage device, or for connection to a GPS receiver for real-time archaeological site mapping

Bluetooth™- equipped GPS device makes the reconnaissance survey and mapping process faster and easier than ever with direct storage of latitude, longitude, and altitude along with the reading results. Further, our optional telescoping Thermo Scientific Extend-a- Pole™ dramatically improves ergonomics and makes it possible to test the ground without ever bending down.

Our instruments identify components of pigments in paintings and glazes, thereby assisting conservators in the preservation and restoration of artifacts. By identifying elements without removing the paintings from the frame, or even the wall, curators are reassured that their pieces can be examined safely, without the potential for physical damage. NITON XL3 analyzers can also be used to measure metal alloy content to analyze objects such as statues, jewelry, silverware, and weaponry.

Because our analyzers have been specifically engineered to provide superior archaeometric data, totally nondestructive analysis can be used for characterization of soil, in-situ site survey, pigments, ceramics, paintings, alloy objects, NAGPRA compliance<sup>2</sup>, numismatics, and other applications.

### Promise to Practice – XRF at Work

#### Archaeological Soils

Whether in-situ or on prepared samples, by performing soil analysis with an XL3 analyzer at a site of suspected prehistoric or historic human activity, the user can delineate and map areas of such activity. This has been shown in certain buried architectural features by elevated (meaning above trend for the whole site) levels of calcium and strontium; in hearth areas and fire pits by elevated levels of potassium and magnesium; and in burial grounds by elevated levels of phosphorus, calcium, and strontium, among other elements.

**La Hacienda y Presidio de Bobocomari and U.S. Army Fort Wallen<sup>3</sup>** – Our analyzer can be an invaluable tool for archaeological site survey such as its use in helping to establish the locations of the sites of Fort Wallen – dated from post-U.S. Civil War – and the Hacienda y Presidio de Bobocomari – dated from the Spanish Colonial period – near Sierra Vista, Arizona. Because of incomplete and conflicting documentation, the exact position of these sites was uncertain, though historic literature reported their locations as being the same.

Aerial imagery of the area and field inspection confirmed that the Fort and the Hacienda/Presidio were two separate sites located 14 miles west of the reported location(s) and were remarkably well preserved.

However, chemical evidence was required to establish the identity and uniqueness of each location. Historical evidence implied that there should be a significant difference between the archaeochemical and archaeogeophysical signatures of these sites.

For Phase I of the investigation, a series of Class I handheld NITON XRF surveys were made of each site. The surveys showed elevated phosphorous levels in an

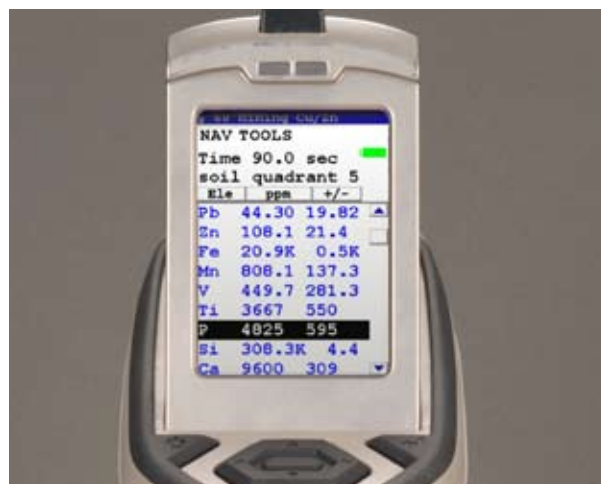


Figure 2: NITON XRF analyzers detect and quantify phosphorus in soil samples with ease, using the He Purge analysis package.

area of Fort Wallen, while P, calcium (Ca), and various metal concentration data at the Hacienda/Presidio site suggested living and activity areas within that site.

Phase II consisted of three investigation methods: resistivity, radiometrics, and XRF, collectively called the Combined Survey Format. The Combined Survey Format uses various modern technologies in concert to non-invasively characterize a site. The radiometrics and the soil chemical analysis done using our analyzer show a strong correlation. Low values around the 5 meter mark correspond to an adobe wall. Higher values around the 11 meter mark correspond to a proposed plaza area. The NITON XRF instrument made it possible to simultaneously assay and analyze many elements at one time, facilitating correlative studies.

As shown in Figure 3, peaks or depressions in the abundance of elements of interest were interpreted for possible archaeological significance. The graph indicates a concentration peak of potassium at the 4 meter sample location; elevated levels of potassium have been associated with hearths and other features. The reading is suspected to indicate a buried feature, which is also suggested by the Combined Survey Format. Surface concentration of artifacts further supports this interpretation. Although excavation must confirm the activities at this location, possible areas of buried features were indicated without disturbing the site.

#### Museum Health and Safety, NAGPRA, Toxins

Until relatively recently, materials that we now know to be toxic – such as arsenic (As) and mercury (Hg) – were used in museum conservation. These preservatives were used to preserve taxidermy specimens, cloth and leather artifacts, and others. Now, these objects can pose a threat to the health and safety of museum workers. Our analyzers allow the user to test for such toxic elements quickly and nondestructively so that special handling precautions can be taken or an effort to clean the object of the toxic substances can be made.

Because of the potential for objects to contain these toxic preservatives, the air quality in a museum conservation lab or collections area may

#### Archaeometry – A Field of Sample Types

- Clays and ceramics
- Soils
- Lithic materials
- Textiles
- Alloys
- Paintings/pigments/glazes
- Construction materials
- Clothing
- Bones, teeth
- Precious metals

#### Saving Time and Money with XRF

##### Cost/Sample:

- Lab: \$600-\$1200
- XRF: \$0.5

##### Time:

- Lab, inside: 1 day
- Lab, outside: ~1 week
- XRF: 5 seconds to 6 minutes

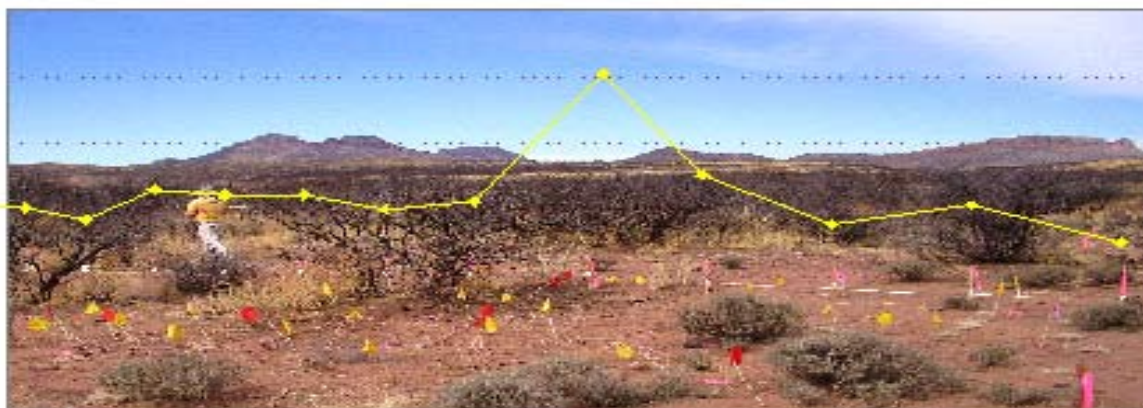


Figure 3: The XRF data were correlated to the survey lines. Here, the PPM values of potassium are visualized over the north survey line.

be compromised. To ensure the safety of museum staff, the ambient air can be tested with the Thermo Scientific NITON analyzer directly via testing air filters, or indirectly via the dust wipe method.

Further, when repatriating items for NAGPRA compliance, our instruments are well-suited to measuring the residual quantities of lead, arsenic, and mercury, thereby allowing suitable precautions to be taken while handling them and appropriate clean-up to be performed, when possible.

#### Ceramics

XRF analysis of ceramic artifacts also boasts a variety of applications. Ceramic artifacts can be subjected to comparative study for sourcing and grouping based on elemental composition of the ceramic substrate; pigments and paints on ceramics can be analyzed for composition; residues found inside ceramic vessels can be analyzed to help determine how the object was used; and more (see Figure 4).

**El Hibeh Project<sup>4</sup>** – As part of its geoarchaeological research program, the El Hibeh Project of the University of California, Berkeley, conducted field tests at the site of El Hibeh, northern Middle Egypt. The tests were done to assess the utility of using a handheld EDXRF unit, specifically a Thermo Scientific NITON analyzer, for obtaining geochemical analyses of pottery suitable for provenance and other ceramic classification studies. When the geochemical ceramic data from the field test were combined with basic petrographic analysis for the pottery sample set, compelling results were generated. In particular, a triangular scattergram using elemental iron, strontium, and rubidium data (in parts per million) provided excellent temporal and spatial separation of ceramic fabrics type, origin, and date.

#### Alloy Objects

When it comes to analysis of alloys – weaponry or jewelry, statues or coins – the Fundamental Parameters-based software algorithm, integral to our analyzers, helps provide accurate, precise results, every time, quickly and consistently.

**National Bank of the Republic of Macedonia<sup>5</sup>** – The contemporary city of Ochrid in Southwest Macedonia is a descendant of the ancient town of Lychnidus, a town in the empire of King Philip II of Macedon. It was located along the Via Egnatia, which connected



Figure 4: Caitlin O'Grady analyzes ceramic artifacts at the Arizona State Museum<sup>6</sup> conservation laboratory.

the Adriatic port Dyrrhachium (present-day Dures) with Byzantium. Lychnidus was one of the economic centers that produced its own coins, called “Lychnids,” in the period from 187 to 171 BC (see Figure 5). Only 30 coins are known to exist worldwide.

The results for the “Lychnids” analysis show that the coinage process and chemistry were different. One reason might be the different period and process of coinage. Moreover, the statistically significant difference in Sn concentration as measured on each side of the coin suggests nonhomogeneity of tin distribution within the coin (see Figure 6). Lower Sn concentration is associated with slightly higher Cu concentration. One possible reason for this may be the preferential leaching of Sn caused by the environmental conditions to which the coin was exposed over centuries. This “inhomogeneous” trend is noticeable also on ancient silver and gold coins.

Likely evidence of alloy corrosion was also found, as indicated by the presence of chlorine and sulfur on the coin surfaces. Our He Purge analysis package allows analysis of light elements in alloys, including Mg, Al, P, S, and Cl.

#### Paintings

Our analyzers are the premier handheld XRF tools for paintings conservation. With an optional integrated camera to see the exact area you are analyzing,



Figure 5: Lychnids from National Republic Bank of Macedonia circa 187-171 B.C.

| SAMPLE | Cu    | Cu Error | Co   | Co Error | Fe   | Fe Error | Sn    | Sn Error | Pb   | Pb Error |
|--------|-------|----------|------|----------|------|----------|-------|----------|------|----------|
| Shield | 80.39 | ±0.63    | 0.11 | ±0.02    | 0.24 | ±0.03    | 16.03 | ±0.26    | 2.54 | ±0.07    |
| Prow   | 81.09 | ±0.59    | 0.09 | ±0.02    | 0.22 | ±0.03    | 15.03 | ±0.23    | 2.59 | ±0.07    |

Figure 6: Results of measurements of composition of two sides of a single "lychnid" coin.

the greatest precision, the unique capability of detecting and quantifying barium, as well as the lowest published limits of detection for all elements, XL3 Series analyzers aide painting conservators, art historians, and others in a number of applications including:

- Pre-treatment studies – Knowing the composition of paints and identifying previous conservation efforts before beginning treatment allows the conservator to make better decisions about how to proceed.
- Authentication/Forgery Identification – Historically, paints and pigments were made differently and had different elemental compositions during different periods and in different places. By examining the elemental composition of paints, a conservation scientist can gather useful information about whether the proposed age of a work is likely to be correct.
- Museum studies, art history, and materials characterization – Characterize an artist's palette, learn about the methods of pigment manufacture of an ancient culture, and much more.

**Eastern Poland (Bieszczady Region)** – An icon typical for the time period of the late 17th century was analyzed. The points marked by the numbers shown in Figure 7 indicate where spectra (see Figure 8) were collected with a collimated system.

## Summary

Thermo Scientific NITON XL3 analyzers are the most accurate and robust handheld XRF instruments ever offered for art conservation and archaeometric analysis. Whatever the task, NITON analyzers provide quick, nondestructive analysis of samples in either the lab or the field. Whether your project involves sourcing, conservation, or characterization, put the power of research in your hand with NITON XL3 analyzers, the ideal tools for in-situ chemical analysis of art and artifacts.

## References

1. Dhaliwal, Muninder and Brackett, Claudia. The Use of X-ray Fluorescence (XRF) Technology to Aide Archaeological Investigations to Locate Evidence of Human Occupancy of Prehistoric Sites in Arizona. Stanislaus State University, CA. 2006.
2. Native American Graves Protection and Repatriation Act, 25 U.S.C. 3001 et seq. [Nov. 16, 1990] (Final Regulations, 43 CFR 10 as amended and published in the Code of Federal Regulations October 1, 2003).
3. We would like to thank Richard J. Lundin, director, Wondjina Research Institute, Sonora, Calif., and Claudia Brackett, associate professor, chemistry, and Muninder Dhaliwal, student, California State University - Stanislaus.

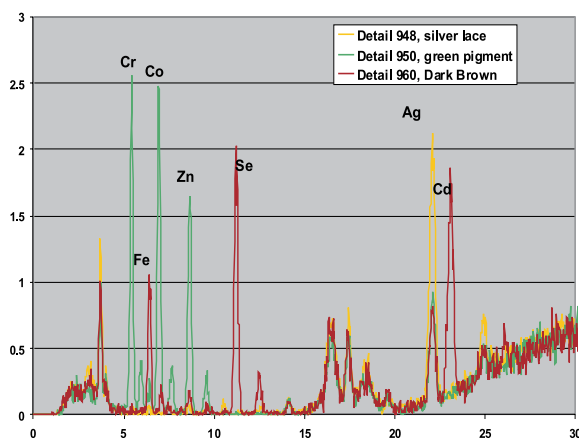
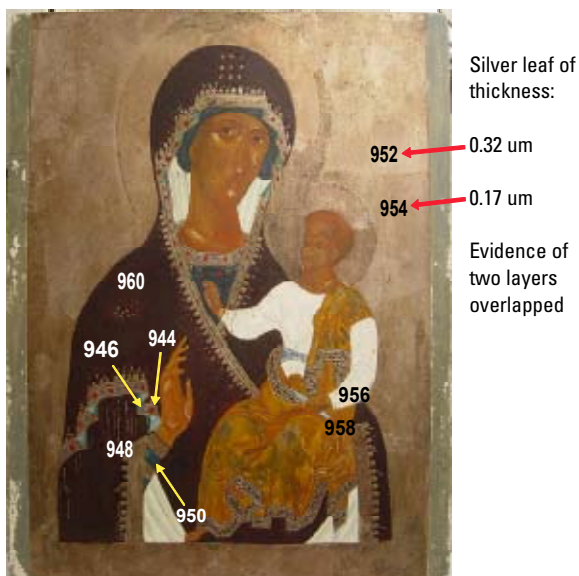


Figure 7 and 8: Spectra of three of the pigment colors on the icon. Composition of the green pigment (Cr, Co), brown pigment (Fe), and silver leaf (Ag), are clearly visible.

4. Morgenstein, Maury and Redmount, Carol A. "Using Portable Energy Dispersive X-ray Fluorescence (EDXRF) Analysis for On-site Study of Ceramic Sherds at El Hibe, Egypt" Journal of Archaeological Science, 32 (2005), pp. 1613-1623.
5. We would like to thank the National Bank of Macedonia for permission to use the data obtained with coins from their collection.
6. We would like to thank Caitlin O'Grady, National Science Foundation Fellow in Archaeological Science; Teresa Moreno, assistant conservator; Nancy Odegaard, conservator and head of the Preservation Division, Arizona State museum, University of Arizona, Tucson, Ariz.

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All competitive references are based on an internal direct comparison of commercially available handheld XRF analyzers, July 2007.

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