X-Ray Fluorescence Spectroscopy of Heritage Copper Alloys

Energy dispersive X-ray fluorescence spectroscopy (ED-XRF) is a method of elemental analysis that has numerous advantages for the study of cultural heritage materials. It is rapid, nondestructive, and capable of simultaneous multi-element analysis. In the last 15 to 20 years, miniaturization and mass production have made the technique widely available to the scientific and conservation laboratories of arts and heritage institutions. Although the generation of an XRF spectrum is a straightforward undertaking, the conversion of an XRF spectrum to an accurate quantitative estimate of elemental composition is a challenging undertaking. As a result, the collaborative study of large classes of objects is hindered by poor interlaboratory reproducibility. This long-term research project addresses the collaborative application of XRF to the study of historic copper alloy artifacts with a particular focus on French gilt bronzes of the seventeenth through twenty-first centuries. The main goal for the project is to improve the accuracy, precision, and inter-laboratory reproducibility of quantitative X-ray fluorescence spectroscopy as applied to the study of copper alloy artifacts. This goal may be met by encouraging informed and responsible practice along with the use of appropriate certified reference materials, good analytical software, and robust calibration procedures.

The results of an early interlaboratory round robin study demonstrated that without the benefit of appropriate standards and a well-designed, shared, calibration protocol, interlaboratory reproducibility for XRF analysis of historic copper alloys can be expected to be dismal.

Two important remedies for this situation have been developed. First, a new set of certified reference standards has been developed (the copper CHARM set), specifically tailored to the study of historic copper alloys. Second, a detailed calibration protocol has been defined that utilizes the new CHARM standards along with a freely available, open-source software for spectral analysis (PyMca). We refer to the complete calibration protocol as CHARMed PyMca. A second interlaboratory study, using a wide variety of instruments in use by cultural heritage institutions, demonstrated the dramatic improvements in reproducibility that may be expected by following the protocol.

The first Copper Cultural Heritage Alloy Reference Material (CHARM) Sets; each set pictured contains the core set of twelve certified reference materials (CRMs) plus two supplementary high-arsenic CRMs.

Finally, the potential benefits of collaborative study using the proposed protocol have been highlighted by applying machine learning techniques to a large reference dataset of French gilt bronze compositional data acquired using five different ED-XRF instruments over a ten-year period. The machine learning analysis outperforms more traditional statistical methods in providing an estimate of the date of manufacture for undated French gilt bronzes with a well-defined confidence interval.

Ongoing research is focused on:

1. The automated evaluation of XRF spectra to detect layering inhomogeneity in analyzed samples (and computational methods that may be used to compensate for such inhomogeneity)
2. The development of a shared database of copper alloy artifact compositions, bringing together research results from a consortium of museums and cultural heritage institutions around the world
3. The use of statistical methods and machine learning to interpret results in more sophisticated ways