The Use of Portable X-ray Fluorescence Spectrometry for Analyzing Ancient Ceramics

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Archaeology has always benefitted from advancements in other scientific fields. The development of new instruments for use in geology and biology has often resulted in the use of these instruments for archaeological applications. Portable X-ray fluorescence spectrometers, originally designed for the mining industry, are an example. These instruments are becoming more and more useful for archaeology, as many artifacts and objects cannot be removed to a laboratory for analysis or destroyed during examination.

Portable XRF (pXRF) allows the chemistry of these objects to be assessed in the field, but the quality of the data is dependent on a number of variables. For analyzing ceramics, particularly those that cannot leave their country of origin or were recovered from burial contexts, researchers have turned to pXRF. However, the utility of pXRF for chemically characterizing ceramics continues to be debated (see bibliography below). Several key issues have been identified: (1) can these instruments provide quantitative chemical data on a complex silica-based material; (2) what standards are needed to calibrate the pXRF for ceramic analysis, and what protocols of use need to be established; (3) how does the heterogeneity of tempered ceramics affect the data; and (4) do the surface irregularities of a sherd compromise the data. Fundamentally, these are questions of pXRF's accuracy, precision, and reliability for analyzing ceramics.

In my experience, the success of pXRF for analyzing ceramics is determined by the material being analyzed and the research questions being asked. This is based on the results of my own research into the limitations of nondestructive XRF. As a part of my Master's research at University College London, I made four ceramic test tiles that were first analyzed through standard destructive XRF (EDXRF) and were then analyzed using nondestructive XRF (Ownby 2006). The test tiles included one that was only the terracotta clay, one with clay and added sand, one with clay and added calcium carbonate, and one with clay, sand, and calcium carbonate. Statistical analysis of the chemical data from the destructive XRF showed that repeat analyses of each of the tiles yielded consistent and replicable results that could be clearly separated and placed into a tight cluster by sample. When a similar statistical procedure was done on the nondestructive XRF data, the repeat analyses from the different tiles were separated, but the clusters were much looser.

This study highlights a major issue with nondestructive XRF: the measurements have a wider standard deviation because the method is not as precise as standard destructive XRF. One reason for this, though less of an issue with EDXRF, is the surface morphology that causes scattering of the secondary electrons emitted after the sample has been exposed to the X-rays. These electrons are captured by the XRF's detector and multichannel analyzer and used to determine the elements and their amounts in the sample. For lighter elements, their characteristic secondary electrons may not reach the detector or may be absorbed by the ceramic material if the sample is not perfectly flat. Variable distance of the samples from the detector will also play a role in the precision of the data. However, as the chemical differences between the test tiles were quite notable, the nondestructive XRF results were still useful in separating them by their composition. If the analyzed samples had been chemically similar, the results may not have been so successful.

Recently, I was involved in an archaeological application of portable XRF. The instrument was used by the Institut Français d'Archéologie Orientale to analyze prehistoric pottery (ca. 4000–2000 B.C.) from the Kharga Oasis in Egypt. The goal was to chemically characterize a large sample of pottery produced from different clays and inclusions, and then select a smaller sample to be petrographically analyzed. Using a petrographic microscope, I was able to separate the thirty-two analyzed samples into three major groups based on the characteristics of their clay and inclusions. When the pXRF data were examined statistically in comparison to the petrographic results, most of the samples placed into a petrographic group were also put together into a chemical group. Notable, however, was the wide dispersion of the samples in each chemical group, although this was not enough to cause the groups to overlap. While these results are encouraging, they are once again due to the chemical distinctiveness of the analyzed samples. One group contained a very calcium-rich clay with inclusions of nummulite shells (a foraminifera); another group derived from an eroding shale with few inclusions; the third group comprised a few samples made from Nile River clay; and the final group was made from a limestone-derived clay. In fact, the samples were visually distinct, and the ceramist had placed them in groups that were nearly identical to the petrographic/chemical groups. Therefore, the pXRF provided chemical data that confirmed the visual and petrographic assignments of the samples.

Based on these personal experiences, and the results of several published studies on the applicability of pXRF for ceramic analysis, some guidelines for its use can be suggested. Perhaps most importantly, this instrument is not designed for ceramic analysis, and this must be considered in utilizing it for archaeological research. While some instruments are being adjusted through the use of standards and programming to be better suited for archaeological applications (see the discussion of obsidian pXRF), such useful manipulations have not yet been worked out for ceramics. Secondly, ceramics are often very heterogeneous, so the area of analysis (typically 1 mm^2) may include large mineral or rock fragments that are not representative of the chemical composition of the whole sample. This means pXRFs with large areas of analysis are desirable and analysis of multiple spots per sample is absolutely required. In fact, successful studies of ceramics with pXRF have analyzed fine-paste wares with little temper (Ballie and Stern 1984). The surface irregularities of sherds are also problematic, as previously mentioned. To overcome this issue, smoothing the area of analysis with fine-grained sandpaper or another such abrasive until it is very flat is recommended. However, this often negates the nondestructive aspect of pXRF. Finally, if the goal is to chemically separate ceramic samples into groups, differences in their chemical composition will need to be significant enough for the data to separate and overcome the large standard deviations. Knowing if this has been achieved is the challenge. Therefore, with the right research questions, a good methodology, and an appreciation of the limitations of pXRF, this instrument can be useful for providing information on the production and exchange of ancient ceramics.

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