FINGERPRINTING POTTERY WITH X-RAY FLUORESCENCE CHEMISTRY

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Abstract

Chemical and isotopic signatures have been used to provenience geological and archeological materials. Traditionally wet chemistry analysis had to be performed to obtain compositional information. XRF-based methods are advantageous due to their non-destructive nature and rapid data collection. Scans can be performed on various spots of an artifact for validation. In this study, a portable XRF Environmental Analyzer was used to examine late 18th century pottery fragments found at City Hall Park of New York City, as well as Raeren stoneware that is known to originate from Germany. It is reasonable to assume that there was only very limited producers of such potteries during that time period. Therefore the clay likely can be traced back to few sources. Three types of surfaces were analyzed: unglazed surfaces likely reflect the composition of clay material; glazed surfaces are more controlled by the salt used; while the ink is known to be a different material that often contains heavy metals (such as cobalt) that give color. Rb-Sr ratio appears to be a reliable parameter to distinguish stoneware originated from New York City or Germany. For samples from NYC, Unglazed (n=11) surfaces gave Rb-Sr of 1.54±0.16, while for glazed surfaces (n=11) and the ink (n=19) this ratio is 1.28±0.16 and 0.56±0.28, respectively. For samples from Germany (n=3), both unglazed and glazed surfaces showed an Rb-Sr ratio of lower than 1. Our preliminary results indicate that data obtained by portable XRF scanner may be a promising tool for the provenience of potteries . There are many collections of ceramics that can potentially be scanned, and a database can be established without involving high cost.

Background

Conventional methods of connoisseurship and typology, while well developed for ceramics, can sometimes not distinguish between local and imported wares. Chemical composition of archeological materials have been used in the past, although sporadically, to identify samples of different origin (e.g., Price and Burton, 2011). However, these data were mainly collected through the destruction and acid digestion of a portion of the samples. This method cannot be widely applied to large numbers of artifacts, thereby has limited value due to its destructive nature, as well as the cost associated with such analyses.

X-ray fluorescence spectrometry, which bombards materials with high energy particles to cause the emission of characteristic secondary X-rays, is often used in industrial operations for quality control and to detect the elements present in a sample. In most applications a large number of elements must be determined in order to characterize the sample's composition. This usually requires a large, highly sensitive spectrometer. The development of small handheld XRF instruments in recent years, while less sensitive, allowed the machine to come to the samples rather than vice versa. The portable XRF analyzer is much more flexible in that it can perform spot analysis for samples of virtually any size, shape and at any location.

Samples

❑ Salt glazed ceramics are created by the addition of salt dissolved in water during the kiln firing process of stoneware. The glassy glaze can range in color from clear to brown due to iron oxide impurities or even decorative blue and purple from the addition of cobalt or manganese oxides.

❑ This process originated in Germany in the 14th century. By the late 18th early 19th century the method of making salt glazed pottery was brought to North America with German immigrants and it became the dominant form of ceramics used in every day utilitarian wares.

❑ The Crolius and Remmey families were some of the first potters to produce salt glazed wares in New York City. They were likely trained in the production before immigrating to New York. Between 1742 to 1814 they operated a professional kiln on a hill that was located just outside what is City Hall Park today.

❑ As a preliminary study, a portable XRF Analyzer was used to examine 18th Century pottery sherds found at City Hall Park of New York City, as well as some Raeren stoneware that was known to originate from Germany. It is reasonable to assume that there was only very limited sources of clay for such ceramics during that time period. Three types of surfaces were analyzed: unglazed surfaces likely reflect the composition of clay material; glazed surfaces are more controlled by the salt used; while the decorative slip is known to be a different material that often contains heavy metals (in particular cobalt) that give color.

New York City Samples
City Hall Park Excavations

A large percentage of 250,000 artifacts are the remains of salt glazed ceramics. The assemblage that makes up the City Hall Park ceramic collection is predominantly of utilitarian. Storage jars, and crocks, jugs, and pots make up most of the ceramic forms, however, more rarely seen shapes such as, mugs, and pitchers are also present. A unique, shallow dish, previously unseen in New York City assemblages was also discovered. Most of the artifacts were decorated with simple spirals, and flowers painted on using cobalt blue oxide.

The kiln, used to produce these goods, stood in a documented location for many years, however, it was not recovered during the excavations. It is believed that it may have been destroyed or confiscated by British soldiers during their occupation of Manhattan during the Revolutionary War.

Instrument and Methods

We used a portable XRF Environmental Analyzer (Innov-X Delta Classic) for the measurements of metals in the ceramics. These include about 20 metals of interest. Each scan took about 3 minutes. Some metal concentrations fell below detection limit therefore they were not reported.

Forty readings were taken on ten samples of New York stoneware and five samples of German-origin stoneware. These range in size from complete jars to small fragments. In the case of larger samples, readings were taken in multiple spots on a single piece. This was conducted in order to account for chemical differences associated with varying levels of glaze density in these different areas.

Beam diameter is 1 cm. The beam can penetrate to about 1 mm depth. Each scan of about 20 metals only requires 2-3 minutes. Uncertainty for Rb and Sr concentrations are normally 1-5%.

Results

❑ Forty readings were taken on ten samples of New York stoneware and five samples of German-origin stoneware. These range in size from complete jars to small fragments. In the case of larger samples, readings were taken in multiple spots on a single piece. This was conducted in order to account for chemical differences associated with varying levels of glaze density in these different areas.

❑ Rb-Sr ratio appears to be a useful parameter to distinguish stoneware originated from New York City or Germany.

❑ For samples from NYC, Unglazed (n=11) surfaces gave Rb-Sr of 1.54±0.16, while for glazed surfaces (n=11) and the ink (n=19) this ratio is 1.28±0.16 and 0.56±0.28, respectively.

❑ For German samples, both unglazed and glazed surfaces as well as the ink showed remarkably consistent ratio of 0.7-0.8.

Table 1. Comparison of Rb/Sr ratios of NYC and German stoneware

	NYC			German		
	n	Mean	±	n	Mean	±
Unglazed	11	1.54	0.16	8	0.78	0.19
Glazed	11	1.28	0.16	5	0.75	0.16
Ink	19	0.56	0.28	5	0.78	0.29

Interpretations

❑ In the 18th Century it is likely that there were relatively few production centers, and few sources of clay materials that make the fingerprinting possible.

❑ From a geochemical perspective, Rubidium (Rb) in clay is probably associated with residual mica content, and thereby parent rock composition. In New York City area, there were abundant mica schist (as parent rock) which would lead to high Rb content (and hence high Rb/Sr ratio) in clay material.

❑ This portable XRF Analyzer combines its non destructive nature and fast data acquisition for convenient analysis of large numbers of stoneware samples without having to transport/move the samples themselves.

❑ The portable XRF method can add to the existing technical tools for archeologists and economic historians, and may be used for the analysis of a wide array of archaeological materials. This might be a simple way to provenance the ceramics by detecting a smaller suite of elements.

Further Research

❑ Verify data accuracy: for some samples that can be sacrificed, conduct acid digestion and ICP-MS analysis, and compare the data with what's obtained with XRF scanner.

❑ Analyze a large number of stoneware artifacts (>300) with known origin, and initiate a database of chemistry data by portable XRF scanners for such artifacts. In the short term we'll focus on samples from museums and collectors in the New York City Metropolitan area.

❑ Examine and make use of other metal ratios and metal concentrations, for which data has been and will be collected.

❑ Better understand the link between clay chemistry and pottery material, e.g., can we find local clay source that have the same chemistry as we found in stoneware; how salt glazes affect the readings.

❑ Identify production centers, and trace colonial trading patterns.

❑ Expand to redware, bricks and tombstone, etc.

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