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Use of portable X-ray fluorescence instrument for bulk alloy analysis on low corroded indoor bronzes

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ABSTRACT

One of the most often used non-destructive methods for elemental analysis when performing field measurements on bronze sculptures is X-ray fluorescence (XRF) analysis based on portable instrumentation. However, when performing routine in-situ XRF analysis on corroded objects obtained results are sometimes considerably influenced by the corrosion surface products.

In this work the suitability of portable XRF for bulk analysis of low corroded bronzes, which were initially precisely characterized using sophisticated and reliable laboratory methods, was investigated and some improvements in measuring technique and data processing were given. Artificially corroded bronze samples were analyzed by a portable XRF instrument using the same methodology and procedures as when performing in-situ analysis on real objects. The samples were first investigated using sophisticated complementary laboratory techniques: Scanning Electron Microscopy, Proton-Induced X-ray Emission Spectroscopy and Rutherford Backscattering Spectrometry, in order to gain precise information on the formation of the corrosion product layers and in-depth elemental profile of corrosion layers for different aging parameters. It has been shown that for corrosion layers of up to ca. 25 μm a portable XRF can yield very accurate quantification results.

1. Introduction

Bronze artifacts are vulnerable to outdoor and indoor corrosion environments — from acid rain containing sulfates and carbonates in urban–industrial environment, to chlorides in marine environmental exposure, which are main cause of "bronze disease"[1,2]. Indoor corrosion environments (museums) are less aggressive, however, it has been reported that indoor corrosion seems to be affected by a greater number of air pollutants than the outdoor corrosion, especially when indoor sources of corrodents are present [3].

Chloride ions and sulfur compounds are the most common and important atmospheric corrosive agent, as has been reported [4]. Chloride ions can contribute to many corrosion problems associated with museum objects and can originate from different sources: from soil (archaeological bronzes), human perspiration or from materials and objects that contains chlorinated compounds.

In addition, bronze artifacts are usually very heterogeneous in composition, and thus various corrode forming and inhomogeneous corrosion product surface layers (patinas) [5]. To get full information of ongoing corrosion processes on the bronze surface it is essential to know composition (and structure) of the original bronze material (intrinsic corrosion parameters) [6].

Handling archaeological, historical or recent artistic bronzes demands some special conservation–restoration requirements when it comes to choosing a measurement method: (i) the method should be non-destructive (only small sample can be taken and it should not be destroyed during measurements) or (ii), preferably, the method should be non-invasive (measurements should be done on the object without sampling). This is especially important when it comes to small plastic bronze objects with fine ornamental or figural relievo.

Nevertheless, surface treatments prior to measurement (especially for techniques such as Proton-Induced X-ray Emission Spectroscopy (PIXE) or X-ray fluorescence Spectrometry, XRF) still include the washing of bronze in formic acid followed by glass bristle brushing [7] or abrading using a corundum burr [8] or a rotating rubber tip, impregnated with alumina grains as abrasive [9] for the micro-polishing.

Furthermore, it has been demonstrated by Swann et al. [8] that the mentioned surface treatment of copper archaeological objects does not insure that the area of analysis is corrosion free. They have noted that even bright-colored metal may not be sufficiently corrosion free to satisfy the needs of the techniques such as PIXE and XRF. From the standpoint of the restoration–conservation practice, any aggressive cleaning of these objects has been determined to be an unacceptable intrusion to the object. It is, therefore, a great advantage to be able to analyze bulk metal composition of bronze artifacts without disrupting patina formed on surface. When investigating bronze corrosion products, where the patina layers can reach thicknesses of 1–2 mm, and the X-ray penetration depth is limited to max. 100–200 μm, XRF can

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essentially be regarded to as a surface technique. Therefore, there is a reasonable concern that measurements can be affected by the presence of corrosion product layers which could not be removed due to conservation–restoration requirements. As it is known, the influence of corrosion processes on data reliability in some cases (archaeological bronzes with thick corrosion layers) can be significant [8]. However, if the thickness of the corrosion layer is very small, analytical techniques revealing the chemical composition of the bulk, like X-ray fluorescence, may be applied [10–13].

Of course, one should be aware that there may be other factors affecting the suitability of surface techniques such as XRF for bulk analysis, e.g. electrochemical deterioration of bronze surface exposed to the seawater [14], or particle size and surface irregularity effects [15], but here we investigate only the effects due to corrosion. Only one technique, Prompt Gamma Activation Analysis, can provide the composition of the bulk of corroded metal [16], but the necessary decay time after activation involves additional problems.

The purpose of this work is to explore the contributions that quantitative elemental analysis using portable XRF can make (to resolve these questions) within the constraints that the analysis has to be totally non-invasive. We concentrate on the corrosive environmental processes which lead to the formation of a smooth, usually brown–reddish thin corrosion layers characterized as type I. corrosion processes [17]. These types of corrosion layers form usually in low aggressive conditions such as museum environment or other indoor environments.

The samples were first investigated using sophisticated and reliable laboratory methods: Scanning Electron Microscopy (SEM), micro-PIXE and Rutherford Backscattering Spectrometry (RBS) in order to gain precise information on the formation of the corrosion product layers and in-depth elemental profile of the corrosion layer. Precise characterization of the corrosion layers was essential for exact interpretation of XRF spectra which allowed assessment of capability of portable XRF equipment for the quantitative bulk analysis of corroded bronze objects. The possibilities and limitations of micro-XRF portable spectrometer in the analysis of low corroded bronze artifacts are also discussed.

2. Materials and methods

CuSn6 binary bronze alloy was chosen as it is commonly used for artistic castings. The bronze CuSn6 coupons, sized 5.0 × 3.0 × 0.3 cm, were cut out from the standard certificated alloy (Cu 93.66 wt.%; Sn 6.10 wt.%; P 0.11 wt.%; Zn 0.10 wt.%; Fe 0.02 wt.%; and Pb 0.01 wt.%). Corrosion layers were formed artificially by immersion in 0.012 M sodium–chloride solution (0.7 g/l NaCl aqueous solution) simulating chloride corrosion environment for a specified period of time (longest immersion time was 60 days). In this way we were able to get well formed and defined corrosion layers. Solution of 0.012 M NaCl was chosen to simulate the type of pollutants found in museum environments [18]. Coupons were taken out every 24 h successively for a period of 1 to 60 days, dried and stored in desiccator. Prior to immersion, the coupons were mechanically treated with P 800 abrasive paper, then polished with P 1200 paper, degreased with ethanol, immersed in 10% (wt) H2SO4 for 3 min and finally dried at room temperature. All corrosion layer formation experiments were carried out in a 1 dm^3 laboratory vessel, at room temperature (25 ± 1 °C). The volume-to-surface specimen area was 20 $mL\ cm^{-2}$ according to the ASTM G 31 (1990) standard [19].

The Philips XL 30 scanning electron microscope (SEM) was used to present secondary electron images of the samples surfaces — related images show surface morphology and we have not performed Energy Dispersive X-ray Spectroscopy analysis since the penetration depths of the incoming electrons are such that the related X-ray depth information is just at the level of about one micrometer.

PIXE and RBS measurements were performed using 2 MeV proton beam from the 1.0 MV Tandetron electrostatic accelerator at the Ruđer Bošković Institute (RBI) in Zagreb. The measurements were performed at the general purpose ion beam analysis chamber, and at the ion microbeam. At the general purpose ion beam analysis end-station PIXE spectra were recorded by two solid state silicon detectors. The detector dedicated for recording higher energy parts of PIXE spectra is 80 mm^2 Canberra Si (Li) detector with rather large working solid angle (0.03 sr). At the same time, low energy parts of PIXE spectra were detected by 10 mm^2 Ketek SDD detector having 8 μm Be window and small solid angle (0.0005 sr), with the installed permanent magnet system for deflection of backscattering protons to prevent their detection by the SDD detector. Si (Li) detector is positioned at 135° scattering angle in horizontal plane, while SDD detector is positioned at 150° scattering angle in vertical plane. An RBS detector (0.01 sr) installed in vertical plane at the scattering angle of 165° was used to record proton backscattered spectra. The accelerated proton beam coming from the accelerator into the end-station was collimated by the set of circular collimators to the diameter of 3 mm. Data from detectors were collected by using conventional charged particle spectroscopy chain connected to the homemade multiparameter data acquisition and analysis system SPECTOR [20]. Measured elastic backscattering spectra were analyzed by using reliable and well known ion beam analysis and simulation software SIMNRA [21]. For the analysis we used evaluated elastic backscattering cross sections for 12C(p,p)12C and 16O(p,p)16O calculated using the on-line SIGMACALC calculator [22] for the scattering angle of 165°. Measured PIXE spectra were analyzed using PIXE analysis software GUPIXWIN, the Windows version of the well known and reliable GUPIX software [23].

At the RBI ion microbeam facility [24], 2 MeV proton beam of about 50 pA current was focused to μm dimensions. The beam was scanned over the samples by the computer-controlled scan generator. The copper mesh with repetition of 25 μm was used to check the beam diameter and to adjust the scanned area to 50 × 50 μm^2. Areal and lateral scans over the samples were performed to investigate the corrosion layers. For this purpose a small specimen cut from samples after 0, 14 and 26 days of immersion was embedded in epoxy resin and polished with paper grade P1200 in order to obtain clearly visible cross sections. The proton beam used for scanning was focused to 2.5 μm. The collection time for each two-dimensional (2D) elemental map was about 20 min. 2D elemental maps for copper and tin were created using the homemade SPECTOR data acquisition and analysis software. Penetration depth of 2 MeV protons in Cu is about 18.3 μm and 27.5 μm in CuO (calculated by SRIM code). Proton microbeam X-ray elemental images presented were taken on the sample cross sections. During the scanning the proton beam was passing through the pure Cu matrix or at the surface through the corrosion layer matrix (mainly Cu oxides). RBS measurements were taken with the surface of the samples being perpendicular to the beam (i.e. the beam was first passing through the Cu oxide layers and fully stopped in Cu bulk).

The samples were then investigated using a portable XRF instrument, which was developed at the Laboratory of the Academy of fine arts in Zagreb. It consists of a 50-kV Rh excitation tube, a Peltier-cooled silicon drift detector with energy resolution of 145 eV at the Mn $K\alpha$ excitation line. Depending on the analytical needs, the device can provide either mili or micro X-ray beam for sample excitation, by employing a motorized collimator interchanger to switch between a pinhole collimator (spot size ca. 1.5 mm) and a polycapillary lens (spot size ca. 45 μm). The operating parameters for tube voltage and anode current during the measurements were set to 40 keV and 150 μA, respectively, and the acquisition real time was 200 s. The diameter of the beam was set to 1.5 mm. Quantitative analysis of the XRF spectra was performed using the XRF-FP software from Amptek, USA, based on the fundamental parameter approach. To minimize errors in quantitative analysis due to improper matrix X-ray absorption correction a calibration of individual elemental sensitivities was performed. The calibration coefficients were obtained from a measurement of a known CuSn6 reference material.