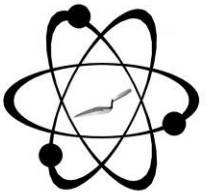
Title
X-RAY FLUORESCENCE (XRF) ANALYSIS OF HISTORIC ALLOYED METALARTIFACTS FROM PECOS NATIONAL HISTORICAL PARK, NORTHERNNEW MEXICO

Author
Shackley, M. Steven

Publication Date
2018-09-25



GEOARCHAEOLOGICAL XRF LAB
A GREEN SOLAR FACILITY

GEOARCHAEOLOGICAL X-RAY FLUORESCENCE SPECTROMETRY LABORATORY
8100 Wyoming Blvd., Ste M4-158 Albuquerque, NM 87113
USA

X-RAY FLUORESCENCE (XRF) ANALYSIS OF HISTORIC ALLOYED METAL ARTIFACTS FROM PECOS NATIONAL HISTORICAL PARK, NORTHERN NEW MEXICO

by

M. Steven Shackley, Ph.D., Director
Geoarchaeological XRF Laboratory
Albuquerque, New Mexico

Report Prepared for

Charles Haecker
Heritage Partnership Programs
National Park Service
Santa Fe, New Mexico

25 September 2018

INTRODUCTION

The analysis here of 9 metal artifacts from Spanish Colonial contexts at Pecos National Historic Park, northern New Mexico indicates mainly copper based (copper to ancient bronze) metals and one lead pewter object. There could be some similarity to the earlier study, but that XRF analysis was apparently performed without the analysis of international standards, so no direct comparison was attempted (Scott, Bleed, and Haecker 2014).

LABORATORY SAMPLING, ANALYSIS AND INSTRUMENTATION

Given the nature of prehistoric copper/lead production, major and minor oxides and trace elements were acquired with a method specific for metals generated for the prehistoric and historic contexts in the Southwest (http://swxrflab.net/anlysis.htm).

All the samples are analyzed whole. The results presented here are quantitative in that they are derived from "filtered" intensity values ratioed to the appropriate x-ray continuum regions through a least squares fitting formula rather than plotting the proportions of the net intensities in a ternary system (McCarthy and Schamber 1981; Schamber 1977). Or more essentially, these data through the analysis of international rock standards, allow for inter-instrument comparison with a predictable degree of certainty (Hampel 1984; Davis et al. 2011; Shackley 2011).

All analyses for this study were conducted on a ThermoScientific *Quant'X* EDXRF spectrometer, located at the Geoarchaeological XRF Laboratory, Albuquerque, New Mexico. It is equipped with a thermoelectrically Peltier cooled solid-state Si(Li) X-ray detector, with a 50 kV, 50 W, ultra-high-flux end window bremsstrahlung Rh target X-ray tube and a 76 µm (3 mil) beryllium (Be) window (air cooled), that runs on a power supply operating 4-50 kV/0.02-1.0 mA at 0.02 increments. The spectrometer is equipped with a 200 l min^{-1} Edwards vacuum pump, allowing for the analysis of lower-atomic-weight elements between sodium (Na) and scandium

(Sc). Data acquisition is accomplished with a pulse processor and an analogue-to-digital converter. Elemental composition is identified with digital filter background removal, least squares and quadratic empirical peak deconvolution, gross peak intensities and net peak intensities above background.

Metal Oxide Analysis

Analysis of the major metal specific oxides of Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, Au, and Pb is performed under the multiple conditions elucidated below. This fundamental parameter analysis (theoretical with standards), while not as accurate as destructive analyses (pressed powder, fusion disks or polished samples) is usually within a few percent of actual, based on the analysis of the MBH Analytical standards (see also Shackley 2011). The fundamental parameters (theoretical) method is run under conditions commensurate with the elements of interest and calibrated with 16 metal and rock standards: Mo pure, Pb pure, Cu pure, US Mint 2007 US Dollar, and US 2017 Nickel; and the following copper based MBH Analytical bronze and brass standards: 33XGM21A3, 32XSN7A, 33XGM4AB6, 32XSN6A3, 32XSN5A1, 32XLB14F6, 32XLB10E3, 32XLB10E331XTB5A4, 31X7835.9A5, 31X7835.8A3, and USGS DGPM-1 gold ore standard.

Conditions Of Fundamental Parameter Analysis[1]:

Mid Zb (As, Ag, Mo, Sn, Sb)

Voltage	30 kV	Current	Auto
Livetime	60 seconds	Counts Limit	0
Filter	Pd (0.06 mm)	Atmosphere	Air
Maximum Energy	40 keV	Count Rate	Medium

High Zb (Mn, Fe, Co, Ni, Cu, Zn, Au, Pb)

Voltage	50 kV	Current	Auto
Livetime	60 seconds	Counts Limit	0
Filter	Cu (0.559 mm)	Atmosphere	Air
Maximum Energy	40 keV	Count Rate	High

[1] Multiple conditions designed to ameliorate peak overlap identified with digital filter background removal, least squares empirical peak deconvolution, gross peak intensities and net peak intensities above background.

[2] Current is set automatically based on the mass absorption coefficient.

The data from the WinTrace software were translated directly into Excel for Windows software for manipulation and on into JMP 12.0.1 Windows for statistical analyses. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. MBH Analytical 32XLB17 leaded bronze standard was run with the samples to insure instrument accuracy (Table 1). Trace element data exhibited in Table 1 is reported in percent by weight (see also Figure 1).

DISCUSSION

While this assemblage is dominated by copper based objects, many of the artifacts contain iron as well. Iron is easily procurable and can strengthen an alloy. Many of the artifacts are technically bronze (Cu-Sn), but not by modern standards. The proportion of copper to tin was variable during the 17th and 18th centuries, and this seems evident here. Tin, like iron decreased the malleability of copper. The one lead pewter object exhibits a composition, again different from many more modern pewter materials (Sn-Cu) with the inclusion of lead in the smelt. This was probably a money saving practice.

Referring to Figure 1, it appears that all the objects with substantial proportions of copper including the bronzes exhibit intersecting compositions. This could mean that they were produced

in the same shop or were produced in similar fashion in the Old World or Mexico. A metallurgist could shed light on this possibility.

REFERENCES CITED

Davis, M.K., T.L. Jackson, M.S. Shackley, T. Teague, and J. Hampel
2011 Factors Affecting the Energy-Dispersive X-Ray Fluorescence (EDXRF) Analysis of Archaeological Obsidian. In *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, edited by M.S. Shackley, pp. 45-64. Springer, New York.

Govindaraju, K.
1994 1994 Compilation of Working Values and Sample Description for 383 Geostandards. *Geostandards Newsletter* 18 (special issue).

Hampel, Joachim H.
1984 Technical Considerations in X-ray Fluorescence Analysis of Obsidian. In *Obsidian Studies in the Great Basin*, edited by R.E. Hughes, pp. 21-25. Contributions of the University of California Archaeological Research Facility 45. Berkeley.

Mahood, Gail A., and James A. Stimac
1990 Trace-Element Partitioning in Pantellerites and Trachytes. *Geochemica et Cosmochimica Acta* 54:2257-2276.

McCarthy, J.J., and F.H. Schamber
1981 Least-Squares Fit with Digital Filter: A Status Report. In *Energy Dispersive X-ray Spectrometry*, edited by K.F.J. Heinrich, D.E. Newbury, R.L. Myklebust, and C.E. Fiori, pp. 273-296. National Bureau of Standards Special Publication 604, Washington, D.C.

Schamber, F.H.
1977 A Modification of the Linear Least-Squares Fitting Method which Provides Continuum Suppression. In *X-ray Fluorescence Analysis of Environmental Samples*, edited by T.G. Dzubay, pp. 241-257. Ann Arbor Science Publishers.

Shackley, M. Steven
2011 An Introduction to X-Ray Fluorescence (XRF) Analysis in Archaeology. In *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, edited by M.S. Shackley, pp. 7-44. Springer, New York.

2017 X-Ray Fluorescence (XRF) Analysis Major, Minor, and Trace Elements of Copper and Lead Artifacts from Sevilleta Pueblo (LA 774), Central New Mexico. Report prepared for Michael Bletzer.

2018 X-Ray Fluorescence (XRF) Analysis Major, Minor, and Trace Elements of Metal Artifacts from Sevilleta Pueblo (LA 774), Central New Mexico. Report prepared for Michael Bletzer.

Scott, D.D., P. Bleed, and C. Haecker (preparers)
2014 The Pecos Trade Fair Area: Archaeological Investigation of Apache, Comanche, and Spanish Related Sites at Pecos National Historical Park, New Mexico. Report prepared for the U.S. National Park Service.

Table 1. Elemental concentrations for the archaeological specimens from Pecos National Historic Park and MBH Analytical Leaded Bronze standard with recommended values. All measurements in weight percent as noted.

Sample	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Ag	Sn	Sb	Au	Pb	Σ	Metal
	%	%	%	%	%	%	%	%	%	%	%	%	%		
29765	0.012	2.187	0.001	0.015	97.448	0	0.015	0.072	0.055	0.015	0.003	0.004	0.174	100	Cu/Fe
28288	0.011	0.643	0.004	0.012	99.192	0.017	0	0.045	0.042	0.001	0.004	0	0.029	100	copper
282777	0.005	0.683	0.015	0.02	98.864	0	0.05	0.02	0.053	0.003	0.13	0	0.156	99.999	copper
28280	0.055	2.651	0.018	0.002	0.502	0.041	0	0	0.028	54.278	0	0	42.425	100	lead pewter
28279	0.024	3.218	0.004	0.007	86.184	0	0	0	0.061	6.205	0.054	0.006	4.238	100	bronze
28284	0.047	6.084	0.014	0.034	69.731	0.033	0	0.026	0.067	16.483	0.027	0	7.454	100	bronze
29764	0.014	2.467	0.002	0.029	96.836	0.137	0.064	0	0.058	0.176	0.138	0	0.079	100	copper
27881	0	0.23	0.008	0.016	99.661	0	0.016	0.001	0.041	0.021	0.003	0.003	0	100	copper
27880	0	0.503	0.001	0.002	99.411	0.003	0.005	0.003	0.045	0.005	0	0	0.022	100	copper
32XLB17	0.158	0.559	0.002	0.432	75.424	0.582	1.177	0	0.922	5.907	4.209	0.01	10.619	100	standard
recommended values	0.296	0.488	0.008	0.465	74.830	0.634	1.510	nr	0.911	5.970	4.100	nr	9.830		

[1] Data normalized to 100%; nr = not reported.

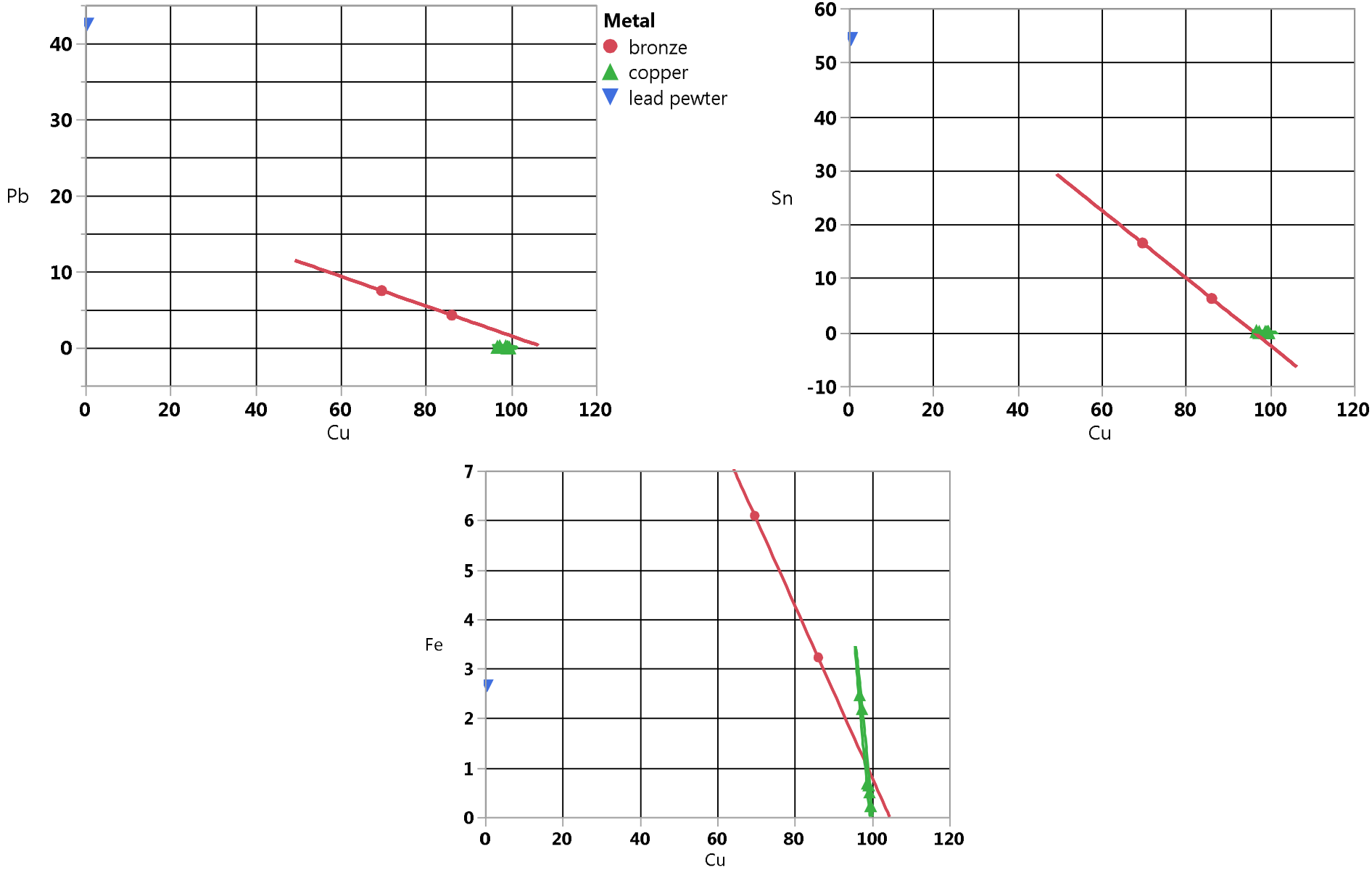


Figure 1. Cu/Pb, Cu/Sn, and Cu/Fe bivariate plots of the archaeological samples. Confidence bars at 95%. Note that the copper based artifacts including the bronzes intersect or nearly so in the three non-copper elements (see text).