# BEAUTIFUL FORMS AND COMPOSITIONS ARE NOT MADE BY CHANCE: EXPLORING THE EFFICACY OF PORTABLE X-RAY FLUORESCENCE TO SORT AND SOURCE ENGLISH LEAD GLAZED CERAMICS 

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By<br>Steven J. Sarich<br>A THESIS<br>Submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE<br>In Industrial Archaeology MICHIGAN TECHNOLOGICAL UNIVERSITY<br>2015<br>© 2015 Steven J. Sarich

This thesis has been approved in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE in Industrial Archaeology

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## Acknowledgements

I would like to extend my deepest appreciation to all those who have helped and supported me during my time at Michigan Technological University. First and foremost, my thanks goes out to my advisor, Dr. Tim Scarlett, who set me on this path and encouraged me throughout. I would also like to thank Dr. John Richards who was kind enough to lend me not only the instruments to carry out this research, but also his time and knowledge. Thanks also to Dr. Mark Rouleau for his advice and guidance and getting me to think differently about the data.

I also thank the Chipstone Foundation, especially Jon Prown who has helped me countless times and whose support has never wavered. Furthermore, this research was conducted with the aid of the Robert and Mary Buttle Scholarship awarded by the American Ceramic Society and I could not be more appreciative.

It is also necessary to mention my fellow graduate students whose good humor helped me get by and whose input was essential for making sense of a bunch of numbers. These people include: Sean Gohman, Dan Schneider, John Arnold, Mark Dice, Robert Anthony, Carol Griskavich, Dan Trepal, Eric Pomber, Adrian Blake, and Dr. Marc Henshaw.

Most importantly I would thank my family who always have my back and help me keep things in perspective. My respect and love go out to my mother, Jackie and my father, Rick.


#### Abstract

Advances in portable X-ray fluorescence (pXRF) technology have made it a viable option for the non-destructive exploration of the underlying chemical composition of ceramic artifacts for the purposes of classification. However, because the literature regarding the use of this instrument on historic artifacts is limited, it is necessary to begin with a broad scale exploratory assessment that might act as a jumping off point for future studies on this topic. Toward that end, this research uses a collection of British and Continental European ceramics ranging from 1650-1920, owned and curated by the Chipstone Foundation in Fox Point, WI, to explore the efficacy of using pXRF to sort and source those materials. The chemical patterns in the data are tested against the known provenance of these artifacts which has been pre-determined by ceramic experts and material culture analysts.

Of the 102 samples that have been tested, primary focus is given to items crafted in London and Staffordshire which account for the largest portion of artifacts in the dataset. Principle component analysis is used to better understand the underlying structure of the entire dataset to ultimately reduce the number of chemical variables to those that best distinguish each group. Using those particular chemical variables, a separate dataset of London and Staffordshire mean intensity readings is subjected to factor analysis which resulted in two components being identified. The calculated factor scores are incorporated into a binary logistic regression model to determine if the samples can be correctly sorted into their pre-established provenance categories. A second model that incorporates the year of production is also presented which shows an improved ability to classify those samples. These results are ultimately situated within the historic context of the pottery making industry in England which was highly influenced by the Industrial Revolution and developments in ceramic technology.


## Chapter 1: Introduction to Archaeological Classification and Portable X-Ray Fluorescence

The characterization and classification of artifacts is a cornerstone of archaeological analysis that entails the detailed examination and description of an object or assemblage. Classification draws on an array of external and internal details of the artifacts. The confluence of that information leads the researcher to conclusions regarding the archaeological record and the groups of people that took part in its creation (Prown 1982). That ancillary or external information is often lacking for historical artifacts, however, or non-existent in prehistoric contexts. Throughout the history of the discipline, this has lead archaeologists to develop means of extracting relevant and valuable information purely from the artifacts themselves. Scholars developed typologies and classification schemes as systems of thought. In other words, these systems became tools for formulating questions by comparing and contrasting the characteristics of artifacts. Subsequent research then answers those questions.

Culture historians, in the early years of archaeology, developed pragmatic and regional systems for making artifact comparisons. Chronologies of cultural and technological developments and diffusion developed as a result. Early examples include Gladwin and Gladwin's (1930) regional chronological classification of southwestern pottery or the Midwestern Taxonomic System used to find confluences of traits that characterized the past cultures in North America (McKern 1939). Later, processual archaeologists endeavored to discover the exact role of artifacts in cultural systems and in
the surrounding environment. Archaeologists began to favor models of cross-cultural human behavior based on the archaeological and ethnoarchaeological record over the recreation of "unique events in all their idiosyncratic detail" (Trigger 2006, 401).

An interest in human agency in the conceptualization and production of things, however, led archaeologists to a post-processual school of thought. An artifact in an historic or prehistoric context was seen as "an active element" within the society where it was produced (Trigger 2006, 453). Post-processual archaeologists emphasize artifacts as symbols and identify traits reflective of an individual's role in society. The classification of artifacts therefore became a tool to gain insight into race, class, and gender in a given society or to reveal the minds of the makers. The artifacts themselves are not of central importance necessarily, but rather the primary focus is on the individual who is crafting them.

These elements, along with particular tenets of preceding paradigms, are being incorporated into the contemporary archaeological toolkit. The classification of artifacts in modern archaeology has taken on a more pragmatically minded processual-plus flavor. This approach views material culture from multiple theoretical perspectives to achieve a holistic understanding of past cultures and human behavior. This framework also incorporates a multitude of methods that are most productive for answering a given research question.

Any artifact research, no matter the theoretical framework for classifying artifacts, must ultimately confront the practical realities of archaeology. Archaeologists draw their conclusions from things. This necessitates developing tools for examining and organizing those material remains. For much of the history of the discipline there has been a reliance
on diagnostic characteristics of artifacts that can be seen with the naked eye or through an optical microscope. Material science techniques in archaeology have gained a great deal of traction over the last few decades and are useful lines of research. Systems of classification based on the chemical fingerprint of artifacts can serve to reinforce existing systems or uncover variation that would otherwise go unnoticed.

## The Benefits of Material Science and Portable X-Ray Fluorescence

Techniques in material science allow archaeologists and material culture analysts to understand artifacts at a mineralogical and elemental level. This is most useful in the absence of macroscopic diagnostic features which would typically be used for identifying and classifying artifacts. Several of these techniques, including pXRF, involve concentrating x-rays into a fine beam which interacts with the material under analysis. Given enough energy, an electron is dislodged from an M, L, or K electron orbital. To maintain neutrality, a higher shell electron drops into the gap. The binding energy of electrons increases the further they are from the nucleus. The difference in energy as a higher shell electron drops into a lower shell, determined by the distances between the M , L , and K shells, leads to the emission of radiation in the form of photons which are detected by the instrument (Figure 1.1) (Piorek 1997; Rice 1987). As the atomic structure of each element is different, the energy emitted will be characteristic of that element and result in $M, L$, and $K$ spectral peaks. The instrument and software also calculates counts, or net intensities of an elemental which act as a measure of the amount of that element in the artifact. This information factors into a patterned "fingerprint" that can be linked with artifacts or raw material of similar composition.


Figure 1.1 Basic diagram of $X$-ray fluorescence. A) Emitted $X$-rays eject an inner shell electron. B) A higher shell electron fills the gap to maintain electrical neutrality which causes the emission of characteristic radiation.

This approach to artifact analysis operates under the assumption that objects or groups of objects made by people can be distinguished based on their elemental fingerprint. This distinction is based on alternative approaches to the production of items even though the same basic end may be achieved. In other words, one potter may produce a similarly shaped vessel or another, however each may be utilizing different raw materials for both fabric and glaze as well as using varying amounts of those raw materials in their recipes. This divergence in approaches to production is shown to manifest itself in differing chemical signatures allowing archaeologists to sort and "source" objects to particular individuals, pottery shops, or ceramic producing regions (Forster and Grave 2013; Hou et al. 2004). The development of these types of technologies for analyzing materials marks a sizeable expansion of the archaeologist's toolkit for understanding the archaeological record.

An array of features characterize field portable X-ray fluorescence (pXRF), shown in Figure 1.2, that are highly attractive to material culture analysts and archaeologists. As the name suggests, the device can be transported to a location such as


Figure 1.2 Basic instrument setup with complete software package, vacuum pump, and instrument stand.
a museum or into the field to perform in situ, non-destructive artifact characterization. In cases of delicate, highly valuable, or non-transportable items this is of great benefit as they do not have to be handled or moved apart from positioning the object for analysis or transitioning from one reading location to another. The pXRF instrument is also capable of performing an analysis non-destructively by reading the surface characteristics of objects, however, homogenized or powdered samples can be used as well to randomize the distribution of constituents. Furthermore, this technology has evolved in recent years to achieve greater accuracy and detect a wider array of constituent elements relative to its earlier incarnations while still maintaining its portability (Potts 2008). Given these features coupled with its lower operating costs and short reading times relative to most bench instruments it is worthwhile to assess its ability to chemically classify artifacts. Through the use of a curated collection of intact British and Continental European ceramics, attributed to manufacture dates from approximately 1650 to 1915 , this study tests the efficacy of the pXRF instrument for archaeological analysis. This is meant to be a proof-of-concept study that will demonstrate the use of pXRF and factor analysis to sort
ceramic artifacts by provenance using the chemical signature of the surrounding tinopacified lead-oxide glaze of each artifact.

## A Brief Overview of Glaze Constituents

Many British ceramics from the seventeenth to the nineteenth century feature earthenware fabrics fired at a lower temperature with a relatively high degree of porosity. The permeable fabric necessitates the application of a non-permeable glaze in order to hold liquid and for aesthetic effect. There are several types of ceramic glazes, but the artifacts at the heart of this study were coated with a lead based tin-opacified glaze. Lead oxide acts as a flux to lower the melting point of the clay to encourage the formation of a smooth glassy surface. Aluminum and silicon are also fundamental constituents which help to stabilize the surface. That is to say keep the glassy surface from running or cracking and help the glaze adhere to the fabric surface (Rice 1987).

Potters from the Netherlands introduced tin-glazing to England in the middle of the sixteenth century (Black 2001). It is a variation on the primarily lead based glazes which have a long history in pottery production. This became a popular glazing strategy as the tin, when fired, interacts with the other glaze constituents to form tiny air bubbles in the glaze which scatter light and thus create a glossy, white surface that imitated fine imported porcelain finishes. The basic combination of lead, aluminum, and silicon along with tin was applied to the vessels and fired in a glost kiln. Colorants would subsequently be dusted or painted depending on the desired outcome. Common colorants include cobalt, iron, copper, nickel, or manganese. Table 1.1 lists common stabilizers, fluxes, opacifiers, and colorants. The use of colorants as well as the underlying, fundamental lead or tin-glazed coating was subject to experimentation over the years in Britain and

Continental Europe to achieve an aesthetically pleasing and white product. An extensive number of these artifacts can be found among the collections at the Chipstone Foundation.

Table 1.1 List of common stabilizers, fluxes, opacifiers, and colorants.

| Stabilizers | Fluxes | Opacifiers | Colorants |
| :--- | :--- | :--- | :--- |
| Silicon | Lead | Tin | Copper |
| Aluminium | Calcium <br> Potassium <br> Sodium <br> Magnesium <br> Zinc | Titanium | Cobalt <br> Manganese |
| Iron |  |  |  |
| Nickel |  |  |  |

## The Benefits and Limitations of the Chipstone Ceramic Collection

In the middle of the twentieth century, Stanley and Polly Stone started collecting seventeenth and eighteenth century British and European ceramics. In the 1980s the Chipstone Foundation was formed to manage this collection and educate people about the importance of these items. Approximately 505 ceramic objects are curated by the Chipstone Foundation. The artifacts chosen for this analysis have known provenance information assessed by experts in the field of historic British and Continental European ceramics (Hume 2001, Martin 1999). This information is catalogued in an online database managed by the University of Wisconsin-Madison, a permanent record of which resides at the Chipstone headquarters. The valuable nature of artifacts held in this collection make pXRF ideal for extracting elemental data without damaging any of the items. The volume of objects curated by the foundation allows for the examination of a substantial number of samples in a single location without significantly disturbing artifacts or transporting them great distances. The Archaeological Research Laboratory at
the University of Wisconsin-Milwaukee very kindly agreed to lend the instrument for the purposes of carrying out this study.

This study is meant to demonstrate the viability of using the pXRF instrument, i.e. act as a proof-of-concept study, to sort ceramic artifacts based on their respective chemical signatures. This study comes with certain limitations however. Because the initial collector, Stanley Stone, was interested in a certain subset of ceramic artifacts, it is open to question whether they are truly representative of the population of tin-opacified and lead glazed wares made in these ceramic producing regions. Additional concerns include differential preservation of ceramic vessel types. Furthermore, this study itself focused on a particular subset of the collection. Nevertheless, the research strategy employed here was deemed acceptable as a useful starting point to gain some insight into the effectiveness of the instrument to characterize these artifacts.

## Document Structure

The five subsequent chapters of this thesis build on one another and culminate in a synthesized assessment that situates this work among the archaeological systematics and ceramic classification literature. Chapter 2 entails a retrospective review of systematics and classification over the course of the archaeological discipline. This is meant to provide some context on those topics as well as emphasize the absolute importance of artifact, and more specifically, ceramic classification in the archaeological realm. This is also meant to highlight the need for a constant re-examination of the toolkit available to the archaeological researcher for organizing and describing material culture as it is the foundation for all subsequent research into the archaeological record. This chapter will also feature a discussion of the use of material science techniques, with a
focus on portable X-ray fluorescence, in contemporary archaeology. However, theoretical concepts regarding pragmatism in classification and having an understanding of the mind of the maker are essential in sorting artifacts effectively regardless of the technique for so doing.

Having established the usefulness of pXRF for material culture analysis, Chapter 3 introduces the methodological elements of the study of the Chipstone collection. This includes a review of the instrument specifications, the samples and the sample size, the process of data collection, and the data analysis procedure and protocols set down by the University of Wisconsin-Milwaukee Archaeological Research Lab. Chapter 4 will detail the results of that data analysis including the trends shown in the principle component analysis, the subsequent ANOVA and post-hoc tests linking the clusters of data to their provenance designations., and the focused factor analysis and regression models for the Staffordshire and London artifacts. With these results in hand, Chapter 5 explores the implications of the findings and situates them within the literature on glaze raw materials and chemical analysis. Finally in Chapter 6, a reflexive examination of the gleaned results leads to new questions manifested as a results of the experiments and features closing remarks on the benefits of arcaeometric analysis.

## Chapter 2: The Disciplinary Evolution of Systematics and Classification

Approaches to artifact classification have taken on many iterations over the years as new paradigms and frameworks are introduced into the archaeological discipline. In all these instances the classification of artifacts was meant to better understand the movements, behaviors, and habits of people and the changing nature of the culture or cultures engaged in the production of particular items by viewing the often subtle variations in form or decoration of artifacts. Classification helps to make sense out of the vast amounts of materials in the world. Once sorted, archaeologists can start to ask questions about the past. Despite this common goal, the means by which these phenomena are understood has been open to much debate, largely between processually minded archaeologists with defined types which become the primary units of analysis (Dunnell 1971; 1986), cognitive scholars who see the mind of the maker among variations in artifacts (Renfrew 2005) and post-processual thinkers who view the changing meanings of artifacts over time and utilize more relativistic vernacular labels or folk taxonomic systems to better understand the emic values imbued in objects (Shanks 1998).

In recent years, these debates have subsided to a certain extent, having been reconciled in the minds of many scholars who see value in pragmatically driven research designs to classify and interpret artifacts in the archaeological record (Read 2009). Not only are interpretive frameworks being developed to unpack the meanings surrounding particular formal or stylistic choices, but there appears be a resurgence in the application
of natural science techniques to the study of artifacts influenced in large part by advancements in technology. Material science and archaeometric techniques have been introduced into the realm of systematics and artifact classification that bring into the fold an alternate means of differentiating cultural items through the use of chemical data (Kingery 1996; Orton and Hughes 2013). This does not eliminate the need for macroscopic diagnostic information of, in the case of the research presented here, whole or partial ceramic artifacts. The chemical classifications are meant to supplement those other systems or provide contrast to them.

Archaeologists organize artifacts in an iterative process. New technology or alternate thinking forces necessary reconceptualization of relationships among objects. New groupings of objects, or awareness of new traits, alters archaeologist's understanding of the people that made or used them. It is worthwhile to chart the trajectory of intellectual thought related to this topic to assess the established toolkit available to the contemporary archaeologist. This continual reconceptualization of artifact classification gave rise to this pragmatic paradigm that utilizes macroscopic as well as elemental information. It is useful to keep this context in mind when determining where the research presented here might fit within the larger realm of systematics and classification.

This discussion is organized by paradigmatic shifts in the archaeological discipline which influenced not only the organization of objects, but also the types of questions archaeologist's asked of the archaeological record. This discussion necessarily begins within the realm of culture-historical archaeology, a period which laid the foundation for typological debates subsequently brought about by the processual and
post-processual turn in archaeology. The many complexities archaeologist's uncovered as a result of those debates went a long way toward influencing the current state of archaeology. In a sense, the discipline has returned to the central tenet of the anthropological field as a holistic pursuit which brings to bear systematic, interpretive, and material science approaches to the study of past human behavior.

## Culture-Historical Archaeology and the Development of Classificatory Systems

The central goal of the culture-historical paradigm has been to "trace historical relations through time and space. Such historical findings are the necessary prerequisites for evolutionary generalizations about the process of change" (Trigger 2006, 313). Concepts like acculturation, assimilation based on the degree of contact, and the organization of cultures across space and over time were developed based on the similarities and differences of styles and forms. However, the application of these ideas was largely focused on prehistoric and contact period contexts with less regard for historic sites. For example, Quimby and Spoehr (1951) looked at the regular changes in form of native-made objects over time among museum collections during the contact period in North America to see the steady assimilation of Western ideas into the material culture of Native groups. The tenets of culture-historical archaeology are reflected also in Culture and Acculturation of the Delware Indians by William Newcomb (1956) which narrowed the scope to changes among a particular group of Native Americans. These authors traced steady cultural changes based on the materials being produced. In other words, it was thought that one culture would transition into another form based on the degree of contact, though with a certain disregard for the complexities of these changes. For example, an article by Jörgen Meldgaard (1960) featured a straightforward and
simple model that showed a temporally broad and steady progression, based on tool materials and house forms, from Late Archaic groups in the Eastern Arctic to Early Woodland who then became the Dorset people. Over time, however, scholars began to recognize the complexities inherent in the archaeological record and this led to both cladistic and reticulation models to trace evolving artifact features and therefore demonstrate cultural transitions over time (O'Brien et al. 2012; Tëmkin and Eldredge 2007). At its core, the cladistic model argues that a single population over time begins to branch out to produce multiple new populations, languages, cultural values, etc. This allows archaeologists to trace representative artifacts in the archaeological record back to a common ancestral culture (Tehrani and Collard 2002). On the other hand the reticulation model puts forth the idea that multiple groups or populations are responsible for the rise of multiple modern populations, languages and cultural values and can be seen as a more convoluted "braided stream" (Moore 1994; O’Brien et al. 2002). These later years of culture-historical archaeology set the stage for a more systematic approach to the study of artifacts; one that would more accurately depict the observed changes in the archaeological record taking place over time.

As a result of these disciplinary developments, archaeologists created classification systems for an array of artifact classes including ceramics. One early example is Gladwin and Gladwin's $(1930 ; 1931 ; 1933)$ classificatory system of pottery of the southwest that was "based on relative degrees of trait similarities, its dendritic pattern involved geographical considerations and it was implicitly chronological; roots formed before stems and stems before branches" (Trigger 2006, 284). Will C. McKern (1939) created an alternate system called the Midwestern Taxonomic Method. This system
divided units of occupation into components then foci which, in turn, were further subdivided. At the time of their inception, these systems separated cultures into a rough chronological framework or situated them in approximate geographic space. Ford's (1962) seriation method required careful observations of stratigraphy and detailed artifact descriptions, and this led scholars to a continual re-examination of classification systems.

Issues surrounding classification erupted with the Ford-Spaulding debate. Albert Spaulding (1953) argued that types were discovered and thus real to makers. Classification should, therefore, fit the cultural context. James Ford (1954), on the other hand, saw types as being constructed by the archaeologist as a practical solution to the sometimes chaotic nature of culture change. Charles Ewen $(2003,70)$ noted that Ford and Spaulding's approaches "were designed to answer different questions...One could argue that Ford was promoting paleoethnology... while Spaulding championed paleoethnography." Because of these discussions culture-historical archaeologists were able to give a firm description and history to particular groups or past cultures.

A number of classificatory systems in historical archaeology were also devised, applied, and refined. These include the type-variety system (Dunnell 1971; Gifford 1960; Sabloff and Smith 1969), the SHA typological systems that establish date of manufacture based on technology history (Lindsey 2015), and more focused systems addressing a particular region such as the Potomac Typological System (Beaudry et al. 1983). Furthermore, industrial archaeology still maintains a firm foothold in the regional nuts-and-bolts approach to classification. Becher and Becher (2004) developed a typology of industrial structures based on formal changes over time. Bayley and Rehren (2007) offer a classification of crucibles based largely on differences in function.

In the realm of ceramics, the type-variety system was developed and is a popular way of describing an assemblage of pottery. It is designed to deconstruct ceramic artifacts into ware, type, variety, and group and analyze the interrelationship between these variables to establish ceramic complexes and chronologies (Sabloff and Smith 1969). The type-variety system has been criticized for being too rigid in its definition of types which often times have a great deal of overlap. Hammond $(1972,452)$ noted that,

> This loss of effectiveness may perhaps be partly resolved by treating the Ceramic Group as a polythetic set of attributes... within which the possession of any one attribute is neither sufficient nor necessary for membership. Thus neither a common vessel form, nor the color, nor even the presence of slip, nor the absence, presence, or variety of ornament matter provided that the specimen possesses a certain number of the defined attributes which encapsulate the group.

This debate speaks to the core concern of archaeologists at this time which centered on making sense of the material world. Classification in the culture-historical realm is focused largely on description and identifying certain patterns. New intellectual developments in anthropology and archaeology would challenge the straightforward narratives presented by the culture-historian, approaches that acknowledged a number of other cultural and ecological factors that influenced the nature of the archaeological record as well as the form and function of artifacts.

## A Systematic Approach to Artifact Classification

Moving forward to the middle decades of the $20^{\text {th }}$ century, culture-historical archaeology dominated the study of material culture and the archaeological record. However an alternate approach was taking shape in the form of the processualist paradigm (Binford 1989). Scientific practice was incorporated into archaeological research and patterns in the archaeological record were being studied using computers
and multivariate statistics. This technological and methodological change mirrors the current evolution in contemporary archaeological practice influenced by material science studies.

This paradigm is discussed in several articles by Binford (see Binford 1983; Binford and Quincy 1972), but his 1962 article "Archaeology as Anthropology" is notable for a number of reasons, one of which is his deconstruction of material culture into the technomic, socio-technic, and ideotechnic. According to Binford $(1962,217)$ "change in the total cultural system must be viewed in an adaptive context both social and environmental, not whimsically viewed as the result of 'influences,' 'stimuli,' or even 'migrations' between and among geographically defined units." The cultural system is revealed through the study of the three classes of material culture stated above. This new framework resulted in a more systematic and process oriented approach to culture change and the study of the archaeological record. This developing framework was explored, again, by Binford (1965) who advocated for the use of particular artifacts, ceramics among them, to reveal the workings of given subsystems of a culture and basing classification on formal, decorative and primary and secondary functional elements.

Robert Dunnell's (1971; 1986) work exemplified these intellectual trends and outlined a strategy for utilizing artifact types as the basic unit of analysis. This approach also used etic classifications that would be universal to the assemblage of items made by individuals in a given culture. In the words of Dunnell (1971):

If several objects hold features in common, and those features are of human origin, there is but a single plausible account. Intentionally or unintentionally, consciously or unconsciously, the objects were made to look alike by people who can be treated as possessing similar ideas about them and who have the same categories of features and ways of
articulating the features into whole artifacts. In short, the objects can be treated as expressions of the same mental template (132).

In this sense, the individual is exchanged for culturally guided groups and focus is placed on common classes of traits rather than particular details of a given artifact (Read 2009). The concept of commonalities between material objects is central to the approach of this research. The sorting of artifacts chemically operates under the assumption that particular groups of potters utilized like glaze recipes that are independent of those developed in another pottery producing region. However, questions regarding the exact nature and cause of those shared features are addressed in greater detail by cognitive and postprocessual scholars who seek to understand the mind of the maker and the evolution of the sequence of operations to achieve a desired outcome in the creation of objects.

## Cognitive and Post-Processual Approaches to Artifact Types

Cognitive approaches to the archaeological record were influenced by developments in the broader discipline of cognitive anthropology and related fields. The paradigm endeavored to utilize material culture to better understand the mental processes at work as people crafted objects which would subsequently make their way into the archaeological record (Abramiuk 2012; Renfrew 1993, 1998). Cognitive archaeology borrows many of the theoretical underpinnings of cognitive anthropology and psychology. A goal of cognitive archaeology is to craft networks of typologies often based on the vernacular terminology of makers and craftspeople to see how ideas regarding the production of objects might develop and be transferred. In other words, the idea is to "develop a secure methodology by which we [cognitive archaeologists] can
hope to learn how the minds of the ancient communities in question worked and the manner in which that working shaped their actions" (Renfrew 2005,41).

Often cognitive interpretations take on a dialectical flavor with back and forth interaction between the mental conceptualization of the maker and real world practice. The strengths and limitations of the material strongly influences the form as the final outcome is re-conceptualized as skill and technology develops (Bleed 2001; Keller and Keller 1996; Schlanger 1996). In this sense, individual action plays a role in the construction of forms and styles, all of which are factored into the organization of the artifacts. James Deetz (1977) saw these slight style differences as variations on a theme, however, and returned to the concept of shared ideas of material culture. Deetz considered artifacts as "reflections of the mental templates of the makers" though this normative framework has been criticized as too formulaic (Neuwirth et al. 2002, 113). Certain concepts, though, overlap with the central dictates of the post-processual paradigm in archaeology which, at its core, attempts to account for human agency and individuals as major influencing factor in the variation found in the archaeological record (Johnson 2010, 108).

As noted above, throughout the 1960s and 70s the archaeological discipline was rich with processual concepts including Binford's (1965; Binford 1968) middle range theory and framing culture as consisting of multiple interacting systems all of which factor into the interpretation of the archaeological record. In the 1980s and 1990s, however, a paradigm shift took place (Kuhn 1962) primarily led by archaeologists influenced by the postmodern turn in the social sciences (Hodder 1982; 1985), who raised a number of questions regarding processual thought in archaeology. The idea of cultures
as systems was considered particularly problematic, or as Matthew Johnson (2010, 102) stated, "in particular, they pointed to the need to address cognitive factors, the difficulties of positivist epistemology, and the problems with developing middle-range theory..." Ian Hodder, for example, was a processualist, and believed that processes in modern cultures could be associated with the processes of the past as reflected in the archaeological record (Hodder and Orton 1976; Johnson 2010, 102). Over the course of his research in Africa, however, he came to several conclusions that led him to believe that processual concepts were no longer adequate in explaining patterns in the archaeological record and past human behavior (Johnson 2010, 103). Hodder (1991) explained that:

From a hermeneutic point of view, the failure of the processual archaeology of the 1970s and early 1980s was that it too often took a cavalier, externally based approach where the data were simply examples for the testing of universal schemes, with too little attention paid to context and to understanding the data in their own terms. The possibility that radically different processes might be encountered was thus difficult to entertain. From the point of view of critique, the failure of processual archaeology was its blindness to its own ideologies (12).

Post-processualism began to focus, to a much greater extent, on the context of material culture and considers the social factors embedded within a past culture.

Processual thinkers argued that the archaeological record is a reflection of systems operating within a society, and can give insight into the interaction between these systems that were part of a particular culture. Lewis Binford $(1983,25)$ stated, "the archaeological record is a static contemporary phenomenon. It is structured matter motionless and noninteractive in terms of the properties of historical interest to the archaeologists" (Binford 1983, 25). Material remains offer a snapshot of the systems functioning with one another and any changes that may be perceived are extrasomatic in
nature (Binford 1962). In contrast, one of the emphases of post-processualism is that cognitive processes as well as a number of other non-behavioral factors influence material culture, and objects are imbued with certain meanings and, over time, these meanings change. Where processualism narrows the focus to certain extrasomatic means of adaptation, a number of distinct frameworks within the post-processualist paradigm attempt to understand the beliefs and symbols that may give insight into the social structure or interaction between groups and individuals. Ultimately, the physical objects found in the archaeological record embody the beliefs and values of people. This adds a level of complexity to the organization of objects which may fill a particular cultural or societal role among one group of individuals, but not another.

The debates in historical archaeology have largely centered on topics well within the post-processual realm that typically involve research into race, class, gender, symbolic interpretation, and power relations (Shackel and Little 1992). However, in recent years there appears to be a reemergence of interest in the creation of typological systems facilitated in large part by a desire for flexibility in design and the utilization of alternate methods and technology which offer an alternate perspective on the organization of artifacts (See Fluzin et al. 2012; Smith et al. 2014).

On the topic of classifying artifacts, Michael Shanks and Ian Hodder (2007) explain that,

Classification operates under a 'rule of the same.' Taxa are characterized by relative homogeneity. This is a legitimate strategy for coping with the immense empirical variety and particularity that archaeologists have to deal with. However, we should be clear that classification does not give the general picture; it gives the average. It is not a general picture because there is no provision in classification for assessing the norm, the taxa..., not the variation within a class, nor the variability of variability.

Classification is less interested in coping with particularity...Why are the members of a class of pots all in fact slightly different? (150).

This assertion is worthwhile to keep in mind when approaching the topic of classifying artifacts and does indeed factor into the broad epistemological framework of the research presented here. Particularities, to a degree, are not the end goal for the study of chemical data in the case of this exploratory examination of historic ceramic glazes. Rather the trends that manifest themselves are of central importance as they will inevitably lead to more focused questioning and a readjustment of the current lens of inquiry. Determining the reason for commonalities and divergence in glaze chemistry requires further research into the societal, economic, technological, and cognitive factors at play during the time these historic ceramic materials were being produced.

## Potentials of Material Science and Archaeometry

Because particular constituent materials were chosen for a given end, material science techniques investigate the structure of assemblages. Formal, stylistic, spatial, chemical as well as other forms of evidence can be used to understand the association, context, and meaning of objects. Various techniques have been developed to analyze the constituent elements of an artifact to source those materials or understand the microstructure and begin to understand the processes involved in its creation (Henderson 2000; Rice 1987). A researcher can also undertake a detailed phase analysis to understand the properties and interactions of the material and thereby enter the mind of the maker who was forming educated decisions based on their ever-developing principled knowledge. However, in the words of Kingery $(1996,196)$, "there is always tacit knowledge embodied in artifacts, and it is not easy to interpret the function and use of a
complex construction without culture-specific knowledge or specific instruction." This means that the approach to the study of material culture always entails a confluence of evidence drawn from both the artifact itself in the form of chemical data as well as anthropological and historical information.

Nevertheless, there is an ever growing body of archaeological projects and scholarly literature using material science technology and techniques to characterize or "fingerprint" artifacts from the archaeological record including ceramic artifacts and assemblages (Maggetti 2012; Maggetti et al. 2014; Papadopoulou et al. 2007). Though the literature on historic fabric and glaze analysis is not as extensive as that involving prehistoric artifacts, several studies using French faience, i.e. French tin-glazed earthenware, have been undertaken. Work by Marino Maggetti, for example, contains a great deal of contextual and chemical information regarding French samples collected from several pottery shops. Maggetti analyzed these faience sherds to develop chemical reference groups which researchers can use to determine the provenance of archaeological samples by comparing the chemical signature of the artifact in question to the reference group (Maggetti 2012; Maggetti et al. 2014). In an effort to distinguish between pottery workshops, Maggetti, Rosen and Serneels (2014 utilized both X-ray fluorescence and X-ray diffractometric techniques to the study of French faience samples of sherds. While these techniques have certain advantages in terms of their abilities to provide high quality chemical and mineralogical information, both are destructive techniques that require that lab staff mill the samples to a fine powder.

Other archaeometrists have established non-destructive alternatives that do not require damage to artifacts and offer other useful features. Recent literature addressed
issues of reliability as it relates to portable instruments like pXRF analyzers. These articles emphasize the need for quality standards to check the instrument is operating consistently, performing multiple runs at appropriate reading locations on the artifact, and taking precautions to reduce attenuation, i.e., loss of x-ray intensity by absorption, during analysis (Craig et al. 2007; Shackley 2010; Speakman et al. 2011; Speakman 2012). This research was mindful of these necessary standards, and analytical practice followed the protocols established by the University of Wisconsin-Milwaukee Archaeological Research Lab.

Archaeologists are now utilizing field portable X-ray fluorescence instruments heavily in prehistoric contexts and in analysis driven by research designs from Art History. Hand-held pXRF analyzers provide data to sort and source materials beyond their macroscopic diagnostic characteristics at a level of accuracy that is adequate for the purposes of the archaeologist who is interested in the averaged patterns, as Shanks and Hodder (2007) would state, that are present in the data (Liritzis and Zacharias 2011; Shugar and Mass 2012). Researchers have used pXRF devices on a wide range of ceramic artifacts including Neolithic Grecian pottery (Papadopoulou et al. 2007), glazed stonewares from north-east Asia (Mitchell et al. 2012), cuneiform tablets from the Near East (Goren et al. 2011), and pre-colonial pottery from Sao Luis, Brazil (Ikeoka et al. 2011). Each of these studies has achieved some level of success for "sourcing" artifacts, at least at the regional level, usually in conjunction with neutron activation or mass spectroscopic techniques used for comparative purposes. Nicola Forster and Peter Graves (2013) undertook a pilot study of lead glazed Byzantine vessels from Cyprus and noted that some of the compositional groups matched well with particular pottery
manufacturers, though this was not the case for all groups. Nevertheless, these results encouraged the authors to pursue a larger characterization study of Cypriot ceramics $(2013,485)$. These studies have shown field portable XRF has a great deal of potential for non-destructive, in-situ analysis of ceramic materials, though the literature is sparse with regards to the application of this technique to the study of historic artifacts in general and ceramics in particular. The research presented here is intended to add to the literature on classification and pXRF with a focus on historic rather than prehistoric materials.

## Chapter 3: Methods for Assigning Provenance Using Glaze Constituents

This proof-of-concept study uses portable X-Ray fluorescence (pXRF) to source historic ceramic materials through the use of a body of data with known production location information. This case study focuses on lead-glazed and tin-opacified wares housed in the Chipstone Foundation collection of British and European ceramics. As stated earlier, the premise is to gain elemental net intensity data both non-destructively and in situ. In other words, the entirety of the pXRF instrument readings are performed at the facility where all the samples are currently curated with little sample preparation. This is meant to demonstrate to the archaeological community that useful, reliable, and meaningful information can be obtained quickly, cost effectively, and without affecting the integrity of these valuable cultural resources.

Speakman and Shackley (2013) have recently commented on pXRF studies that they characterize as examples of "silo science" due to the use of uncalibrated data. Speakman and Shackley argue that the result is not good science as these studies lack reproducibility and inter-laboratory comparability. Because my study relies upon uncalibrated net intensity values, it might be argued that the result is an example of this genre. Certainly, my results would be more broadly comparable if my data represented calibrated values for analyzed elements. However, the instrument available to me lacked that capability, as the appropriate calibrations had not been loaded at the time I collected and analyzed the data. Consequently, this work must be seen as a preliminary "proof of concept" study valid only at the level of the Chipstone collection. However, if one assumes: 1) that the analyzed sample is representative of Staffordshire and London wares
in general and; 2) that the net intensity values are a reasonable proxy for the elemental concentrations in the samples, results suggest a statistically valid separation between London and Staffordshire wares based on the variation in tin content. While this result cannot be generalized to other collections (i.e, recorded net intensity values cannot be used to suggest the real range of difference because a different instrument will likely return different net intensity values), other researchers can attempt to replicate my basic finding that tin concentrations vary significantly. This variation is further supported by observed shifts in production, distribution, and social vogues during the time the pottery in the Chipstone sample was produced and used. Thus, the results presented here should have analytical utility beyond the Chipstone collection and the present study.

Toward that end, I analyzed the readings using R Statistical Software to establish the chemical fingerprint of the samples and used factor analysis to link those signatures to the known provenance designations. Clusters, on the one hand, need to be identified among the intensity readings which act as an indirect measure of the variation in glaze production strategies utilized by the various production centers. I can then compare the extracted factors and samples designated as coming from the Staffordshire region and London region, two major pottery manufacturing areas with the former located in the north of England and the latter in the South (shown in Figure 3.1). The geographical separation, the development of independent pottery manufacturing techniques, and the tin glazed industry's waning in London should produce distinguishable chemical signatures. In SPSS, I used factor analysis to study a reduced dataset of only London and


Figure 3.1 Map showing major pottery manufacturing sites in the 17th and 18th centuries.
Staffordshire materials with averaged net intensities of stabilizers and fluxes to determine differences in glaze production strategies. Two binary logistic regression models, utilizing the factor scores, determined the probability of samples being correctly assigned to either Staffordshire or London. Other researchers can test this model in future studies using similar lead and tin-glazed ceramic artifacts held by Chipstone and other facilities.

## An Initial Exploration of the Chipstone Data

Prior to determining the relationship between the Staffordshire and London materials this research aims to utilize the entire dataset of analyzed samples from Britain and Continental Europe. Analysis of the complete dataset seemed a natural starting point for getting a sense of the data and the interaction between chemical variables before refining the approach. Though the number of Continental European artifacts is small and cannot be included in the factor analysis and regression models, their inclusion in the principle component analysis and analysis of variance is useful. Principle component scores coupled with ANOVA and Tukey post-hoc tests for determining potential differences between groups provided some sense of the divergence in compositions between the artifacts. I posit that English ceramics, broadly speaking, are not the same compositionally as Continental European ceramic artifacts in the Chipstone dataset. The major influencing variables that help to capture the greatest trends in the data were retained while removing redundant or unnecessary variables to further distinguish the English and Continental European artifacts from one another.

With this broad geographical understanding that English ceramics are unique from those in Europe, the question then turns to whether the two major sets of artifacts from Staffordshire and London have unique compositional characteristics determined through factor analysis and logistic regression. This allowed for an appraisal of the level of geographical focus that can be achieved with the instrument starting with a broad assessment of all the data and moving toward a narrower regional assessment.

A reduced dataset with all representative samples, but using only data of elements uses as glaze stabilizers and fluxes, was examined using PCA and ANOVA. I was able to determine the appropriateness of using those fundamental glaze constituents for the final regression model that focuses on distinguishing London and Staffordshire made materials. The reason for retaining the stabilizers and flux components in the second principle component analysis and subsequent factor analysis of the London and Staffordshire materials is based on the assumption that the glaze manufacturing process became more standardized over time. The fundamental constituents of the lead based glazes were retained, but variability in decorative colorants will be present even in a single pottery shop (Hale 2008; Owen and Sutherland 1901). I offer further discussion of this topic in the subsequent chapters.

## A Note Regarding the Relationship between Glaze Chemistry Readings

Glaze is a vitreous, non-permeable coating in which elements are not represented randomly. Particular elements will correlate because of the nature of glaze production. Silicon and aluminum, for example, are fundamental constituents of the glaze composition which act as stabilizers to keep the glaze from running or from cracking. Lead and tin also likely correlate as an increase in the percent of lead will require a decrease in tin or vice versa depending on the level of opacity or translucence that the potter would like to achieve. Despite these correlations between elements, other forms of analysis are required to make a determination if particular production factors have an effect on the classification of artifacts into one category or another. It is highly useful, nevertheless, to analyze the chemical variables using principle component analysis to
understand the exact underlying structure of the chemical data which can be taken into consideration when determining which variables to include in the regression models.

## The Instrument and Instrument Specifications

The University of Wisconsin-Milwaukee Archaeological Research Lab (ARL) loaned the pXRF instrument for the purposes of this experiment. ARL's instrument is a Bruker AXS Tracer IIIv + with a Si pin detector, and an X-ray tube featuring a Rh target. As such, the analysis followed the UW-Milwaukee pXRF protocols. I chose not to use a filter in order to gain a wide spectrum of chemical information, and after consultation with UW-Milwaukee ARL staff and consultants at Bruker Corporation, determined that the instrument should be set at 15 KeV and $25 \mu \mathrm{~A}$. Depending on the amount of lead, a 15 KeV beam under vacuum could penetrate up to 5 mm , so this protocol was meant to minimize depth of penetration. Readings were taken under vacuum and without a beam filter to reduce the amount of atmospheric attenuation and a voltage regulator was put in place to maintain a steady power output allowing the instrument to operate consistently. The voltage regulator stopped functioning midway through the experiment, so power levels were checked regularly to ensure that fluctuations were not occurring.

Three flat or approximately flat areas were chosen on each vessel to accommodate the collimated $3 \times 4 \mathrm{~mm}$ X-ray beam. Furthermore, plain white areas or low colorant areas were targeted. All vessel locations were scanned for three continuous runs at 180 seconds per run totaling nine minute scans for each location ( $180 \mathrm{~s} \times 3=540 \mathrm{~s}$ ). The scan time for a single sample, therefore, was 1,620 seconds or 27 minutes yielding 9 cases of net intensity readings to gain a representative overview of the glaze surface. Before and after each analysis session a kaolinite clay standard (Kaolin KGa-2) was used to be certain that
the instrument was running consistently. Precise chemical compositional data for this standard has been published in the Data Handbook for Clay Materials and Other Nonmetallic Minerals (Van Olphen and Fripiat 1979) and is shown below in Table 3.1.

Table 3.1 Characteristics of the kaolin clay standard used to check consistent instrument performance.

| Kaolin Kga-2, (high-defect) |
| :---: |
| Origin: Probably lower tertiary (stratigraphic sequence uncertain) <br> County of Warren, State of Georgia, USA <br> Location: 33019' N-82028' W approximately, topographic map Bowdens Pond, Georgia N 3315-W 8222.5/7.5, Collected from face of Purvis pit, October 4, 1972. <br> Chemical Composition(\%): SiO2: 43.9, Al2O3: 38.5, TiO2: 2.08, Fe2O3: 0.98, FeO: 0.15, MnO: n.d., $\mathrm{MgO}: 0.03, \mathrm{CaO}: \mathrm{n} . \mathrm{d} ., \mathrm{Na} 2 \mathrm{O}:<0.005, \mathrm{~K} 2 \mathrm{O}: 0.065, \mathrm{P} 2 \mathrm{O} 5: 0.045, \mathrm{~S}: 0.02$, Loss on heating: $-550 \mathrm{oC}: 12.6 ; 550-1000 \mathrm{oC}: 1.17, \mathrm{~F}: 0.02$. <br> Cation Exchange Capacity: $3.3 \mathrm{meq} / 100 \mathrm{~g}$ <br> Surface Area: N2 area: $23.50+/-0.06 \mathrm{~m} 2 / \mathrm{g}$ <br> Thermal Analysis: DTA: endotherm at 6250 C , exotherm at 10050 C , TG: dehydroxylationweight loss $13.14 \%$ (theory $14 \%$ ) indicating less than $7 \%$ impurities. <br> Infrared Spectroscopy: Typical spectrum for less crystallized kaolinite, however the mineral is not extremely disordered since the band at $3669 \mathrm{~cm}-1$ is still present in the spectrum. <br> Structure: (Catr Ktr)[Al3.66 Fe(III). 07 Mntr Mgtr Ti.16][Si4.00]O10(OH)8, Octahedral charge: .16, Tetrahedral charge: 0.00, Interlayer charge: .16, Unbalanced charge: .15, Extra Si: . 04 |

## The Chipstone Ceramic Samples

The Chipstone Foundation owns and curates all the objects used in this study. The foundation began in the 1980s with an endowment from the Stone family dedicated to maintaining the large ceramic, furniture, and print collections accumulated by Stanley and Polly Stone or purchased during the years since they created their foundation. The Chipstone Foundation now owns and curates approximately 505 ceramic objects. The ceramic materials are primarily seventeenth, eighteenth, and nineteenth century English lead and tin-opacified wares with comparable earthenware fabrics. Through the eighteenth and nineteenth centuries a transition to cream-colored wares and whiter improved earthenwares occurred, and these types are dominant in the Chipstone collection. Of the many vessels in the collection, I analyzed $102(\mathrm{~N}=102)$ using the Bruker pXRF instrument. Table 3.2 lists the Chipstone vessel types and the number of
each analyzed. For more detail regarding individual vessels and vessel images see
Appendix A and B.
Table 3.2 Chipstone vessels types and the number analyzed using the pXRF instrument.

| Chipstone Vessel Types |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Chargers | Plates | Bottle/Jugs | Cups/Tankards | Pots/Teapots | Jars | Bowls | Figurines | Wall Pockets | Fruit Stands | Handwarmers | Total |
| 21 | 17 | 9 | 14 | 18 | 8 | 4 | 6 | 2 | 2 | 1 | 102 |

The analyzed samples can be subdivided into English and Continental European made artifacts with $32(\mathrm{n}=32)$ attributed to London based potteries, $41(\mathrm{n}=41)$ produced in Staffordshire, and $7(\mathrm{n}=7)$ from Bristol. Experts attributed objects to Kent (n=2), Essex $(\mathrm{n}=1)$, Liverpool $(\mathrm{n}=1)$, the general Midlands area $(\mathrm{n}=2)$, Stoke-on-Trent $(\mathrm{n}=4)$, Derbyshire ( $\mathrm{n}=1$ ), England generally ( $\mathrm{n}=2$ ), and Glasgow ( $\mathrm{n}=1$ ). Ceramicists have also identified samples from European pottery shops including the Netherlands (n=4), France $(\mathrm{n}=2)$, Italy ( $\mathrm{n}=2$ ), Portugal ( $\mathrm{n}=1$ ), and Czechoslovakia ( $\mathrm{n}=1$ ). One vessel has been traced to Massachusetts $(\mathrm{n}=1)$ and one is unknown $(\mathrm{n}=1)$.

## Net Intensity Readings and Initial R Preparation

Once analyzed, I imported the resulting spectra into the Bruker Artax software to begin the Bayesian deconvolution process which helps to identify the most probable compositional components of the historic glazes and their associated net intensities. The Artax software can only analyze 100 spectra at one time resulting in several project files that were combined in Microsoft Excel. I created a new characterization method using the software by identifying components in a random selection of spectra to craft a preset list of elements. This was an iterative process that entailed selecting a spectrum, identifying the elements, and testing the updated method on a subsequent spectrum to determine if additional elements should be included. The final method was used to analyze all the remaining spectra in each project set. Net intensities were extracted for 18 elements
including: Al, Co, $\mathrm{Cr}, \mathrm{Cu}, \mathrm{Fe}, \mathrm{Ga}, \mathrm{K}, \mathrm{Mn}, \mathrm{Ni}, \mathrm{Pb} \mathrm{L}, \mathrm{Pb}$ M, Rh, Rh L, $\mathrm{Si}, \mathrm{Sn}, \mathrm{Sn} \mathrm{L}, \mathrm{Ti}, \mathrm{Zn}$. A majority of identified elements and their associated net intensities come from K shell readings unless otherwise labeled. The instrument detected only the L and M shell spectral peaks for lead as greater power levels are needed to detect K shell lead readings. This analysis uses the lead $L$ shell counts as a measure of lead in the artifacts. Because of the Rh target, this element will always appear in the list of identifiable components and therefore subsequent analyses did not use either the K shell or. A qualitative scan of the data also lead to the removal of certain other elements from the analysis including $\mathrm{Cr}, \mathrm{K}$, Pb M , and Sn K because they appeared at negligible levels or presented as 0 or negative values which are essentially noise in the spectrum requiring correction. This left a total of 12 remaining major glaze elements that were used in the initial principle component analysis and tests of significance.

I removed particular artifacts in the dataset due to the ambiguity of their assigned provenance designations and low sample sizes. Those items included the England (general) materials and the samples from Liverpool, Essex, Kent, Derbyshire, the Midlands, Massachusetts, Czechoslovakia, and the unknown sample. The sample from Glasgow was retained due to the suggested relationship between London and Glasgow pottery shops which entailed the occasional movement of potters between those two locations. The dataset now featured 90 samples. Subsequent to this qualitative culling, a letter designation was assigned to the remaining British and Continental European samples (presented in Table 3.2), included in a new field in the R prepared dataset. A unique artifact identifier was assigned to each item that consisted of the artifact

Table 3.3 List of provenance designations and number of samples.

| Provenance | R Designation | \# of Samples |
| :--- | :--- | :--- |
| London | L | 32 |
| Staffordshire | S | 41 |
| Bristol | B | 7 |
| Glasgow | G | 1 |
| Italy | I | 2 |
| France (Rouen) | FR | 1 |
| France (Nevers) | FN | 1 |
| Portugal | P | 1 |
| Netherlands | N | 4 |

designation, the reading number, and the reading location. After converting the spreadsheet to a .txt file, I uploaded the data into the R Statistical Software.

## Removing Anomalous Readings with $\mathbf{R}$

The Mahalanobis distance metric was applied in order to remove extreme or anomalous chemical readings from the dataset. According to Hulit (2012:32) "the Mahalanobis distance is a robust metric designed to measure the distance of each reading from the center of all the readings for the artifact. It differs from Euclidean distance metrics in that it takes into account the nature of chemical data to tend towards elliptical shapes when projected in two dimensions." In this case, I analyzed the three measurements that comprise a single case (i.e. a single reading location) to check for consistency among those measurements. The software removed cases from the dataset that deviated greatly from other measurements leaving readings that represent the net intensities of the glaze components across the surface of the ceramic object. As a result of the Mahalanobis distance metric analysis, the software identified and removed 63 readings in this initial broad analysis. Furthermore, a software function identified any cases that included net intensity values less than or equal to zero and removed those as
well. As a result 750 readings remained after applying the distance metric and 721 after removing zero or negative net intensities for all 102 samples. Having culled any outliers from the dataset, the remaining cases were ready to be examined using principle component analysis.

## R Statistical Software Analysis

I used principle component analysis (PCA) to analyze relationships among elements to see if they are indicative of variations in the glaze production process or some other latent variable(s) linked to particular sites of manufacture. PCA allows a researcher to see correlations among multiple variables and identify compositional differences between artifacts based on its position in multidimensional space. A principle component is essentially a line that fits the greatest spread among data points in a cloud. The line is a representation of variation among two or more variables. Within the R software, I applied the GrayILRv2 function contained within the Hulit Source for clustering and compositional analysis (Hulit 2012). As a result, the function produced a biplot "which aims to represent both the observations and variables of a matrix of multivariate data on the same plot" (Hulit 2012, 48). Rather than thinking in so many dimensions, the plot provides a more intuitive two dimensional representation. The number of dimensions is equivalent to the number of elemental variables and with each component more of the variation in the data is explained, i.e. particular trends in the data are being captured. The first principle component explains the highest percentage of variation. The elements (i.e. variables) in the first principle component with high loading values have the greatest influence on the distribution of the data. Subsequent principle components capture the remaining variation characterized by alternative sets of variables
that influence the respective components. The amount of variation captured by each component is represented visually in the form of a screeplot. Focus is given to those components up to the point of a horizontal leveling as these components represent a majority of the variation among the artifacts.

Furthermore, the correlation between elements is representative of a latent variable that cannot be measured directly. Ultimately, those elemental variables with the highest loading values, i.e. those elements with the highest level of interaction and explanatory power, can be looked at in greater detail while ignoring others in an effort to reduce the dimensionality of the overall dataset. Archaeometric convention states that explaining $50-60 \%$ of the variation is adequate and follows UW-Milwaukee ARL standards.

# Chapter 4: Results of Dimension Reduction and the Development of a Glaze Chemistry Regression Model 

The following section provides the results of the statistical analysis of the Chipstone ceramic data and presents two logistic regression models used to predict the provenance of London and Staffordshire materials. Prior to principle component analysis the Mahalanobis distance metric function removed anomalous readings from the dataset. After running the distance metric function, 750 readings remained for subsequent culling. Another function in the Hulit (2012) package that identified zero or negative intensity readings removed them from the dataset. Upon running this package 721 cases remained for use in the principle component analysis that included all remaining readings and utilized all of the relevant, identified elements. I created a subset of net intensity measures and the GrayILRv2 command, developed by Dr. J. Patrick Gray (Hulit 2012), provided the loading values, individual reading scores or standing on each component, and the percent of variation explained by each component. It also automatically generated a biplot and a screeplot for the data.

The screeplot in Figure 4.1 shows four principle components that account for a majority of the variance, however the first three components are adequate per ARL standards. Analyzing the percent of variation explained by each of the four components, I determined that Component 1 accounts for $\sim 29 \%$. Each additional component explains an increasing amount of variation with all four major principle components accounting for a cumulative sum of $70 \%$ of the variation (Table 4.1). In studying the PCA biplot, the data appears to

Screeplot of Chipstone Ceramic Data


Figure 4.1 Screeplot of entire Chipstone dataset. This plot indicates four major principle components.

Table 4.1 Percentage of the variation for each principle component and the associated cumulative sum for the entire Chipstone dataset.

| Percent Variation of Chipstone Ceramic Data |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 | Comp. 7 | Comp. 8 | Comp. 9 | Comp. 10 | Comp. 11 |
| 29.429362 | 18.514763 | 12.673716 | 9.466257 | 7.761725 | 6.438849 | 5.317259 | 3.905716 | 3.467725 | 1.994504 | 1.030124 |
| Cumulative Sum of Percent Variation Chipstone Ceramic Data |  |  |  |  |  |  |  |  |  |  |
| Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 | Comp. 7 | Comp. 8 | Comp. 9 | Comp. 10 | Comp. 11 |
| 29.42936 | 47.94412 | 60.61784 | 70.0841 | 77.84582 | 84.28467 | 89.60193 | 93.50765 | 96.97537 | 98.96988 | 100.00000 |

be elliptical in shape with several possible clusters being apparent (Figure 4.2). The loading values indicate the explanatory weight of particular variables on the distribution of the data. This information factors into the decision to retain certain variables or remove them to reduce dimensionality when conducting subsequent tests. The analysis focused on the loadings of the four major components identified which are listed in Table 4.2 with notable values highlighted. Viewing the loading measures, overall the higher values are often associated with fundamental glaze constituents, i.e. stabilizers such as aluminum and silicon, along with fluxes such as lead, particularly in the first principle component. It is possible then to say that the principle components with these variables


Figure 4.2 PCA biplot showing multiple clustering indicating possible compositional differences.

Table 4.2 PCA loadings for the entire Chipstone dataset with high loading values indicated.

| PCA Loadings for All Data |  |  |  |  |  |  |  |  |
| ---: | ---: | ---: | ---: | ---: | :---: | :---: | :---: | :---: |
| Comp. 1 |  |  |  |  |  | Comp. 2 | Comp. 3 | Comp. 4 |
| Al | $\mathbf{- 0 . 5 9 8 0 3 6 5 2}$ | $\mathbf{- 0 . 4 1 2 5 6 1 7 5}$ | -0.16168662 | 0.03282603 |  |  |  |  |
| Co | -0.12710500 | -0.03273245 | -0.12366019 | $\mathbf{- 0 . 3 0 4 3 1 4 8 1}$ |  |  |  |  |
| Cu | -0.03810563 | 0.24323265 | 0.16036956 | $\mathbf{- 0 . 4 7 0 0 4 2 7 3}$ |  |  |  |  |
| Fe | 0.14959512 | 0.14602156 | -0.29178832 | -0.20848093 |  |  |  |  |
| Ga | 0.19149149 | $\mathbf{- 0 . 3 2 0 4 5 6 6 1}$ | 0.18731731 | 0.29321967 |  |  |  |  |
| Mn | -0.07252857 | $\mathbf{0 . 4 8 3 9 7 0 1 3}$ | -0.19274925 | $\mathbf{0 . 6 9 0 7 7 0 7 6}$ |  |  |  |  |
| Ni | 0.26524659 | -0.06133849 | $\mathbf{0 . 4 2 4 7 0 5 5 6}$ | -0.12335846 |  |  |  |  |
| Pb | $\mathbf{0 . 3 7 2 4 3 6 4 6}$ | -0.11802426 | 0.22688753 | 0.11601712 |  |  |  |  |
| Si | $\mathbf{- 0 . 3 9 4 6 1 5 3 7}$ | -0.19603727 | 0.08444303 | 0.05249406 |  |  |  |  |
| Sn | -0.25612610 | $\mathbf{0 . 4 7 2 2 6 5 3 4}$ | $\mathbf{0 . 4 0 7 6 2 3 6 1}$ | -0.02214774 |  |  |  |  |
| Ti | 0.27781315 | $\mathbf{- 0 . 3 3 8 0 5 3 9 0}$ | -0.12613309 | 0.12187723 |  |  |  |  |
| Zn | 0.22993438 | 0.13371504 | $\mathbf{- 0 . 5 9 5 3 2 9 1 3}$ | -0.17886021 |  |  |  |  |

captured the greatest amount of variation in the data. In other words, the opposition of aluminum and silicon to lead represents the greatest trend in the data.

Furthermore, aluminum and tin oppose one another in the second principle
component and a correlation between tin and manganese as well as titanium and gallium.
Nickel and tin cluster in the third principle component and are in opposition to zinc.

Cobalt and copper cluster in the fourth component and oppose manganese. Based on these results it is difficult to conceptualize the groupings of variables apart from the loading scores on PC1 which does not feature any colorants. However, Components 2 and 3 show tin as positively correlated with particular colorants which may be some indication of a conscious decision by the pottery to create a colored opaque glaze for purely artistic reasons or to better cover the coarse earthenware fabric. This is discussed further below.

To determine if the compositions of categorical groups differ significantly from one another it is necessary to run an ANOVA test with a $95 \%$ confidence interval ( $\alpha=.05$ ) on all four components. Each of the four ANOVA tests show statistically significant results $(\mathrm{PC} 1: \mathrm{p}=1.24 \mathrm{e}-13 ; \mathrm{df}=8 ; \mathrm{PC} 2: \mathrm{p}=<2 \mathrm{e}-16, \mathrm{df}=8 ; \mathrm{PC} 3: \mathrm{p}=<2 \mathrm{e}-16, \mathrm{df}=8 ; \mathrm{PC} 4$ : $\mathrm{p}=<2 \mathrm{e}-16, \mathrm{df}=8$ ). The p -values and associated ANOVA information is shown in Table 4.3. Because the analysis concluded that at least one significant grouping is present in

Table 4.3 ANOVA results of the entire Chipstone dataset.

| ANOVA Results for Chipstone Ceramic Data |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  | Df | Sum Sq | Mean Sq | F value | $\operatorname{Pr}(>\mathrm{F})$ |
| ANOVA PC1 | 8 | 196.1 | 24.51 | 10.26 | $1.24 \mathrm{e}-13^{* * *}$ |
| Residuals | 712 | 1701.3 | 2.39 |  |  |
|  | Df | Sum Sq | Mean Sq | F value | $\operatorname{Pr}(>\mathrm{F})$ |
| ANOVA PC2 | 8 | 267.8 | 33.47 | 15.82 | $<2 \mathrm{e}-16^{* * *}$ |
| Residuals | 712 | 1506.3 | 2.12 |  |  |
|  | Df | Sum Sq | Mean Sq | F value | $\operatorname{Pr}(>\mathrm{F})$ |
| ANOVA PC3 | 8 | 273 | 34.12 | 12.62 | $<2 \mathrm{e}-16^{* * *}$ |
| Residuals | 712 | 1925 | 2.70 |  |  |
|  | Df | Sum Sq | Mean Sq | F value | $\operatorname{Pr}(>\mathrm{F})$ |
| ANOVA PC4 | 8 | 356.5 | 44.56 | 26.36 | $<2 \mathrm{e}-16^{* * *}$ |
| Residuals | 712 | 1203.7 | 1.69 |  |  |

each principle component, I applied a Tukey post-hoc test to determine significant differences between each of the individual provenance categories. Those pairings with significant values less than $\alpha=.05$ have been consolidated in Table 4.4. It is particularly

Table 4.4 Tukey post-hoc results for the entire Chipstone dataset with provenance designation key.

noteworthy that compositional differences exist between British artifacts and several
Continental European artifacts across all four principle components. Furthermore, in the case of the second, third, and fourth principle components there are significant differences between Staffordshire and London materials based on the associated chemical variables for those components.

These components feature several colorants and in the case of Component 2
gallium and tin load highly. The p-value $=.0000$ in the Tukey post-hoc test indicates there are some compositional differences between artifacts involving these variables which appear to be negatively correlated. It is curious that Staffordshire and London materials do not differ significantly in the first principle component, yet Bristol and Staffordshire materials do. Because the first component is characterized by fundamental glaze elements it is of interest to see how retaining those variables and removing particular colorant
variables effects the loadings and subsequent ANOVA results. Furthermore, the presumed variability in the application of color to each item during production makes it worthwhile to investigate those constituents that are necessary to achieve a glaze that will behave appropriately when fired and therefore be more consistent throughout the production of successive items.

## Reducing the Dataset to Fundamental Glaze Constituents

Because of the assumed high degree of variability in the application of colorants, which are subject to the whims of the artist and the desires of the mass market, I reran the principle component analysis with a reduced number of variables based on the higher measures for stabilizing and fluxing agents particularly in the first principle component. For this subsequent analysis aluminum, copper, gallium, lead, silicon, tin, and zinc were retained as variables. I chose to retain copper, despite being a colorant, for its fluxing effect. Once again, the analysis identified four components as accounting for a majority of the variance as shown in the screeplot (Figure 4.3). The screeplot shows that these first


Figure 4.3 Screeplot of Chipstone stabilizer and flux dataset.
four principle components capture $\sim 95 \%$ of the variation, summarized in Table 4.5.

Table 4.5 Percentage of the variation for each principle component and the associated cumulative sum for the reduced chipstone dataset.

| Percent Variation of Stabilizer and Flux Data |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 |
| 38.334161 | 24.404741 | 22.567737 | 9.815842 | 3.156235 | 1.721285 |
| Cumulative Sum of Percent Variation Stabilizer and Flux Data |  |  |  |  |  |
| Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 |
| 38.33416 | 62.7389 | 85.30664 | 95.12248 | 98.27871 | 100.00000 |

Furthermore, the first two PCS account for $\sim 63 \%$ of the variation. Looking forward to the factor analysis, it is possible to see some overlap in how certain variables load, notably gallium in the second PC and second Factor component. The biplot shows two larger clusters, however, surrounded by smaller groupings (Figure 4.4). This is potentially


Figure 4.4 PCA biplot of the reduced dataset showing two clusters.
explained by the much larger number of Staffordshire and London samples also hinted at by the unusual shape of the screeplot that plateaus after components 1 and 2 and descends between components 3 and 4 .

Loading measures for this reduced dataset are presented in Table 4.6 which show
Table 4.6 PCA loadings for the stabilizer and flux Chipstone data with major loading values indicated.

| PCA Loadings for Stabilizers and Fluxes |  |  |  |  |
| :--- | ---: | ---: | ---: | ---: |
|  | Comp. 1 | Comp. 2 | Comp.3 | Comp. 4 |
| AlK | $\mathbf{0 . 5 5 9 7 4 5 7 1}$ | 0.26484550 | -0.04283422 | -0.19295304 |
| CuK | -0.07348023 | $\mathbf{- 0 . 3 4 1 3 7 8 7 0}$ | $\mathbf{- 0 . 3 5 8 3 6 9 8 0}$ | $\mathbf{- 0 . 7 3 5 5 0 8 8 3}$ |
| GaK | -0.28498131 | $\mathbf{0 . 3 6 7 1 0 9 2 0}$ | $\mathbf{0 . 3 3 7 9 3 1 0 3}$ | -0.08806853 |
| PbL | $\mathbf{- 0 . 5 2 6 9 5 4 2 3}$ | 0.18568500 | $\mathbf{0 . 3 2 6 3 7 0 1 5}$ | -0.03844671 |
| SiK | $\mathbf{0 . 5 1 5 7 1 1 7 3}$ | 0.17644760 | 0.16014641 | 0.21628085 |
| SnL | 0.04349591 | $\mathbf{- 0 . 7 7 3 5 2 3 9 0}$ | $\mathbf{0 . 3 0 5 0 0 5 2 7}$ | $\mathbf{0 . 3 3 5 4 4 7 7 6}$ |
| ZnK | -0.23353758 | 0.12081530 | $\mathbf{- 0 . 7 2 8 2 4 8 8 4}$ | $\mathbf{0 . 5 0 3 2 4 8 5 0}$ |

higher values and a positive correlation of aluminum and silicon and opposition to lead in Component 1. Copper and gallium are negatively correlated in Component 2 with a high value for tin as well. Gallium, lead, and tin correlate in Component 3, though oppose copper. There is also a high value for zinc. Component 4 features a high loading value for copper and slight clustering of tin and zinc. To determine whether this reduction helps to explain the compositional differences, I used ANOVA once more to determine compositional differences among the four principle components. All four components returned significant values indicating at least one significantly different provenance grouping based on this set of variables (PC1: $\mathrm{p}=1.73 \mathrm{e}-11, \mathrm{df}=8 ; \mathrm{PC} 2:<2 \mathrm{e}-16, \mathrm{df}=8 ; \mathrm{PC} 3$ : $\mathrm{p}=<2 \mathrm{e}-16, \mathrm{df}=8 ; \mathrm{PC} 4: \mathrm{p}=9.1 \mathrm{e}-14, \mathrm{df}=8$ ) detailed in Table 4.7. The Tukey post-hoc test

Table 4.7 ANOVA results for the Chipstone stabilizer and flux data.

| ANOVA Results for Stabilizer and Flux Data |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  | Df | Sum Sq | Mean Sq | F value | $\operatorname{Pr}(>\mathrm{F})$ |
| ANOVA PC1 | 8 | 120.8 | 15.099 | 8.788 | $1.73 \mathrm{e}-111^{* * *}$ |
| Residuals | 6695 | 1194.2 | 1.718 |  |  |
|  | Df | Sum Sq | Mean Sq | F value | $\operatorname{Pr}(>\mathrm{F})$ |
| ANOVA PC2 | 8 | 210.8 | 26.344 | 12.56 | $<2 \mathrm{e}-16^{* * *}$ |
| Residuals | 695 | 1457.6 | 2.097 |  |  |
|  | Df | Sum Sq | Mean Sq | F value | $\operatorname{Pr~(>F)}$ |
| ANOVA PC3 | 8 | 361.5 | 45.19 | 194.8 | $<2 \mathrm{e}-16^{* * *}$ |
| Residuals | 695 | 161.2 | 0.23 |  |  |
|  | Df | Sum Sq | Mean Sq | F value | $\operatorname{Pr~(>F)~}$ |
| ANOVA PC4 | 8 | 94.2 | 11.779 | 10.36 | $9.1 \mathrm{e}-14^{* * *}$ |
| Residuals | 695 | 789.9 | 1.137 |  |  |

showed that the number of pairings which present as being significantly different increase in the case of the second, third, and fourth principle components. Significant pairings increase from eight to 14 for Component 2, five to 13 for Component 3, and seven to eight for Component 4. The number of pairings drops from 14 to 12 for Component 1. The p-value for the Staffordshire and London pairing in Principle Component 1, which together represent the greatest number of artifacts analyzed, drops from $\mathrm{p}=.2530$ to $\mathrm{p}=.0731$. While this is not statistically significant based on the assigned confidence interval, however it is an improvement. Table 4.8 shows these results.

Table 4.8 Tukey post-hoc results for the Chipstone stabilizer and flux data with provenance designation key


| S=Staffordshire | L=London | B = Bristol | G=Glasgow | I=Italy | FR=France (Rouen) | FN=France(Nevers) | P=Portugal |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{N}=$ Netherlands |  |  |  |  |  |  |  |

Based on the outcome of this second analysis it appears that the removal of
particular colorants improves the ability to detect differences between groups of both

British and Continental European made artifacts. Furthermore, the analysis showed potential compositional distinctions between those materials made in Britain which had highly significant values, particularly in those components with higher lead, tin, gallium, zinc, and copper loadings. With this knowledge in mind regarding the relationships between fundamental glaze constituents, the focus turns to the Staffordshire and London materials in particular to determine those glaze constituents that best factor into each group and if those artifacts can be sorted into their respective provenance categories. Factor Analysis of Staffordshire and London Mean Net Intensity Readings

Due to the results of the principle component analysis of the overall dataset, I determined that the analysis should be re-focused to emphasize fundamental glaze elements of the Staffordshire and London made materials. Toward that end, I placed those measures into a separate dataset and averaged the multiple readings for each pot to achieve a single representative reading of each glaze constituent variable. Furthermore, I removed copper from the analysis so as to have a dataset that included only those variables which constituted the fundamental aspects of the glaze, i.e. stabilizing and fluxing agents. Within SPSS, I conducted a factor analysis to see if these observed variables hint at some broader unobserved variables such as different glaze production strategies. Variables now correlate positively or negatively with the factor, i.e. the latent variable. The factor analysis utilized the Anderson-Rubin method "in which the least squares formula is adjusted to produce factor scores that are not only uncorrelated with other factors, but also uncorrelated with each other." (DiStefano et al. 2009, 5). This aids in the elimination of multicollinearity which is understandable given that there are necessary elements in the glaze chemistry to achieve a given end. (DiStefano et al. 2009).

As a result, the factor analysis extracted two components that cumulatively
account for $\sim 71 \%$ of the variance. Table 4.9 details these values and Table 4.10 shows
Table 4.9 Factor loading values for the Staffordshire and London data.

| Factor Loadings |  |  |
| :--- | :---: | :---: |
|  | Comp. 1 | Comp. 2 |
| Alkavg | 0.892 |  |
| GaKavg |  | 0.893 |
| PbLavg | -0.852 | 0.348 |
| SiKavg | 0.974 |  |
| SnLavg | 0.516 | -0.397 |
| ZnKavg |  | -0.617 |

Table 4.10 Factor analysis results of the Staffordshire and London mean intensities.

| Factor Analysis of Staffordshire and London Mean Net Intensities |  |  |  |  |  |  |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Initial Eigenvalues |  |  | Extraction Sums of Squared Loadings |  |  |
| Component | Total | \% of Variance | Cumulative $\%$ | Total | \% Variance | Cumulative \% |
| 1 | 2.78 | 46.375 | 46.375 | 2.782 | 46.375 | 46.375 |
| 2 | 1.5 | 25.022 | 71.396 | 1.501 | 25.022 | 71.396 |
| 3 | 0.97 | 16.151 | 87.547 |  |  |  |
| 4 | 0.54 | 8.976 | 96.524 |  |  |  |
| 5 | 1.64 | 2.732 | 99.255 |  |  |  |
| 6 | 0.05 | 0.745 | 100.000 |  |  |  |

the associated factor loadings. Of particular note is the positive correlation between Factor 1 and tin. This is to say that as the Factor 1 score of an artifact increases, i.e. an artifacts standing on a factor goes up, the amount of tin will also increase. Furthermore, aluminum, lead and silicon have a strong association with the first factor.

Gallium is a major characteristic of Factor 2 and positively correlates with that factor. Gallium has a very high loading value and is a distinctive characteristic of Factor 2. A positive correlation also exists between Factor 2 and lead. Furthermore, Factor 2 is negatively correlated with tin. Those artifact glazes that have a high Factor 2 score will have greater intensities of gallium and lead though feature much less tin in their compositions resulting in a clear finish rather than an opaque one.

## Developing a Model for Predicting Staffordshire or London Provenance

In light of this information regarding the notable variables for Factor 1 and Factor 2, it is now possible to use the factor scores to develop a binary logistic regression model that utilizes the London and Staffordshire provenance designations as the dependent variable. Not taking into consideration any other information, the regression analysis assumed the model would correctly predict the provenance by chance alone $56.2 \%$ of the time. When including the factor scores in the model the chi-square test $(\alpha=.05)$ of the null hypothesis shows $p$ value $=.000$ indicating that the model can make some distinction between Staffordshire and London materials as a result of the inclusion of the factor scores in the analysis. However, when looking at the Cox \& Snell R Square value it is low showing that only $23.2 \%$ of the variability of the data is being explained. In this instance, the model correctly categorized $79.5 \%$ of the samples overall with $75 \%$ of the London materials correctly predicted to be from London and 82.9\% of Staffordshire samples correctly predicted to come from Staffordshire (Table 4.11).

Table 4.11 Logistic regression Model 1 showing the number of correctly predicted samples using factor scores.

| Classification |  |  |  |
| ---: | :---: | :---: | :---: |
|  | London | Staffordshire | \% Correct |
| London | 24 | 8 | 75 |
| Staffordshire | 7 | 34 | 82.9 |
| Overall |  |  | 79.5 |

Only the Factor 2 scores of the chemical variables that constitute the second factor contribute to the predictive ability of the model, as seen in Table 4.12.

In an effort to improve upon this model, I re-ran the logistic regression analysis with the variables in the previous model as well as the addition of the estimated year of production. In this case the Cox \& Snell R Square value improves significantly which

Table 4.12 Details of significant variables that contribute to the predictive ability of Model 1.

| Variables in the Equation |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | B | S.E. | Wald | df | Sig. | $\operatorname{Exp}(B)$ |
| Factor 1 | -0.148 | 0.263 | 0.316 | 1 | 0.574 | 0.863 |
| Factor 2 | 1.322 | 0.381 | 12.033 | 1 | 0.001 | 3.751 |
| Constant | 0.295 | 0.271 | 1.189 | 1 | 0.276 | 1.344 |

now indicates that $50.1 \%$ of the variability in the data is now being explained. The overall percentage of correctly predicted samples also increases to $87.7 \%$ with $84.4 \%$ of London samples correctly attributed to London and 90.2\% of Staffordshire materials correctly predicted as coming from Staffordshire (Table 4.13). Factors 1 and 2 as well the
Table 4.13 Logistic regression Model 2 showing the number
of correctly predicted samples using factor scores and year of production.

|  | Classification |  |  |
| ---: | :---: | :---: | :---: |
| London | 27 | 5 | 84.4 |
| Staffordshire | 4 | 37 | 90.2 |
| Overall |  |  | 87.7 |

estimated year of production are significant and therefore are contributors to the ability of the model to make an accurate prediction of provenance. Table 4.14 details this

Table 4.14 Details of significant variables that contribute to the predictive ability of Model 2. All variables are significant contributors.

| Variables in the Equation |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | B | S.E. | Wald | df | Sig. | $\operatorname{Exp}(\mathrm{B})$ |
| Factor 1 | -1.755 | 8.717 | 8.717 | 1 | 0.003 | 0.173 |
| Factor 2 | 0.807 | 3.665 | 3.665 | 1 | 0.056 | 2.242 |
| Est. Year | 0.043 | 0.011 | 15.035 | 1 | 0.000 | 1.044 |
| Constant | -74.219 | 19.234 | 14.889 | 1 | 0.000 | 0.000 |

information. The results of this exploratory analysis into making provenance attributions based on the constituent chemical fingerprints of these ceramics can now be considered in the light of historical trends in the British pottery industry to gain a better understanding of why particular glaze constituents aid in distinguishing between groups.

## Chapter 5: The Evolution of the Pottery Industry in the Eighteenth and Nineteenth Centuries

It is of interest to examine the historical context of ceramic production and consumption in England to gain a deeper understanding of the results of this study. As a corollary to this, further consideration should be paid to the reasons behind the improved results when I removed the lead and tin-opacified glaze colorants from the principle component analysis, ANOVA, Tukey post-hoc tests, and the regression models. Because of the notable difference between pottery groups, particularly the distinction between Staffordshire and London artifacts, it is useful to consider industrial pottery practice in England during the eighteenth and nineteenth centuries. During this time, changes wrought by the Industrial Revolution led to alterations in pottery fabric and glazes and led to the large scale commodification of decorative ceramics.

Changing ceramic markets necessitated a higher degree of production resulting in a pervasiveness of ceramic objects during the eighteenth and nineteenth centuries. These changes go a long way toward explaining many of the observed patterns and differences in the data. Standardization of glaze processes led to regional commonalities, but technological change in pottery and glaze production resulted in national distinctions. From a disciplinary perspective these results strengthen the justification for a refined archaeological toolkit and utilizing chemical analysis to aid in sorting through these materials, in particular taking advantage of the beneficial features of the portable X-ray fluorescence instrument.

## English Ceramic Economy in the Eighteenth and Nineteenth Centuries

The eighteenth century marked a period of industrialization and expansion of population and wealth in England. Entrepreneurs began investing in the development of technologies to facilitate the extraction of raw materials and the creation of finished products of greater variety in order to satisfy a growing national and global market place. Very early in this period, the production of pottery was one industry among many that was influenced by these forces, though maintained a fascination with exotic goods and stylistic elements. In the early decades of the 1700s, many pottery manufacturers tried developing imitations of Chinese, Japanese, and Mediterranean designs that often featured fine porcelain fabrics and delicate aesthetic qualities that caught the eye of many consumers (Hume 2001). However, organizations attempting to encourage domestic developments in the sciences and arts such as the Royal Society of Arts, founded in 1754, advocated for a movement away from the imitation and importation of these Eastern and Mediterranean ceramic traditions toward innovative English-made styles (Berg 2002).

London based potteries at Southwark and Lambeth were producing tin-glazed wares that attempted to approximate the appearance of overseas porcelain and later production expanded to a large degree particularly in Liverpool (Ostermann 2006). Not only were these potters conducting experiments on ceramic technologies and processes of manufacture, but new styles were emerging as well. Rosemary Troy Krill $(2010,135)$ noted that "some obvious evidences of development include sgraffito-decorated earthenware, influenced by an ethnic tradition; various white-bodied tea and dinner wares, affected by cross-cultural influences and social practices; and the diversity of transfer-printed wares, stimulated by the desire to expand ceramic markets." Because of
the advancements made by these individuals, a flowering of styles and forms flooded into the marketplace to meet the demands and tastes of a rising middle and upper class.

Pottery production during this period of English ceramic reflects shifts in societal and consumer aesthetics and cultural and cross-cultural influences that resulted in the production of new artifact forms. In tandem with new domestic scientific and technological developments, by the late 1700s "the number of forms had been extended to include a variety of objects for the home such as rectangular flower-holders, pen-andink stands, puzzle jugs, and a full complement of tea-drinking items..." (Cooper 2000, 155). A number of factors converged in the 1700s in England that altered the ways in which people were able to purchase goods and maintain and present themselves within society. Agricultural difficulties, population shifts, and the development of factories and mass production all served to alter the landscape of Britain (Mokyr 1985). A growing urban middle class was on the rise bolstered by a strengthened entrepreneurial spirit and characterized by a strong desire to express themselves to other members of their socioeconomic rank by purchasing decorative additions to display in their homes and on their dress (Berg 2007). Bermingham and Brewer $(2013,13)$ explained that "of the character models available to the late eighteenth century it was the ideal of the 'bohemian' or 'romantic' that most predisposed its types to consume. The romantic creed of self-expression, Campbell believes, aligned easily with consumption's promise of hedonistic self-gratification" (citing Campbell 1987).

While the ceramic market, and the market for other luxury goods fluctuated throughout the first decades of the 1700 s, by the end of the eighteenth century the marketplace had evolved to meet the tastes and demands of the middle class consumer,
whose home was "rich in material goods which signified much about the social and cultural values of its occupiers..." (Richards 1999, 71). According to Dean et al. (2004) among households in Kent the percentage of those that owned plates increased from 14\% in the early 1600s to $85 \%$ by the early eighteenth century, and in Cornwall this number went from $4 \%$ to $85 \%$. The authors note similar increases among many other ceramic consumer goods in those same areas indicating changing tastes and greater affordability (Dean et al. 2004).

The eighteenth and nineteenth centuries marked an evolution of the consumer who was now able to obtain desirable goods for display as well as engage in leisure activities that gave individuals the opportunity to demonstrate their social rank through such a display (Bermingham and Brewer 2013). These sorts of engagements were certainly a product of the time which was characterized by shifting social, cultural, and economic circumstances. This new population of consumers exhibited a growing degree of extravagance and excess reflected in conspicuous consumptive behavior. Such behavior may have been an expression of identity, or to distinguish oneself among a growing population of similarly well-to-do people. During this time elements of Georgian high style had an important influence on the goods being sought, and with each passing decade the means were being put in place to meet the whims of the buyers.

## Standardization and Rethinking the Ceramic Production Process

In order to meet the demands of a rising mass market, the English ceramic industry experimented with new forms of factory organization. Writing in the nineteenth century, Simon Shaw (1900[1829]) noted that by the middle of the eighteenth century the
organization of workers in Staffordshire pottery factories changed significantly and was one factor that facilitated increased production. According to Shaw:

The increase of workmen, the subdivision of labour in every process; and the dexterity and quickness consequent on separate persons confining themselves solely to one branch of the Art, with the time saved in the change of implements and articles, instead of retarding, greatly promoted the manufacture, by increasing its excellence and elegance (166).

Given this reorganization that separated workers into particular activity areas of the overall manufacturing process, it is assumed that those engaged in the glazing process would follow the dictates of the master. This individual would have extensive knowledge regarding the necessary proportions of glaze constituents most appropriate to achieve a desired appearance, and this knowledge would be passed down to their apprentice(s).

Apart from the re-organization of workers to increase productivity, it is also the case that the production process itself, i.e., the operational sequence of making ceramic items, was becoming increasingly standardized. Jessica Hale (2008) offers a condensed list of seven production tasks that are described by Malcom Graham (2000, 13[1908]), a Staffordshire Vicar who published a photo-essay of nineteenth century earthenware production. Hale's list includes clay preparation, shaping, biscuit firing, application of glaze, glost firing, application of decoration, and a final firing. The glazing process can be further subdivided, as described by Owen (1901), beginning with the dipping of wares into a glaze bath, a subsequent inspection by the ware-cleaner, and a firing in the glost oven. During each firing, saggers were used to protect the wares in both early wood-fired kilns and subsequent larger coal-fired bottle kilns (Burton 1902). The application of colorants by blowing, painting, or dusting happened subsequent to the glost firing. After the addition of color and decoration the wares were placed in the kilns for the final firing.

Despite this newly specialized workforce that engaged in the glazing process, these craftsmen were becoming increasingly disconnected from the actual experimentation with and production of the glaze. This task was increasingly being taken over by chemists or other materials specialists. Goodfellow and Booth, for example, developed an improved fluid glaze and John Greatbatch is credited with the development of so-called China Glaze for Wedgwood that further refined Goodfellow and Booth's method (Miller 1987; Shaw 1900[1829]). Looking back over the course of the nineteenth century up to the time of publication of A Potter's Book, Bernard Leach $(1976,134)$ made note of the changes that resulted from this evolution of the English pottery craft and states "industrialization of pot making has involved such a heightened degree of standardization of material that it is now no longer the universal practice for potters to know their glaze materials and to make their own glazes." With such contextual information in mind it is now possible to make linkages between English pottery making history and the information derived from the pXRF chemical analysis.

## Situating Glaze Chemistry in its Historical Context

Affordable material substitutes for porcelain were in growing demand by English consumers during the late eighteenth century. However, these ceramics featured a coarse earthenware fabric which necessitated the heavy use of tin glazing in order to produce a porcelain-like finish. Black $(2001,8)$ notes "it is impossible...to estimate how much tinglazed earthenware was produced in the seventeenth and eighteenth centuries, but Peter Francis...estimates 44 million pieces between 1723 and 1781 from factories outside London alone (citing Francis 2000). The desire of consumers for improvements to fabric and glaze alike did not fall on deaf ears, however. Josiah Wedgwood, for example, was
beginning to utilize a growing body of scientific knowledge on the production of pottery. Glenn Adamson (2007) noted a paradigm shift in the eighteenth century from secretive alchemy to modern science in several realms, including pottery production, which was to the benefit of industrialists and entrepreneurs. Scientific experimentation allowed better precision and control over the constituent elements of the clay, the firing temperature and atmosphere, and the glaze. Eventually, this would result in a product to rival expensive, imported porcelains (Musson and Robinson 1969). As the nature and behavior of materials related to pottery production became public knowledge, it was possible to refine manufacturing techniques and apply that knowledge to industrial production (Adamson 2007).

With the development of cream-colored ware in the mid-1700s, the English, and in particular the Staffordshire ceramic industry saw a massive expansion and by the later decades of the eighteenth century "Josiah Wedgwood...achieved undisputed preeminence, and became the greatest agent in the world-wide distribution of the creamcoloured earthenware of North Staffordshire" (Miller 1980; Wedgwood 1913, 85). Originally using Dorsetshire ball clay with a mixture of other local clay, the Wedgwood recipe was altered with the discovery of kaolin deposits in Cornwall. The use of kaolin clays improved the fabric even more and allowed production of a much refined ware (Wedgwood 1913, 84). This development shook the British ceramic industry at this time as "the introduction and success of industrially manufactured cream-coloured wares in the second half of the eighteenth century led to a decline in the popularity of tin-glazed ware, and by around 1800 production of it had virtually ceased" (Bagdade and Bagdade 2004; Cooper 2000, 155).

Taking this into consideration, it is possible to look at the elements that best characterize the respective factors extracted through the factor analysis. Of greatest interest are the loading values of tin on Factors 1 and 2 of the Staffordshire and London stabilizers and fluxes. The fact that tin does not characterize Factors 2 to such a high degree relative to the tin value in Factor 1 seems to reflect the historic developments of glaze production in that region. Furthermore, tin is negatively correlated with Factor 2, but positively correlated with lead indicating that London and Staffordshire can be distinguished based on separate glaze production processes. Tin, as an opacifier, was no longer needed to produce a lustrous porcelain-like appearance in Staffordshire-made wares as they transitioned from the rougher local clays to the finer kaolinite material. However, Factor 1 is noteworthy for its greater loading value for tin and the associated higher intensity measures and factor scores for the London artifacts. As pointed out above, tin-glaze production was initiated among London based pottery shops and continued for many decades afterward before production experiences a sharp decline. Thus, the difference in tin is one of the most distinguishing characteristics of ceramic objects made in Staffordshire or London. Given the use of Cornwall kaolinite deposits by Staffordshire factories, it is also worthwhile to consider the presence of gallium in the second factor of the factor analysis which is linked to the Staffordshire glaze production strategy. Gallium is relatively uncommon; however, it is found in greater concentrations in association with aluminosilicate minerals, including those that constitute kaolinite, and is found during the extraction of alumina and zinc (Gray et al. 2000). Gray et al. (2000) states that:

The early stages of weathering of primary host rocks is characterized by leaching of alkalis, alkali-earths and silicon, consequently, gallium and aluminum may remained linked in secondary minerals, typically kaolinite and gibbsite, retaining in part the originally affinity in the lateritic cover (339).

While gallium may not be an intentional component of the glaze recipe, its presence hints at the change in raw materials used by Wedgwood and the Staffordshire potters, namely the use of kaolin clays. Coupled with the overall intensities of the other highly loaded elements these materials can be sorted into their respective places of manufacture.

## Chapter 6: Future Research Using pXRF to Study Glaze Chemistry

As a result of this analysis a number of intriguing questions remain to be considered, in particular, future testing of the exploratory model that has been presented here. The principle component analysis focused the study to the major glaze constituents. Subsequent tests indicated compositional differences that encouraged further exploration. The factor analysis refined my understanding of the glaze chemistry which allowed for the characterization of the factors as London and Staffordshire glaze production strategies. Though the first of the two logistic regression models assigned the artifacts to the correct provenance or production area to a fair degree, the inclusion of the year of production allowed the model to achieve a greater level of statistical significance and improved the pseudo- $\mathrm{R}^{2}$ values. Such results encourage the use of the pXRF as one tool for gaining a deeper understanding of the Chipstone collection as well as other ceramic assemblages. While this analysis could be reproduced, it would only be useful for drawing further conclusions about this collection, however, alterations to the research design and further testing is worthwhile.

To refine the model for predicting provenance it would be beneficial to use the pXRF instrument to scan not only more of the British artifacts in the Chipstone collection, but also branch out to other repositories of historic British and Continental European ceramics to see if a greater number of readings of materials will support the conclusions drawn from this initial model. It is necessary to determine a research strategy that eliminates the sampling bias issue inherent in this study (Speakman and Shackley 2013). One possible solution is to use collections of sherds and wasters in a blind study
and subsequently compare groups to known provenance information. In addition, Hunt and Speakman (2015) discuss the issues of measuring low Z elements and propose certain protocols for the analysis of ceramics and sediments as raw materials.

A new research design would begin by calibrating the existing dataset and the analysis would be re-run using parts per million values. Sherds in Chipstone's collection would be analyzed using pXRF and destructive analytical techniques to derive detailed compositional fingerprints of the glaze. A filter might be developed, in collaboration with Bruker, to target the specific constituents of lead glazes. Furthermore, a comparative study could be conducted using the ELIO Bruker analyzer that produces an XRF map of complex design surfaces. Should this line of research prove fruitful, the analysis could expand to sherds or whole vessels that do not yet have provenance information associated with them. This would further support the portable X-Ray Fluorescence instrument as a useful tool, both in the field and the lab, for sorting historic archaeological ceramics.

Apart from refining the model, developing greater knowledge about the raw materials used for the production of glaze and how those constituents interact with one another as well as confirming the link between raw material source and the pottery shop would be a productive avenue for research. On the one hand, it would reveal the nature of the kaolinite clay deposits that Staffordshire potters used in the late eighteenth century and determine if gallium and specific isotopes of other elements are present both in the those clay sources and in the glaze being made from those sources. It is an opportunity to assess the depositional effects on glaze chemistry by comparing the raw material chemistry to the fired artifacts. This may stretch beyond the abilities of the pXRF
instrument, though it would be interesting to utilize it as one tool among many for that research.

Such research would begin to fill in the entire commodity chain from raw materials to production and ultimately distribution into the mass market. This would give some insight into the spread of goods at every stage facilitated by the influences of the Industrial Revolution and the rise of consumerism. Tracing these goods chemically and archaeologically leads to multiple avenues to assess consumer choice as well as have knowledge of production. Archaeologists could reopen the issue of modeling consumer behavior discussed by Henry (1991), Klein (1991), Spencer-Wood (1987), and Wurst (1999). Furthermore, making basic national attributions to ceramic assemblages at archaeological sites based on the chemical fingerprinting of artifacts would be worthwhile given the strictures of mercantilism in the seventeenth and eighteenth centuries. Mercantilism lead to the expansion of trade routes, but restrictions on trade itself. Many European nations, including Britain, expanded their reach by establishing colonies and footholds across the world (Ormrod 2003). Materials were extracted and produced, but trade with foreign nations restricted (Ormrod 2003). Undertaking chemical analysis at a British colonial site and finding goods produced by a foreign nation may reveal occurrences of smuggling or deviations from established foreign relation policies. Such as research strategy could be expanded to other contexts including Roman and Mayan sites to reveal the exchange of goods, illicit or otherwise.

Furthermore, having that understanding of the raw and finished materials would help in potentially recreating the glaze recipes. This would entail not only an understanding of those raw sources, but also a careful chemical analysis of the glaze. A
detailed reading of the historical record is also necessary that would provide insights into the specific ratios of constituents. This would likely involve a battery of tests and the use of a calibrated pXRF instrument as well as other techniques for gaining quantitative percentages of elements in the glaze.

Having an understanding of the glaze, coupled with the knowledge gained from the study of each stage of production, leads to interesting questions regarding technology transfer and the sharing of knowledge of practice. These transferences can be attained in a variety of ways including the traditional master and apprentice relationship. It might also be accomplished through industrial espionage or the movement of skilled workers to an alternate ceramic producing factory or region. Materials based research also provides an opportunity to assess the loss of diversity in glaze production strategies and recipes as that knowledge is concentrated into a smaller group of skilled glaze chemists and material scientists.

## Concluding Remarks on Glaze Analysis using Portable X-Ray Fluorescence

This exploratory foray into determining provenance based on the chemical compositions of British and Continental European lead and tin-opacified glazes is very much reliant on an understanding of the technical and methodological material science techniques, and in particular the nature of portable X-Ray fluorescence. This is coupled with a firm grounding in the historical literature that contextualizes the presence or absence of certain glaze elements. In this particular case, the trajectory of English made ceramics and the influence of industrialization on that process offer powerful insights into the patterns this study produced as a result of the principle component analysis, the subsequent factor analysis and the final logistic regression models.

The archaeologist or material culture analyst has an opportunity to utilize pXRF and other analytical tools to gain a better understanding of materials through the study of their underlying distinctions and similarities. These studies may provide new knowledge regarding the producers and the users of items manufactured from the materials studied. It should be stated outright that the portable X-Ray Fluorescence instrument cannot be considered a magic wand that will instantly generate conclusions regarding the archaeological record. A study such as this one must draw on a multitude of tools in the archeaological toolkit to achieve a holistic understanding of the material under study. Furthermore, generating that understanding is an iterative process whereby new information leads to a reexamination of the dataset, and seemingly anomalous results may force the researcher to alter the framework through which they view events in history.

Coupled with this, the importance of collaboration, drawing on the specialized knowledge of other researchers in various fields, and linking that knowledge together to craft an effect research design should be emphasized when approaching a study such as this one. This research is, on the one hand, situated well within the discipline of archaeology, but it also draws heavily on the material science of ceramics. There are elements of the industrial historical past and a solid understanding of the disciplinary history of archaeology regarding systematics and artifact classification. This study is ultimately operating from a processual-plus or historical-processual worldview. That is to say, that to understand the distinguishing and overlapping characteristics of these ceramics, which leads to effective classification schemes, it is necessary to utilize multiple perspectives and methods, explore the practices of the people who made them,
and have broader cultural and societal knowledge. This deeper understanding, in other words, "will be found only through the cumulative, painstaking, data-rich, multi-scalar studies of proximate causation" (Pauketat 2001, 87). As this study shows, people, technology, and society have an effect on glaze chemistry and ceramic production. Portable X-ray fluorescence offers a window into that broader story and can deepen our knowledge of archaeological materials and their chemistry. It is a tool for revealing the similarities or differences among an assemblage of ceramics. This information can factor into the formation of classification systems that will be useful in future archaeological research. Archaeometric approaches to material culture studies, broadly speaking, are one beneficial avenue of ceramic classification research as well offer the opportunity to bridge the divide between the natural and social sciences.

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## Appendix A: Chipstone Sample Log

The Chipstone sample log with details for each artifact used in the analysis.

| Chipstone Sample Log |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| UWM Protocols |  |  |  |  |  |  |
| $15 \mathrm{KeV} / 25 \mu \mathrm{~A}$ | Full glaze area |  |  |  |  |  |
| 180 sec runs | 3 areas/3 runs |  |  |  |  |  |
| No filter | Kaolin Kga-2 Std |  |  |  |  |  |
| Vacuum |  |  |  |  |  |  |
| Volt regulator |  |  |  |  |  |  |
| Sample \# | Identifier | Origin | Est. Date | Item Type | Glaze Type | Scanned Areas |
| STD1 | Kaolinite_Start_\# | USGS |  |  |  | Sample Case |
| CS1 | 1993.3 | London | 1628-1650 | Charger | White tin-glaze | Flat inner base |
| CS2 | 1991.13 | London | 1680-1710 | Porringer | White tin-glaze | Flat inner base |
| CS3 | 1997.24 | London | 1650 | Charger | Blue lead-glaze | Flat inner base |
| CS4 | 1990.6 | London | 1690-1720 | Charger | Blue tin-glaze | Flat inner base |
| CS5 | 2011.7 | Bristol | 1700-1720 | Charger | Blue tin-glaze | Flat inner base |
| STD2 | Kaolinite_End_\# | USGS |  |  |  | Sample Case |
| STD3 | Kaolinite_Start2_\# | USGS |  |  |  | Sample Case |
| CS6 | 2013.1 | Portuguese | 1670 | Charger | Blue tin-glaze | Flat inner base |
| CS7 | 2000.58 | England | 1600 | Charger | Blue tin-glaze | Flat inner base |
| CS8 | 2006.7 | Italy | 1620-1640 | Charger | Tin-glaze | Flat inner base |
| CS9 | 1995.7 | London | 1660-1680 | Hand warmer | White tin-glaze | Flat surface of books |
| CS10 | 1962.16(1) | London | 1670-1685 | Charger | Blue tin-glaze | Flat inner base |
| STD4 | Kaolinite_End2_\# | USGS |  |  |  | Sample Case |
| STD5 | Kaolinite_Start3_\# | USGS |  |  |  | Sample Case |
| CS11 | 1962.16(2) | London | 1670-1685 | Charger | Blue lead glaze | Flat base |
| CS12 | 1993.15 | London | 1628 | Bottle | White tin-glaze | Body |
| CS13 | 1992.20 | London | 1650-1670 | Posset pot | White tin-glaze | 2 body/ 1 Lid |
| CS14 | 1992.21 | London | 1680 | Posset pot | White tin-glaze | 1 handle lid/2 body |
| CS15 | 2013.2 | London | 1660 | Charger | Green lead-glaze | Front edge |
| CS16 | 1995.16 | London | 1681 | Charger | Blue tin-glaze | Flat of area edge |
| CS17 | 1965.10 | Staffordshire | 1695 | Owl jug | Lead-glaze | 2 top head/ 1 body |
| CS18 | 2005.13 | Massachusetts | 1780-1820 | Storage jar | Tin-glaze | 1 Top lid/2 body |
| CS19 | 1969.11 | Liverpool | 1750-1770 | Punch bowl | White tin-glaze | 2 base/ 1 body |
| STD6 | Kaolinite_End3_\# | USGS |  |  |  | Sample Case |
| STD7 | Kaolinite_Start4_\# | USGS |  |  |  | Sample Case |
| CS20 | 1988.24 | England | 1670-1710 | Charger | Lead glaze | Edge on front |
| CS21 | 1990.12 | Staffordshire | 1680-1720 | Charger | Lead glaze | Flat inner base |
| CS22 | 1993.23 | Staffordshire | 1677 | Charger | Lead glaze | Flat inner base |
| CS23 | 1993.16 | Staffordshire | 1715 | Charger | Lead glaze | Flat edge on front |
| CS24 | 1998.3 | Midlands? | 1720-1740 | Dish | Lead glaze | Flat inner base |
| CS25 | 1990.17 | Kent | 1722-1727 | Tyg | Lead glaze | Rim |
| CS26 | 1970.4 | Staffordshire | 1670-1690 | Charger | Lead glaze | Flat edge front |
| CS27 | 1989.12 | Staffordshire | 1650-1680 | Charger | Lead glaze | Edge on front |
| CS28 | 1999.4 | Staffordshire | 1690 | Charger | Lead glaze | Flat inner base |
| STD8 | Kaolinite_End4_\# | USGS |  |  |  | Sample Case |
| STD9 | Kaolinite_Start5_\# | USGS |  |  |  | Sample Case |
| CS29 | 1991.8 | Staffordshire | 1730 | Charger | Lead glaze | Flat inner base |
| CS30 | 1967.13 | Staffordshire | 1695 | Cup | Lead glaze | Body |
| CS31 | 1993.6 | Staffordshire? | 1733 | Puzzle jug | Lead glaze | Body |
| CS32 | 1984.3 | Midlands? | 1731 | Cup with cover | Lead glaze | Body |
| CS33 | 1994.3 | Staffordshire | 1710 | Cup | Lead glaze | Body |
| STD10 | Kaolinite_End5_\# | USGS |  |  |  | Sample Case |

The Chipstone sample log with details for each artifact used in the analysis continued.

| Chipstone Sample Log (Continued) |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| STD11 | Kaolinite_Start6_\# | USGS |  |  |  | Sample Case |
| CS34 | 1963.15 | Kent | 1649 | Tyg | Lead glaze | Body |
| STD12 | Kaolinite_End6_\# | USGS |  |  |  | Sample Case |
| STD13 | Kaolinite_Start7_\# | USGS |  |  |  | Sample Case |
| CS35 | 2009.10 | Netherlands | 1690-1710 | Plate | Tin-glazed | Inner base |
| CS36 | 1965.11 | Netherlands | 1700-1799 | Jar | Delftware | Body |
| CS37 | 1996.125 | Netherlands? |  | Plate | Delftware | Flat inner base |
| CS38 | 1952.18 | Unknown |  | Barber's Bowl |  | 2 inner base/1 base |
| CS39 | 1964.10 | Italy | 1600 | Plate | Majolica | 2 inner base/1 front |
| CS40 | 1966.8 | London | 1725 | Punch bowl | Blue tin-glaze | 2 body/1 base |
| CS41 | 1960.6 | France (Rouen) | 1700 | Bleeding bowl | Faience | Body |
| CS42 | 2000.44 | Staffordshire | 1700-1725 | Fuddling cups | Lead-glaze | Body |
| CS43 | 2001.71 | Bristol | 1710-1730 | Plate | Delftware | Flat inner base |
| CS44 | 2001.74 | Bristol | 1710-1730 | Plate | Delftware | Flat inner base |
| CS45 | 2001.69 | Bristol | 1750 | Plate | Delftware | Flat inner base |
| STD 14 | Kaolinite_End7_\# | USGS |  |  |  | Sample Case |
| STD15 | Kaolinite_Start8_\# | USGS |  |  |  | Sample Case |
| CS46 | 2009.9 | Bristol | 1760-1775 | Plate | Delftware | 2 inner base/1 base |
| CS47 | 2001.63 | Staffordshire | 1775-1785 | Plate | Lead glaze | 2 inner base/ 1 base |
| CS48 | 2000.32 | Staffordshire | 1775-1785 | Plate | Lead glaze | 2 inner base/1 base |
| CS49 | 2001.1 | Staffordshire | 1780-1790 | Compote | Lead glaze | Flat inner base |
| CS50 | 2000.38 | Staffordshire | 1780 | Loving Cup | Lead glaze | Body |
| CS51 | 2000.36 | Staffordshire | 1810 | Tankard | Lead glaze | Outer base |
| STD16 | Kaolinite_End8_\# | USGS |  |  |  | Sample Case |
| STD17 | Kaolinite_Start9_\# | USGS |  |  |  | Sample Case |
| CS52 | 2000.33 | Derbyshire | 1774-1780 | Plate | Lead glaze | 2 inner base/1 base |
| CS53 | 2003.35 | Carlton China | 1915 | Ship Figurine | Lead glaze | Body |
| CS54 | 2003.38 | Carlton China | 1914-1915 | WWI Figurine | Lead glaze | Flat Back |
| CS55 | 2003.36 | Shelley China | 1917 | Camel Figurine | Lead glaze | Body |
| CS56 | 2003.40 | Victoria China | 1918 | Tank Figurine | Lead glaze | Body |
| CS57 | 2003.37 | Grafton China | 1914-1918 | WWI Figurine | Lead glaze | Body |
| CS58 | 2000.48 | Staffordshire | 1800 | Jug | Lead glaze | Body |
| CS59 | 2006.15 | Staffordshire | 1800-1840 | Mini Pitcher | Lead glaze | Body |
| CS60 | 2003.39 | Arcadian China | 1914-1918 | WWI Figurine | Lead glaze | Body |
| STD18 | Kaolinite_End9_\# | USGS |  |  |  | Sample Case |
| STD19 | Kaolinite_Start10_\# | USGS |  |  |  | Sample Case |
| CS61 | 2006.16 | Staffordshire | 1800-1830 | Mini Pitcher | Lead glaze | Body |
| CS62 | 2000.49 | Staffordshire | 1755-1775 | Teapot | Lead glaze | Body |
| CS63 | 1990.18 | Staffordshire | 1760 | Teapot | Lead glaze | Body |
| CS64 | 1978.6 | Staffordshire | 1745-1765 | Teapot | Lead glaze | Body |
| CS65 | 2012.17 | Staffordshire | 1782-1785 | Loving Cup | Lead glaze | Body |
| CS66 | 2012.16 | Staffordshire | 1782-1785 | Teapot | Lead glaze | Body |
| CS67 | 2000.14 | Staffordshire | 1755 | Tea Bowl/Saucer | Lead glaze | Bottom of Saucer |
| CS68 | 2012.15 | Staffordshire | 1782-1785 | Portrait Mug | Lead glaze | Body |
| STD20 | Kaolinite_End10_\# | USGS |  |  |  | Sample Case |
| STD21 | Kaolinite_Start11_\# | USGS |  |  |  | Sample Case |
| CS69 | 2000.52 | Staffordshire | 1755 | Teapot | Salt glaze | Body |
| CS70 | 1966.23 | Nevers, France | 1700s | Jardiniere | Salt glaze | Body |
| CS71 | 1983.6 | Staffordshire | 1760 | Coffeepot | Salt glaze | Body |
| CS72 | 2005.1 | Staffordshire | 1755-1760 | Teapot | Salt glaze | Body |
| CS73 | 1992.16 | London | 1680 | Jardiniere | Tin-glaze | Body |
| CS74 | 1968.2 | London? | 1705 | Charger | White tin-glaze | Flat inner base |
| CS75 | 2001.25 | Essex | 1893 | Charger | Lead glaze | Flat inner base |
| CS76 | 1968.8 | London | 1702-1714 | Charger | Tin-glaze | Flat inner base |
| CS77 | 1967.15 | London | 1695 | Charger | Tin-glaze | Flat inner base |
| STD22 | Kaolinite_End11_\# | USGS |  |  |  | Sample Case |

The Chipstone sample log with details for each artifact used in the analysis continued.

| Chipstone Sample Log (Continued) |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| STD23 | Kaolinite_Start12_\# | USGS |  |  |  | Sample Case |
| CS78 | 1963.28 | Netherlands | 1670-1700 | Charger | White tin-glaze | Flat inner base |
| CS79 | 1961.13 | Bristol | 1727-1740 | Charger | Blue tin-glaze | Flat inner base |
| CS80 | 1997.1(1) | London | 1760 | Sauce Boat | Tin-glaze | Body |
| CS81 | 1997.1(2) | London | 1760 | Sauce Boat | Tin-glaze | Body |
| CS82 | 2000.55 | Staffordshire | 1760 | Sauce Boat | Tin-glaze | Body |
| CS83 | 2002.21 | London | 1740 | Plate | Tin-glaze | Flat inner base |
| CS84 | 1964.31 | London | 1670-1700 | Apothecary Jar | Tin-glaze | Body |
| CS85 | 1964.30 | London | 1670-1700 | Apothecary Jar | Tin-glaze | Body |
| CS86 | 1967.18 | London | 1670-1700 | Apothecary Jar | Tin-glaze | Body |
| CS87 | 1992.18 | London | 1700 | Plate | Tin-glaze | Flat inner base |
| CS88 | 1964.29 | London | 1675-1700 | Lozenge Jar | Tin-glaze | Body |
| STD24 | Kaolinite_End12_\# | USGS |  |  |  | Sample Case |
| STD25 | Kaolinite_Start13_\# | USGS |  |  |  | Sample Case |
| CS89 | 1989.10(1) | Staffordshire | 1760 | Fruit Basket/Stand | Green lead glaze | Flat inner base stand |
| CS90 | 1989.10(2) | Staffordshire | 1760 | Fruit Basket/Stand | Green lead glaze | Flat inner base stand |
| CS91 | 2008.1 | Staffordshire | 1770 | Plate | Green lead glaze | Flat inner base |
| CS92 | 2001.51 | Staffordshire | 1790-1810 | Dish | Green lead glaze | Flat base |
| CS93 | 1989.4(2) | London | 1760 | Wall Pockets | Delftware | Flat base |
| CS94 | 1989.4(1) | London | 1760 | Wall Pockets | Delftware | Flat base |
| STD26 | Kaolinite_End13_\# | USGS |  |  |  | Sample Case |
| STD27 | Kaolinite_Start14_\# | USGS |  |  |  | Sample Case |
| CS95 | 1995.4 | Staffordshire | 1775 | Tumbler | Lead glaze | Body |
| CS96 | 1972.7 | London | 1669 | Armorial Cup | Delft | Body |
| CS97 | 1991.7 | London | 1775-1785 | Tankard | Delft | Body |
| CS98 | 1964.41 | London | 1765 | Plate | Blue tin-glaze | Flat inner base |
| CS99 | 1999.16 | Glasgow | 1760 | Plate | Tin-glaze | Flat inner base |
| CS100 | 1975.10 | Bristol | 1753 | Armorial Cup | Blue delft | Body |
| CS101 | 1969.20 | London | 1676 | Plate | Delft | Flat inner base |
| CS102 | 2000.66 | London | 1761 | Plate | Delft | Flat inner base |
| STD28 | Kaolinite_End14_\# | USGS |  |  |  | Sample Case |

## Appendix B: Selected Photos of Chipstone Samples

Available images of artifacts used in the analysis taken from the Chipstone
Foundation archives. See Appendix D for permission letter.


Images of analyzed Chipstone artifacts continued.


Image of analyzed Chipstone artifacts continued.


Images of analyzed Chipstone artifacts continued.


Images of analyzed Chipstone artifacts continued.


Images of analyzed Chipstone artifacts continued.


## Appendix C: Raw Net Intensity Data for Chipstone Materials

Raw net intensity data for the artifacts used in the statistical analysis.

















Raw net intensity data for the artifacts used in the statistical analysis continued.


















Raw net intensity data for the artifacts used in the statistical analysis continued.

















Raw net intensity data for the artifacts used in the statistical analysis continued.


















Raw net intensity data for the artifacts used in the statistical analysis continued.


















Raw net intensity data for the artifacts used in the statistical analysis continued.













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Raw net intensity data for the artifacts used in the statistical analysis continued.



















Raw net intensity data for the artifacts used in the statistical analysis continued.


















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Raw net intensity data for the artifacts used in the statistical analysis continued.

















Raw net intensity data for the artifacts used in the statistical analysis continued.


## Appendix D: Permissions

Permission letter to reprint images in Appendix B.
Academic Office Building
Michigan Technological University
1400 Townsend Drive
Houghton, MI 49931
April 13, 2015
Jon Prown
Chipstone Foundation
7820 N Club Cir
Milwaukee, WI 53217

Dear Jon Prown:

I am completing a Master's thesis at Michigan Technological University entitled " BEAUTIFUL FORMS AND COMPOSITIONS ARE NOT MADE BY CHANCE: EXPLORING THE EFFICACY OF PORTABLE X-RAY FLUORESCENCE TO SORT AND SOURCE ENGLISH LEAD GLAZED CERAMICS." I would like your permission to reprint in my thesis images of ceramics held by the Chipstone Foundation in the section titled "Appendix B" of the document. These images depict the samples analyzed during my research.

The requested permission extends to any future revisions and editions of my thesis, including nonexclusive world rights in all languages, and to the prospective publication of my dissertation by ProQuest through its ProQuest ${ }^{\circledR}$ Dissertation Publishing business. ProQuest may produce and sell copies of my dissertation on demand and may make my dissertation available for free internet download at my request. These rights will in no way restrict republication of the material in any other form by you or by others authorized by you. Your signing of this letter will also confirm that the Chipstone Foundation owns the copyright to the above-described material.

If these arrangements meet with your approval, please sign this letter where indicated below and return to me the physical letter via mail and a scanned digital copy via email. Thank you very much.



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[^1]:    
    

