

THE COPPER CHARM SET: A NEW SET OF CERTIFIED REFERENCE MATERIALS FOR THE STANDARDIZATION OF QUANTITATIVE X-RAY FLUORESCENCE ANALYSIS OF HERITAGE COPPER ALLOYS*

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This paper introduces a new set of certified reference materials designed to aid scientists and conservators working in cultural heritage fields with quantitative X-ray fluorescence analysis of historical and prehistoric copper alloys. This set has been designated as the Copper CHARM Set (Cultural Heritage Alloy Reference Material Set). The Copper CHARM Set is designed to be used by a wide range of museum-, art- and archaeology-oriented scientists and conservators to help improve the accuracy and range of their calibrations for quantitative ED–XRF spectrometry of copper alloys, and also increase the number of elements that can routinely be quantified. In addition, the common use of a single core set of the reference materials is designed to significantly improve inter-laboratory reproducibility, allowing greater data sharing between researchers and thus furthering possibilities for collaborative study.

KEYWORDS: X-RAY FLUORESCENCE SPECTROSCOPY (XRF), CERTIFIED REFERENCE MATERIAL (CRM), CALIBRATION, COPPER ALLOY

INTRODUCTION

This paper introduces a new set of certified reference materials (CRMs) designed to aid scientists and conservators working in cultural heritage fields with quantitative X-ray fluorescence (XRF) analysis of historical and prehistoric copper alloys (hereafter referred to as ‘heritage alloys’). This set of CRMs has been designated as the Copper CHARM Set (Cultural Heritage Alloy Reference Material Set). The core Copper CHARM Set contains 12 discs of precisely characterized metal, each approximately 35 mm in diameter and 15 mm thick. In addition, two optional supplementary sets have been designated, one for arsenical coppers

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(two additional standards) and the other for cupro-nickel alloys (three additional standards) (Fig. 1).

Since at least the late 1950s, a great number of studies have been published in the art and archaeometric literature that include quantitative analyses of heritage copper alloys based on analysis by X-ray fluorescence spectroscopy. Recent advances in the miniaturization of X-ray tubes and X-ray detectors, accompanied by steep reductions in cost, have meant that the use of X-ray fluorescence instrumentation in art and archaeology has increased exponentially in the past several years and that use is likely to accelerate further. This introduces the possibility for large, well-coordinated international teams of collaborating scientists, conservators and archaeologists to produce, share and archive large amounts of compositional data. As this body of compositional data on heritage copper-alloy artefacts grows temporally, geographically and typologically, so does the potential for new insights as a result of increasingly sophisticated analysis of the data.

In principle, this development should augur the beginning of a golden age for elemental analysis of copper-alloy artefacts. However, certain serious obstacles must be overcome before this potential can become a reality. One of the most significant is the necessity that data are

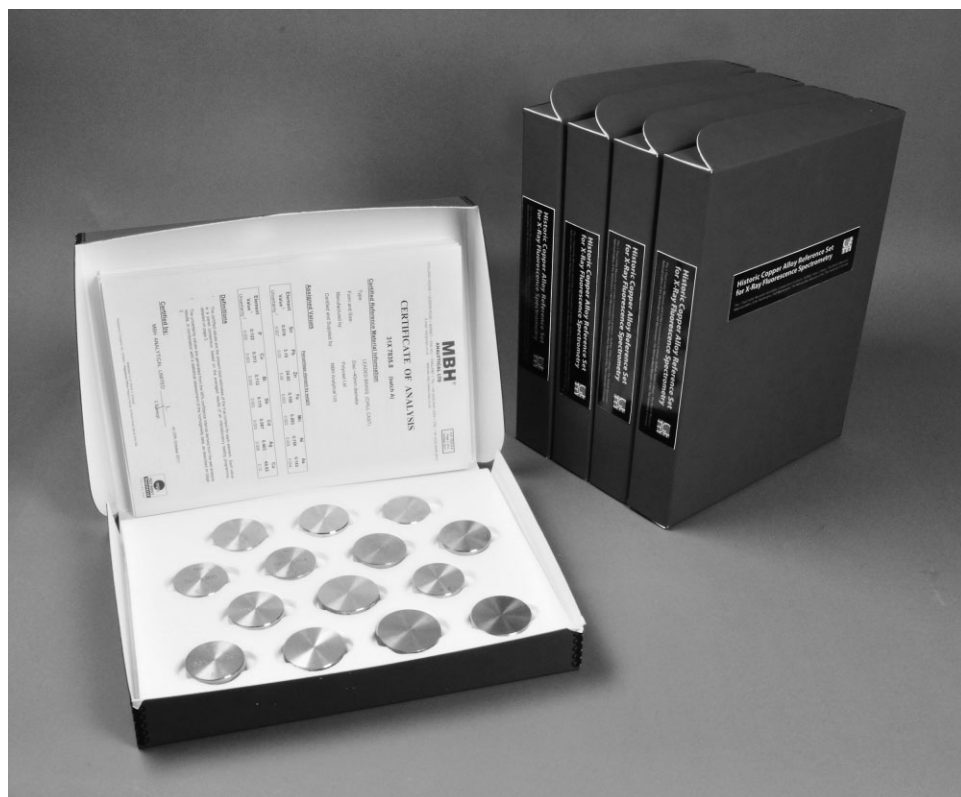


Figure 1 The first Copper Cultural Heritage Alloy Reference Material (CHARM) Sets; each set pictured contains the core set of 12 certified reference materials (CRMs) plus two supplementary high-arsenic CRMs.

obtained by valid methods that are comparable and reproducible between collaborators. The reproducibility of quantitative XRF results between laboratories, particularly for copper alloys, has proven difficult to ensure (Chase 1973). A 14-institution inter-laboratory reproducibility study published in 2011 demonstrated that current quantitative XRF alloy analysis of copper artefacts by museums and university laboratories is not sufficiently reproducible for collaborative research. According to this study, the average per cent relative reproducibility ($R_{rel}\%$) is greater than 50% for Fe, Ni, As, Sb and Pb, ranging as high as 185% for Sb (Heginbotham *et al.* 2011). This severely limits the pursuit of statistically rigorous studies by multiple institutions and hinders development of the large data sets that such collaborative studies could provide.

The results of the 2011 inter-laboratory reproducibility study indicated that the most accurate and reproducible quantitative XRF results on heritage copper alloys were obtained by software based on fundamental parameters (FP) algorithms in combination with a calibration using reference standards. The use of FP software is beyond the scope of this paper. However, with regard to reference standards, the authors of the study concluded that

the use of a . . . common and readily available set of reference materials could further improve the reproducibility of results within the group. Many participants expressed a desire to have a set of certified reference materials, replicated for the various institutions that wish to share data, which includes a range of major and trace elements appropriate for historic alloys. Although a selection of available standards might fill a portion of this range, such a set would certainly require some standards to be newly manufactured.

Many of the participants agreed that minor elements commonly present as impurities in heritage copper alloys are under-represented in commercially available reference materials. These elements are either absent or present at levels lower than commonly found in actual artefacts, especially for Fe, As, Bi, Ag and Sb. Even when present in commercial reference materials at suitable levels, they are often incorporated into non-representative modern alloy types (such as aluminium or silicon bronzes). Difficulties in obtaining appropriate standards for XRF analysis of historical copper alloys have also been noted in recent publications (Martin 2001; Smith 2012).

Reference materials for XRF analysis of historical copper alloys were previously produced as part of an EU project—Improvement of Means of Measurement on Archaeological Copper Alloys for Characterisation and Conservation (IMMACO), which was supported by the European Commission's Standards, Measurements and Testing (SMT) programme: Protection of the Cultural Heritage. A set of five standards was produced, designated BCR-691 (Ingelbrecht *et al.* 2001). The design of this set had two significant shortcomings for the calibration of XRF instruments. First, although the standards contained up to nine elements, the set was only certified for four per standard (Pb, Sn, Zn and As). The second shortcoming of the set was that each of the five standards was designed to reproduce a 'representative' historical alloy type based on a statistically determined mean composition. This resulted in a set that provided a relatively limited calibration range since, by definition, it included only 'typical' elemental values and did not attempt to cover the wide variety of concentrations that may be encountered in heritage copper alloys.

In 2010, the authors of this paper began the process of designing and commissioning a new set of reference materials, optimized for quantitative X-ray fluorescence analysis of heritage copper alloys, using existing standards where possible, and commissioning new castings as necessary.

DESIGN OF THE SET

Certification

The authors agreed that the set should be comprised of *certified* reference materials (CRMs). Uncertified reference materials (RMs) and/or reference standards are often used in XRF calibrations, but these are sub-optimal for generating high-quality calibrations, as the uncertainty associated with the nominal values is usually not known. Well-characterized CRMs provide values that are accurate with a high degree of precision and should therefore be suitable for generating rigorous regression-based calibrations. In order for classical regression equations to be used in the calibration of XRF instrumentation, the independent variable (the values associated with the standard) should have a negligible uncertainty (Ellison *et al.* 2009, 93). If the independent variable has unknown uncertainty or if the uncertainty is not negligible in comparison to the uncertainty associated with the dependent variable (the measured concentration by XRF), then a calibration should more properly be calculated using regression statistics applicable to *association* relationships rather than *functional* relationships. The former will yield larger errors and confidence intervals than the latter (Anderson 1987, 108–21).

Availability and longevity

It was agreed at the outset that many, verifiably homogeneous copies of each CRM should be produced and that the set should be available for widespread distribution. To ensure that the set remains available into the foreseeable future, the producer should agree to prepare additional batches when any individual CRM is sold out. These additional CRMs would reproduce the original set values as closely as possible and would be independently certified.

Number of standards

The number of reference materials included in the set represents a balance between cost and effectiveness. A relatively small standard set keeps the cost low and reduces the time required for acquiring calibration spectra. Calibrations based on too few standards, on the other hand, can result in excessively large errors of prediction. Six or seven independent standards are widely considered to be sufficient for the calibration of a single analyte where instrumental response is not significantly influenced by matrix effects (Ellison *et al.* 2009; Institute for Reference Materials and Measurements 2010). In this case, however, the standard set should be suitable for the calibration of many elements simultaneously, *and* matrix effects are known to be significant for XRF analysis of copper alloys (de Vries and Vrebos 2002, sections 8-1 to 9-14; Willis and Duncan 2008). To account for these factors, the authors increased the number of standards to include a greater variety of matrix types resembling those encountered in heritage copper alloys.

The inter-laboratory study discussed above also offered some guidance in determining the number of standards to include in the set. The study found that

increasing the number of standards used for quantification does not necessarily improve the accuracy of results. In fact, the vast majority of the best performing laboratories used 20 standards or fewer, and most used fewer than 10 . . .

Specifically, for the major elements (Cu, Zn, Sn and Pb) the average number of standards used by the six top-performing participants in the round robin (all of whom used fundamental parameters

software with standards) was 14. For minor elements (Fe, Ni, As and Sb) the top performers averaged 16 standards (Heginbotham *et al.* 2011).

Taking these various issues into consideration, the first proposed iteration of specifications included 12 standards, with the understanding that more could be added later if deemed necessary.

Alloy types

In order to include a suitable variety of matrix types, the authors chose to base the composition of the standards on 12 common heritage alloy types as determined by the combined experience of the working group. These included low-zinc casting brass, mid-zinc casting brass, high-zinc casting brass, sheet brass/brazing metal, impure copper, low-tin bronze, mid-tin bronze, high-tin bronze, leaded bronze, high-arsenic leaded bronze, tin-zinc bronze (gunmetal or red brass) and quaternary bronze (leaded gunmetal or leaded red brass). These designations are admittedly very ill defined. It is unfortunate that there is little consensus on appropriate terminology for categorizing alloy types.

Element selection

The selection of elements to include in the set was made based on the experience of the authors and on a review of the published literature (Tylecote *et al.* 1977; Glinsman and Hayek 1993; Pernicka 1998, 1999; Mille and Bourgarit 2000). The selection was, of course, designed to include all elements commonly found in heritage copper alloys (Cu, Zn, Sn, Pb, Fe, Ni, As, Ag and Sb). The authors also chose to include several elements that are encountered only occasionally (notably S, Cr, Co, Se, Cd, Au and Bi).

Cobalt was included in the copper CHARM specifications because it appears as an impurity in European tin ores (Tylecote 1976), certain copper bearing ores from the Harz mountains (Asmus 2012) and also copper ores from Zaire and Zambia (Fabian 1993).

The inclusion of selenium in the set was based on the potential of this element to be brought into copper metal during the smelting of sulphidic ores and its resultant potential to distinguish early smelted copper from native copper (Pernicka 1990).

Cadmium is not routinely reported in published XRF analyses of heritage copper alloys. It was included in the CHARM Set, however, because of published work that suggests that the analysis of cadmium levels may help to distinguish brass produced by cementation from brass produced by the direct addition of metallic zinc (Craddock and Eckstein 2003; Craddock and Zhou 2003; Zhou 2007).

The inclusion of some gold in the standard set was considered to be desirable by some authors; however, the addition of all but the smallest percentages of gold into a large production run proved to be financially untenable. In the end, gold was included in two of the core set CRMs, but at levels that are likely to be well below the detection limits of most ED-XRF analyses, although at levels detectable by other techniques, and especially useful when analysing Shakudo- or Hsmn-Km-type alloys, as well as some Khmer bronzes (Pernicka 1990; Craddock and Giunlia-Mair 1993; Bourgarit *et al.* 2003).

Bismuth was included in the specifications because 18th- and 19th-century British copper (particularly from Cornwall) seems to have contained more bismuth than that from other sources (0.12–0.25% compared to <0.03%) and thus this element may be a useful indicator of British production (Craddock and Hook 1995; Craddock and Hook 2012).

In addition to the elements discussed above, small amounts of Al, Si, P and Mn were included in some standards, primarily because they are found in certain modern commercial copper alloys. No effort was made, however, to cover the wide range of these elements that are found in modern alloy types. In all, 20 elements are included in the core set.

Concentration ranges

Starting with the 12 alloy types specified above, specific elemental concentrations were designated in order to achieve, as far as possible, full coverage of the wide concentration range of elements encountered in the XRF analysis of heritage copper alloys. The concentration range to cover for each element was determined by the authors as a group, based on personal experience, with the goal of providing a calibration range for each element that would include all but the most highly unusual copper alloys.

Two heritage copper-alloy types of special interest were identified that contain elemental values outside the range of the core set of 12. One type is arsenical coppers (up to $\approx 4\%$ As) and the other is cupro-nickel alloys (up to $\approx 30\%$ Ni). Since not all laboratories will require calibrations with extended ranges to accommodate these unusual alloy types, supplementary sets were specified to augment the core set if desired. The Nickel Supplementary Set contains three additional standards and the Arsenic Supplementary Set contains two additional standards.

Matrix variability

The set was designed so that, to the degree possible, similar values of each minor element are present in a variety of matrix/alloy types. This was done to aid in the assessment of calibration errors associated with absorption, enhancement and other matrix effects. For instance, similar levels of arsenic were included in standards with widely varying levels of lead. This should help correct for the possible enhancement of the arsenic fluorescence intensity in the presence of large amounts of lead, the $L\beta$ characteristic lines of which (at 12.011 and 12.620 keV) lie just above arsenic's K absorption edge at 11.860 keV (Willis and Duncan 2008). Specifically, similar arsenic concentrations of 0.196, 0.143 and 0.151 were paired with widely diverging lead values of 0.106, 3.15 and 11.74, respectively; in addition, similar (but much lower) arsenic values of 0.0619 and 0.0524 were paired with radically different lead values of 0.259 and 14.62, respectively.

Similarly, comparable levels of silver were included in several standards with widely varying levels of tin, since some minor enhancement of silver fluorescence intensity might be expected in the presence of large amounts of tin, the $K\beta$ characteristic line of which (at 28.483 keV) lies above silver's K absorption edge at 25.514 keV (Willis and Duncan 2008). Specifically, similar silver concentrations of 0.042, 0.062 and 0.099 were paired with tin values of 8.16, 5.411 and 16.05, respectively, and in addition, silver values of 0.463 and 0.305 were paired with tin values of 0.516 and 12.6, respectively.

Distribution of concentrations

For most of the elements represented in the CHARM Set, the distribution of specified values was weighted towards zero, with the lowest values near to expected detection limits and increasing roughly exponentially to the expected maximum value. This type of concentration distribution is generally not recommended because it exaggerates the leverage of high concentration standards,

potentially leading to lower precision of instrumental calibrations at higher values (Barwick 2003; Institute for Reference Materials and Measurements 2010). For the analysis of heritage copper alloys, the authors felt that this potential difficulty at the highest range of concentrations was outweighed by the benefit of added precision near the detection limit. Forcing the average value of the distribution towards zero helps to deliver smaller uncertainties for values close to the detection limits (Ellison *et al.* 2009, 105). This improvement occurs because the *error of prediction* for a regression is minimized at the centroid of the regression (\bar{x}, \bar{y}) (Burgess 2000).

Weighting the elemental distributions towards zero should also help in the determination of robust and reliable detection limits. Rigorous procedures for determining detection limits, such as ASTM International's new Standard Practice for Determination of the 99%/95% Critical Level (WCL) and a Reliable Detection Estimate (WDE) Based on Within-laboratory Data (D7782 – 12), rely on 'estimate[s] of precision at multiple points in the analytical range, especially in the range of the expected detection limit' (ASTM 2012).

EXPERIMENTAL

MBH Analytical Limited was chosen as the producer and supplier for this set based on their metallurgical expertise and their willingness to undertake the casting of unfamiliar alloy types. In addition, the thoroughness and transparency of MBH's certification process and the completeness of the company's issued certificates were significant factors. MBH routinely lists each of the certifying laboratories on its certificates, along with a complete table of analytical methods and results for each element. Between eight and 15 independent laboratories determine the concentration of each element within any given CRM, using a combination of inductively coupled plasma – atomic emission spectrometry (ICP–AES), flame atomic absorption spectrometry (FAAS) and wet chemical methods. Robust uncertainty values are generated from the raw analytical results, in combination with the results of a separate homogeneity evaluation conducted at MBH using optical emission spectrometry (OES).

Existing CRMs in the MBH inventory were chosen to match the set design criteria described above, and the casting of new CRMs was commissioned to complete the sets. In all, eight new CRMs were specified, cast and certified as part of the core set of 12.

The decision was made to produce the CHARM Set by casting rather than by powder metallurgy/hot isostatic pressing (HIPping). Although HIPping had been used in the preparation of the IMMACO BCR-691 set (see above: Engelbrecht *et al.* 2001), this technique is costly and logistically challenging. The cast discs should also more closely resemble the heritage alloys in their metallographic structure than HIPped discs.

The certified reference materials (CRMs) in this set were made by melting various recipes of commercial metals and master alloys, as follows. Each charge was melted in an open-air induction furnace, and cast into a sequence of multiple chill moulds. The casting process was completed within 30 s, to minimize compositional variation. The moulds were laid on to a heavyweight steel sheet to promote rapid solidification, and thus minimize segregation.

Processing and testing of the castings were carried out in accordance with the requirements of ISO Guides 30–35, which cover the preparation and use of reference materials (ISO 1997, 2000a,b, 2006, 2008, 2009). Further details of the preparation and certification processes can be found in the individual certificates of analysis for each CRM, available at <http://www.mbh.co.uk>.

Many copies of each CHARM CRM were produced, so that the set may be widely distributed. If any 'batch' of CRMs is sold out, MBH has agreed to manufacture additional batches reproducing the original set values. Replacement batches will be independently certified and new

values reported. Thus, in principle, this set should remain available well into the future. The only limitation on this may be with regard to the Arsenic Supplementary Set. The RMs in this set were produced many years ago and current health and safety concerns may preclude their replication in the future.

RESULTS

Twelve CRMs now form the core Copper CHARM Set. The certified elemental concentrations for all elements in these CRMs are given in Figure 2. The final distribution of concentrations by elements is represented in Figure 3. Two additional CRMs comprise the Arsenical Copper Supplementary Set and three additional CRMs comprise the Cupro-Nickel Supplementary Set. The certified elemental concentrations for all elements in the supplementary sets are given in Figure 4.

DISCUSSION

The production of new copper-alloy CRMs is always subject to a certain degree of uncertainty, due to vagaries of the melting and casting process. Although every effort was made to produce a final product that matched the initial specifications, a certain amount of variation in the results was to be expected. As a result, the new castings were produced one or two at a time and preliminary characterization of the batch was done by OES. Any deviations from the intended concentrations in the material were taken into account and the specifications for subsequent castings were adjusted as necessary to maintain an optimal distribution of concentrations for each element.

The production of high-arsenic alloys presents health and safety concerns. The sublimation temperature of arsenic (approximately 610°C) is significantly lower than the melting point of historical copper alloys (usually between 900°C and 1000°C). This raises concerns that arsenic vapour could escape the melt, lowering the final concentration and possibly endangering the health of the foundry workers. Arsenic has historically been added to MBH's products through the addition of a commercial Cu–30%As master alloy (30% arsenic in copper by weight). Experience has shown that all the arsenic added to a melt in this manner has stayed within the solidified metal. However, this experience has only applied to low resultant As levels, below 0.3%. Preparation of the new alloys for the CHARM Set involved adding As at incrementally higher levels, to test As retention without putting safety at risk. The pre-existing Cu–As discs used for the Arsenic Supplementary Set (36× CuAs3A and 36× CuAs4A) were found in the storage of an old foundry, now closed, and their provenance is lost.

The production of alloys with even moderate levels of cadmium also raises potential health and safety concerns, given its low boiling point of about 767°C and its very high toxicity. Loss of cadmium was greatly minimized in the new Copper CHARM Set castings by adding it to the melt in the form of a 50:50 Pb/Cd binary alloy, specially prepared for this purpose. The maximum final concentration attempted was 0.25%.

Several authors have advocated a maximum tin level of around 25%. After considerable debate, the team concluded that above 16% tin, the likelihood of gross segregation and/or surface enrichment was so high that it would be difficult to obtain a CRM that would meet strict homogeneity standards (Meeks 1986). As a result, the maximum tin value in the set is approximately 16%. Similarly, given the insolubility of lead in copper, the maximum lead level for the set was limited to about 15% based on the technical feasibility of producing reasonably homogeneous CRMs.

Element	Core Set (MBH Designation)																				Core Range	
	Value C(95%)	31X 7832.8A	31X 7835.9A	31X 785A	32X LB10E	32X LB14E	32X LB17A	32X SNA	32X SNA	32X SNA	32X SN7A	33X GM44B	33X GM20A	33X GM21A	Low (0.001)	High						
Al	Value	0.092	0.0458	0.091	0.00057	0.00069	0.388	0.474	0.0313	0.032	0.007	-0.001	0.255	0.001	0.474							
C(95%)	Value	0.003	0.001	0.003	0.0001	0.0003	0.011	0.026	0.0013	0.052	0.006		0.005	0.001	0.474							
Si	Value	0.0232	0.0014	0.003	0.0014	0.0017	0.051			0.066	0.0088	0.063	0.0156	0.0156	0.122							
C(95%)	Value	0.009	0.0006	0.003	0.0016	0.0017	0.003			0.053	0.0011	0.003	0.0008	0.0011	0.189							
P	Value	0.122	0.0066	0.00161	0.016	0.0017	0.0088	0.0009	0.018	0.066	0.0088	0.063	0.005	0.0088	0.189							
C(95%)	Value	0.002	0.00161	0.00161	0.016	0.0017	0.0088	0.0009	0.018	0.066	0.0088	0.063	0.005	0.0088	0.189							
S	Value	0.001			0.0011	0.0017	0.0088	0.0009	0.0074		0.005	0.015	0.002	0.005	0.08							
C(95%)	Value				0.0011	0.0017	0.0088	0.0009	0.0074		0.005	0.015	0.002	0.005	0.08							
Cr	Value						0.0008	0.0002	0.0014			0.015	0.002	0.0008	0.0585							
C(95%)	Value						0.0008	0.0002	0.0014			0.015	0.002	0.0008	0.0585							
Mn	Value	0.093	0.0009	0.445	0.0004	0.005	0.296	0.72	0.0024	0.001	0.0007	0.219	0.004	0.0004	0.72							
C(95%)	Value	0.003	0.0001	0.008	0.0001	0.0003	0.005	0.004	0.0001	0.0001	0.0001	0.005	0.004	0.0004	0.72							
Fe	Value	0.1	0.408	0.178	0.013	0.0669	0.488	1.2	0.099	0.06	0.053	0.57	0.751	0.013	1.2							
C(95%)	Value	0.003	0.003	0.005	0.001	0.0028	0.006	0.02	0.004	0.002	0.002	0.008	0.006	0.013	1.2							
Co	Value	0.313	0.0813	0.0229	0.0456	0.212	0.0083	0.138	0.665	0.443	0.259	0.0382	0.0083	0.0083	0.665							
C(95%)	Value	0.003	0.0013	0.0011	0.0014	0.005	0.0005	0.003	0.003	0.007	0.007	0.0006	0.0006	0.0083	0.665							
Ni	Value	0.158	0.1	0.079	0.687	0.312	0.465	0.502	0.203	0.175	1.795	0.999	0.129	0.079	1.795							
C(95%)	Value	0.005	0.002	0.002	0.01	0.005	0.005	0.006	0.002	0.001	0.016	0.017	0.002	0.079	1.795							
Cu	Value	69.93	78.48	55.84	77.98	78.08	74.83	78.96	86.39	80.3	82.96	87.58	76.90	55.84	87.58							
C(95%)	Value	0.12	0.11	0.13	0.1	0.11	0.08	0.12	0.08	0.06	0.06	0.14	0.12	55.84	87.58							
Zn	Value	24.83	14.34	40.63	0.566	0.0421	0.634	1.17	1.96	1.96	7.13	3.87	5.05	0.0421	40.63							
C(95%)	Value	0.06	0.06	0.15	0.009	0.0024	0.0024	0.005	0.02	0.02	0.04	0.04	0.04	0.0421	40.63							
As	Value	0.143	0.107	0.349	0.151	0.0524	1.51	0.0619	0.764	1.071	0.287	0.196	0.464	0.0524	1.51							
C(95%)	Value	0.004	0.002	0.003	0.003	0.0018	0.02	0.0013	0.006	0.012	0.008	0.003	0.006	0.0524	1.51							
Se	Value	0.34												0.194	0.34							
C(95%)	Value	0.02												0.194	0.34							
Ag	Value	0.463	2.12	0.213	0.042	0.0619	0.911	0.099	1.159	0.305	0.0265	0.141	0.004	0.0265	2.12							
C(95%)	Value	0.006	0.04	0.003	0.002	0.0014	0.006	0.003	0.012	0.005	0.0015	0.003	0.007	0.0265	2.12							
Cd	Value	0.087	0.0673	0.501	0.073	0.501	0.151	0.145	0.0903	0.0385	0.0229	0.255	0.007	0.0229	0.501							
C(95%)	Value	0.003	0.0015	0.005	0.0015	0.005	0.003	0.002	0.0012	0.0012	0.0005	0.002	0.007	0.0229	0.501							
Sn	Value	0.516	1.48	0.107	8.16	5.411	5.97	16.05	7.31	12.6	2.56	4.07	4.55	0.107	16.05							
C(95%)	Value	0.007	0.0045	0.003	0.09	0.034	0.04	0.09	0.03	0.09	0.05	0.02	0.02	0.107	16.05							
Sb	Value	0.115	0.445	0.174	0.591	0.0628	4.1	0.664	0.323	0.263	0.0261	2.004	1.049	0.0261	4.1							
C(95%)	Value	0.002	0.003	0.004	0.008	0.0014	0.06	0.005	0.004	0.005	0.0012	0.015	0.01	0.0261	4.1							
Au	Value													0.0005	0.0102							
C(95%)	Value													0.0005	0.0102							
Pb	Value	3.15	1.024	0.576	11.74	14.62	9.83	0.259	1.559	2.6	4.69	0.106	6.99	0.106	14.62							
C(95%)	Value	0.03	0.017	0.007	0.07	0.06	0.22	0.004	0.015	0.03	0.04	0.002	0.05	0.106	14.62							
Bi	Value	0.112	0.81	0.314	0.0608	0.974	0.22	0.097	0.158	0.052	0.084	0.031	0.452	0.031	0.974							
C(95%)	Value	0.005	0.02	0.006	0.001	0.014	0.005	0.002	0.002	0.002	0.002	0.002	0.007	0.031	0.974							

Figure 2 Elemental compositions for the Copper Cultural Heritage Alloy Reference Material (CHARM) Set, including uncertainties based on a 95% confidence interval. Values given in parentheses are not certified. The overall range of the set is also given on the right.

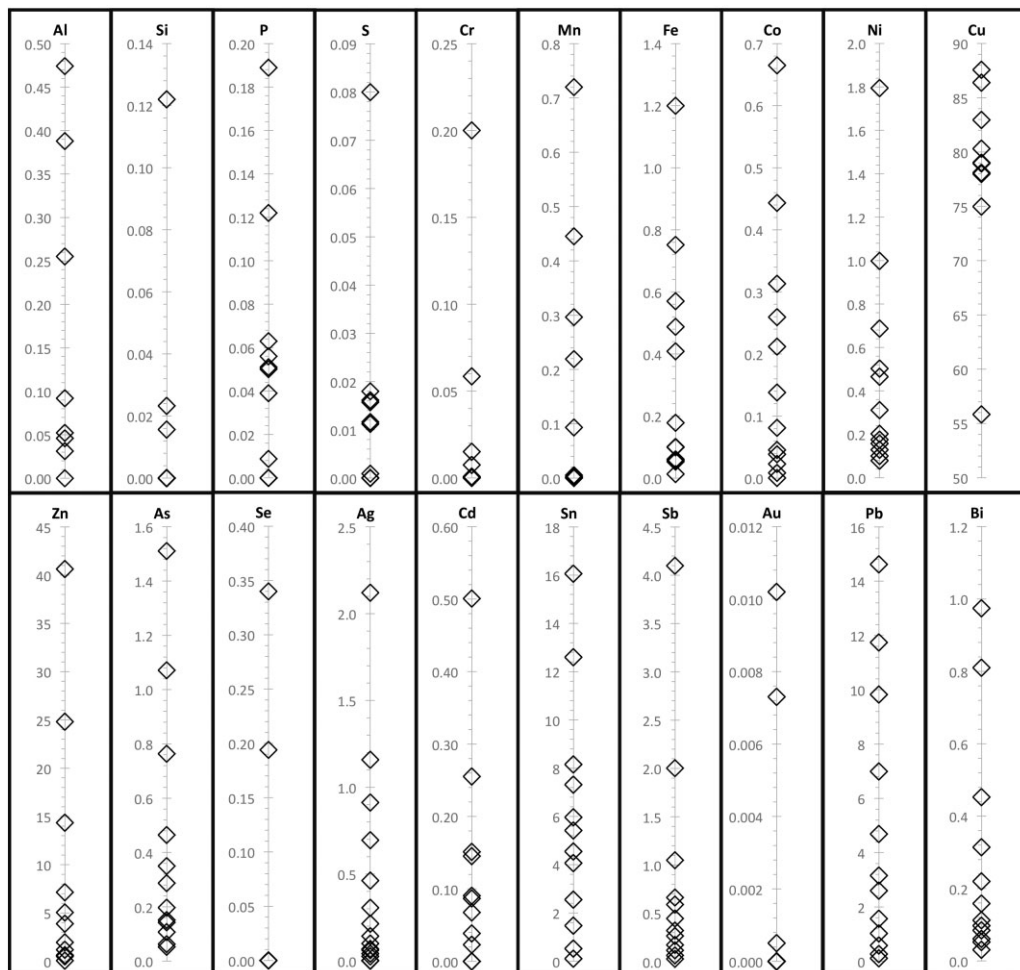


Figure 3 Graphs showing the distribution of concentrations, by element, for the core Copper CHARM Set. All values are shown in weight per cent.

Aluminium was included in the specifications for the set for two primary reasons. First, it is present in some modern alloys, and given vacuum or helium purge conditions, it should be detectable by XRF. Second, aluminium also serves to stabilize iron in molten copper alloys. The author team had expressed interest in having iron values up to 1.5%; however, the recovery of iron in copper alloys has been found to be highly variable—in all instances, but for unknown reasons, iron tends to be lost from the metal. In the case of the CHARM Set, iron was added to each melt as a commercial Cu–10Fe binary master alloy (10% iron in copper by weight) and the producer followed conventional wisdom by adding small amounts of aluminium to improve iron retention in the standards with relatively high iron contents.

CONCLUSIONS

The CHARM Set presented here should not necessarily be considered to be definitive or static, and deficiencies may be discovered that might be remedied through the inclusion of additional

Element	As Set (MBH Designation)		Ni Set (MBH Designation)			Range with Supplemental Sets		Element
	36X CUAS3A	36X CUAS4A	34X NS1F	36X CN2J	36X CN4K	Low	High	
Al	Value		(0.003)	0.005	0.001	0.001	0.474	Al
	C(95%)			0.001	0.0002			
Si	Value		(0.002)	0.044	0.025	(0.002)	0.122	Si
	C(95%)			0.003	0.002			
P	Value		0.014	0.015	0.0079	(0.001)	0.189	P
	C(95%)		0.0013	0.002	0.0009			
S	Value		(0.0004)	0.035	0.0076	0.0004	0.08	S
	C(95%)			0.003	0.0009			
Cr	Value		0.0003	0.24	0.022	0.0003	0.24	Cr
	C(95%)		0.0001	0.008	0.001			
Mn	Value		0.0009	1.26	0.164	0.0004	1.26	Mn
	C(95%)		0.0002	0.02	0.004			
Fe	Value	(0.001)	0.064	1.7	2.67	0.001	2.67	Fe
	C(95%)	0.0012	0.002	0.03	0.06			
Co	Value		0.052	0.264	0.052	0.0083	0.665	Co
	C(95%)		0.002	0.008	0.002			
Ni	Value	0.0007	7.81	15.47	27.49	0.0003	27.49	Ni
	C(95%)	0.0002	0.0001	0.07	0.1			
Cu	Value	97.09*	58.63	80.78	69.48	55.84	97.0878	Cu
	C(95%)	95.85*	0.1	0.11	0.19			
Zn	Value		33.41	0.0358	0.041	0.0358	40.63	Zn
	C(95%)		0.1	0.0014	0.003			
As	Value	2.9				0.0524	3.66	As
	C(95%)	0.03	0.03					
Se	Value					0.194	0.34	Se
	C(95%)							
Ag	Value		0.069			0.0265	2.12	Ag
	C(95%)		0.002					
Cd	Value	(0.0003)				0.0003	0.501	Cd
	C(95%)	0.109						
In	Value	0.0054				0.0054	0.093	In
	C(95%)	0.0006	0.093					
Sn	Value	0.009	0.011	0.061	0.009	0.009	16.05	Sn
	C(95%)	0.002	0.0009	0.004	0.001			
Sb	Value					0.0261	4.1	Sb
	C(95%)							
Au	Value					0.0005	0.0102	Au
	C(95%)							
Pb	Value	0.0012	0.0141	0.048	0.023	0.0009	14.62	Pb
	C(95%)	0.0003	0.0013	0.002				
Bi	Value			0.0045	0.0077	0.0045	0.974	Bi
	C(95%)			0.0008	0.0011			

Figure 4 Elemental compositions for the Copper Cultural Heritage Alloy Reference Material (CHARM) supplemental sets, including uncertainties based on a 95% confidence interval. Values given in parentheses are not certified. Values marked with an asterisk (*) are calculated by difference. The overall range of the core set plus the supplemental sets is also given on the right.

standards. However, the authors believe that these standards represent a major step forward in the production of accurate and reliable calibrations for XRF analysis of heritage copper alloys and also towards increasing the number of elements that can routinely be analysed.

Furthermore, the authors hope that the Copper CHARM Set will be used by a wide range of museum-, art- and archaeology-oriented scientists and conservators to dramatically improve the inter-laboratory reproducibility of their results. Such improvement should have a significant impact on research in the field, allowing greater data sharing between laboratories and fostering growth in collaborative research.

The Copper CHARM Set has already been successfully integrated into the ED-XRF calibrations of several of the authors, as well as a number of other laboratories. A planned follow-up round robin, based on the methodology used in Heginbotham *et al.* (2011), will evaluate

quantitatively the impact of the set on accuracy and inter-laboratory reproducibility among the new adopters.

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The National Gallery of Art in Washington hosted a seminal meeting in 2007 of representatives from seven museums to address issues surrounding the sharing and comparability of quantitative XRF data between institutions. That meeting, sponsored by Robert H. Smith and the Center for Advanced Study in the Visual Arts, focused on these issues, particularly as they relate to the analysis of Renaissance bronze sculpture. Moderated by Nicholas Penny, then Senior Curator of Sculpture, and Shelley Sturman, Head of the Object Conservation Department, the participants agreed that the ability to compare data would be valuable, but enumerated a host of problems and obstacles to be overcome before meaningful inter-laboratory comparisons could be made. This study is a direct product of that meeting.

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