doi:10.1017/S1431927611009871
Microsc. Microanal. 17 (Suppl 2), 2011

Compositional Analysis of Corrosion Products from Rodin's Eve

Amy Hemmati [*,1], Jeffrey M. Davis[1], Amy Marquardt[2], Edward Vicenzi [1,2]

1) National Institute of Standards and Technology, Surface and Microanalysis Science Division (837), 100 Bureau Drive, Stop 8372, Gaithersburg, MD 20899-8372
2) Smithsonian Museum Conservation Institute, 4210 Silver Hill Road, Suitland, MD 20746

The cleaning and restoration of statues and other works of art are primary duties for most art preservation specialists. Frequently, researchers rely on spectroscopic methods such as X-ray powder diffraction, X-ray fluorescence, and gas chromatography (1) in order to analyze corroded materials sampled from various works of art. Compositional analysis of corroded materials often provides information about the corrosion process, and can assist with the selection of solvents for cleaning and restoration.
An X-ray microanalysis based study was conducted to determine the composition of particles taken from the surface of a bronze statue displayed outdoors. Surface samples were scraped from three areas of the statue and the particulates were dispersed onto double stick carbon tape. Once in the electron microscope, several areas were selected for analysis based on their high concentration of particles. X-ray maps of each area (Figure 1) were used to aid the selection of a statistically significant number of particles for point analysis.

Spectra from the particles were quantified using the DTSA II (2) software package and elemental standards. Spectra that showed carbon over thirty percent of total counts were omitted from weight percent analysis. Spectra that had obstructed background affects due to shielding were also omitted.
In order to better summarize the data, a series of statistical tools were used. k-ratios derived from DTSA II were analyzed using the hierarchical clustering of principal component feature of the R "R Commander" software package (3). Four distinct compositional clusters were consistently identified: carbonaceous material, a copper rich material, highly oxidized metals, and a nickel rich material. The k-ratio analysis yielded an additional cluster characterized by oxidized copper, trace metals, and sulfides. Interrogation of the identified clusters using p-value correlation tests indicated strong clustering, especially with copper and sulfur data (Figure 2).

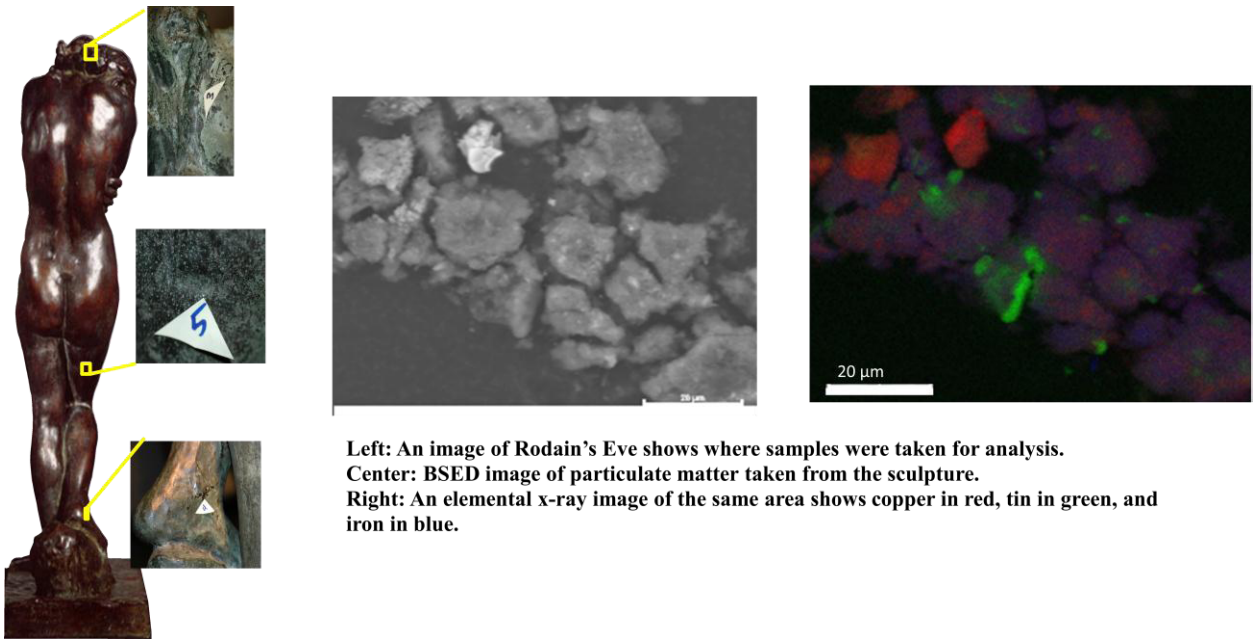
As is frequently the case with forensic analysis of historical objects, the limited sample size and lack of a bulk, flat polished section present a challenge for X-ray microanalysis. The method described here can be applied to other heterogeneous samples with rough surface characteristics or unusual preparation artifacts. By comparing spectra using only k-ratio data (thereby eliminating the potential for errors introduced by matrix correction), it is possible to summarize the data in a statistically relevant way. Further, by first collecting coarse X-ray maps to identify the regions of interest and then using a sampling of point spectra, the data size, time and processing requirements are significantly reduced.

*Corresponding author: amy.hemmati@nist.gov
Certain commercial equipment is mentioned in this abstract to further understanding of the work conducted. Its mention does not imply recommendation or endorsement by NIST or the U.S. Government.

References:

(1) Selwyn LS, Binnie NE, Poitras J, Laver ME, Downham DA (1996) Outdoor bronze statues: analysis of metal and surface samples. Stud Conserv 41:205
(2) DTSA-II (2011) http://www.cstl.nist.gov/div837/837.02/epq/dtsa2/index.html, last accessed 2/16/2011.
(3) Fox, J (2009). R Commander. Comprehensive R Archive Network.

Acknowledgements: Andrew Lins and Sally Malenka, Philadelphia Museum of Art



Left: An image of Rodain's Eve shows where samples were taken for analysis.
Center: BSED image of particulate matter taken from the sculpture.
Right: An elemental x-ray image of the same area shows copper in red, tin in green, and iron in blue.

Figure 1: (Left) An image of Rodin's Eve where samples were taken for analysis. (Center) BSED image of particulate matter taken from the sculpture. (Right) A color overlay of copper (red), tin (green) and iron (blue) X-ray images.

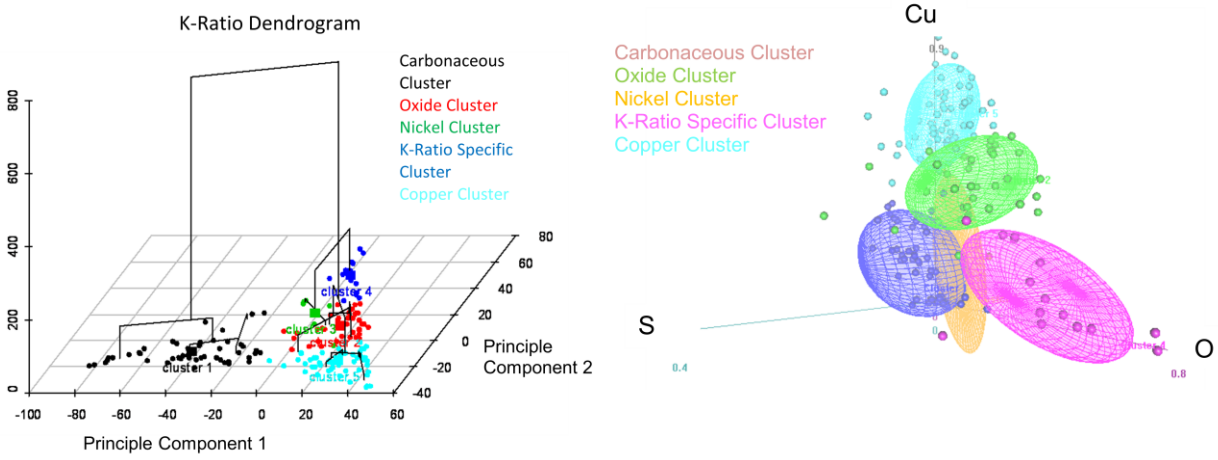


Figure 2: (Left) A dendrogram represents the clustering patterns yielded from hierarchical clustering of principle components of the k-ratio quantitative analysis of spectra taken from the sample. (Right) A three dimensional scatter plot displays the percent composition of sulfur, oxygen, and copper of each cluster derived from the dendrogram.

https://doi.org/10.1017/S1431927611009871 Published online by Cambridge University Press