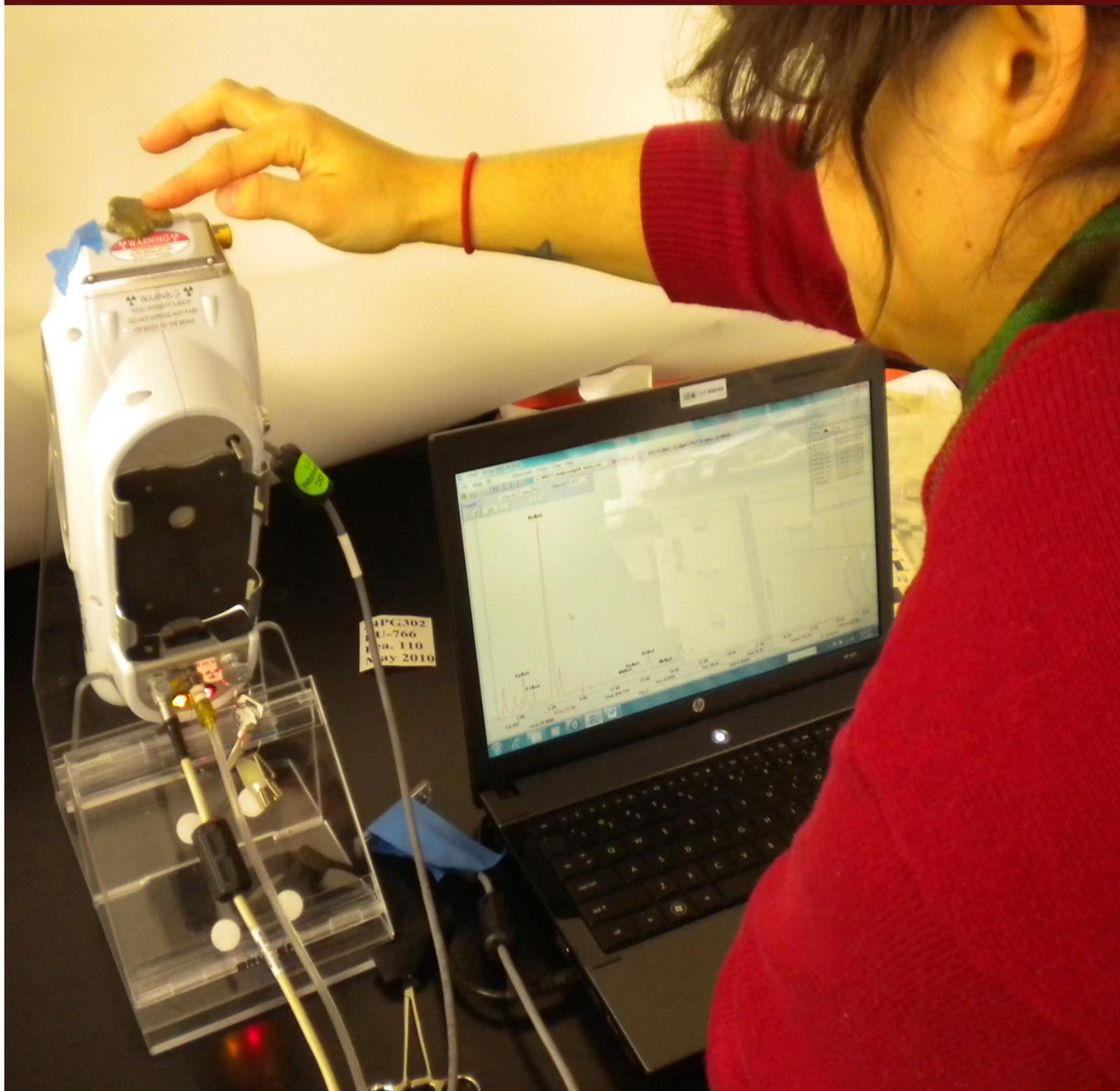




# Development of Ceramic Reference Materials for Calibration and Qualification of Portable XRF Data | 2011-06

Virginia Department of Historic Resources



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### Executive Summary (400 words)

The DHR proposed to develop and establish a set of uniform museum ceramic reference materials replicating common low-fired ceramics. Recent efforts have focused on the development of reference materials related to the identification and quantification of heavy-metal pesticides on Native American artifacts. To date there have been no projects focusing on the development of ceramic reference materials for NDT-XRF instrumentation. During the course of the project, a number of staffing changes, unexpected modifications to employment responsibilities and lack of access to comparative reference materials made it difficult to complete the proposed activities in the original grant application. Therefore, over the course of the funded project, the following activities were conducted and reported.

#### Phase I

- Native American ceramic type collections, curated at the Department of Historic Resources, were photographed, catalogued and analyzed to characterize paste temper and surface decoration.
- Accokeek, Keyser, Mockley, Potomac Creek, Stony Creek, and Varina ceramics, located in Department of Historic Resources type collections, were tested to characterize physical and chemical properties including hardness, density and porosity.
- Selected Native American ceramic wares (Accokeek, Keyser, Mockley, Potomac Creek, Stony Creek and Varina) analyzed with portable X-ray Fluorescence instrumentation (Bruker S1 Tracer III-V+ with Rhodium tube).
- Initial experiments conducted to determine manufacturing parameters of ceramic reference materials using proxy materials.
- Supplies purchased to manufacture proposed ceramic reference materials.

#### Phase 2

- Selected Native American ceramics and purchased reference material supplies analyzed with portable X-ray Fluorescence (XRF) instrumentation [Bruker S1 Tracer III-V+ with Rhodium (Rh) tube source].
- Collected portable XRF data results compiled and compared for analyzed archaeological and reference material samples in order to determine accuracy and precision of data collection.
- Calibration protocol developed using portable XRF instrumentation and proprietary software.
- Tests conducted to determine efficacy of developed calibration protocol.

### Phase 3

- Collected data and results of the project have been gathered for preparation of presentations and peer-reviewed publication.
- A presentation was made to the College of William & Mary graduate seminar series in the Department of Anthropology.
- An abstract has been submitted to the Archeological Society of Virginia (2011) annual meeting.

### Introduction

Over the past 10 years, there has been a dramatic rise in the popularity of using non-destructive portable x-ray fluorescence (portable XRF) analysis in conservation, archaeological and other cultural heritage applications. The ability to produce compositional data that is completely non-destructive, does not require sampling and can be acquired in the laboratory or field setting has become an increasingly important feature in the analysis and conservation of archaeological materials since the passage of the Native American Graves Protection and Repatriation Act (Public Law 101-601) in 1990. Over the years, the use of portable XRF instrumentation in the analysis of museum and repository collections has intensified dramatically to include identification of pesticides, as well as compositional studies of ceramic, metal, pigment/paint and other cultural artifact materials. Additionally, current research questions focusing on the migration and origins of people and artifacts necessitate an efficient, non-destructive and easy method for the analysis of large ceramic collections.

Currently, there are significant research questions associated with the temporal and regional interface of sand-tempered Stony Creek Ware and Accokeek Ware in the Potomac River basin, as well as the transmission of crushed quartz-tempered Potomac Creek Ware and the shell-tempered Keyser Ceramic series across the mid-Atlantic landscape. Due to the fact that the archaeological and historic use of these ceramics is specific to a relatively contained geographic region, they provide an excellent case study for the development of ceramic reference material standards to improve non-destruction analytical methods.

The limitations of commercially-produced portable XRF instrumentation in the analysis of cultural heritage materials have been reported in the literature (Dussubieux et al. 2005, Gianoncelli and Kourousias 2007) and make acquisition of accurate compositional data difficult. Efforts to improve interpretation of NDT-XRF compositional data are necessary through the creation of reference materials that reflect ceramic materials found in archaeological repository and museum collections.

Currently, the DHR is actively engaged in major research projects focusing on the analysis of low-fired ceramics found in the Potomac River basin and how these materials reflect the migration of people, objects and technology over the landscape. The question of migration and ceramic production in this region is particularly important given the fact that these low-fired ceramic wares were produced over a period of 3000 years (1200 BC - A.D.1600) (Gallivan 2003). Identified ceramic series of interest include Accokeek Ware, Keyser Ware, Mockley Ware, Potomac Creek Ware, Stony Creek Ware and Varina Ware. These six ceramic wares reflect the range and variety of low-fired ceramics in the James River and Potomac drainages, as well as the variety of clays and tempering materials used to produce them. Clays are iron-rich and range in degree of percent clay content, while tempering materials include fresh and marine shell, burnt shell, sand, prepared quartz, etc.

Given the importance of archaeological and historic ceramics research in each project, DHR has focused on the development of ceramic reference materials to improve the interpretation of XRF analysis through increased accuracy and precision. Review of the literature indicates the majority of southeastern ceramics incorporate iron-oxide bodies. NIST standard materials have been selected based on their compositional consistency with the majority of prehistoric and historic low-fired ceramic technologies commonly found

in Virginia. Prepared samples replicating ancient, low-fired (600 - 900° C) ceramic compositions will utilize NIST standards in order to make archaeological reference materials.

The manufacture of reference materials is critical towards the creation of homogeneous reference materials with consistent chemical/physical properties including composition, density, porosity and thickness. Any changes in these properties will affect the consistency of instrumental sampling and data collection. Selected archaeological artifacts from the DHR collections will be tested to determine the efficacy of the produced calibration curves. As such, the collection has been researched extensively and there is a strong body of compositional and technological data for southwestern archaeological ceramics. This commitment to archaeological and conservation ceramic research combined with the DHR's dedication to the development of portable XRF protocols for analysis makes it an ideal place to produce museum ceramic reference materials.

Please note that some grant progress has been delayed due to uncertainty about the future of the Commonwealth of Virginia budget in spite of the origin of funds. There has been reticence for the VA DHR to make large material purchases in the current economic climate. Other difficulties encountered during the process of research activity covered by this grant include obtaining access to some archaeological ceramics of interest located in collections outside of the VA DHR, as well as significant changes in staff. These administrative issues have made it difficult to achieve the stated goal of this grant to produce low-fired ceramic reference materials. Furthermore, analytical results indicate that manufacture of low-fired ceramic reference materials would not be successful regardless of administrative changes throughout the grant period.

## **Methods and Materials**

### **Materials:**

#### *1. Native American archaeological ceramic samples*

The VDHR holds significant archaeological ceramic collections from a number of sites across the Commonwealth of Virginia, as well as a modest ceramic type collection. Identified ceramics of interest include Accokeek, Keyser, Mockley, Potomac Creek, Stoney Creek and Varina wares. These six ceramic wares reflect the range and variety of low-fired ceramics in the James River and Potomac drainages, as well as the variety of clays and tempering materials used to produce them.

Additional ceramics selected for analysis were excavated from a number of archaeological sites in Virginia associated with the James and Potomac River drainages. James River drainage sites include the Bartlett (44NK166), Big Island (44NK5), Croaker Landing (44JC70), Great Neck (44VB7), Hatch (44PG51), Irwin (44PG4), Lilly Point (44NK3), Maycock's Point (44PG40), and Newington (44KQ6), as well as several unnamed sites including 44NK1, 44NK11, 44PG5, and 44SX32. Potomac River drainage sites include the Cabin Run (44WR3), Keyser Farm (44PA1), Potomac Creek (44ST2), and Trittipoe (44LD10).

These ceramics were also chosen to reflect the range and variation in tempering materials found in these drainages. Identified temper types include grit, mica, quartz, sand, and shell, as well as combinations. Temper combinations are also observed including grit/sand, grit/shell, sand/quartz and shell/mica. Grit and sand classifications refer to the degree of intentional processing of lithic material for temper – which is generally composed of quartz, quartzite or sandstone (Blanton et al. 1999: 47).

All selected sherds were characterized for physical properties including hardness, density and porosity, as well as their structure and composition analyzed using stereo- and polarized light microscopy and portable XRF instrumentation.

## *2. Ceramic Clays and Reagent Grade Chemicals*

Experiments were conducted to determine the most efficient method to produce the proposed low-fired ceramic reference materials using readily available artist quality ceramic clays and reagent grade chemicals. Selection of clays and reagent grade chemicals was dependent of their availability in local artist supply stores and chemical stock located in the DHR conservation laboratory. Utilized ceramic clays included low-fired and regular formulations (Main Art Supply, Richmond, VA), while reagent grade chemicals included FCC Ca(OH)<sub>2</sub> (calcium hydroxide) powder (Macron<sup>TM</sup> Chemicals and Avantor<sup>TM</sup> Performance Materials), 100 mesh iron powder (Macron<sup>TM</sup> Chemicals and Avantor<sup>TM</sup> Performance Materials), and KCl (potassium chloride) powder (JT Baker<sup>®</sup> and Avantor<sup>TM</sup> Performance Materials).

## *3. National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM)*

Standard Reference Materials (SRM), produced by the National Institute of Standards and Technology (NIST), were selected to manufacture low-fired ceramic reference materials based on their similarity in composition and preparation as powders. SRM 98b, plastic clay, is an “air-dried, ball-milled and blended powdered clay.” Potassium (K), iron (Fe) and titanium (Ti) are present in higher concentrations (National Bureau of Standards Certificate of Analysis SRM 98b). SRM 679, brick clay, “consists of a brick clay that was air-dried, ball milled and passed through 200-mesh sieve” (National Bureau of Standards Certificate of Analysis SRM 679). Fe and K are present in high concentrations. SRM 165a, glass sand, is a blended glass powder with Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> oxides present (NIST Certificate of Analysis SRM 165a).

## **Methods:**

### *1. Physical Characterization of Archaeological Ceramic Samples*

All selected archaeological sherds were characterized for physical properties including hardness, porosity, and bulk density. These physical properties were selected, as they influence the penetration, absorption and attenuation of X-rays and produced X-ray fluorescence. Efforts to develop accurate reference materials depend on the accurate reproduction of observed properties in archaeological samples.

Analyzed samples were selected as representatives of the six ceramic types under investigation including Accokeek, Keyser, Mockley, Potomac Creek, Stony Creek and Varina wares. Due to the limited number of samples in the DHR Native American ceramic type collection, the number of analyzed sherds varied. Additional archaeological samples were analyzed to determine the range and variation in ceramic paste and temper composition from sites located in the James and Potomac River drainages. A table of analyzed sherds was included in previous sections.

### *Hardness*

Sherd surface hardness was estimated through comparison to metals picks of known hardness values equal to 2 – 6 on the Mohs' hardness scale (gypsum, calcite, fluorite, apatite, and orthoclase feldspar). Recto and verso surfaces, which can vary in compaction and surface density due to ceramic finishing method (unfinished, smoothed, polished, burnished, impressed, striated), were tested by scratching the surface with metal picks of various and known hardness. Surface hardness values were estimated by

identifying the hardness range at which the sample surface can be scratched. This method was selected over alternatives due to the limited number of samples in the DHR Native American type collection. There was the curatorial desire to avoid sample breakage due to compression, tensile or shear fracture, which often results from the inclusion of temper in paste compositions. Results are summarized in Table 1.

Ware (# samples)	Hardness Range
Accokeek (2)	3 – 4
Keyser (6)	3.5 – 4.5
Mockley (8)	3 – 4
Potomac Creek (6)	3.5 – 4.5
Stony Creek (5)	2.5 – 3.5
Varina (1)	2 – 3

Table 1: Estimated ware hardness ranges based on experimental results.

#### *Porosity*

Sherd porosity was estimated using the liquid immersion technique described in American Society for Testing and Materials (ASTM) standard C830-00 (2011). Following oven drying at 230°C until constant weight is achieved, the sample is placed under vacuum for 30 minutes. Deionized water is introduced into the vacuum chamber - covering the sample – and the saturated sample remains under vacuum pressure (ca. 30 psi) for 120 minutes – modified from the recommended 60 minutes. Percent porosity,  $P$ , can be calculated using the following formula:

$$P = \frac{W - D}{W - S}$$

where  $W$  is the weight of the saturated sample (grams),  $D$  is the weight of the dry sample (grams) and  $S$  is the weight of the sample suspended in deionized water (grams). This is an appropriate method for the analysis of low-fired ceramics, where there is little paste vitrification and minimal pore closure. This method was selected over water absorption (ASTM C830-00), in spite of research indicating water absorption is more accurate (Harry & Johnson 2004). Preliminary tests indicated that archaeological samples, exposed to boiling deionized water sustained for long periods, sustained edge and surface rounding suggesting some degree of solubility. Porosity results are summarized in Figure 1 and Table 2.

#### *Bulk Density*

Sherd bulk density was estimated using the bulk density technique described in American Society for Testing and Materials standard C830-00 (2011). Following oven drying at 230°C until constant weight is achieved, the sample is placed under vacuum for 30 minutes. Deionized water is introduced into the vacuum chamber until the sample is completely covered. The saturated sample remained under vacuum pressure (ca. 30 psi) for 120 minutes – modified from the recommended 60 minutes. Bulk density,  $B$  ( $\text{g}/\text{cm}^3$ ) is calculated using the following formula:

$$B = \frac{D}{V}$$

where  $D$  is the weight of the dry sample (grams) and  $V$  is the exterior volume ( $\text{cm}^3$ ) calculated by subtracting the suspended weight ( $S$ ) from the saturated weight ( $W$ ). Bulk density results are summarized in Figure 2 and Table 3.

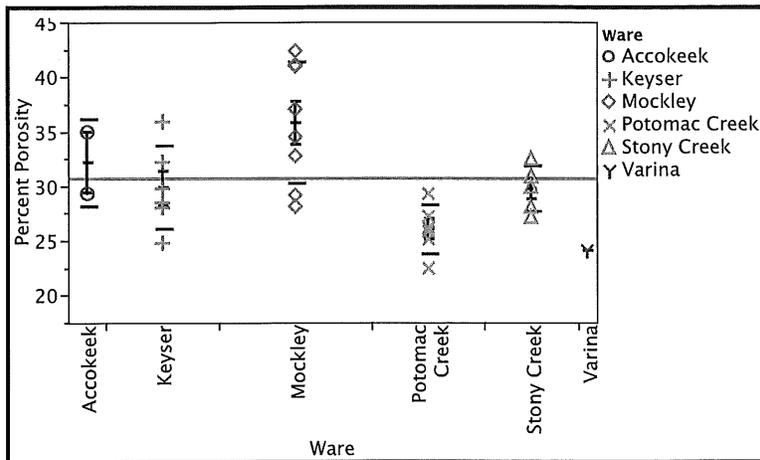


Figure 1: Ware type graphed against calculated sherd porosity. Mean and standard deviation indicated by black bars.

Ware (# samples)	Mean Porosity	Standard Deviation
Accokeek (2)	32.17%	3.98
Keyser (6)	29.84%	3.83
Mockley (8)	35.75%	5.51
Potomac Creek (6)	26.00%	2.27
Stony Creek (5)	29.74%	2.10
Varina (1)	24.124	n/a

Table 2: Ware mean porosity and standard deviation calculated based on experimental results.

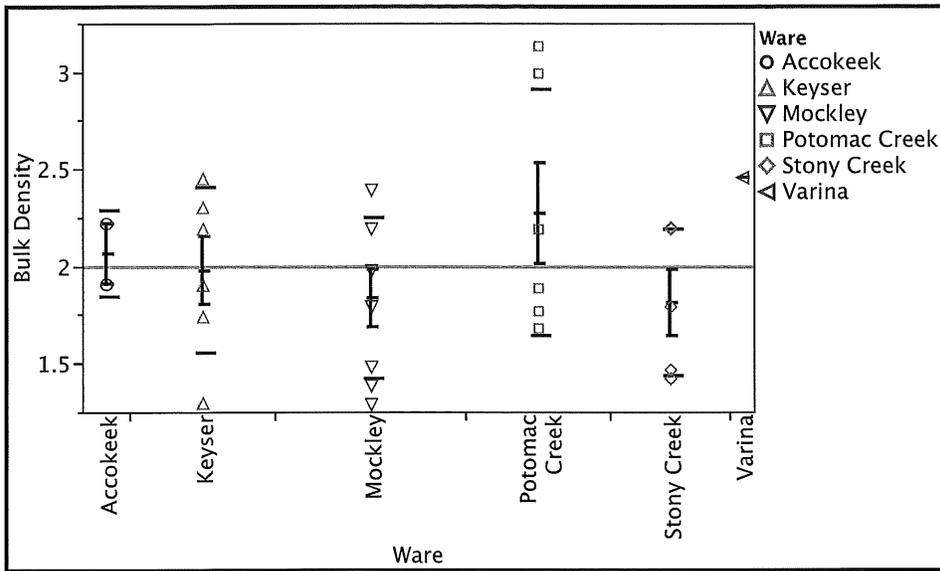


Figure 2: Ware type graphed against calculated sherd bulk density. Mean and standard deviation indicated by black bars.

Ware (# samples)	Mean Bulk Density (g/cm <sup>3</sup> )	Standard Deviation
Accokeek (2)	2.06	0.221
Keyser (6)	1.98	0.424
Mockley (8)	1.84	0.416
Potomac Creek (6)	2.27	0.634
Stony Creek (5)	1.81	0.376
Varina (1)	2.46	n/a

Table 3: Ware mean bulk density and standard deviation calculated based on experimental results.

## 2. Chemical Characterization of Archaeological Samples

Archaeological sherd samples were analyzed to determine their chemical composition using light microscopy to determine present temper and portable X-ray Fluorescence (XRF) to characterize elemental composition. Analyzed samples were selected as representatives of the six ceramic types under investigation including Accokeek (n=2), Keyser (n=6), Mockley (n=8), Potomac Creek (n=6), Stony Creek (n=5) and Varina (n=1) wares. Due to the limited number of samples in the DHR Native American ceramic type collection, the number of analyzed sherds varied.

### *Light Microscopy*

Archaeological samples were examined under magnification in order to characterize temper present in the paste. Identified temper types include grit, mica, quartz, sand, and shell, as well as combinations. Temper combinations are also observed including grit/sand, grit/shell, sand/quartz and shell/mica. Grit and sand classifications refer to the degree of intentional processing of lithic material for temper – which is generally composed of quartz, quartzite or sandstone (Blanton et al. 1999: 47). Results are summarized in Table 4.

<b>Temper</b>	<b>Number of Samples</b>	<b>Ware (if known)</b>
grit	26	Mockley (1), unknown
mica	3	unknown
quartz	6	Potomac Creek (6)
sand	2	unknown
shell	108	Keyser (6), Mockley (25)
grit/sand	48	unknown
grit/shell	2	unknown
sand/quartz	7	Accokeek (2), Stony Creek (5)
shell/mica	2	unknown
unknown	2	unknown

Table 4: Archaeological samples grouped by temper type. Total samples analyzed = 206.

### *Portable XRF Data Collection*

Portable XRF spectra were collected using standard experimental protocols. Data was collected for 300 sections using a Bruker hand held XRF S1 TRACER III-V+ with Rh-tube operated under vacuum at an accelerating voltage of 15 keV and 10.5  $\mu$ A with vacuum and no primary or secondary filters. Data was collected from sherd recto and verso surfaces in order to characterize the influence of sampling volume on date reproducibility. Ceramic forms varied in size and complexity with jars, bowls, plates and other types present. Data collection could not be optimized in all cases. In these instances (concave and convex), artifact-instrument geometry affected data collection through the introduction of air gaps. This results in attenuation of exciting x-rays and decreased collection of associated fluorescence.

Collected spectra and intensity data were visually interpreted to identify spectral artifacts and interferences including escape, sum and diffraction peaks, as well as the presence of Compton and Rayleigh scatter peaks and bremsstrahlung continuum peaks. Data collected from sherd recto and verso were averaged to obtain a uniform composition. Typical spectral patterns can be seen in Figures 3 – 4.

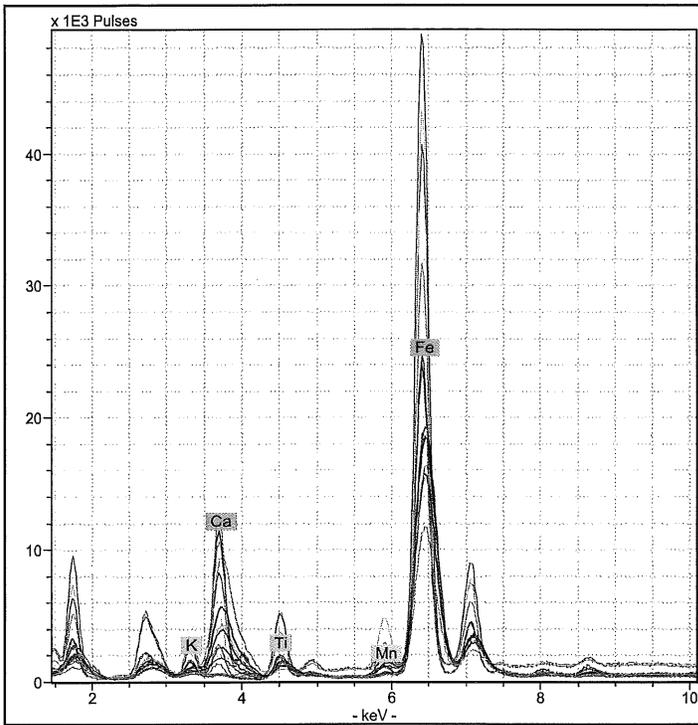


Figure 3: Typical spectra collected for Mockley ceramics.

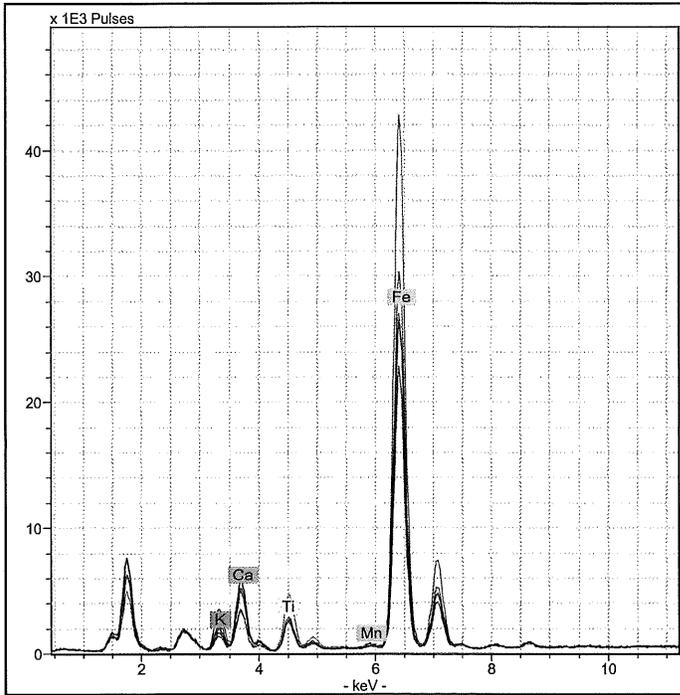


Figure 4: Typical spectra for Potomac Creek ceramics

### *3. Selection of Manufacturing Method for Proposed Low-Fired Ceramic Reference Materials*

Efforts to develop methods for manufacture of the proposed low-fired ceramic reference materials were conducted using readily available artist clays and reagent grade chemicals. Experimental materials were tested to determine their similarity in physical and chemical properties associated with the selected archaeological samples. The selection of NIST standard reference materials was based on previously determined sample compositions collected using portable XRF data.

### *4. Portable XRF Data Correction Procedures*

A number of methods have been proposed to correct XRF data collected from ceramic matrices including Compton scattering correction methods, fundamental parameters or the use of empirical calibration methods and elemental ratios to eliminate inconsistencies in beam parameters. Frequently, Compton methods, which correct spectra through measurement and comparison of background scattered radiation to sample peaks (Nielson 1979), are used to correct data collected from samples with dark matrices, as Compton scattering can be determined for the whole sample (Pessanha et al. 2009). The intensity of Compton radiation can be simplified and determined in cases where the ratio of atomic number to mass number is the same or similar for the sample. Fundamental parameters methods use non-linear XRF equations derived directly from x-ray properties associated with elements and were first developed in the 1950s (Sherman 1955). These equations describe the dependence of x-ray intensity on the concentration and layer thickness of each element present in the sample of known composition correcting for a variety of matrix effects.

Empirical calibration methods calculate region of interests (ROI) for specific peaks by comparing counts per second (CPS) obtained from ROI for specific elemental x-ray lines (Pérez-Arategui et al. 2008). This is corrected through comparison to ROI values collected from samples of known composition. ROI values are proportional to weight concentrations and their square root serves as a measure of experimental error. This allows for comparisons of indirect elemental ratios between artifacts. This technique was selected based on the fact that Compton methods are best suited for samples with dense, crystalline matrices, while fundamental parameter methods rely on specific knowledge, which is unavailable for the DHR archaeological samples, of the interaction of paste constituents to build the complex correction calculations.

### *5. Development of Portable XRF Calibration Protocol*

Portable XRF calibration protocols were developed using ROI and empirical calibration methods constructed from samples of known composition. The ROI values and empirical correction methods relate raw counts collected in known energy channels to selected standard reference materials of known composition (SRM 98b, 679, 165a).

Calibrated portable XRF data was utilized to analyze collected data. Comparisons of Fe concentrations to specific elemental ratios successfully differentiated data collected from the DHR Native American sherd type collection.

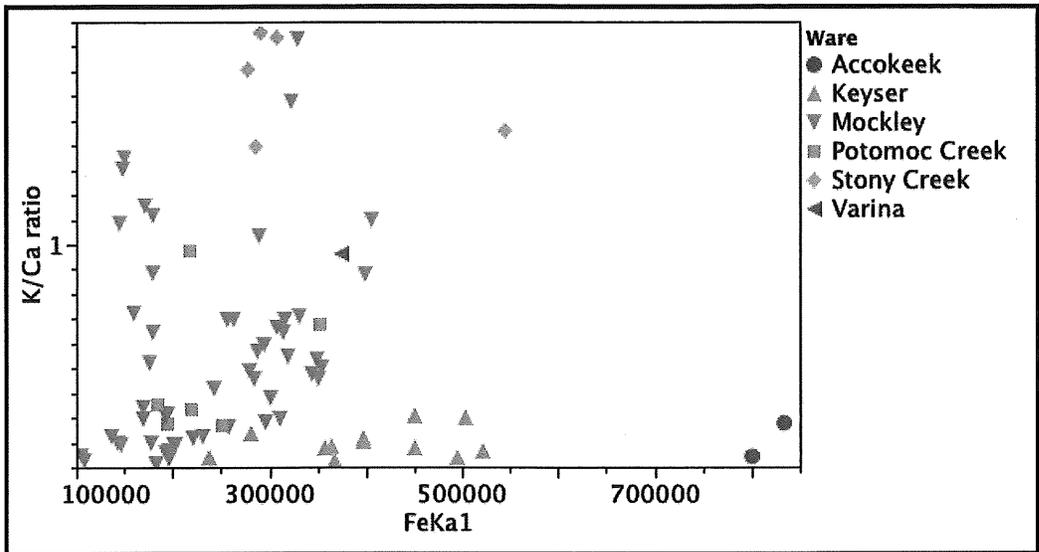


Figure 5: Samples with identified ware classification are graphed by comparing Fe concentrations to K/Ca elemental ratios.

In the above figure, good discrimination between analyzed ceramic ware compositions is achieved for all analyzed wares except Mockley. Collected data suggest that there is a broad range of manufacturing parameters for the fabrication of Mockley ceramics. However, when samples collected from sherds of unknown ware designation, the previously defined compositional regions associated with ware type are not retained.

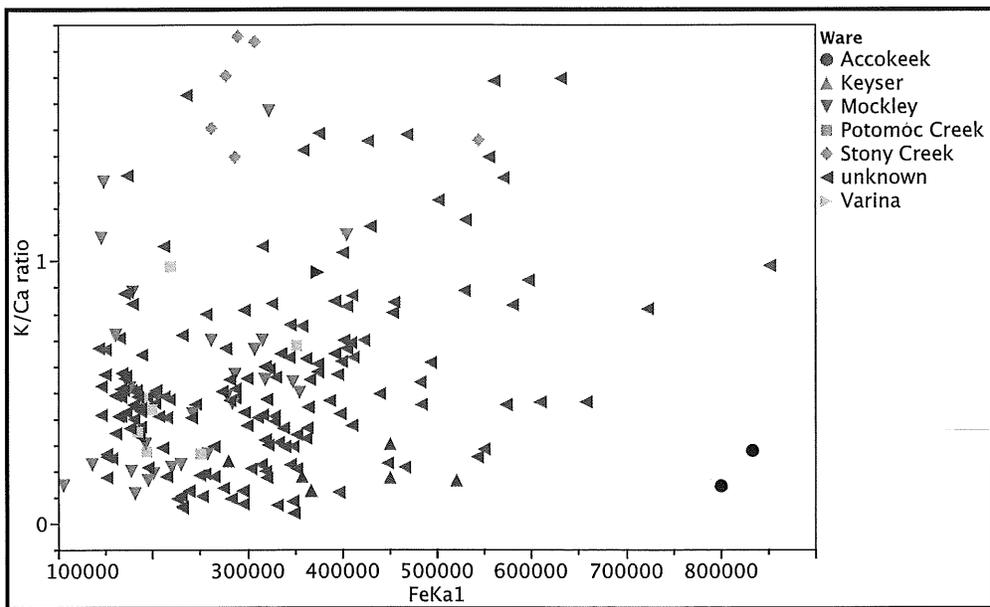


Figure 6: All analyzed samples are graphed by comparing Fe concentrations to K/Ca elemental ratios. Samples are grouped by identified ceramic ware.

Comparison of Fe to K/Ca elemental ratios for all temper types provides the best discrimination of produced data. Unfortunately, it is not very successful in identifying discrete compositional groups. See figure below.

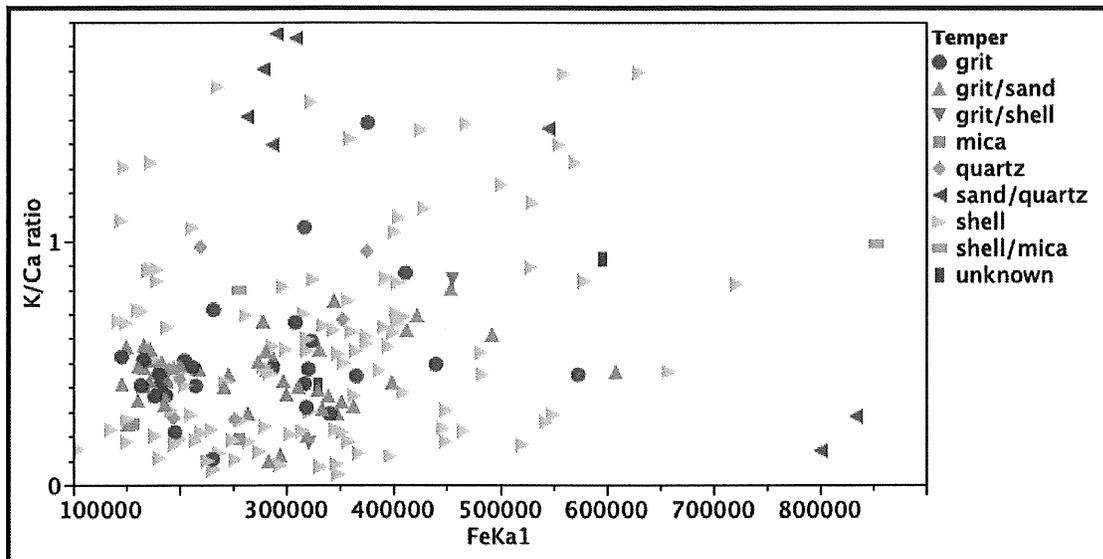


Figure 7: All analyzed samples are graphed by comparing Fe concentrations to K/Ca elemental ratios. Samples are grouped by identified temper.

## Results and Discussion

The production of reference materials requires good analytical data describing material physical and chemical properties. This is particularly critical for reference materials that will be used for calibration of XRF instrumentation. Material hardness, porosity, bulk density, microstructure, elemental and crystalline composition are critical parameters that affect sample interaction with X-ray beams. Produced characteristic fluorescent x-ray energy and its associated ability to escape the sample is dependent on sample thickness, density and the angle of initial x-ray incidence. Sample homogeneity is also critical and characteristics such as composition, mineralogical microstructure and grain size will affect x-ray production either through absorption or enhancement of the intensity of analyte XRF lines (Markowicz 2008: 24). Chemical matrix effects (sample composition) occur when elements present in the sample affect the intensity of the collected spectrum.

Efforts to characterize the physical and chemical properties of analyzed low-fired, archaeological ceramics from the James and Potomac River basin drainages was problematic. Reported hardness, percent porosity and bulk density mean and standard deviation measurements were inconsistent suggesting a wide range of production variability. Variations in hardness measurements reflects final ceramic surface processing and applied decorative effects, which often vary for all six selected ware types (Egloff, personal communication 2009). This also reflects extreme variation in the choice of tempering materials during ceramic manufacture. For example, the degree of temper processing is particularly critical towards recording accurate porosity measurements, as coarse processing often results in larger voids due to leaching of the  $\text{CaCO}_3$  shell temper. This is a problem for both Keyser and Mockley ceramic wares.

Measured chemical composition varies widely and is due to variations in clay and tempering sources used during production. Furthermore, coarse processing of temper will introduce specific microstructure, as well as preferential sampling during portable XRF analysis. Efforts to eliminate this variation would require microstructural analysis using petrographic or scanning electron microscopic methods. Unfortunately, due to curatorial concerns, permission to conduct destructive sampling was not granted, given the relatively small size of the DHR Native American sherd type collection. It is also possible that identified ceramic ware classifications in the Mid-Atlantic region may need to be redefined to reflect these variations.

### **Conclusions**

This project focused on the production of low-fired ceramic reference materials for use with portable XRF instrumentation. In the past decade, the use of portable XRF instrumentation in museums, universities, repositories and other cultural institutions has become universal for the non-destructive analysis of cultural materials. However, produced data must be carefully assessed and analyzed in order to achieve valid and reproducible data. To date, no low-fired ceramic reference materials have been produced. Physical and chemical analyses work completed during the course of this grant suggests that production of low-fired ceramic reference materials, reflecting archaeological samples, is extremely difficult due to problems associated with replicating archaeological samples with a wide range of variation in physical and chemical properties.

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