Comparative measurements on certified reference copper alloys using neutron-based techniques

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Five pieces of IRMM reference copper alloy (BCR-691) [1], originally intended for X-ray fluorescence (XRF) calibration, represent well the composition of ancient bronzes and brasses. Several, preferably non-destructive chemical analytical techniques applicable to real art objects were benchmarked in this study. In addition to prompt gamma activation analysis (PGAA), instrumental neutron activation analysis (INAA) was applied for trace element quantification, and XRF– a widespread non-destructive analytical technique for metals – was involved in the study.

Certified reference values, available for the concentrations of four major additive components (As, Zn, Sn, and Pb), were compared with the results.

Measurements and Methodology

Conventional PGAA measurements were carried out at the Budapest Neutron Centre using a 27% HPGe detector – surrounded by BGO Compton-suppressor system –in a cold-neutron beam with thermal equivalent neutron flux of 9×10^{7} cm^{-2} s^{-1} [2]. We made the following modifications on our conventional PGAA experimental conditions:

(1) A Pb slab γ-ray attenuator with the thickness of 10 mm between the sample and the detector was applied in order to suppress the high count rate from the low-energy peaks of the main component (Cu). This helps to enhance the count rate of higher-energy peaks from the components of interest.

(2) A low-energy germanium detector (LEGe), was applied to analyse the elements with intense lines below 500 keV. Due to its lower efficiency at high energy it allows for a lower overall count rate [3].

The spectrum evaluation was done with the Hypermet-PC software [4]. The concentration calculation was carried out using the Excel package called ProSpeRo [5, 6].

Subsequently, in-beam activation analysis was performed at the cold-neutron PGAA facility of FRM II using a 3×10^{10} cm^{-2} s^{-1} neutron flux. The off-line counting of the induced radioactivity was performed with a HPGe detector in a low-background chamber [7-8], just like in INAA.

For the most precise determination of trace components, INAA was applied [9]. 100 mg of each sample was loaded into polyimide carrier capsule, together with flux monitors. The samples were irradiated using the fast-rabbit irradiation facility of the Budapest Research Reactor for 180 s with 5.3×10^{13} cm^{-2} s^{-1} neutron flux. The samples were measured in a low-background counting chamber applying the zero dead time mode of ORTEC acquisition system.

Complementary XRF measurements were carried out using a handheld XRF analyser Innov-X Delta Premium [10]. Alloy Plus settings were applied, even though this mode of the instrument does report the As content. The X-ray spot was 3 mm in diameter, therefore 5 repetitions were done on both (polished and rear) sides of the alloy samples in order to meet the tolerances specified in the certificate. The composition calculation was done by the built-in software of the device.

Results and Discussion

The applicability of the previously described specific techniques was tested on these certified reference copper alloys. Additional elements to the four major alloying components could be detected, such as Mn, Fe, Sb and Ni. In-beam activation analysis can deliver Cu, Mn, Sn, As, Sb and Zn data (the latter could be determined only as a minor component); high-resolution mode can analyze Sb better, lead-attenuated PGAA is most suitable to improve the Mn, Pb, Fe and Ni data. The combination of all these seems to be capable of improving the analytical merit of PGAA in bronze analysis, still in a non-destructive way. Thanks to different probing volumes of the neutron and X-ray based techniques, inhomogeneity problems, a bias between front and reverse sides can be revealed even for a certified reference material. With INAA, the only destructive method used in this study, the As, Zn, Sn, Sb and Ag content could be determined.

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