IDENTIFYING HISTORIC CERAMICS: APPLICATIONS OF X-RAY FLUORESCENCE SPECTROMETRY IN ARCHAEOLOGY

A Thesis

by

MEREDITH ALAYNE STOOPS

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Donny Hamilton
Committee Members,	Filipe Vieira de Castro
	Jonathan Coopersmith
Head of Department,	Cynthia Werner

August 2018

Major Subject: Maritime Archaeology and Conservation

ABSTRACT

Historic ceramics are some of the most important artifacts in archaeological studies because of their prevalence and the wealth of information they can provide about a site. However, identifying certain types of historic ceramics, such as creamware, pearlware, and whiteware, can be very difficult due to the gradual evolutionary processes that took place in the English ceramic industry during the 18th and 19th centuries. Additional difficulties arise when other white- and off-white-colored ware types, such as porcelain, are also considered. This research tested a potential non-destructive method of ceramic identification using a portable X-ray fluorescence (pXRF) spectrometer by examining the glazes of these four ceramic categories: creamware, pearlware, whiteware, and porcelain.

Multiple XRF configurations were used on each ceramic sherd to target specific ranges of elements. Using both qualitative and semi-quantitative methods of analysis, these scans revealed that, although this method did not offer an irrefutable technique for identifying these ceramics, many aspects of the results indicated promising routes of analysis. Two ware types in particular, porcelain and creamware, were both more easily identifiable based on spectrum analysis for the former and trends in manganese and magnesium net photon counts for the latter. The findings from this investigation offer insights into a potential application of pXRF technology for quick, non-destructive historic ceramic identification.

DEDICATION

To my family.

ACKNOWLEDGMENTS

I would like to thank the members of my thesis committee, including my chair Dr. Hamilton, Dr. Castro, and Dr. Coopersmith for their encouragement and assistance throughout the process of this research. Also, I must thank Dr. Dostal for the opportunity he provided, as well as the guidance he gave about the subject matter.

Thank you to Amelia, for all of your support during this research, and to the Science Ducklings, who have been there with me since the beginning of this journey.

Of course, I want to thank my mom, dad, sister, and aunts, who have helped and guided me to this point. Without them I would be lost. Finally, thank you Eric, for being my other half.

CONTRIBUTORS AND FUNDING SOURCES

This work was supervised by a thesis committee consisting of Professor Hamilton and Professor Castro of the Department of Anthropology and Professor Coopersmith of the Department of History.

The research topic was presented by Professor Dostal of the Department of Anthropology, and the data were collected in collaboration with Amelia Hammond of the Department of Anthropology.

All other work conducted for the thesis was completed by the student independently.

There are no outside funding contributions to acknowledge related to the research and compilation of this document.

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CHAPTER I

INTRODUCTION

Archaeology is a scientific investigation into the past, and the tools and methods used to interpret data are grounded in scientific research; however, within archaeology there is always the possibility for error. Many aspects of studying an archaeological site remain interpretive. Artifact identification is often one of those aspects. Certainly, artifacts can be measured and described in any number of ways, and they can be categorized according to these observations, but often these observations cannot lead the archaeologist to definitive answers. If an archaeologist does not know how to properly identify one type of ceramic ware from another, no amount of measuring will be helpful during visual or physical analysis. Ceramic glazes can be a good diagnostic tool. For instance, certain distinguishing characteristics include blue color pooling in joints on pearlware ceramics and yellow pooling on creamware ceramics. Once again though, if a ceramic sherd is small or possesses no distinguishing visual characteristics, proper identification is made even more difficult. It is therefore necessary that either every archaeologist be extensively trained in ceramic identification, or that a scientific procedure be used for the process that erases any doubt or error concerning proper artifact identification.

This research intends to address this issue by assessing the utility of using X-ray fluorescence (XRF) analysis to test the plausibility of accurately identifying historic ceramic wares based on the composition of ceramic glazes. Ceramics are ubiquitous within archaeological excavations from the historical period, but the transformations and standardizations made in the British ceramic industry during the Industrial Revolution created multiple categories of wares that are visually difficult to distinguish from one another. This difficulty is compounded when only fragments of ceramics are recovered. Decorations may not be visible, or the vessel type may be unknown, and all that the archaeologist has to go off of is an assemblage of white- or slightly off white-colored sherds. Analysis of ceramic pastes requires databases of known kilns and is difficult and often inconclusive. Through elemental analysis of historic ceramic glazes this study will attempt to provide an alternative to the guesswork of ceramic identification. The method was tested with a portable XRF (pXRF) spectrometer. These devices allow for greater flexibility for either *in situ* analysis in the field or off-site analysis in a laboratory. A Bruker Tracer III-SD portable XRF model was used during this research.

Importance of the Project

Part of the importance of this research lies in the practical applications afforded historical archaeologists. X-ray fluorescent spectrometers have been used in archaeology for several decades now. Recently though, the use of X-ray fluorescent spectrometry within archaeology has grown significantly, in part because of the introduction of portable spectrometers. In particular, the trend of decreasing costs for owning and operating a portable XRF device has made them particularly suitable for cultural resource management entities, as well as universities and museums. The ease with which these devices can be used for *in situ* analysis offers greater opportunities for more archaeologists to learn how to implement them in their research. It is important to note that this “point and shoot” ease of use can lead to the false sense that the machine always produces usable results; however, a certain amount of introduction and training must be given to archaeologists in order to understand and analyze the data produced by pXRF spectrometers. With that in mind, meaningful data analysis can be obtained by any archaeologist who has been properly introduced to the basic principles of XRF spectrometry. The use of a pXRF spectrometer for this research would therefore allow for widespread practical applications.

A successful outcome within this research could influence future archaeological investigations, but only if the information were available to the archaeological community. An exciting possibility for this sort of XRF research is the production of a shareable database that can be used by others, as is often done with obsidian XRF data such as the Wavema Archaeological Research Project Obsidian XRF Database from The Digital Archaeological Record (Liebmann 2016). This would allow others to compare research and reference the calibrations used for scanning the ceramic sherds. Sharing data and research is the only way to improve and standardize techniques, particularly for those involving scientific equipment such as XRF spectrometers, which may be widely used but with various settings and calibrations. The potential for this manner of research rests not only in its practicality but also in its ability to be distributed.

A third important element within this research is the importance it holds for the author. Analysis and identification of historic ceramic wares has always been a personal difficulty and I have long hoped to better familiarize myself with them. This research topic, introduced to me by, at the time a PhD candidate and now Dr. Christopher Dostal, a faculty member of Texas A&M University, offered the perfect opportunity to do just that. It also offered a wonderful chance to learn how to operate a portable XRF spectrometer. Due to the increasing use of XRF in archaeology and conservation, learning how to operate this device and analyze the data was an opportunity that could not be missed. The outcome of this research may prove beneficial for future archaeological investigations, and importantly, it has certainly proved beneficial for my understanding of historical ceramics and learning new technical skills.

CHAPTER II

X-RAY FLUORESCENCE SPECTROMETRY, AN OVERVIEW

Concepts: Physics and Chemistry

As previously mentioned, an introduction into the principles of XRF spectrometry is necessary before the device can be used and the data can be interpreted. A brief description of the physics at play and how an XRF spectrometer works follows.

X-rays make up part of the electromagnetic spectrum, which also includes visible light, ultraviolet light, infrared, and radio waves (Moens et al. 2000:56). Just as with visible light, X-rays function both as waves and as particles, called photons, and can be measured in both formats. When described as a wave, electromagnetic radiation is characterized by its wavelength, which directly correlate to the energy of the radiation. The wavelength is determined by the distance between consecutive crests. Shorter wavelengths will have a shorter distance between crests and will therefore travel at a higher frequency. The higher the frequency at which radiation is traveling, the greater the energy it will have. X-rays have high energy, short wavelengths, and high frequency (Shackley 2011:16). The wavelength of electromagnetic radiation is measured in metric units, and the only portion of the X-ray spectral range used for fluorescence analysis falls between 10 and 0.01 nanometers ($1 \text{ nm} = 1 \times 10^{-9} \text{ m}$). In terms of energy, which is measured in electron-volts (eV), this corresponds to between 0.1 and 100 keV, or kiloelectron-volts (Moens et al. 2000:56-57).

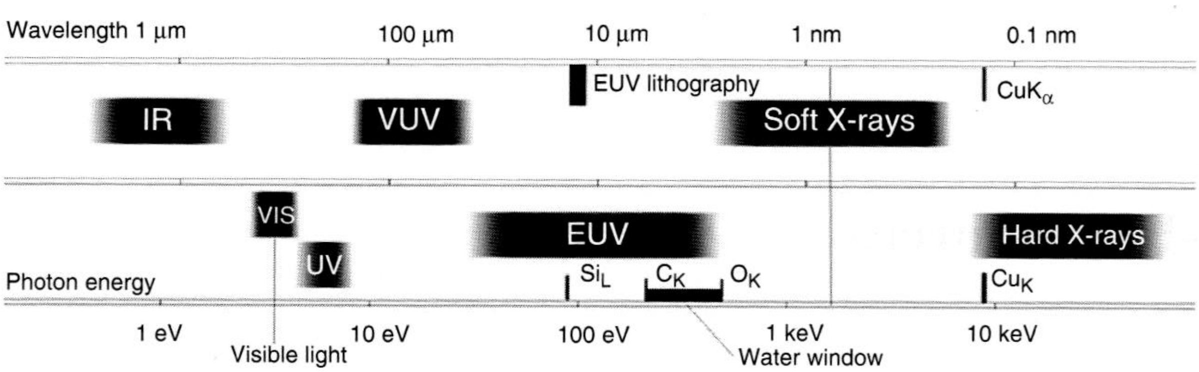


FIGURE 1. Electromagnetic radiation spectrum (IR=infrared, VIS=visible light, UV=ultraviolet, VUV=vacuum ultraviolet, EUV=extreme ultraviolet). (Langhoff and Simionovici 2006: 34)

The purpose of X-ray fluorescence is to "identify and quantify the chemical elements" within a material sample (Artioli 2010:34). This is accomplished by the production of X-rays, which are projected towards the material sample with the objective of removing electrons from the inner shells of the material's atoms. Atoms consist of protons, neutrons, and electrons. The positively charged protons and neutrally charged neutrons make up the nucleus of an atom, and the number of protons within an atom's nucleus dictates its atomic number, or Z number, and the element it represents. These values are arranged numerically in the periodic table of elements. Surrounding the nucleus are the electrons which move around the nucleus in different shells. These shells are groups of atomic orbitals, labeled alphabetically beginning with the letter K; therefore, the shell closest to the nucleus is the K shell, the next closest is the L shell, and so on. In each shell electrons require a different amount of energy to stay in orbit around the nucleus. Electrons closer to the nucleus need less energy to stay in place than electrons further from the nucleus. Additionally, these energy differences are "known and fixed" (Shackley 2011:16).

This knowledge is one of the most important concepts for the foundation of X-ray fluorescence analysis.

The X-rays produced in the XRF analyzer are projected towards the sample being analyzed with enough energy to penetrate the atoms within that sample and remove electrons from the innermost shells (Moens et al. 2000:57). This X-radiation energy must be greater than the binding energy of an electron shell, in order to remove the electron (Čechák and Leonhardt 2006:55). Each shell requires a different amount of energy to dislodge an electron from it, and these energies are different for each element. Removing electrons from a stable atom produces an unstable ion, and electrons from shells further from the nucleus move in to fill that void and stabilize the atom (Shackley 2011:17). During this instance the atom is relaxed from an excited state, where the electron has been dislodged, to a ground state, when the void is filled by outer shell electrons, and the atom stabilizes once again by emitting a photon with characteristic energy (Artioli 2010:30).

In most instances, an electron from the K shell is removed and then replaced by an electron from the adjacent L shell, resulting in a Kα peak on the spectrum. Additionally, though less commonly, an electron from the M shell can replace the one lost on the K shell, resulting in a Kβ peak. Each kind of peak has its own unique energy signature. These basic principles also apply to instances when an electron from the L shell is dislodged. In that instance a Lα peak would represent an electron from the M shell replacing an electron lost on the L shell (Moens et al. 2000:57-58).

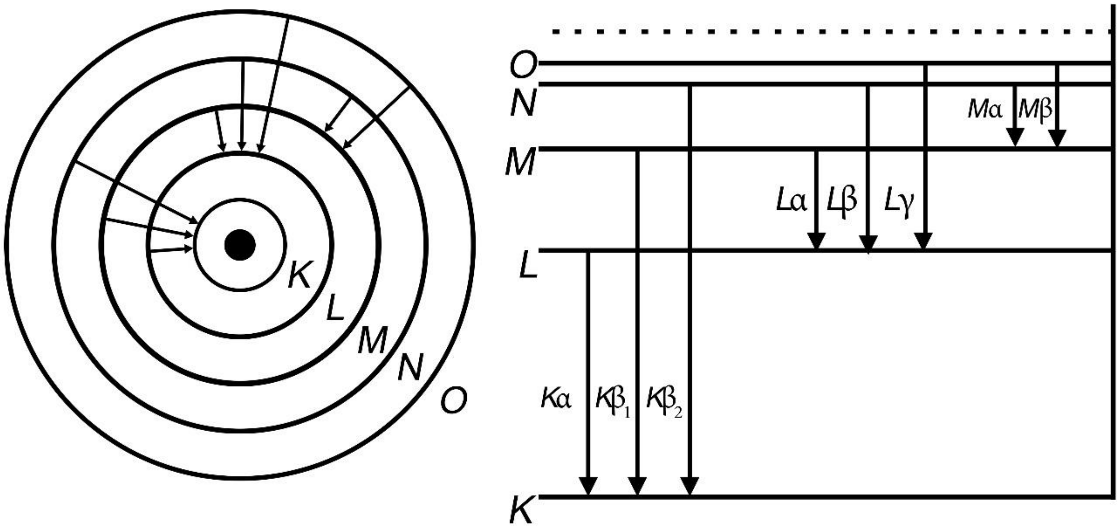


FIGURE 2. Electron shell transitions. (Moens et al. 2000:58)

The importance of the shell's individual energy levels comes into play the moment an electron from an outer shell drops down to an inner shell as it now requires less energy than it originally had to stay in orbit. This excess of energy is released in the form of secondary radiation, or photon particles, in the X-ray region of the electromagnetic spectrum. This process of re-emitting radiation is called fluorescence, referring to the glow emitted by the photons (Moens et al. 2000:57; Artioli 2010:32,34). The wavelength of these secondary X-rays is unique to each element. The elemental composition of a sample is detected by the energy released from secondary radiation, which corresponds to the atomic number of an element. This information is then displayed graphically by an X-ray spectrum (Moens et al. 2000:57-58). The x-axis displays the keV energy, indicating what elements are present, and the y-axis displays the net photon count for each element, which are represented as peaks on the spectrum.

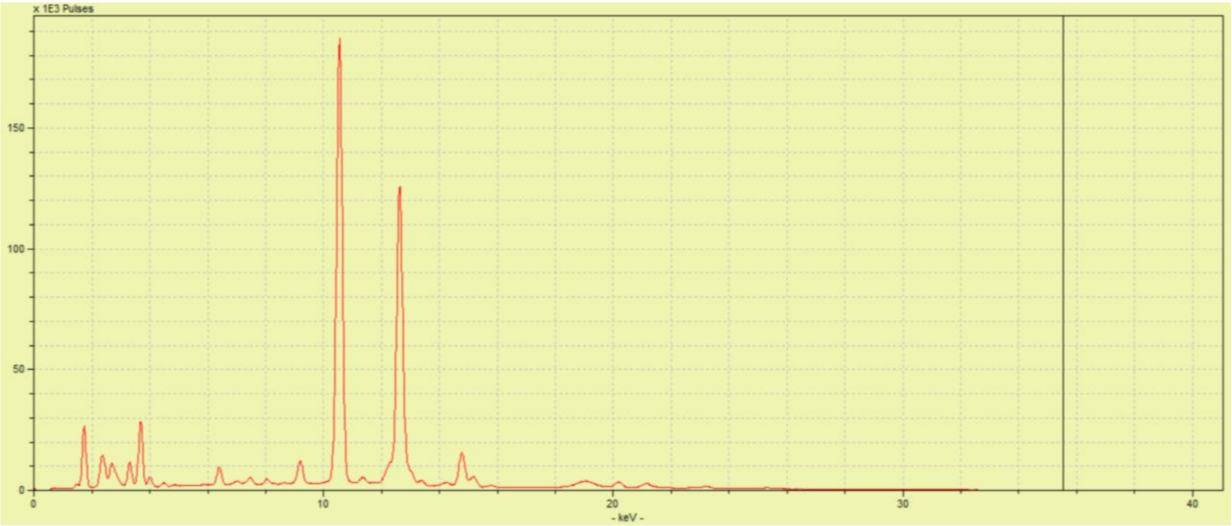


FIGURE 3. A spectrum produced from XRF; each peak represents a different energy level detected by the spectrometer. (Spectrum by author using ARTAX, 2018.)

It is vital to note that a number of things can happen during this interaction other than the one described above. This is the ideal interaction that reveals the chemical composition of the sample; however, the X-rays do not always remove electrons from the inner shell of the atoms. In these instances, either “background” or scattering may be produced, and these will show up on the X-ray spectrum. The term “background” is used to describe “noise that appears in the spectra due to deceleration of electrons as they strike the anode of the X-ray tube” (Shackley 2011:23-24). This “noise” is also referred to as *bremsstrahlung*, German for “braking radiation.” The scattering process taking place causes a continuous background and is more severe when analyzing elements of low atomic numbers. Depending on the instrument being used it may be impossible to analyze any element below atomic number Z=11, sodium (Na), in a reliable way (Bruker 2016:9: Shackley 2011:24).

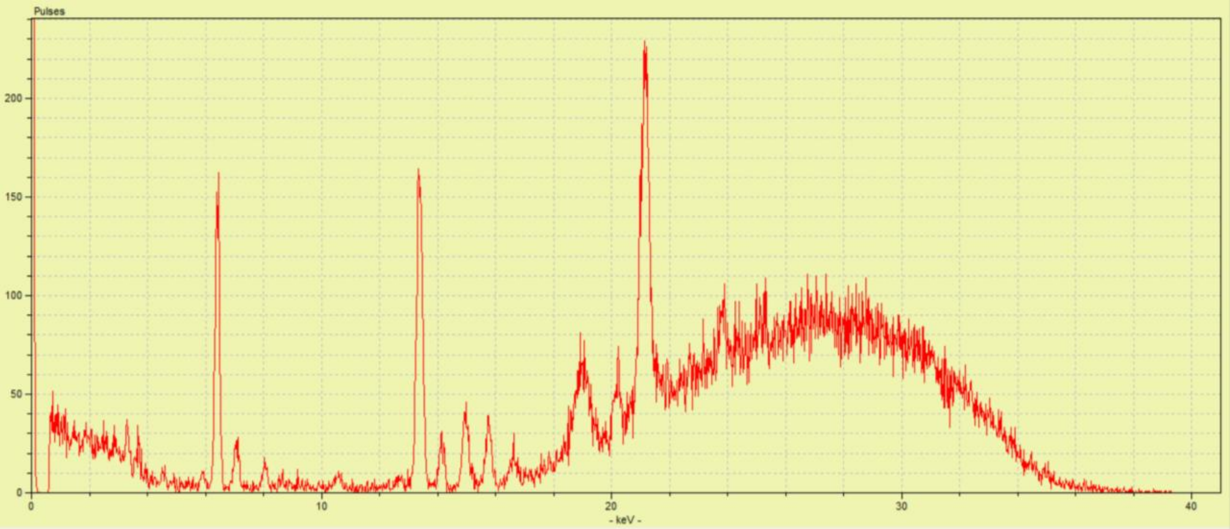


FIGURE 4. Example of *bremsstrahlung* in a spectrum, resulting in a distorted peaking shape on both ends. (Spectrum by author using ARTAX, 2018.)

Two additional forms of scattering, or reflection, appear on the spectra created by XRF. Rayleigh scattering results in the appearance of the peak of the anode material on the spectra. This occurs as X-ray photons coming off of the anode interact with the atoms of the sample without producing secondary fluorescent X-rays. The primary X-rays do not lose energy but are redirected towards the detector of the XRF device, creating a peak on the line spectrum of the anode material. This is also known as elastic or coherent scatter. Compton scattering, also referred to as inelastic or incoherent scattering, will occur as the incident X-rays interact with the atoms of the sample. In this case photons from the X-ray tube do lose energy as they strike an electron from an outer shell. These photons are picked up by the detector with an energy reading slightly below that of the anode material. Each detector will have a different peak, known as a Compton peak, depending on the anode and the settings of the X-ray tube, and these must be known and understood by the operator to ensure accurate data interpretation. The Bruker Tracer III-SD model used in this research has a Compton peak around 19 keV as a result of its rhodium (Rh) anode. The effects of scattering can be reduced by placing filters between the X-ray source and the sample (Bruker 2016:10; Shackley 2011:22-23).

Applications in Archaeology

While portable spectrometers are the latest technology in the field of X-ray fluorescence spectrometry, this method of scientific investigation has been in use for many years. X-ray fluorescence has been used in archaeology for many applications and for many decades. Archaeologists have been supplementing their research with XRF spectrometry since the 1960s for analyzing a range of materials (Frahm and Doonan 2013:1426). These include but are not limited to soils, rocks, metals, ceramics, and obsidian. One of the most important roles XRF has had in archaeology is its use in provenance studies, particularly for ceramic and obsidian artifacts (Davies et al. 2011:46; Moens et al. 2000:68-69). Scientists have used XRF spectrometry on obsidian to determine the specific volcanic locale of the raw material, and they have applied the same principles to clay to find its source of origin for ceramics artifacts. Knowing the source of the material informs researchers as to where the site inhabitants may have come from, travelled to, or traded with, enhancing archaeologists' perspectives on the people they are studying.

Portable X-ray Fluorescence Spectrometers

With the advent of portable XRF spectrometers, the application of this science in archaeological studies became more widespread. There are a variety of portable devices available today, allowing for easier access for archaeologists (Frahm and Doonan 2013:1425). Since archaeology is an amalgamation of several different fields such as history, geology, chemistry, and biology, researchers use techniques and equipment from each of these fields to formulate and supplement their work. The use of pXRF spectrometers, which have grown primarily out of the geology profession, has been no different. Archaeologists were quick to realize its potential for their research because it was developed for timely, non-destructive study of various materials. This allowed for rapid analysis *in situ*, whether at an excavation in the field, or at a museum analyzing materials that must not be destroyed (Liritzis and Zacharias 2011:109; Ceccarelli et al. 2016:253). In addition to the applications XRF was initially used for in archaeology, the growth of portable spectrometers increased the range of its uses to include on-site material characterization. The portability factor had an impact on conservation science, analysis of pigments, and authentication testing (Liritzis and Zacharias 2011:112-114). Without the restrictions of a laboratory setting, archaeologists are able to gather data in a myriad of settings, and the reduction in size of the detector does not equate to a loss of performance. In fact, “many PXRF systems currently on the market have superior detector resolution and electronics than laboratory-based instruments manufactured 5-10 years ago” (Speakman and Shackley 2013:1436).

Limitations Using Portable X-ray Fluorescence Spectrometers

Although portable X-ray fluorescence spectrometers offer a more approachable option for buying and operating this brand of scientific instrumentation, they are not without their own set of limitations. The ease of use of pXRF devices is in fact a growing concern because it promotes a “point-and-shoot” mentality amongst new researchers; these machines appear straightforward enough that little to no proper training seems necessary, simply point the device at a sample, run the scan, and see the results appear on a screen (Hunt and Speakman 2015:638). The opposite is true, but such devices are advertised in ways that can mislead archaeologists. X-ray fluorescence spectrometers work best when properly calibrated to the material being studied. In regards to the analysis of archaeological ceramics,

> The ability to generate accurate and reliable compositional data for archaeological ceramics and sediments by pXRF requires a matrix matched calibration and a material specific analytical protocol. … Analysis of unprepared samples is not fully quantitative using a pXRF spectrometer because of the heterogenous nature of ceramic and sediment samples and matrix effects which prevent X-rays from interacting with the unprepared sample in the same way as the prepared calibration standards. This differential interaction or response to the X-rays causes the analytical software to over or undercalculate elemental concentrations in the sample material (Hunt and Speakman 2015:637).

Hunt and Speakman (2015) were referring to analysis of ceramic body materials and sediments, but the issues concerning pXRF analysis are true for any material and were a factor within this research. Portable XRF spectrometers come with a number of out of the box calibrations, but these are “not always appropriate for archaeological materials analysis” (Hunt & Speakman 2015:626). However, beneficial qualitative data can be obtained through the use of pXRF spectrometers even when the calibrations do not allow for reliable quantitative data. Determining the compositional characterization of ceramic glazes within this research was not intended to ascertain the material point of origin, but rather the human-manufactured categorization of a ceramic ware type. The aforementioned out of the box calibrations were relied upon during this research. These do not provide the high-quality data a specifically calibrated machine could, but this aspect provided another component to test the ease of use for this method of ceramic identification.

One of the most pressing concerns with pXRF analysis was previously mentioned—that of an untrained operator. Not only is safety paramount when operating a radiation producing device, but these concerns also encompass the experience levels of archaeological pXRF users in regards to their knowledge of X-ray physics, statistics, or chemistry, all of which are involved in XRF analysis (Speakman and Shackley 2013:1435). An experienced introduction to the topic is necessary before any analysis should be undertaken, which I too received before beginning this research. As in any endeavor, more experience usually leads to better results. Since this was my first independent research using XRF, this investigation may have suffered from that pitfall. However, this investigative research also tested the difficulty of employing this method of ceramic identification for archaeologists newly trained in X-ray fluorescence spectrometry.

Another limitation that portable XRF spectrometers present is the scatter caused by unprepared samples. Benchtop spectrometer analysis is done with specifically prepared samples that are designed to limit interference. A smooth, flat surface is best, which means that samples are ground and formed into pellets to create this ideal surface for traditional spectrometers. Portable devices are popular because they can be used to test material outside of a laboratory setting and they can be used non-destructively, but these benefits complicate the ideal parameters of X-ray fluorescence analysis. Unprepared samples may suffer from surface contamination such as corrosion products on metals, or their surfaces may be too rough. The use of such samples introduces chemical contamination and matrix effects (Hunt and Speakman 2015:627). The effects from sample flatness and surface texture are recognized as one of the more difficult issues pertaining to *in situ* pXRF analysis (Liritzis and Zacharias 2011:132). All of the sherds used in this research came from collections that have already been cleaned and conserved. While surface contamination from soil or dirt was not an issue, surface flatness still presented a potential difficulty. During every scan the flattest portion of each sherd was set on the spectrometer, but the analysis of unmodified artifacts with rough surfaces still likely contributed to scattering.

There is one limitation of pXRF spectrometer use that could actually favor the focus of this research. It has been debated how successful its application is for studying ceramics due to the scattering caused by their uneven surfaces (Ceccarelli et al. 2016:253). However, one aspect remains advantageous in its use on ceramic glazes. The incident radiation of X-ray fluorescence has limited penetration into the sample. Therefore, the elements found on and near the surface of a sample are predominantly detected, which was ideal for this investigation into ceramic glazes (Ceccarelli 2016:254). There was less chance of detecting elements from the ceramic body for this reason. The depth of analysis increases with higher energy, and elements with higher atomic energies can be detected further into a sample than elements with lower atomic energies. Elements with low energies, or low Z numbers, are less likely to have been affected by the underlying ceramic body and focusing on these could prove more valuable during analysis of surface glazes.

CHAPTER III

HISTORIC CERAMICS

Research Focus: From When and Where

“Pottery was perhaps the first craft to be transformed to an industry” (Rado 1969:207). This research focused on those ceramics that grew from the industrialization processes that swept across Western Europe during the mid-18th century. England was the hub of industrialization during the onset of the Industrial Revolution’s first phase, which began around 1760 and lasted until approximately 1880. A growing population, a portion of which was developing into a newly-founded middle class, contributed to England’s workforce, technological innovations, and changing production systems (Stearns 2013:14-15, 25). The country was transformed, not only in manufacturing, but also in agriculture, trade and economy, and the demand for goods (Young 1999:10-11).

England’s preeminence in industrialization extended to ceramic production, and it dominated the market for refined earthenwares during this period (Majewski and O’Brien 1987:114). It was during this period that creamware, pearlware, and whiteware were developed and popularized; each ceramic type will be individually discussed later in the text. Pottery of this nature is abundant throughout archaeological excavations in the United States and across the globe. There were U. S. ceramic factories during this time, but the dominance of the English products left little room for profitable competition; however, distinguishing between English ceramics and their American imitations can be difficult (Denker and Denker 1982:138).

Ceramics of English origin provided the bulk of the ceramic selection for this study, though several may also have been of U. S. origin.

A contributing factor for the popularity of these ceramic types was the trend to imitate Oriental, or Chinese and Japanese, porcelain. Porcelain influenced European ceramics both aesthetically and technologically, and English potters sought out new materials to lighten the color of their products (Clow and Clow 1958:328; Majewski and O'Brien 1987:116). The quest to create a lighter, whiter ware to imitate porcelain produced a number of early attempts. Tin-enamel glazes, which had long been used by potters, created a white exterior glaze on red or buff clay bodies. Later, a white-firing kaolin clay was used for white salt-glazed stoneware vessels. Mixing white-firing clay with calcined flint produced a suitable earthenware clay body that would later be covered with a clear lead glaze (Clow and Clow 1958:346-347). Following these advancements from the industrial era, traditional ceramic practices such as tin-enamel glazing soon began to disappear (Caiger-Smith 1973:189).

English pottery "went through an evolution in paste and decoration that in theory would make ceramic pieces ideal temporal markers for sorting archaeological assemblages" (Majewski and O'Brien 1987:98-99). The basis for that theory is understandable, that specific ware types have distinctive attributes that tell them apart, but the practice of applying that theory to archaeological studies is where problems arise. This period in ceramic history is revolutionary, marking a dramatic shift in manufacturing techniques and ceramic design. The sheer output of English ceramics also makes this period particularly important to study because these wares are unearthed in most archaeological contexts. However, the level of subjectivity that also arises when categorizing these wares is troubling, strengthening the argument for a scientific approach to ceramic classification.

Ceramic Sample

The ceramic sherds used in this research were gathered from resources readily available within the department. Three ceramic assemblages were pulled from for sampling; these included the Port Royal, Jamaica excavations, the CSS *Georgia* excavations, and a typology collection assembled by Dr. Donny Hamilton. Select sherds that were plainly identifiable as creamware, pearlware, or whiteware based on visual diagnostic criteria, such as blue pooling in crevices on pearlware, were pulled from each assemblage for testing. Included is a brief description of each assemblage.

Port Royal

Port Royal was England's most important economic New World establishment during the latter half of the 17th century. The Jamaican port was successful in part because of its protective harbor as well as its involvement in "officially sanctioned privateering" during that period (Hamilton 1984:11). It was also vital to the trades in sugar, natural resources, and slaves. However, on 7 June 1692 an earthquake struck and about 66% of the city suddenly sank below the water, into the harbor. During the event around 2000 people died and another 3000 perished soon after of disease and injury (Hamilton 1984:12). Indeed, the strength of the Spanish presence in the Caribbean limited the options for English settlements, and the area where Port Royal was established was unfit for a city. It has been continually challenged by natural forces, including "47 hurricanes and major storms, at least nine earthquakes of major or moderate intensity, as well as two major fires" between the years 1597 and 1994 (Dewolf 1998:26). Due to the catastrophic nature of the 1692 earthquake, Port Royal is a uniquely preserved 17th-century site because much of it appears to have sunk straight down without major lateral movement as a result of liquefaction during the earthquake.

The Institute of Nautical Archaeology was invited by the Jamaican government in 1978 to begin new excavations of Port Royal. In cooperation with Texas A&M University and the Jamaica National Heritage Trust, excavations took place from 1981 to 1990 under the direction of Dr. Donny Hamilton (Donachie 2001:20; Hamilton 1984:15). The excavated material has since been used in numerous theses and dissertations at Texas A&M University. Although Port Royal is a 17th-century site, artifacts post-dating the site were recovered as archaeologists excavated down to their target layer. The site consisted of three levels. The uppermost was Layer 1, which contained primarily 20th-century material. Just below that was Layer 2 with artifacts primarily from the 18th and early 19th centuries, mixed in with some 17th-century artifacts. Finally, Layer 3 was the bottommost layer on which the city was actually built. It consisted mostly of the floors of the 17th-century structures and contemporary artifacts (Donachie 2001:21). Ceramics used during this research will likely have been recovered from Layer 2.

CSS *Georgia*

During the American Civil War, in 1862, the ironclad vessel CSS *Georgia* was built for the protection of Savannah. Heavily armored and armed, the vessel was composed of a barge-like structure fitted with an inclined wooden roof that was then covered with interlocking iron railroad T-rails as protective plating. *Georgia* was built through the efforts of the Ladies Gunboat Association; women from Savannah, Augusta, and other areas of Georgia helped to raise over $115,000 for the construction of the vessel. Two years later it was intentionally sunk by the Confederates. On 20 December 1864 the CSS *Georgia* was scuttled in the Savannah River to prevent the Union from capturing it after Union troops had taken Fort Jackson (Garrison and Anuskiewicz:74,78).

Since then the wreck has been damaged by salvaging and dredging activities. Most recently, the planned deepening of the river as part of the Savannah Harbor Expansion Project posed a serious threat to the site as it would completely destroy what remains of the ship. Since the site is listed on the National Register of Historic Places, the threat of destruction warranted the necessity of excavation. Headed by the U.S. Army Corps of Engineers, two field seasons (2015 and 2017) have thus far worked on excavating the vessel and its associated artifacts. These artifacts are currently undergoing conservation at the Conservation Research Laboratory at Texas A&M University. The ceramic assemblage recovered from the site is sizable and diverse, ranging from Native American coarse earthenware sherds to modern ceramic pieces. Ceramic specimen that have already undergone excavation from the 2015 field season were selected for testing in this research.

Typology Collection

Following the excavations at Port Royal, Dr. Donny Hamilton created a ceramic typology to appropriately identify and label sherds for processing and research purposes. Certain ware types were given numerical numbers which were further delineated by decoration type through decimal numbers. For instance, a creamware sherd would be labelled “7” to identify it as creamware. If it were undecorated, “.10” would be added, resulting in “7.10.” Following this method, a pearlware sherd with green transfer printed decoration would be labelled “8.62” and a Chinese porcelain sherd decorated with the Willow pattern would be labelled “1.17.” Every ware type was given a number, and subsequent decimal numbers were applied to describe variations. From these efforts, select ceramic specimens were pulled from the excavation material and used as representative samples. Nearly every category is represented in this separate typology collection. Although Port Royal material forms the core of the typology collection, additional ceramic material has been added to it from other archaeological sources. Since this collection has already been neatly categorized and sorted, selecting suitable material to test was straightforward.

CHAPTER IV

A LOOK AT CERAMICS AND THEIR GLAZES

Glaze Attributes

As previously mentioned, this study will be examining the glazes of different types of ceramics. Therefore, it is important to understand the structural and chemical attributes of glazes and why they are important for ceramic vessels. Glazes become fused to the body of a ceramic vessel by firing them in a kiln; ceramics are generally fired in a kiln twice. The first time the clay body is fired without a glaze in what is known as the bisque, or biscuit, firing. The second firing, known as the glost firing, is done with the glaze applied to the ceramic body (Rice 1987:99). This double-firing technique was not always used in English ceramic production but was introduced to the Staffordshire region by Enoch Booth around 1750. It steadily spread and gained popularity throughout England; potters preferred it over the single-firing method and salt-glazing technique used on stoneware vessels because it was easier and more economical (Clow and Clow 1958:348-349).

Glazes serve multiple functions. They are primarily applied in order to create a non-porous surface. Pottery that is not fired at sufficiently high temperatures to vitrify the clay will remain porous. Glazes serve to make these vessels impervious as well as mechanically stronger, more resistant to chemicals and scratching, smoother, and more attractive (Rhodes 1957:56; Singer and Singer 1963:525). They are able to accomplish this because glazes are a special form of glass that "forms a highly viscous coating melted or fused at high temperatures onto a ceramic body" (Rice 1987:98). The composition of the clay and the glaze must have complimentary rates of shrinkage in order to fuse correctly; if the glaze shrinks too much it can cause crazing and cracking, while shrinking too slowly will not allow it to fuse properly.

Glazes are essentially glass, but in order to adhere to the surface of a ceramic vessel they must be adjusted to meet that particular function. The viscosity of glazes must be increased so that they do not run off the vessel during firing. This is accomplished by the addition of aluminum oxide (Al_2O_3) (Rhodes 1957:55). Chemical components in glazes are utilized and described as oxides; these elements have been chemically combined with oxygen through natural processes (Rhodes 1957:61). The molecular formula for each element described in this section will be given in its oxide form. There are three components that make up a glaze: network formers, network modifiers, and intermediates (Rice 1987:98). The majority of the structure of a glaze is comprised of the network formers, and silica (SiO_2) is the primary former for most glazes. Additional formers include boron (B_2O_3) and phosphorous (P_2O_5). The second component, modifiers, are typically added to lower the melting point of the network formers, thus acting as fluxes. Silica has a very high melting point, around 1710°C, and modifiers such as sodium (Na_2O), potassium (K_2O), lead (PbO), calcium (CaO), and magnesium (MgO) are commonly added to reduce the firing temperature needed to melt the glaze. Finally, intermediates such as aluminum (Al_2O_3), lead (PbO), zinc (ZnO), zirconium (ZrO_2), and cadmium (CdO) "are oxides that replace part of the silica and usually serve one or both of two functions. One is to increase the viscosity (stiffness) of the glaze, which was originally lowered by adding fluxes. … A second function of intermediates is to strengthen the glaze in firing" (Rice 1987:99). In some instances, certain elements serve several purposes and may represent more than one component in a glaze. Lead may act as a modifier by lowering the melting temperature of the glaze, and it may act as an intermediate by strengthening the glaze during firing.

Refined Earthenware

This investigation into ceramic glaze materials focused on three forms of refined earthenware: creamware, pearlware, and whiteware. The fundamental aspects of glazes were mentioned in the previous section; this section will describe the chemical details of refined earthenware glazes in more detail. Earthenware vessels have unvitrified bodies that have not become glass-like, as is the case with porcelain (Rice 1987:5). During the double-firing method, the biscuit firing temperature for earthenwares such as those listed above is around 1050-1150°C. The second glost firing temperature is lower, usually around 950-1050°C (Rado 1969:4).

The reason for this lower glost firing temperature is because of the primary modifier, or flux, used in earthenware glazes. Lead (PbO) has been used as one of the principal fluxing ingredient for glazes across the world because it reliably produces a blemish-free glaze. However, it does become volatile above 1200°C and cannot be used in high-firing glazes (Rhodes 1957:66). It can also cause lead poisoning through the food and drink prepared and served in such dishes if not fired to the correctly determined temperatures. Lead glazes were in use from Rome to China as early as the Han Dynasty (ca. 206 B.C.) (Clow and Clow 1958:332). Its dependability is one reason for its wide-spread use, another is its contribution to appearance. Lead will create a glaze with a brilliant finish (Rado 1969:112). It is also versatile. Alone in a silica glaze, lead creates a clear, colorless product. It can then be easily colored by the addition of ingredients such as iron, cobalt, or manganese. It can also be given a white or opaque appearance with the addition of tin ash, or stannic oxide (Clow and Clow 1958:333).

The three primary ingredients in earthenware glazes are silica, alumina, and lead oxide. Depending on the recipe and material sources for the glaze, proportions of these and the remaining ingredients will differ. Differences will occur naturally within ware types, due to manufacturing differences, but will these be too great to define a specific ware type? The proportions of main ingredients may not reveal significant differences in ware type, but the proportions of minor and trace ingredients may. For an earthenware glaze these ingredients could include feldspars, which have an alumino-silicate framework in which different elements fill the cavities to create different feldspars. Potassium (K_2O) results in potash feldspar ($K_2O.Al_2O_3.6SiO_2$), sodium (Na_2O) in soda feldspar ($Na_2O.\ Al_2O_3.6SiO_2$), and calcium (CaO) in lime feldspar ($CaO.\ Al_2O_3.6SiO_2$) (Rado 1969:31-32). Carbonates may also be present, such as calcium carbonate ($CaO.CO_2$), magnesium carbonate ($MgO.CO_2$), or barium carbonate ($BaO.CO_2$), though the last can cause disproportionate shrinking and is rarely used (Rado 1969:36-37). Table 1 lists various raw materials used in ceramic glazes. X-ray fluorescence will allow us to determine the elements found within a glaze, but not specifically the origin of the raw materials those elements originate from.

TABLE 1 Raw Materials Used in Ceramic Glazes

Oxide Desired	**Raw Material**	**Other Oxides Introduced**
Silica (SiO_2)	Crystal Quartz, Quartz Sand, Flint	-
	China Clay	Al_2O_3
	All Feldspathic and Micaceous Minerals	K_2O, Na_2O, Li_2O, and Al_2O_3
	Wollastonite	CaO
	Talc	MgO
	Zircon	ZrO_2

TABLE 1, CONTINUED

Oxide Desired	**Raw Material**	**Other Oxides Introduced**
Alumina (Al_2O_3)	China Clay	SiO_2
	All Feldspathic and Micaceous Minerals	K_2O, Na_2O, Li_2O, and Al_2O_3
	Corundum	-
	Aluminum Hydrate	-
Potash (K_2O)	Potash Feldspar	Al_2O_3 and SiO_2
	Nepheline Syenite, Cornish Stone	Na_2O, Al_2O_3, and SiO_2
	Potassium Nitrate	-
	Potassium Carbonate	-
Soda (Na_2O)	Soda Feldspar	Al_2O_3 and SiO_2
	Nepheline Syenite, Cornish Stone	K_2O, Al_2O_3, and SiO_2
	Sodium Carbonate	-
	Borax	B_2O_3
Lithia (Li_2O)	Spodumene, Petalite	Al_2O_3 and SiO_2
	Lepidolite	K_2O, Al_2O_3, and SiO_2
	Amblygonite	Al_2O_3, P_2O_5
	Lithium Carbonate	-
Lime (CaO)	Wollastonite (rarely)	SiO_2
	Lime Feldspar (very rarely)	Al_2O_3 and SiO_2
	Calcium Carbonate (viz. Chalk, Limestone, Marble)	-
	Dolomite	MgO
	Calcium Borate	B_2O_3
Magnesia (MgO)	Talc	SiO_2
	Magnesium Carbonate (viz. Magnesite)	-
	Dolomite	CaO
Baria (BaO)	Barium Feldspar (Celsian, very rarely)	Al_2O_3 and SiO_2
	Barium Carbonate	-
	Barium Sulphate (Barytes)	-
Strontia (SrO)	Strontium Carbonate	-
Zinc Oxide (ZnO)	Zinc Oxide	-
	Zinc Carbonate	-
Lead Oxide (PbO)	Lead Oxide, Red Lead, Lead Dioxide, Lead Carbonate, etc.	-
Boric Oxide (B_2O_3)	Boric Oxide	-
	Borax	Na_2O
	Calcium Borate	CaO

TABLE 1, CONTINUED

Oxide Desired	**Raw Material**	**Other Oxides Introduced**
Tin Oxide (SnO_2)	Tin Oxide	-
Zirconia (ZrO_2)	Zirconia Zircon	- SiO_2

Source: Rado (1969:129).

Porcelain

Refined earthenware ceramics were the main focus of this research, and one the reasons for this is the difficulty in distinguishing them by appearance. This difficulty increases when dealing with small, broken sherds. An additional category of ceramics, porcelain, may therefore also be difficult to identify when small and undecorated specimens are being analyzed, particularly for the novice student or technician. A small sample of porcelain ceramics were included in this study for this reason. The sample size was smaller and less emphasis was given to porcelain; the goal was simply to determine the major difference between earthenware and porcelain glazes in order to provide a simple guideline for comparing them.

Less analysis went into the porcelain sample used in this study, but it is important to understand the variances that are present in porcelain studies. There are several categories of ware that are included within the porcelain classification, such as hard-paste porcelain, soft-paste porcelain, and bone china. These differ in ingredients and firing temperatures. The data gathered from the porcelain samples will likely reflect this, but little effort was spent on distinguishing between porcelain types because the emphasis of this research was refined earthenware ceramics. The classic example of porcelain is hard-paste and originated in China and Japan. Most of the sample tested appeared to be of this type. It differs from earthenware because its body is composed of the purest of clays called china clay or kaolin (Rado 1969:7, 15). A traditional composition for this porcelain body is 50% kaolin, 25% feldspathic rock known as china stone or *petuntse*, and 25% quartz (Rado 1969:177; Rice 1987:6; Young 1999:17).

The appearance of porcelain sherds can be difficult to differentiate from white refined earthenware sherds. The clay has little or no additives or discoloring oxides, such as iron oxide, that will discolor it, and therefore fires white. The glaze does not need any additional coloring agents to produce a white finish over the body (Rado 1969:15, 18). The amount of iron is so low, around 0.5%, that the firing atmosphere actually produces a bluish-white tint. Hard-paste porcelain is fired in a reducing atmosphere, which lacks oxygen. Within this atmosphere the small amount of ferric oxide in the clay is reduced to ferrous oxide, providing a bluer tint rather than the greyish-yellow tint iron typically produces in ceramics (Rado 1969:98, 117). During firing, which is usually done in a single operation for hard-paste porcelain, temperatures reach between 1300°-1400°C, causing the body to vitrify and appear translucent. The body and glaze also fuse at such temperatures because the “glaze is chemically allied to the feldspathic materials of the body” (Young 1999:16-18). As this occurs the body “takes up a large amount of the glaze” but the glaze usually appears separate from the body “in a translucent line” (Majewski and O’Brien 1987:128).

Glazes for hard-paste porcelain are typically feldspathic, consisting of silica, alumina, and *petuntse*. They may be mixed with sand, quartz, lime, or potash (Majewski and O’Brien 1987:110). They differ starkly from glazes used on refined earthenware ceramics in that they contain no lead or boron compounds (Rado 1969:179). Hard-paste porcelain is fired at such high temperatures that lead would become volatile and cannot be used. Recognizing porcelain glazes compared to earthenware glazes using XRF should prove straightforward because of this important variation. However, it seemed necessary to briefly include them in this study because of their popularity and the potential to mistake them with refined earthenware types based on visual cues.

CHAPTER V

CERAMIC WARES: DESCRIPTIONS AND BACKGROUNDS

Creamware

A brief overview of each ware types history is necessary in order to appreciate the similarities that make identification challenging. Such challenges stem from the continuity of form and decoration that began in England with white, salt-glazed stoneware, which was prevalent prior to the introduction of creamware, and persisted through the popularity of creamware and pearlware (Majewski and O'Brien 1987:116). As industrial manufacturing transformed the ceramic industry and refined earthenwares became more easily produced, the popularity of the higher priced, white salt-glazed stoneware waned under the influence of less expensive creamware, or cream-colored earthenware (Clow and Clow 1958:353). The perfection of a thin, double-fired, cream-colored earthenware that was dipped in a clear lead glaze was transformative and one of the most important developments for ceramics during the 18th century (Noël Hume 1969:123).

Creamware, a term never used by potters or merchant of the time but instead coined by archaeologists (more on this will be discussed in a later section), owes its pale yellow-cream coloring to the high content of lead present in the glaze (Majewski and O'Brien 1987:117; Cushion 1976:87). After its initial introduction, "production expanded rapidly between 1750 and 1760" (Clow and Clow 1958:350). The ware was not invented by renowned potter Josiah Wedgwood, but he is credited with its refinement and perfection by 1762. It is often referred to as "Queen's ware" after Wedgwood notably sold a tea set to England's Queen Charlotte, an act that helped cement the ware's success and popularity. Earlier products are noted to, generally, be deeper yellow in color. Pieces that date to the late 18th century and early 19th century tend to be paler, nearing the whiteness that later wares would achieve. This difference appears most pronounced by about 1785 (Noël Hume 1969:125-126). The later pieces are some of the more difficult ones to distinguish from pearlware or whiteware. Creamware's popularity continued to rise; by the end of the 18th century it enjoyed massive success in England and abroad (Majewski and O'Brien 1987:117). However, the rate of innovation for ceramics was increasing as quickly as trends were shifting, and creamware's popularity began to fade just as white salt-glazed stoneware's had before it.

Pearlware

In contrast to creamware, pearlware was in fact developed by Wedgwood as he experimented with ways to create a whiter ware. He offset the natural yellow tint of creamware through the addition of a small amount of cobalt to the glaze as well as increasing the flint content in the body. Archaeologists today call it pearlware, Wedgwood termed the ware "Pearl White" (Noël Hume 1969:128). Introduced in 1779, it contributed greatly to the decline in popularity of creamware (Majewski and O'Brien 1987:118). Pearlware is said to resemble hard-paste porcelain, except for its lack of translucency. The desire for porcelain was a contributing factor for its development. Creamware had saturated the market, causing a decline in its demand. Coupled with that was England's protective tariffs against the importation of foreign porcelain. (Miller 1980:15-16). This context allowed pearlware to proliferate the market, and it almost instantly became widespread. On archaeological sites of the early 19th-century pearlware is the most common ceramic type found (Noël Hume 1969:129-130). Typical dates of prominent use range from 1780 to about 1830 (Sussman 1977:105). However, due to continuing developments in the ceramic industry pearlware too was falling out of fashion by 1820 or so (Noël Hume 1969:130).

Prior to pearlware the body of refined earthenware ceramics were still naturally yellow or cream colored. Wedgwood added a small amount of cobalt oxide to the glaze which accomplished two things: first, it whitened the appearance of the ceramics in the same manner that bluing laundry creates a whiter looking product, second, it created a slightly blue-tinted ceramic that was indicative of the highly sought after Chinese porcelain wares. The addition of the cobalt gave the glaze a slight "bluish" tinge that is characteristic of pearlware and a more concentrated blue color that puddles in the crevices and junction of the vessel (Majewski and O'Brien 1987:118). Very little cobalt is needed to act as a bluing agent—less than 0.001% is effective (Rado 1969:145).

Similar to creamware, pearlware displays pattern of change throughout its production, though every manufacturer will differ. Pearlware of the 18th century tends to be "characterized by a light, cream-white fabric covered with a thin, soft, blue- or blue/green-tinged glaze" while 19th-century pearlware "is heavier and whiter with a harder, more brilliant glaze that may vary from deeply blue-tinged to almost colorless" (Sussman 1977:105-106). The trend towards a whiter ware continued as pearlware progressively evolved into whiteware, a gradual and undefinable transition that creates difficulties when attempting to identify ceramics. The clear presence of blue pooling therefore outlined the distinction between pearlware and whiteware in this study.

Whiteware

This English refined earthenware continuum that grew out of industrial techniques culminated with the manufacture of whiteware vessels. As the name suggests, whiteware is almost pure white in color. Its creation is not credited to a single potter nor does it have a single date of conception, instead it developed gradually from various potters during the early 19th century. The transition from pearlware to whiteware is indistinct; the fashion of white ceramics led potters to modify their formulas. For glazes this meant "creating a range of products with gradually decreasing amounts of bluing in the glaze" (Miller 1980:16). In some instances, it is possible that the amount of cobalt in the glaze decreased while the amount of cobalt in the body increased, creating a whiter body (Majewski and O'Brien 1987:120).

While there is not a well-defined transition from pearlware to whiteware, it is clear that whiteware was developing by the 1820s and possibly as early as 1810. (Miller 1980:2). This appears to have been influenced by the rising production of bone china in England, an altered form of porcelain that used bone ash in the body to contribute to its white color (Majewski and O'Brien 1987:119; Young 1999:68). Bone china had been introduced around 1800 and is credited to potter Josiah Spode. The popularity of this product demonstrated the continued appeal for white ceramics, influencing earthenware potters to tinker with their recipes and transition from pearlware whiteware (Miller 1980:17).

Porcelain

The traditional Chinese hard-paste porcelain wares had been imported to Europe since the 14th century, though it was not until the 17th century and increased trading with the Far East that their popularity intensified (Young 1999:14). Hard-paste porcelain had been produced in China since the 9th century and European attempts to re-create it were unsuccessful until about 1718 (Cushion 1976:16). Following the breakthrough of this technological barrier, hard-paste porcelain became widely manufactured throughout continental Europe (Majewski and O'Brien 1987:127). This form of porcelain was unrivalled by most other European ceramics because it was technically superior; vessels were thinner, of a finer quality, waterproof, and could have more elaborate decorations. Only with the introduction of cream-colored wares did hard-paste porcelain have a realistic competitor (Young 1999:15).

While England also had a number of factories producing hard-paste porcelain, imitations known as soft-paste porcelains were widely manufactured. These included bone china, *steatitic* or *soaprock* wares, and a glassy form of porcelain, all of which were made from different ingredients, and fired at lower temperatures, than traditional porcelain (Young 1999:17-18). Of these, bone china became particularly fashionable within England and most English pottery factories were producing this form of porcelain at the beginning of the 19th century (Young 1999:68). It is so named because bone ash was used as an ingredient in the body, roughly 50%; it may have first been used to try and whiten the color of the body, though it also strengthened the paste for firing (Cushion 1976:18; Young 1999:17). Although technological improvements in the manufacture of refined earthenware led to more competition with porcelain, it always retained a favored position in the market.

In reference to this investigation, porcelain samples have not been noted as either hard-paste or soft-paste, though some of them have been reasonably identified. There was no effort to source or date them either. Their inclusion in this investigation was not to distinguish between porcelain types, but rather to offer a comparison against the three refined earthenware types. A short description of the different types of porcelain helps to understand and identify variations that may occur when sampling sherds using XRF. Although not immediately pertinent, it may prove helpful in the future to pursue an investigation like this with porcelain varieties, especially for 19th-century porcelains which are more difficult to categorize according to source (Majewski and O'Brien 1987:127).

Archaeological Classification of Ceramic Wares

As mentioned in the Introduction, fundamental to the topic of this research are the complexities associated with classifying archaeological ceramic specimens. Classifying earlier ceramic material tended to be easier; a typology for 17th- and 18th-century sites was developed that broadly separated ceramics into three categories: porcelain, stoneware, and earthenware. Each of these had their own subdivisions, but the variety of color and decoration made classification fairly straightforward. The changes that took place in England's ceramic manufacturing during the second half of the 18th century and the continuity throughout the following ceramic evolution subsequently meant that classification of 19th-century ceramics became more difficult. Wares had to be classified according to slight variations of color, such as cream or blue, even when the differences could be extremely subtle (Miller 1980:1-2).

According to Miller (1980:17), the typology that was created for 19th-century classification includes three groups: clearly whiteware, clearly pearlware, and something in between. The condition of the sherd and the elements of the vessel still intact may or may not allow an archaeologist to properly identify it as pearlware or whiteware. Although he did not include creamware into his initial categorization, Miller (1991:1) later described the additional difficulties of distinguishing creamware by the 1830s because it was "considerably lighter in color and would be classified as a whiteware by most archaeologists." He referred to creamware as CC ware, for cream-colored, a term used in both potters' and merchants' records by 1790.

These three categories of ware types are widely used in archaeological research, but few sources can actually agree on the criteria and definitions for sorting them (Majewski and O'Brien 1987:99, 105). This stems from the continuous nature of ceramic technological development at the time when ceramic wares were not in fact "static entities" (Majewski and O'Brien 1987:106). Potters were often making subtle and thoughtful changes to their products in order to achieve a desired outcome; the scientific and systematic approach to ceramic production meant that the transition from one ware type to another could be incremental, making current classification standards disputable.

The level of subjectivity in the categorization of these specific ceramics can create problems in any research. The descriptions of these ware types may appear straightforward on paper, but the practice of classifying actual sherds allows for human interpretation to affect the results. Just as Miller (1980:2) described, if you present an assemblage of early 19th-century ceramics to six archaeologists and ask them to sort by ware type, you will receive six different accounts of the assemblage. Despite such a degree of subjectivity, this form of ceramic typology is still widely used, and in the context of this research some very straightforward guidelines were applied for categorizing ceramics. Sherds with crevices in the molded decoration or at the junction of a footring or handle were sought out to identify blue pooling so that whiteware and pearlware could be easily distinguished. Older creamware samples were used because of their tendency to be darker and more clearly recognizable as cream-colored. Yellow pooling in crevices was also used as a means of identifying creamware. Some sherds without crevices or corners had previously been sorted, particularly those from the typology collection, and were included in the sampling. Once again, porcelain samples were not specifically sorted by their variations of ware types.

An important aspect to bear in mind with archaeological ceramic studies is the discrepancies between archaeological terms and historical terms used to describe pottery. As previously mentioned, the term pearlware is heavily used by archaeologists but was rarely used historically. Instead, the original "Pearl White Ware" and variations thereof were used, though it is not always clear as to what kind of pottery was being described in these records (Miller 1980:3). It can be difficult to discern the classification system used by potters and merchants of the time, and the archaeologically assigned typologies "may have little or nothing in common with how ceramics were cataloged, marketed, and purchased" (Majewski and O'Brien 1987:99). Ware-based sorting is historically-based, but not historically-accurate; "terms like pearlware, whiteware … rarely appear in the price lists and account books" (Miller 1980:3). Nonetheless, ware-based sorting is widely used and is an effective form of categorization for archaeological research.

There is a more specific form of ceramic classification centered on decoration and vessel form, and that is arguably a better technique for detailed ceramic identification. Looking back into the historical record, decoration was the determining factor for the prices for pottery by the 1790s (Miller 1980:3). While detailed ceramic analysis should absolutely take decoration and form into account, some ceramic samples cannot be appropriately studied in this way. Broken sherds of all shapes and sizes are recovered from archaeological excavations, many of them without any identifiable features or decorations on them. In these cases, it is necessary to utilize the simplified ware classification that archaeologists have used for years. Projects may also not have the time or funding to conduct in-depth analysis of their ceramic assemblage and may rely on a quick, ware-based typological system. Ceramic ware identification is only one aspect of a more complex ceramic analysis that archaeologists can use, but it is particularly helpful with assemblage chronology and remains a relevant and useful tool for ceramic identification.

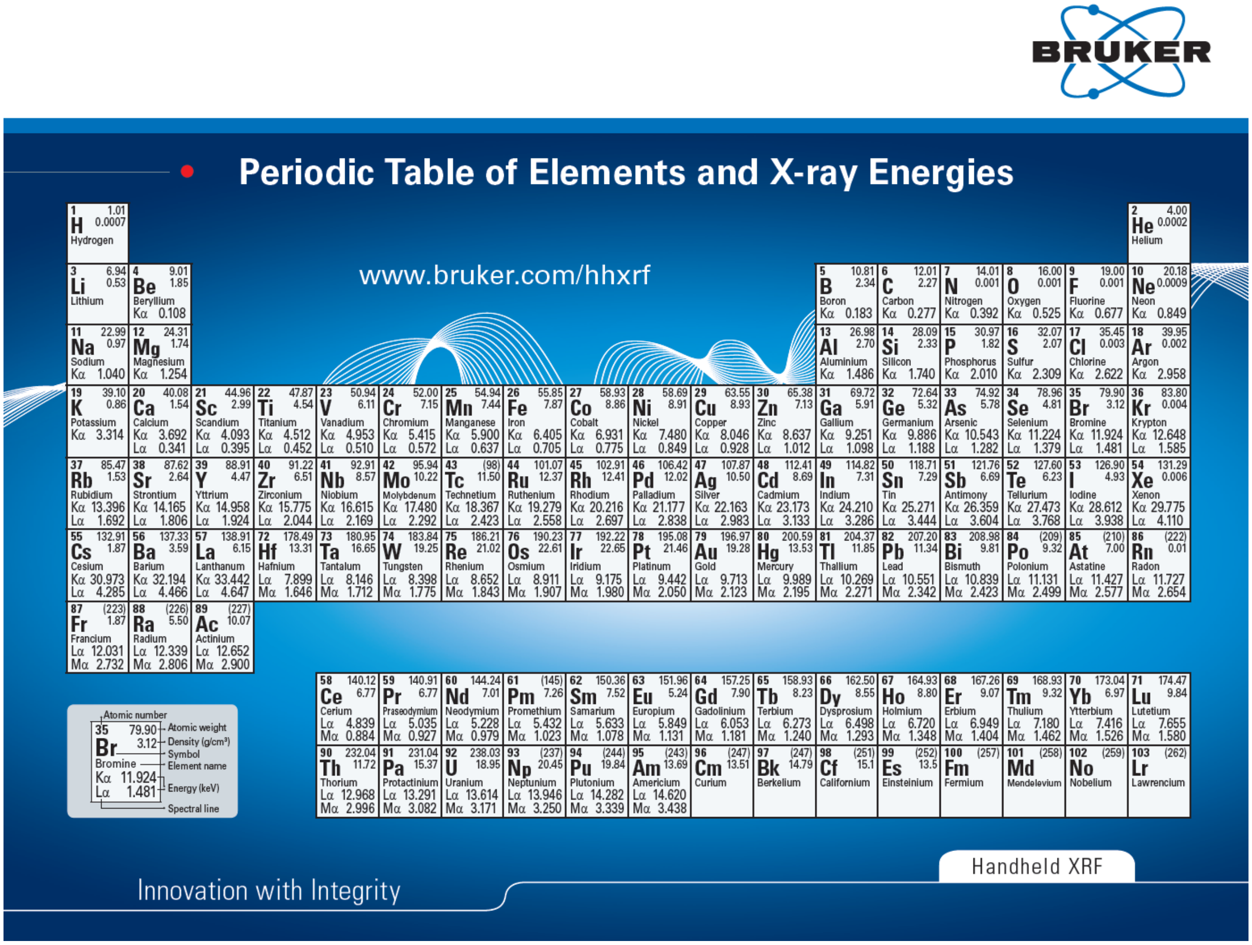
CHAPTER VI

RESEARCH METHODS

Equipment and Settings

As explained above, the project began with the selection of ceramic sherds for testing from the three assemblages previously mentioned in this text. Elemental analysis was conducted using the Bruker Tracer III-SD portable XRF model. This piece of equipment is operated through the Analytical Archaeology Lab in the Center for Maritime Archaeology and Conservation at Texas A&M University. This handheld device was used in a benchtop stand for analysis in the lab, but it is fully capable of functioning in the field or any non-laboratory setting through battery-powered operation. This pXRF spectrometer is fitted with a rhodium (Rh) anode target and a palladium (Pd) collimator, a device that narrows a beam of particles. Therefore, on every spectrum produced from this device there are peaks for rhodium and palladium; in general, when choosing any XRF spectrometer, it is important to know what elements you may encounter and select a machine that is not fitted with components that will interfere with that research. Rhodium and palladium are scarcely found when analyzing archaeological materials, so it is suitably applied to this kind of analysis.

The spectrometer has several settings that can be adjusted to target specific elements for analysis. Three different scans were taken of each sherd to focus on a range of elements. Adjustments to voltage, expressed in kilo-electron volts (keV), determine the energy of the X-rays being sent towards the sample and thus the elements that will be detected. Higher voltages can detect elements with higher energies, or elements with higher Z (atomic) numbers. These higher energies are also able to penetrate further into a sample than the lower energies.



Periodic Table of Elements and X-ray Energies

www.bruker.com/hhxrf

1 1.01 H 0.0007 Hydrogen																	2 4.00 He 0.0002 Helium
3 6.94 Li 0.53 Lithium	4 9.01 Be 1.85 Beryllium Kα 0.108											5 10.81 B 2.34 Boron Kα 0.183	6 12.01 C 2.27 Carbon Kα 0.277	7 14.01 N 0.001 Nitrogen Kα 0.392	8 16.00 O 0.001 Oxygen Kα 0.525	9 19.00 F 0.001 Fluorine Kα 0.677	10 20.18 Ne 0.0009 Neon Kα 0.849
11 22.99 Na 0.97 Sodium Kα 1.040	12 24.31 Mg 1.74 Magnesium Kα 1.254											13 26.98 Al 2.70 Aluminium Kα 1.486	14 28.09 Si 2.33 Silicon Kα 1.740	15 30.97 P 1.82 Phosphorus Kα 2.010	16 32.07 S 2.07 Sulfur Kα 2.309	17 35.45 Cl 0.003 Chlorine Kα 2.622	18 39.95 Ar 0.002 Argon Kα 2.958
19 39.10 K 0.86 Potassium Kα 3.314	20 40.08 Ca 1.54 Calcium Kα 3.692 Lα 0.341	21 44.96 Sc 2.99 Scandium Kα 4.093 Lα 0.395	22 47.87 Ti 4.54 Titanium Kα 4.512 Lα 0.452	23 50.94 V 6.11 Vanadium Kα 4.953 Lα 0.510	24 52.00 Cr 7.15 Chromium Kα 5.415 Lα 0.572	25 54.94 Mn 7.44 Manganese Kα 5.900 Lα 0.637	26 55.85 Fe 7.87 Iron Kα 6.405 Lα 0.705	27 58.93 Co 8.86 Cobalt Kα 6.931 Lα 0.775	28 58.69 Ni 8.91 Nickel Kα 7.480 Lα 0.849	29 63.55 Cu 8.93 Copper Kα 8.046 Lα 0.928	30 65.38 Zn 7.13 Zinc Kα 8.637 Lα 1.012	31 69.72 Ga 5.91 Gallium Kα 9.251 Lα 1.098	32 72.64 Ge 5.32 Germanium Kα 9.886 Lα 1.188	33 74.92 As 5.78 Arsenic Kα 10.543 Lα 1.282	34 78.96 Se 4.81 Selenium Kα 11.224 Lα 1.379	35 79.90 Br 3.12 Bromine Kα 11.924 Lα 1.481	36 83.80 Kr 0.004 Krypton Kα 12.648 Lα 1.585
37 85.47 Rb 1.53 Rubidium Kα 13.396 Lα 1.692	38 87.62 Sr 2.64 Strontium Kα 14.165 Lα 1.806	39 88.91 Y 4.47 Yttrium Kα 14.958 Lα 1.924	40 91.22 Zr 6.51 Zirconium Kα 15.775 Lα 2.044	41 92.91 Nb 8.57 Niobium Kα 16.615 Lα 2.169	42 95.94 Mo 10.22 Molybdenum Kα 17.480 Lα 2.292	43 (98) Tc 11.50 Technetium Kα 18.367 Lα 2.423	44 101.07 Ru 12.37 Ruthenium Kα 19.279 Lα 2.558	45 102.91 Rh 12.41 Rhodium Kα 20.216 Lα 2.697	46 106.42 Pd 12.02 Palladium Kα 21.177 Lα 2.838	47 107.87 Ag 10.50 Silver Kα 22.163 Lα 2.983	48 112.41 Cd 8.69 Cadmium Kα 23.173 Lα 3.133	49 114.82 In 7.31 Indium Kα 24.210 Lα 3.286	50 118.71 Sn 7.29 Tin Kα 25.271 Lα 3.444	51 121.76 Sb 6.69 Antimony Kα 26.359 Lα 3.604	52 127.60 Te 6.23 Tellurium Kα 27.473 Lα 3.768	53 126.90 I 4.93 Iodine Kα 28.612 Lα 3.938	54 131.29 Xe 0.006 Xenon Kα 29.775 Lα 4.110
55 132.91 Cs 1.87 Cesium Kα 30.973 Lα 4.285	56 137.33 Ba 3.59 Barium Kα 32.194 Lα 4.466	57 138.91 La 6.15 Lanthanum Kα 33.442 Lα 4.647	72 178.49 Hf 13.31 Hafnium Lα 7.899 Mα 1.646	73 180.95 Ta 16.65 Tantalum Lα 8.146 Mα 1.712	74 183.84 W 19.25 Tungsten Lα 8.398 Mα 1.775	75 186.21 Re 21.02 Rhenium Lα 8.652 Mα 1.843	76 190.23 Os 22.61 Osmium Lα 8.911 Mα 1.907	77 192.22 Ir 22.65 Iridium Lα 9.175 Mα 1.980	78 195.08 Pt 21.46 Platinum Lα 9.442 Mα 2.050	79 196.97 Au 19.28 Gold Lα 9.713 Mα 2.123	80 200.59 Hg 13.53 Mercury Lα 9.989 Mα 2.195	81 204.37 Tl 11.85 Thallium Lα 10.269 Mα 2.271	82 207.20 Pb 11.34 Lead Lα 10.551 Mα 2.342	83 208.98 Bi 9.81 Bismuth Lα 10.839 Mα 2.423	84 (209) Po 9.32 Polonium Lα 11.131 Mα 2.499	85 (210) At 7.00 Astatine Lα 11.427 Mα 2.577	86 (222) Rn 0.01 Radon Lα 11.727 Mα 2.654
87 (223) Fr 1.87 Francium Lα 12.031 Mα 2.732	88 (226) Ra 5.50 Radium Lα 12.339 Mα 2.806	89 (227) Ac 10.07 Actinium Lα 12.652 Mα 2.900															

58 140.12 Ce 6.77 Cerium Lα 4.839 Mα 0.884	59 140.91 Pr 6.77 Praseodymium Lα 5.035 Mα 0.927	60 144.24 Nd 7.01 Neodymium Lα 5.228 Mα 0.979	61 (145) Pm 7.26 Promethium Lα 5.432 Mα 1.023	62 150.36 Sm 7.52 Samarium Lα 5.633 Mα 1.078	63 151.96 Eu 5.24 Europium Lα 5.849 Mα 1.131	64 157.25 Gd 7.90 Gadolinium Lα 6.053 Mα 1.181	65 158.93 Tb 8.23 Terbium Lα 6.273 Mα 1.240	66 162.50 Dy 8.55 Dysprosium Lα 6.498 Mα 1.293	67 164.93 Ho 8.80 Holmium Lα 6.720 Mα 1.348	68 167.26 Er 9.07 Erbium Lα 6.949 Mα 1.404	69 168.93 Tm 9.32 Thulium Lα 7.180 Mα 1.462	70 173.04 Yb 6.97 Ytterbium Lα 7.416 Mα 1.526	71 174.47 Lu 9.84 Lutetium Lα 7.655 Mα 1.580
90 232.04 Th 11.72 Thorium Lα 12.968 Mα 2.996	91 231.04 Pa 15.37 Protactinium Lα 13.291 Mα 3.082	92 238.03 U 18.95 Uranium Lα 13.614 Mα 3.171	93 (237) Np 20.45 Neptunium Lα 13.946 Mα 3.250	94 (244) Pu 19.84 Plutonium Lα 14.282 Mα 3.339	95 (243) Am 13.69 Americium Lα 14.620 Mα 3.438	96 (247) Cm 13.51 Curium	97 (247) Bk 14.79 Berkelium	98 (251) Cf 15.1 Californium	99 (252) Es 13.5 Einsteinium	100 (257) Fm Fermium	101 (258) Md Mendelevium	102 (259) No Nobelium	103 (262) Lr Lawrencium

Innovation with Integrity

Handheld XRF

FIGURE 5. The periodic table of elements with X-ray energies provided for each element. The atomic number in the top left corner of each element tile represents its Z number. (Bruker 2015)

Amperage is a measurement of the intensity of an electric current, or the flow of electrons towards the anode target. Increasing the amperage increases the number of electrons produced and the number of interactions that occur with the sample, though this will cause more *bremsstrahlung* interference. When analyzing elements with higher Z numbers the amperage should be lower to reduce that background radiation. The count time for each scan was kept the same in this instance. Times may generally range from 10 seconds to 10 minutes, with shorter count times used for qualitative analysis and longer count times used more for quantitative analysis, searching for PPM (parts per million) concentrations of minor elements (Shackley 2011:31). The Bruker Tracer III-SD has the option to pull a vacuum within the chamber of the machine in order to cut down on interference from elements within the air, and this is preferred for analysis of low Z elements. The air around the sample is not under vacuum, just the air within the device. Filters may be used to help block certain elements from dominating the spectrum and allow others to be seen. Only one filter was used on one scan performed during this research. The green filter provided by Bruker is 1 mm aluminum (Al), 1 mm titanium (Ti), and 6 mm copper (Cu), and is used to help block low energy X-rays and concentrate on high Z number elements. The details for each scan are listed in Table 2.

TABLE 2 Spectrometer Specifications for Each Scan

Scan	**Voltage (keV)**	**Amperage (µA)**	**Time (seconds)**	**Vacuum**	**Filter**
1- General Analysis	40	30	60	Yes	No
2- High Z Numbers	40	11.5	60	No	Yes - Green
3- Low Z Numbers	15	30	60	Yes	No

Each of these voltage and amperage settings were chosen for their appropriateness for targeting certain elements and programmed into the spectrometer. The samples were placed on the scanner as flatly as possible to minimize atmosphere interference. If a sherd had any form of color decoration in the glaze, this area was avoided. Areas with undecorated glaze were selected to compare the differences from one ware type to the next; painted and transfer-printed decorations give very different concentrations of coloring elements in comparison to samples with a basic clear glaze. The first scan was done in order to obtain a general analysis of the samples, providing a wider range of elemental analysis. The second scan concentrated on high Z number elements. This scan may prove to be the least helpful simply because of the overwhelming amount of lead (Pb) in the earthenware glazes; there may be little additional information beyond the concentrations of lead. The third scan focused on elements with low Z numbers, concentrating on the elements with atomic numbers below copper (Z=29) on the periodic table of elements. This scan may be the most significant because of its narrow focus on low Z elements. The fact that this scan was at a lower energy also ensures that it did not penetrate very far into the sample. This helped to concentrate on the glaze and minimize the chances that elements from the ceramic body were detected.

The computer program used during analysis with the spectrometer was S1PXRF. The Bruker Tracer III was run from the computer using this software, and a spectrum was produced from each scan. While this software also has analytical capabilities, it was not used to analyze the spectrums produced from the ceramic sampling. Instead, another Bruker program called ARTAX was used for spectrum analysis. Within each category of ware type the spectrums were examined and elements were identified according to the X-ray peaks on the spectrums. The results of these analyses were then exported into Excel spreadsheets for further statistical evaluation.

Forms of Analysis

It is important to note that XRF data can be used for different levels of analysis: qualitative, semi-quantitative, and quantitative. Qualitative measurements are the simplest and reveal what elements are in the sample; quantitative measurements reveal the amount of each element in the sample (Dostal 2015:6). Quantitative analysis requires specifically calibrated reference data obtained from known specimens to compare data and obtain parts per million (ppm) elemental measurements. This is the most precise form of measurement. Semi-quantitative measurements can be obtained with uncalibrated data; while it will not give precise measurements for each element, it can still be used to produce net photon counts for each element, which can then be compared and used in statistical analysis. Both qualitative and semi-quantitative measurements were used in this research. Qualitative data was measured directly from the spectrums produced from each scan and primarily involved elemental identification. Semi-quantitative analysis was used to compare net photon counts of specific elements to determine if there were any identifiable differences. These last kinds of measurements are only comparable if the same settings are used to scan each sherd, which in this case they were.

Testing Goals and Considerations

In the event that a successful method of ware identification is found using this method, the next stage to test the legitimacy of this method would involve blind testing. First the author would analyze spectrums from sherds scanned by others using the same equipment and settings to see if they could be accurately identified. If that proves successful, the next stage of testing would involve participants with little to no XRF experience. The author would educate them on the theory, the methods, and the results of this study, and would provide spectrums for them to analyze. The importance of this study lies not only it the ability to scientifically identify ceramic wares, but in the replicability of this method by others.

There are a few factors to consider during analysis, in addition to the concerns mentioned earlier about the archaeological classification system of ware types. The first has been previously mentioned but bears repeating. This study is investigating the differences in glaze composition, but there is always the possibility that the X-rays are interacting with elements from the body of the ceramic. Penetration distance cannot be accurately measured in this case, but it is known that XRF scans performed at higher energies will penetrate further into the sample than those at lower energies. The third scan, targeting low Z numbers, will therefore have the least amount of interference from the ceramic body than any of the other scans. Another consideration is what effect conservation has had on these sherds. Cleaning and consolidating sherds may put them into contact with various chemicals and substances, and the effects of this process on XRF data is unknown. No effort was made to try and account for those effects in the data collected in this study, but it is an important consideration to keep in mind. Lastly and once again, there may be user error due to the fact that this is the first XRF study performed by the author.

CHAPTER VII

ANALYSIS

Once the ceramics were collected from the three sources of archaeological material previously listed, they were sorted by ware type and assigned a new sample number for easy identification purposes. Table 3 lists every sample of creamware, pearlware, whiteware, and porcelain that was tested. Repeated artifact numbers indicate that there was more than one sherd with this number. The additional sherds are indicated by a number in parentheses after the artifact number. Also, several sherds selected from the typology collection did not have an artifact number so these were simply referred to as "Unlabeled" and assigned a corresponding number.

TABLE 3 Ceramic Sample Selection

Sample #	**Artifact #**	**Ware Type**
1	CSSG 3226.3 (1)	Whiteware
2	CSSG 3226.3 (2)	Whiteware
3	CSSG 2295.1	Whiteware
4	CSSG 3278.1	Whiteware
5	CSSG 2251.1	Whiteware
6	CSSG 3058.2	Whiteware
7	CSSG 2010.2	Whiteware
8	PR87 582 9.10	Whiteware
9	PR87 572 9.10	Whiteware
10	PR87 311 9.10	Whiteware
11	PR89 891 9.10	Whiteware
12	PR87 282 9.10	Whiteware
13	PR87 284-1 9.10	Whiteware
14	PR87 351 9.10	Whiteware
15	CSSG 2746.2	Pearlware
16	CSSG 2624.4	Pearlware
17	CSSG 2286.3	Pearlware
18	PR89 884-3 8.61	Pearlware

TABLE 3, CONTINUED

Sample #	**Artifact #**	**Ware Type**
19	PR89 7/6-3 8.72	Pearlware
20	PR89 602 8.72	Pearlware
21	BG 5-1-3 8.41	Pearlware
22	Unlabeled 1	Pearlware
23	Unlabeled 2	Pearlware
24	BG 5-1-0	Pearlware
25	5-2-1 (1)	Pearlware
26	5-2-1 (2)	Pearlware
27	CSSG 3294.3	Creamware
28	7.24	Creamware
29	PR 5-4-3	Creamware
30	7.21	Creamware
31	4-1-3	Creamware
32	5-4-2 (1)	Creamware
33	5-4-2 (2)	Creamware
34	Unlabeled 3	Creamware
35	Unlabeled 4	Creamware
36	Unlabeled 5	Creamware
37	Unlabeled 6	Creamware
38	CSSG 3083	Porcelain
39	1.11	Porcelain
40	1.12	Porcelain
41	Unlabeled 7	Porcelain
42	Unlabeled 8	Porcelain
43	Unlabeled 9	Porcelain
44	1.22 (1)	Porcelain
45	1.22 (2)	Porcelain
46	1.23	Porcelain
47	1.21	Porcelain

Qualitative Analysis

Identifying Porcelain

A few significant points were made apparent through qualitative analysis of the spectrums. The most noteworthy was the stark difference between the refined earthenware ceramics and porcelain, particularly on both the general analysis and high Z scans. The lead present in the glazes of these refined earthenware types translated into the high Lα peaks at 10.5

keV and Lβ peaks at 12.6 keV for lead dominating these spectrums. Except for Sample 5, which appeared to be the only refined earthenware sample with a notable Kα (8.6 keV) peak for zinc, every other spectrum had its most prominent peaks for lead.

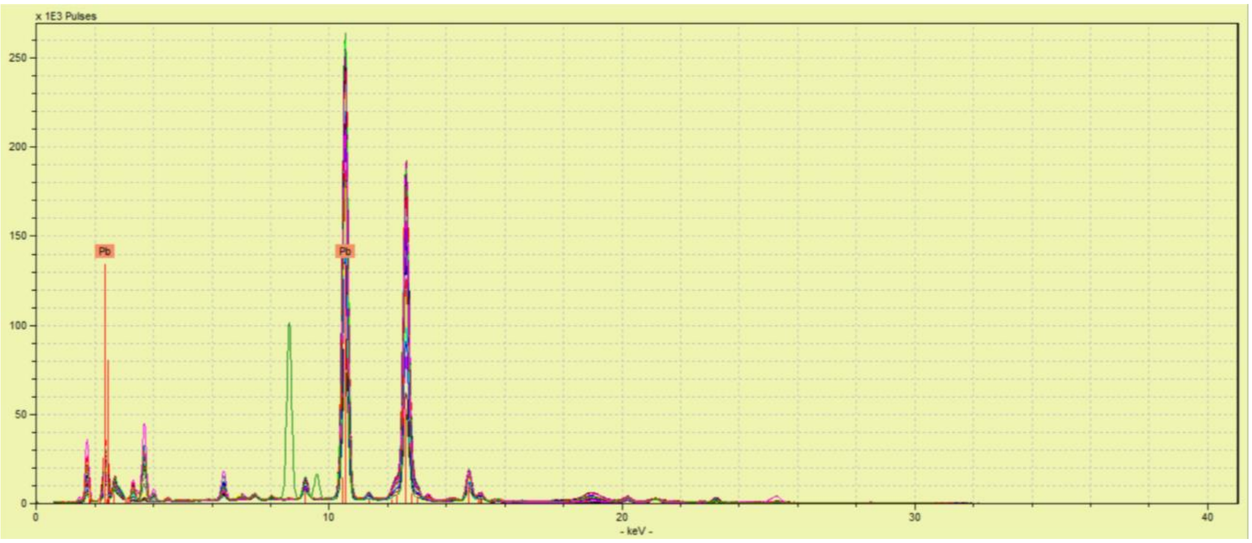


FIGURE 6. All refined earthenware general analysis spectrums, with prominent Lα (10.5 keV) and Lβ (12.6 keV) lead peaks. (Spectrum by author using ARTAX, 2018.)

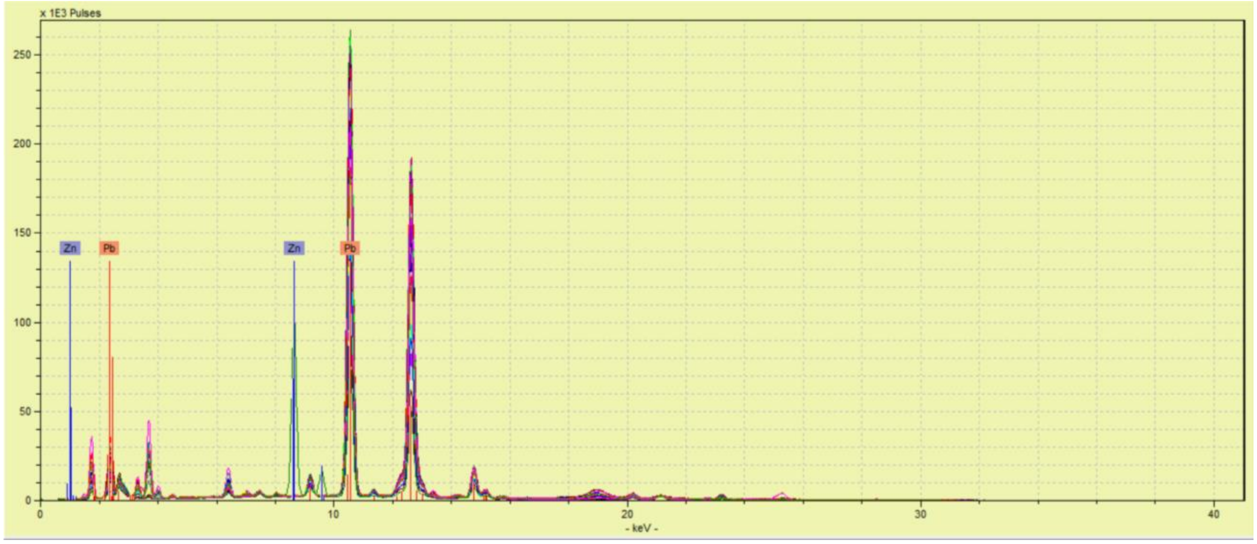


FIGURE 7. All refined earthenware general analysis spectrums, including a label for the noticeable Kα (8.6 keV) peak for zinc for sample 5. (Spectrum by author using ARTAX, 2018.)

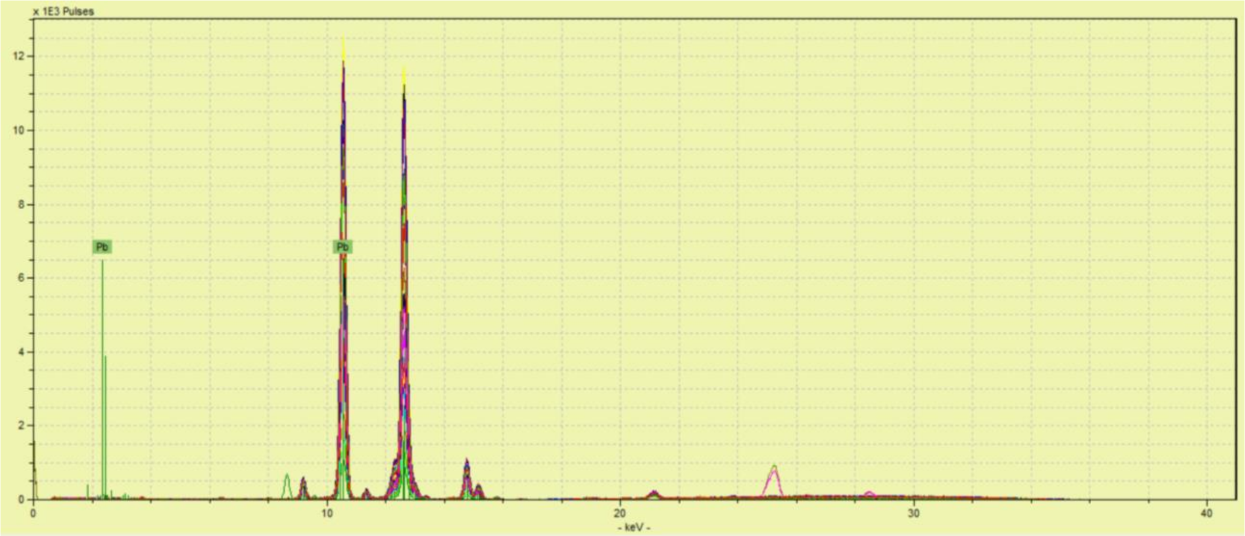


FIGURE 8. All refined earthenware high *Z* spectrums, with prominent Lα (10.5 keV) and Lβ (12.6 keV) lead peaks. (Spectrum by author using ARTAX, 2018.)

By comparison, porcelain glazes should contain no lead. The general analysis spectrums for porcelain differed markedly from those for any of the refined earthenware types in that both iron (Kα, 6.4 keV) and silicon (Kα, 1.7 keV) peaks were the most prominent. The high Z spectrums were even more distinguishable through the intensity of the *bremsstrahlung*. Porcelain glazes contain fewer high Z elements than those for creamware, pearlware, and whiteware. Although it is within the *bremsstrahlung* region, the peak for palladium (Kα, 21.1 keV), caused by the palladium collimator within the spectrometer instrumentation, was the most significant within the high Z spectrums for porcelain. The next two noticeable elements were rubidium (Kα, 13.3 keV) and iron (Kα, 6.4 keV). An interesting note among these samples was that there were significant Lα and Lβ lead peaks for samples 40 and 47. The source of this lead was unclear, but it is clear that there was much less of it detected in the porcelain glazes than the refined earthenware glazes.

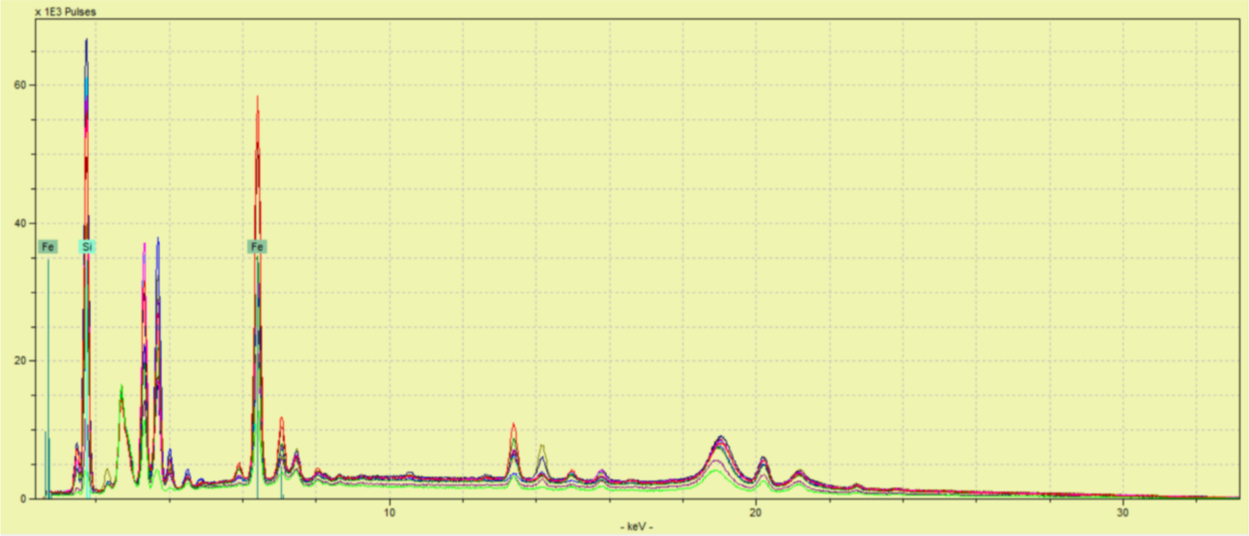


FIGURE 9. Porcelain general analysis spectrums. Labels indicate the most prominent peaks, silicon and iron. (Spectrum by author using ARTAX, 2018.)

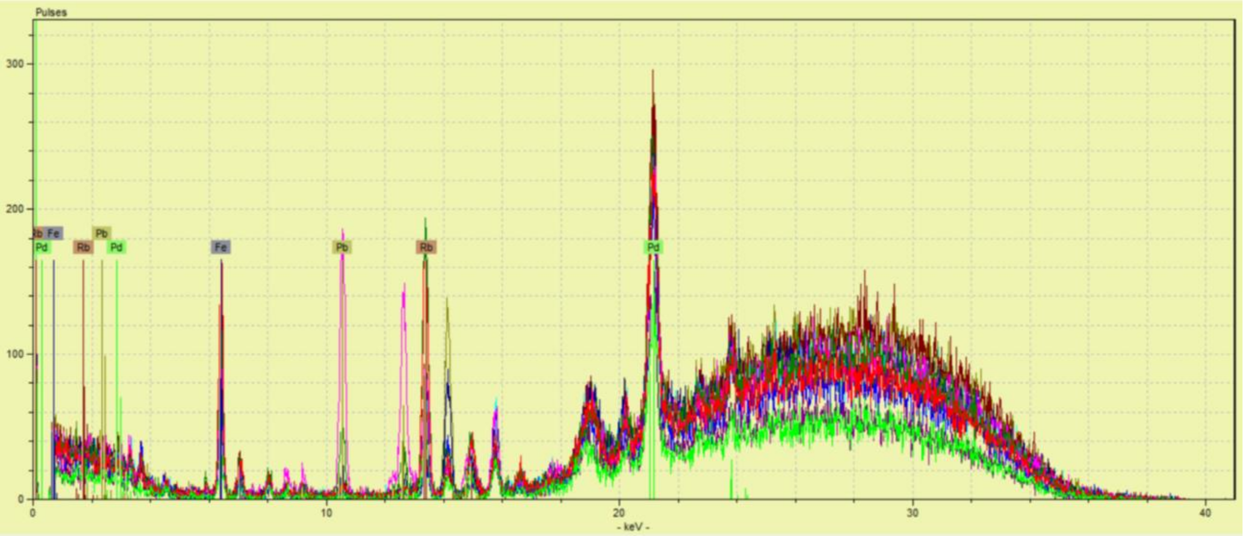


FIGURE 10. Porcelain high Z spectrums. The most distinguishable peak is palladium (Kα, 21.1 keV) in the *bremsstrahlung* region. Other notable peaks include iron (Kα, 6.4 keV) and rubidium (Kα, 13.3 keV). Samples 40 and 47 both display strong Lα and Lβ peaks for lead. (Spectrum by author using ARTAX, 2018.)

Qualitatively, using this method of analysis, it was very easy to distinguish between refined earthenware glazes used on creamware, pearlware, and whiteware and those used on porcelain. Although a couple of porcelain sherds appeared to have lead peaks on the high Z scan, the overall composition of the porcelain spectrums was very different than that of the refined earthenware spectrums. Both the high peak for palladium and the strong *bremsstrahlung* curve in the porcelain high Z spectrums made them distinguishable. Similarly, the high peaks for iron and silicon made the porcelain general analysis spectrums distinguishable from the other wares. If an archaeologist cannot appropriately categorize a sherd as either porcelain or one of these similarly light-colored refined earthenwares, this method offers an option for suitable ceramic ware identification.

In a similar manner, lead also allowed us to differentiate the porcelain glazes when analyzed using the low Z settings. Every spectrum representing refined earthenware glazes displayed Lα and Lβ lead peaks on the right side of the spectrum, whereas there were no such peaks present on the porcelain low Z spectrums. For each of these methods, porcelain has been undeniably identifiable when comparing spectrums against those of refined earthenware. In some cases, when a sherd is too small to have any identifiable features, or when an archaeologist is not proficient in distinguishing porcelain from other white-colored, lead-glazed ceramics such as creamware, pearlware, or whiteware, the use of any of these XRF parameters should be sufficient in quickly determining if the sherd is porcelain or not.

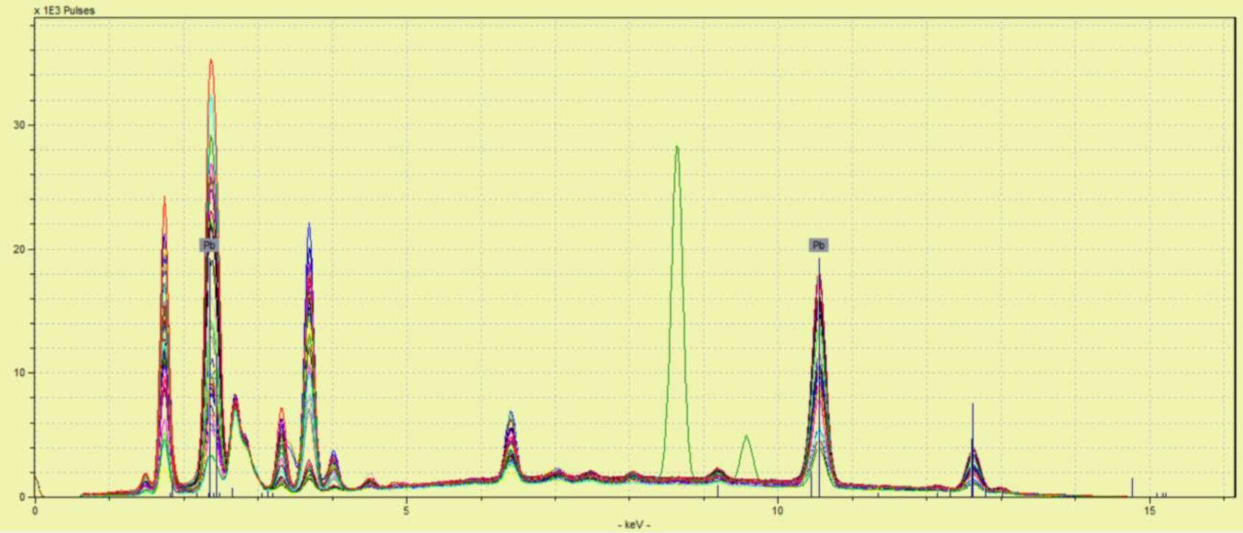


FIGURE 11. All refined earthenware low Z spectrums, with label to indicate Lα (10.5 keV), Lβ (12.6 keV), and Mα (2.3 keV) lead peaks. (Spectrum by author using ARTAX, 2018.)

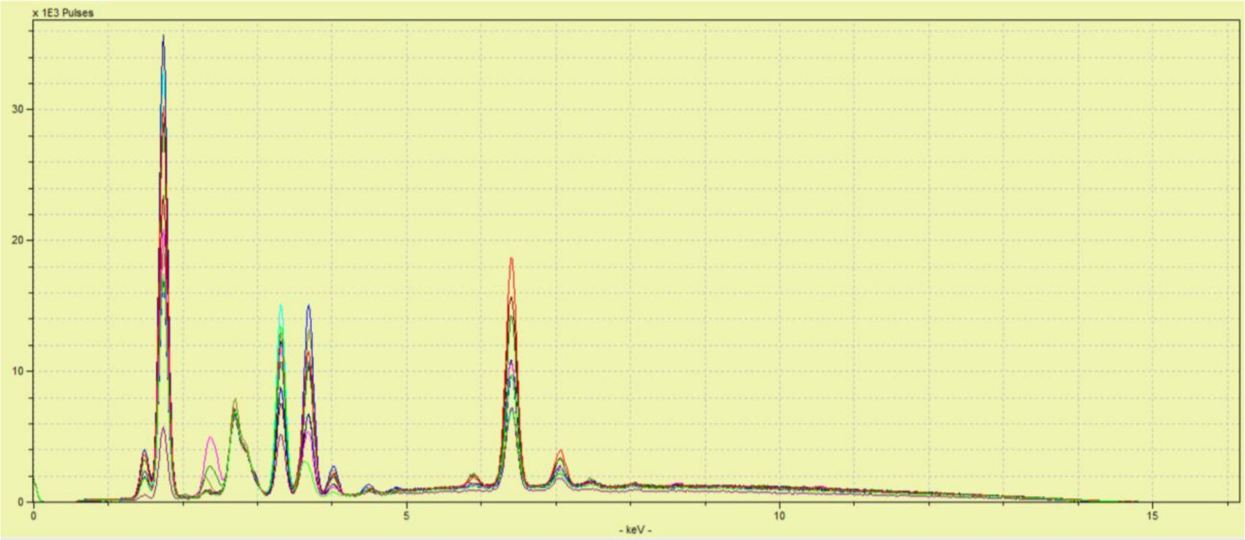


FIGURE 12. Porcelain low Z spectrums. None of these have Lα (10.5 keV) or Lβ (12.6 keV) lead peaks, indicating one way to identify porcelain using this technique with these settings. (Spectrum by author using ARTAX, 2018.)

Refined Earthenware

Differentiation between creamware, pearlware, and whiteware through qualitative analysis of the spectrums produced with X-ray fluorescence spectrometry was less straightforward and produced ambiguous results. The overall elemental composition of the glazes was so similar to one another, except for a few of the sherds sampled, that attributing a ware type to a specific spectrum seemed impossible. Each of the three scans produced similarly vague results, and the only anomalies were three whiteware sherds, samples 3, 4, and 5. Samples 3 and 4 displayed noticeable peaks for tin (Sn) in all three scans, and sample 5 stood out as the only sherd with very high zinc (Zn) peaks appearing on all three scans. In an industry that was always seeking improvement, these variations may stem from differences in glaze formulas, or they may be attributed to the fact that lead, tin, zinc, and pewter, an alloy of tin and copper, can be difficult to distinguish visually and could have easily been confused in manufacture, during the mixing of the glazes.

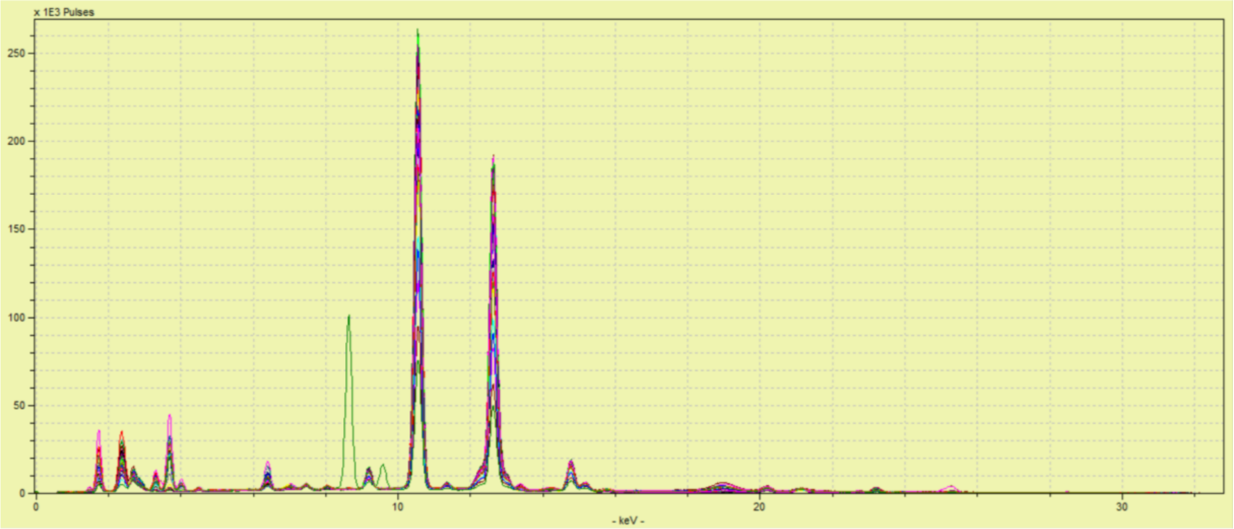


FIGURE 13. All refined earthenware general analysis spectrums. There is very little difference beyond peak intensity between the spectrums of the three ware types. (Spectrum by author using ARTAX, 2018.)

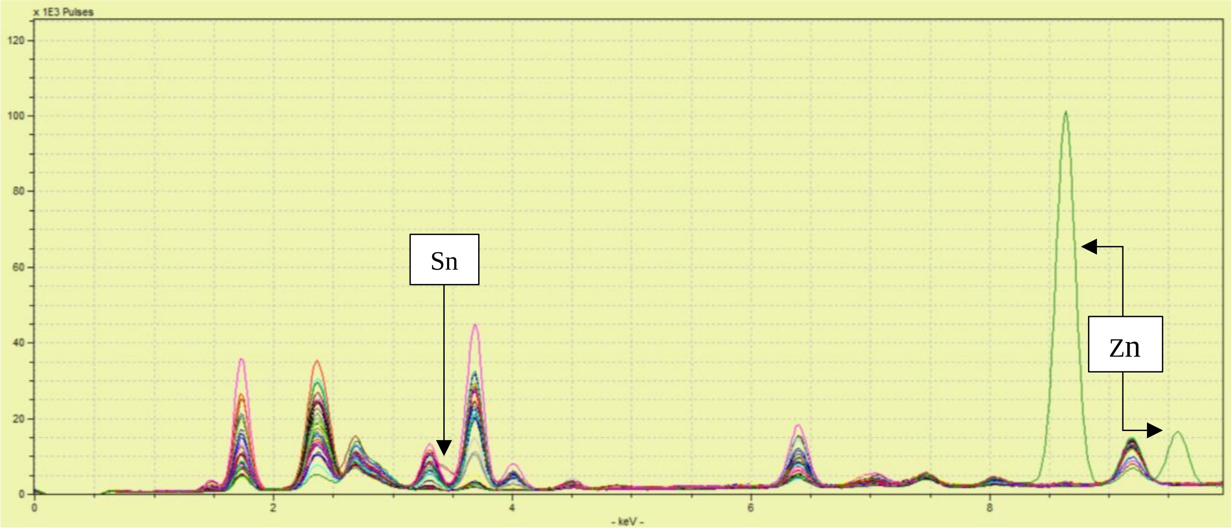


FIGURE 14. A closer look at the low voltage range of all refined earthenware general analysis spectrums. Both tin (Lα, 3.4 keV) peaks from samples 3 and 4 and zinc (Kα, 8.6 keV and Kβ, 9.5 keV) peaks from sample 5 are indicated; these are the only striking variations in all of the refined earthenware spectrums. (Spectrum by author using ARTAX, 2018.)

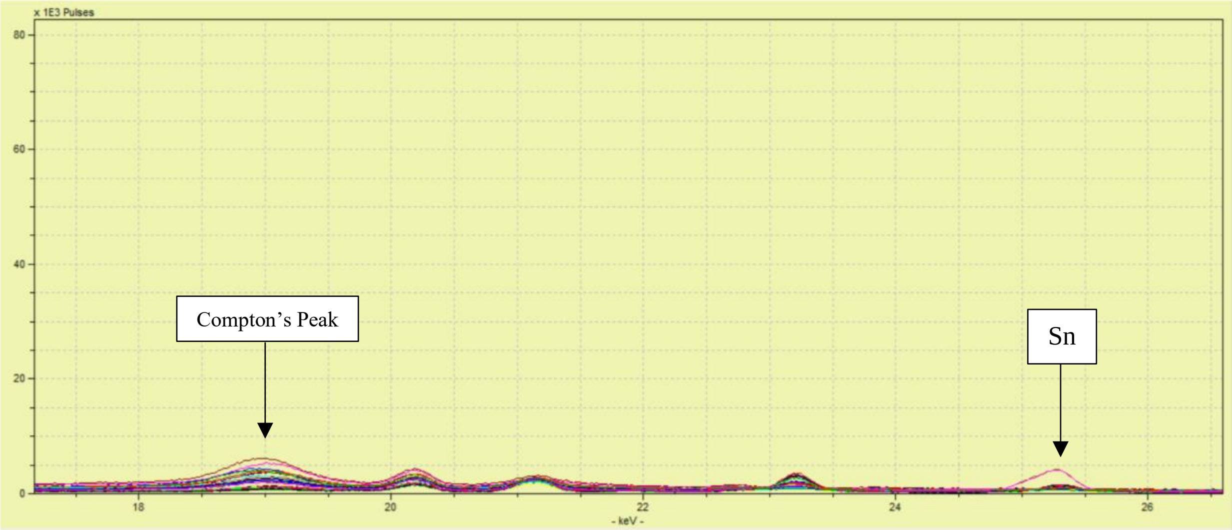


FIGURE 15. A closer look at the high voltage range of all refined earthenware general analysis spectrums. Compton’s peak, which appears because of inelastic scattering in every spectrum, is highlighted. Tin (Kα, 25.2 keV) peaks are also highlighted for samples 3 and 4. (Spectrum by author using ARTAX, 2018.)

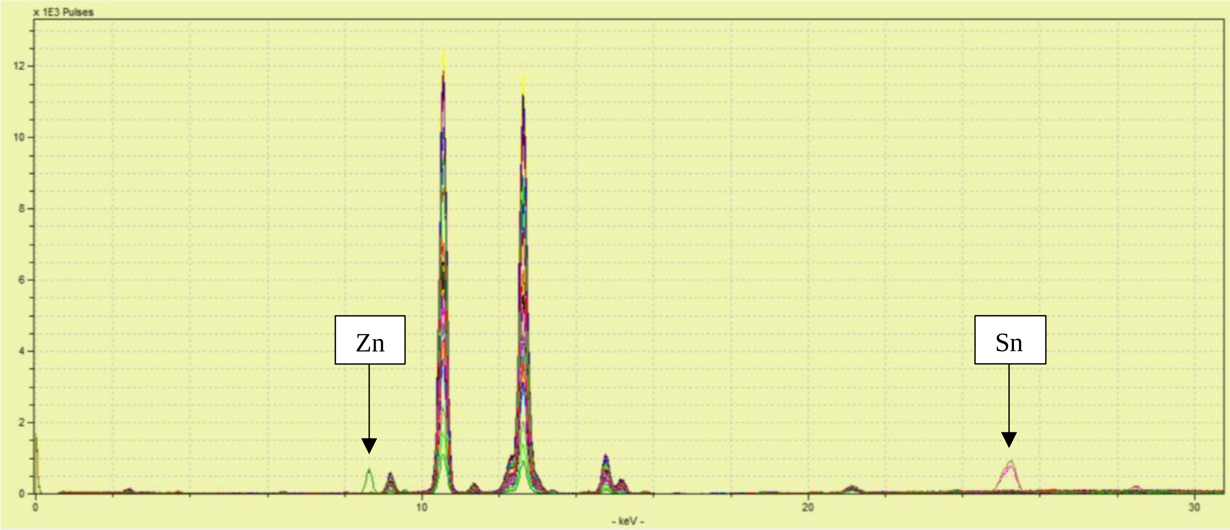


FIGURE 16. All refined earthenware high Z spectrums. As with the general analysis spectrums, the zinc (Kα, 8.6 keV) peaks for sample 5 and tin (Kβ, 28.4 keV) peaks for samples 3 and 4 are the only obvious differences. (Spectrum by author using ARTAX, 2018.)

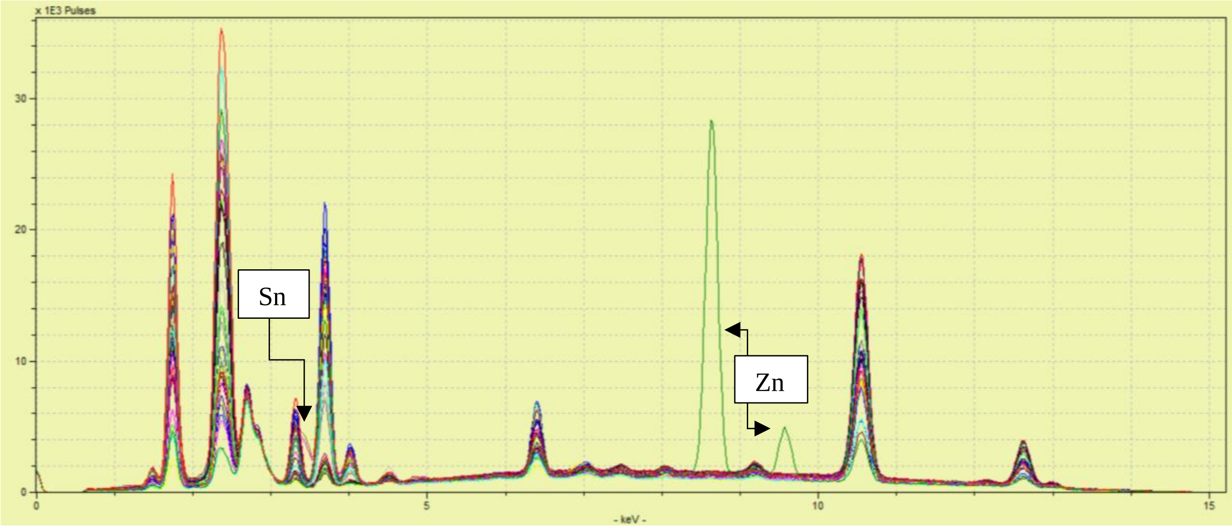
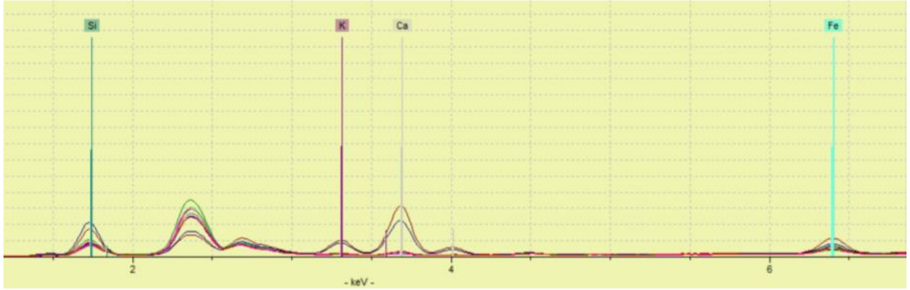


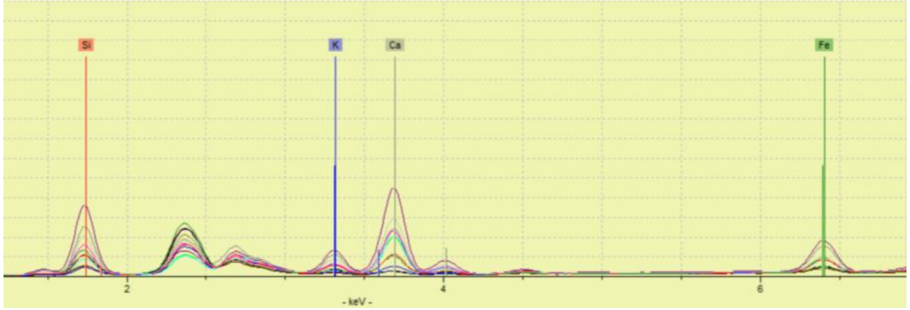
FIGURE 17. All refined earthenware low Z spectrums. Samples 3 and 4 are highlighted with their tin (Lα, 3.4 keV) peak and sample 5 is highlighted with its zinc (Kα, 8.6 keV and Kβ, 9.5 keV) peaks. (Spectrum by author using ARTAX, 2018.)

Although it may seem that there was a substantial amount of peak height variation when looking at all of the refined earthenware spectrums at once, that variation did not disappear when looking at the spectrums of individual ware types. Creamware, pearlware, and whiteware each appeared to have the same elemental peaks and there was noticeable peak height variation within each ware type. Through qualitative analysis of peak height, it was not possible to differentiate between these three ceramic wares based on their glazes.

Creamware



Pearlware



Whiteware

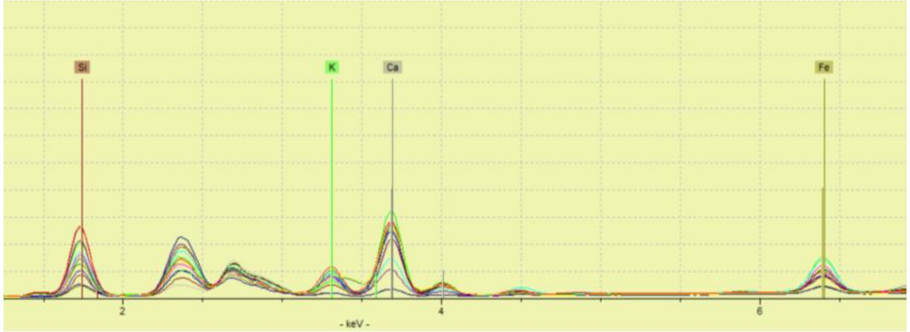


FIGURE 18. A portion of the general analysis spectrums of each ware type. There are similar peak height variances in each ware type for different elements such as silicon (Si), potassium (K), calcium (Ca), and iron (Fe). (Spectrums by author using ARTAX, 2018.)

Semi-Quantitative Analysis

Data exportation from ARTAX to Excel allowed for more in-depth statistical analysis. These spreadsheets displayed the net photon count of every element associated with a peak on the spectrum of each ceramic sample. This research compared broad categories of ceramic wares and therefore the XRF data did not have specific calibrations and could not be quantitatively analyzed as % concentrations or parts per million measurements. In fact, data obtained from pXRF spectrometers are not necessarily ideal for that form of analysis as the samples are not prepared specifically and there is more chance for interference from other sources. Despite this fact, the data gathered from pXRF spectrometers can still be used in semi-quantitative analysis and handheld/portable XRF spectrometers are commonly used in archaeological research. Statistical tools can be used to interpret the data and assumptions may be made about the data based on the use of these tools. The data used in the following graphic representations have been normalized. Each elemental net photon count has been normalized to, or divided by, the net photon count for rhodium (Rh), our anode X-ray target material, to help partially correct for sample density differences and X-ray absorption.

Characteristics of Porcelain

Qualitative analysis already showed that porcelain spectrums were easily recognizable compared against creamware, pearlware, and whiteware spectrums. Porcelain spectrums had higher peaks at different energies because of the differences in glaze composition and were readily distinguished by these features. In addition to the positive results of this qualitative analysis, a few semi-quantitative characteristics were explored for additional comparative purposes.

Since porcelain ceramic glaze composition was quite different from that of creamware, pearlware, and whiteware, X-rays interacted with certain elements more or less often than they did for the lead-based glazes. As illustrated by the general analysis spectrums above, refined earthenware spectrums were distinguishable by their lead peaks whereas porcelain spectrums generally had higher peaks for silicon (Si), potassium (K), calcium (C), and/or iron (Fe). In a few of these instances this also translated to higher average net photon counts for these elements, when compared to the other ceramic ware types using the general analysis settings. This is true for silicon, potassium, and iron, as well as aluminum (Al).

The box and whisker charts below illustrate the photon count range of each of these elements. Potassium counts in porcelain were much higher with the general analysis scan than they were for any of the other ceramic types. They had a normalized range of 2.2-4.6, while the highest normalized measurement for any of the refined earthenware samples was 1.5. With the exception of potassium, there was overlap between ware types for each of the other elements. In porcelain, each of the other elements displayed had higher average normalized photon counts than the averages of creamware, pearlware, and whiteware; while this is an interesting observation about porcelain glazes, the overlap between each of the ware type categories means that analyzing these elements would not necessarily grant much clarity about what kind of ceramic is being tested. Using semi-quantitative analysis, in this instance only potassium seemed a likely indicator for a positive porcelain identification.

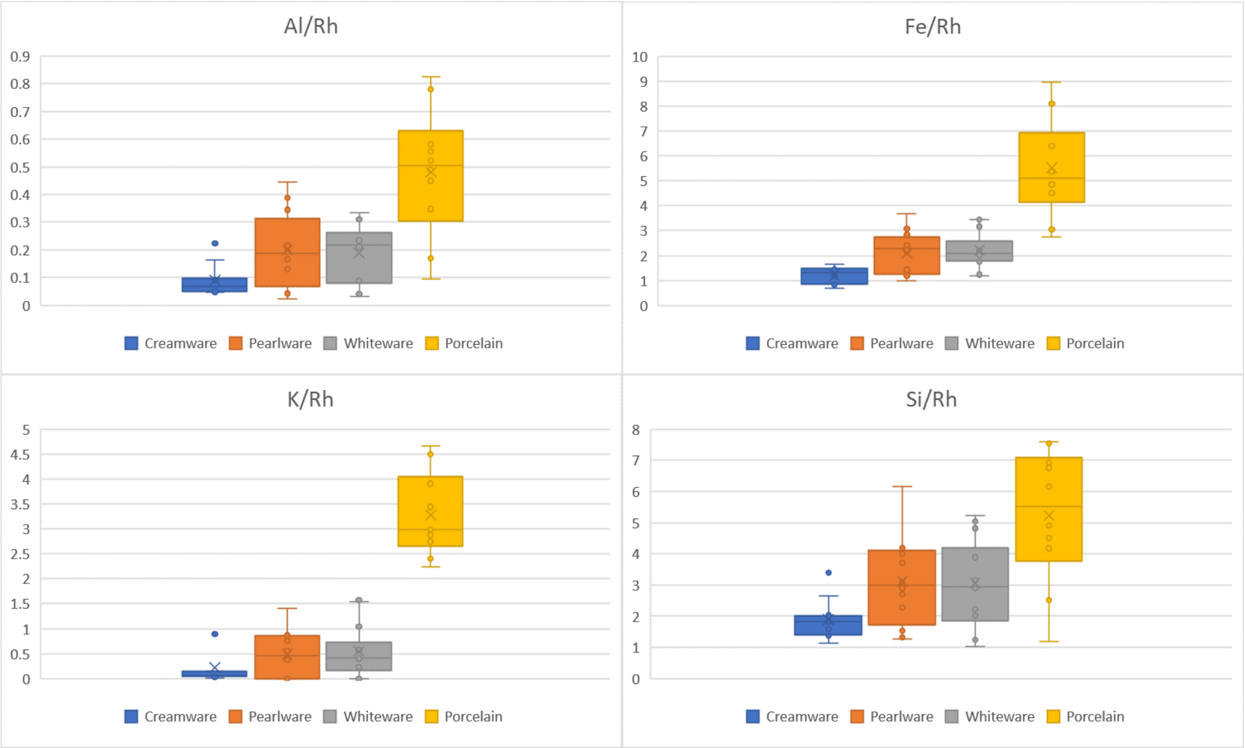


FIGURE 19. Box and whisker plots for each ware type with the general analysis scan. Normalized net photon counts for aluminum (Al), iron (Fe), potassium (K), and silicon (Si). (Graphs by author using Excel, 2018)

There were similar results in regards to potassium when looking at the low Z data. The majority of the normalized net photon counts for porcelain was greater than those for the three refined earthenware categories. Only one sample was low enough to overlap. These results were less conclusive than those of the general analysis test but helped to reinforce the potential usefulness of observing potassium levels to identify porcelain. Other elements of interest included copper (Cu) and nickel (Ni). In the porcelain samples these two elements had the opposite characteristics of potassium and had some of the lowest net photon counts of the four ceramic ware types. There was still overlap with other ceramic wares, particularly with the whiteware samples, but the low counts for copper and nickel in porcelain appeared to be important properties to consider when comparing ceramic wares using XRF data.

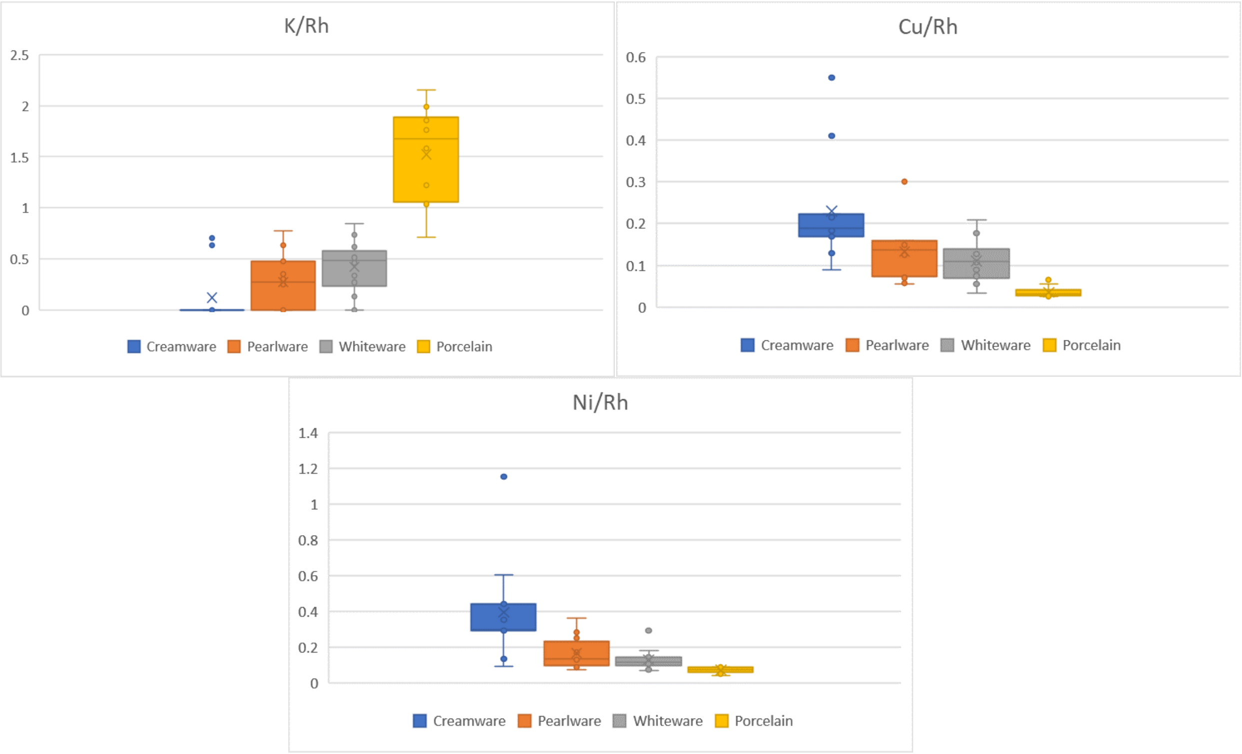


FIGURE 20. Box and whisker plots for each ware type with the low Z scan. Normalized net photon counts for potassium (K), copper (Cu), and nickel (Ni). (Graphs by author using Excel, 2018)

Creamware, Pearlware, and Whiteware

The qualitative observations made of the refined earthenware data did not provide insightful information into defining XRF characteristics for each ware category. The semi-quantitative analysis of the refined earthenware categories offered more discerning qualities about each ware type, but it too proved unsuccessful in revealing a method for ware identification. One of the biggest challenges in this research was the variability in the sample selection. Each selection of sherds from a particular ware group was varied in its origin and therefore its source materials. Differences in materials can still produce comparable ceramics that are categorized equivalently by archaeologists. This diversity of origin that led to complications in establishing an identification method using these techniques. Regardless of the inconclusive nature of these results, there were still several observed trends in these data that bear mentioning.

The general analysis scan seemed to indicate that the ingredients in the glazes on creamware were more different from pearlware and whiteware than the latter two were from each other. There were many instances when the levels of elements detected in the creamware samples were consistently lower than the levels detected in the pearlware and whiteware samples. These included aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), and manganese (Mn). In almost every case there was overlap in the amount of photon counts between the ware types; however, this overlap could at times be attributed to an outlier within the creamware samples. The exception was manganese, which had no overlap of values. The highest normalized net photon count for creamware was .048 while the lowest count for whiteware was .051 and the lowest for pearlware was .067. While these values were very close in scale, the lack of overlap and the very small range of values for manganese in creamware measured using this scan suggest that it may be a useful element to observe in further attempts at ware identification.

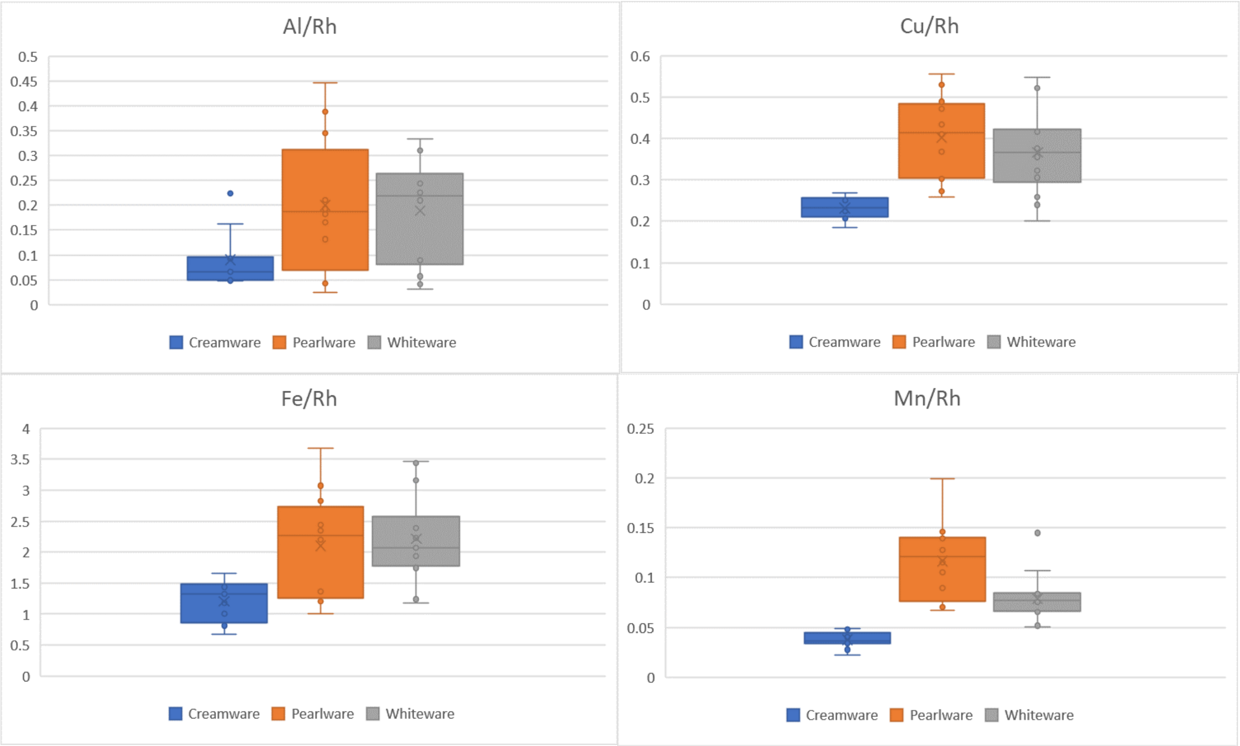


FIGURE 21. Box and whisker plots for each refined earthenware type with the general analysis scan. Normalized net photon counts for aluminum (Al), copper (Cu), iron (Fe), and manganese (Mn). Creamware has consistently lower photon counts for each of these elements, particularly manganese. (Graphs by author using Excel, 2018)

When the values from the porcelain samples were added, almost each of these trends remained the same. Creamware had reliably low photon counts compared to the other ware types for each of these elements except copper, which porcelain shared similarly low counts for. Manganese remained the most promising element for observation in distinguishing creamware with normalized net photon values of 0.05 and lower.

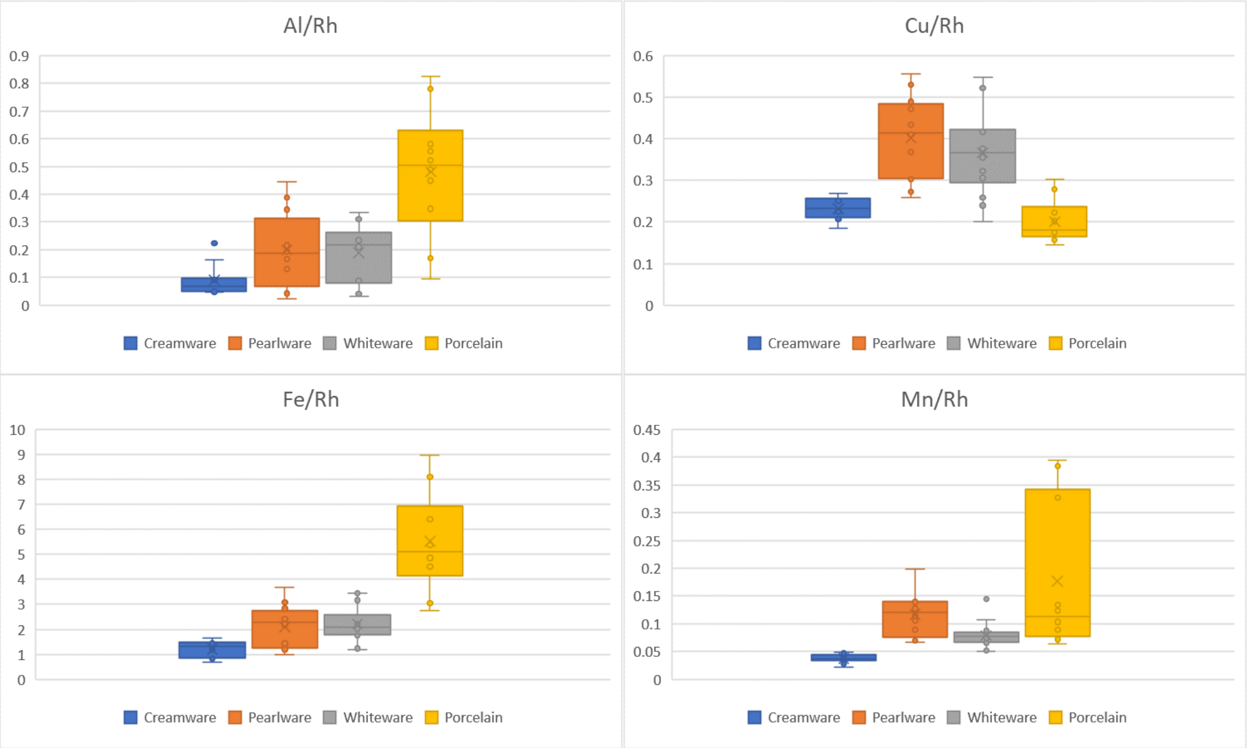


FIGURE 22. Box and whisker plots for all ware types with the general analysis scan. Normalized net photon counts for aluminum (Al), copper (Cu), iron (Fe), and manganese (Mn). (Graphs by author using Excel, 2018)

Calcium also had a very small range of values in the creamware general analysis scan if two outlier samples were excluded, sample 27 and sample 28. On the other hand, pearlware and whiteware had a much wider range of photon detection values. Even with the outliers included, the highest normalized photon value for creamware was 3.92. Half of the pearlware samples valued higher than that and over 70% of the whiteware samples were higher. When excluding the outliers, 83% of pearlware and 100% of whiteware samples had higher calcium values than that of creamware. The range of pearlware and whiteware values set them apart from creamware in this instance.

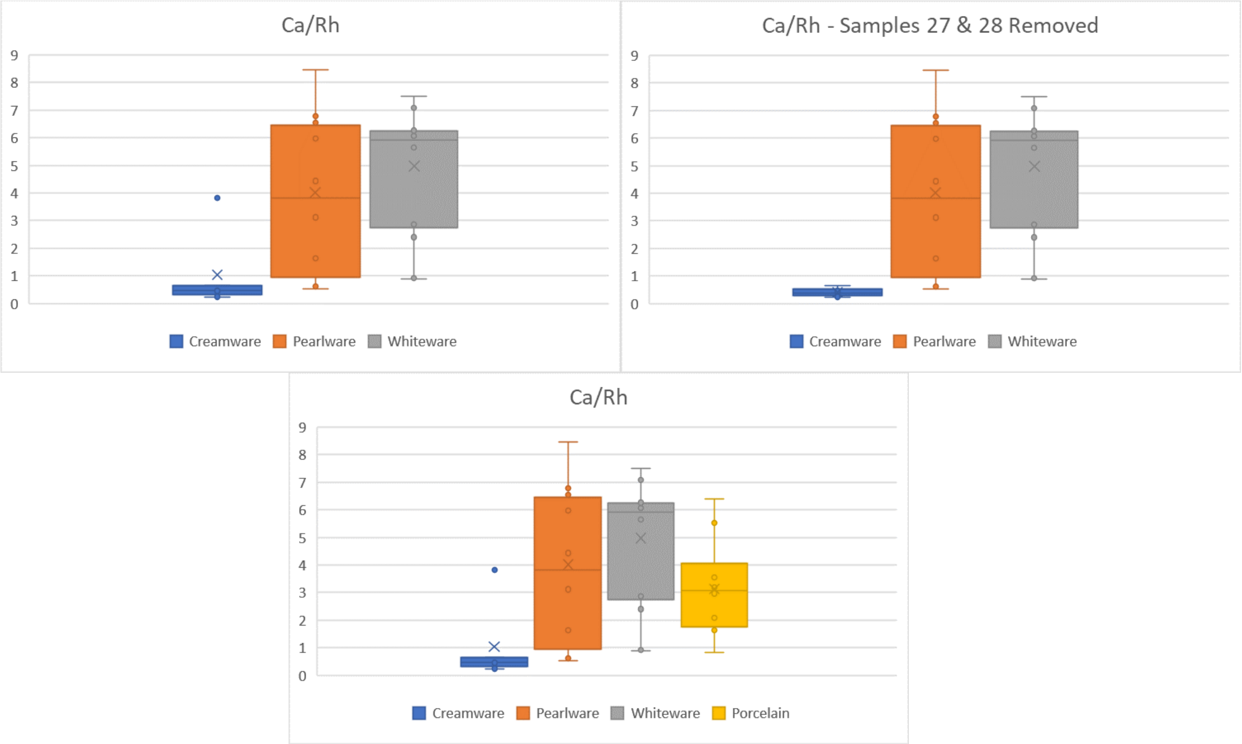


FIGURE 23. Box and whisker plots of normalized net photon counts for calcium (Ca) for each refined earthenware type with the general analysis scan. Samples 27 and 28, outliers in the creamware data, were excluded from the second graph. The third graph includes porcelain calcium values. (Graphs by author using Excel, 2018)

As already mentioned, lead was a base for refined earthenware ceramic glazes during the 18th century and into the 19th century, and the qualitative analysis demonstrated that lead was overwhelmingly detected in the general analysis and high Z scans. Observations from the high Z scan revealed that all three ware types had net photon counts for lead at the Lα energy level that fell within similar ranges. This was particularly true for pearlware and whiteware, though more pearlware samples sat higher in this range and more whiteware samples were found lower in the range, so their averages differed greatly. Interestingly, most of the creamware samples had the highest lead counts and only two samples had lower values than the average value for pearlware. These averages seemed to indicate a trend for lower levels of lead in earthenware glaze through time, with creamware having the highest average and whiteware having the least average. This is an expected trend to observe in glaze compositions, though it should be reiterated that these numbers do not represent % concentrations of elements in the glaze.

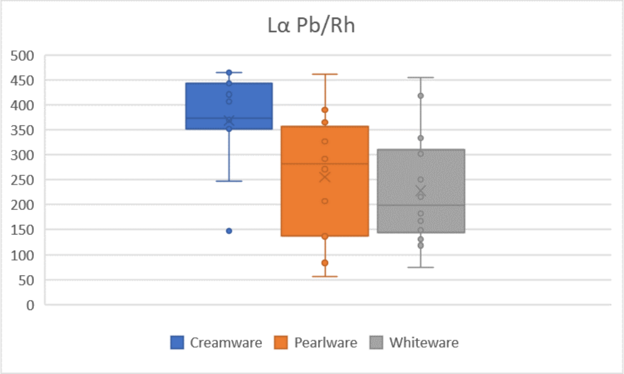


FIGURE 24. Box and whisker plots of normalized net photon counts for lead (Pb), at the Lα energy level, for each refined earthenware type with the high Z scan. (Graphs by author using Excel, 2018)

One of the elements of interest at the beginning of this research was cobalt. Cobalt was added to refined earthenware lead-based glazes used on creamware to give it a whiter appearance, leading to the production of what is today called pearlware. An early hypothesis during the onset of this investigation was that analysis of cobalt might prove an important element in distinguishing these wares from one another. Data from the low Z scan did not support this hypothesis. On average, pearlware did have higher photon counts than the other two ware types, but both creamware and whiteware each had an outlier with very high cobalt photon counts. Removing these outliers revealed that whiteware had a consistently lower photon count for cobalt and creamware photon counts resided almost entirely within the range of pearlware counts. This form of data analysis, which is meant to be relatively quick and straightforward, did not provide a means of distinguishing between these three ware types. A more detailed analysis into the % concentration of cobalt within each sample might lead to success, but analysis of that kind would require specific calibrations for each ceramic type that go beyond the means of this investigation.

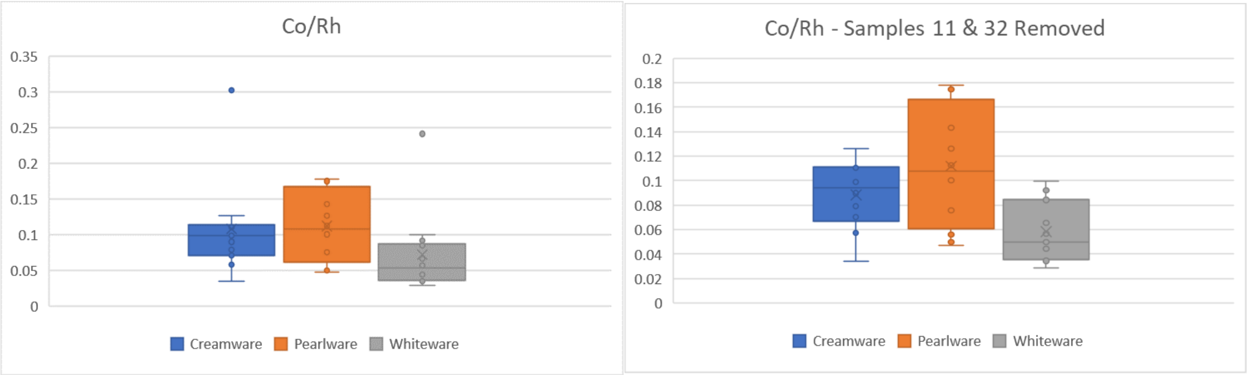


FIGURE 25. Box and whisker plots of normalized net photon counts for cobalt (Co) for each refined earthenware type with the low Z scan. Outliers in the creamware (sample 32) and whiteware (sample 11) data were excluded from the second graph. (Graphs by author using Excel, 2018)

While examination into cobalt did not yield definitive differences between creamware, pearlware, and whiteware, another element did present interesting data. Looking once again at the low Z data, magnesium (Mg) counts in both pearlware and whiteware were generally very low compared to those of creamware. There was an outlier in pearlware and in whiteware, but aside from these, every other sample had a lower magnesium photon count than the average count for creamware. Whiteware in particular had consistently low counts of magnesium. There was overlap for all three ware types, but higher magnesium normalized net photon counts, predominantly 0.02 or higher, appeared to be likely indicators that the sherd was creamware.

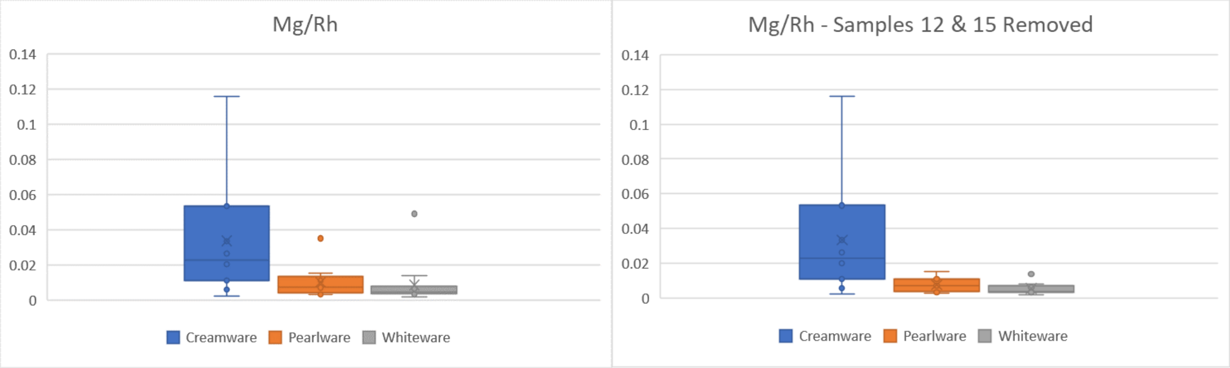


FIGURE 26. Box and whisker plots of normalized net photon counts for magnesium (Mg) for each refined earthenware type with the low Z scan. Outliers in the pearlware (sample 15) and whiteware (sample 12) data were excluded from the second graph. (Graphs by author using Excel, 2018)

CHAPTER VIII

CONCLUSION

The premise of this investigation was to determine if, using a portable X-ray fluorescence spectrometer, it is possible to easily identify the ware type of certain kinds of historic ceramics by analyzing their glazes. The ceramics in question included creamware, pearlware, whiteware, and porcelain, which can often be misidentified by archaeologists due to either the archaeologist's lack of experience with ceramics or the ceramic sherds limited diagnostic attributes. The popularity of porcelain from China and Japan led to an evolutionary trend in European ceramics, which England spearheaded during the Industrial Revolution, and spawned the creation of whiter and whiter refined earthenware ceramics. These three ware types, creamware, pearlware, and whiteware, are abundant on archaeological sites worldwide due to the domination of the English ceramic industry during the 18th and 19th centuries. Although other features such as vessel type and decoration can be more informative about the socio-economical aspects of an archaeological site, the identification of ware type, particularly distinguishing between these three refined earthenware types, is most important in developing a chronology and age of a site.

The analysis of both qualitative and semi-quantitative data yielded mixed results. Due to these results and the lack of a well-defined identification method, the blind tests were omitted from the testing procedure. The qualitative examination of spectrums produced from the pXRF spectrometer allowed me to conclude:

1. Porcelain was easily distinguishable from the other wares because these refined earthenwares have lead-based glazes and lead peaks surpassed all others on their

spectrums. In addition, porcelain was recognizable in the high Z scan by the strong *bremsstrahlung* region around 18-25 keV.

2. Qualitative analysis of creamware, pearlware, and whiteware spectrums did not offer conclusive evidence for identification as each ware type shared similar peak patterns and peak heights differed throughout all three of the sample selections.

Semi-quantitative analysis revealed additional information about trends in the normalized net photon counts of particular elements:

1. Potassium (K) was the most informative element of interest for distinguishing porcelain; the range for potassium values from the general analysis scan was isolated at 2.2-4.6 with no overlap from the lower values of the other ware categories.
2. Manganese (Mn) was similar for creamware as a distinguishing element; creamware had the lowest values which ranged from 0.021-0.048.
3. Cobalt (Co) had been an element of interest at the onset of the study, but the data from the low Z scan did not indicate that it can be used in this method to distinguish between creamware, pearlware, and whiteware.
4. Magnesium (Mg) counts were much more revealing, indicating that pearlware and whiteware usually have a much smaller range of values than creamware.

Although the primary goal of this research was not achieved, valuable information was gathered nonetheless:

a) The easiest of the white- and cream-colored ceramics to identify using this method was porcelain.

b) Of the refined earthenware categories, creamware was the most distinct and may be identifiable through analysis of a few different elements such as manganese and magnesium, using different spectrometer settings.

Portable XRF spectrometers are not a standard piece of equipment for every archaeological investigation, but their applications in archaeology continues to expand due to the ease of use, portability, and cost-effectiveness of these machines. The ease with which XRF data may be shared is also beneficial for the entire archaeological community. Although the outcome of this research was mixed, the data collected could prove beneficial to other researchers, and providing access to this data would be one of the next stages of this research. Sites such as The Digital Archaeological Record offer resources for researchers to share and access data such as these. Applications such as this may not necessarily be immediately practicable, but as the employment of XRF and pXRF devices in archaeology increases and researchers are educated on the processes utilized in XRF analysis, similar procedures may become common practice in future settings.

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