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Analytical Note

Minimally-invasive Laser Ablation Inductively Coupled Plasma Mass Spectrometry analysis of model ancient copper alloys

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ABSTRACT

This work describes an evaluation of a strategy for multi-elemental analysis of typical ancient bronzes (copper, lead bronze and tin bronze) by means of laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS).The samples originating from archeological experiments on ancient metal smelting processes using direct reduction in a 'bloomery' furnace as well as historical casting techniques were investigated with the use of the previously proposed analytical procedure, including metallurgical observation and preliminary visual estimation of the homogeneity of the samples. The results of LA-ICPMS analysis were compared to the results of bulk composition obtained by X-ray fluorescence spectrometry (XRF) and by inductively coupled plasma mass spectrometry (ICPMS) after acid digestion. These results were coherent for most of the elements confirming the usefulness of the proposed analytical procedure, however the reliability of the quantitative information about the content of the most heterogeneously distributed elements was also discussed in more detail.

1. Introduction

A chemical analysis plays the key position in archeometric investigations [1], providing unique information about the studied artifact. Due to the unique cultural and material value of historical objects, studies of them require a specific approach for planning and performing investigations. Archeometric studies cannot be used routinely and there is a common need to apply a number of different physical and chemical methods of analysis. The specificity of archeological samples requires development of the most appropriate procedures and adoption of a methodology of measurements individually fit for each artifact. The demands for the best analytical techniques to elemental analysis of archeological objects have been reviewed by Resano et al. [2]. Minimal-invasive or non-destructive multielemental/isotopic techniques are preferred with respect to preservation of ancient objects [3]. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) is one of the methods of choice for the analysis of historical objects. However, since LA-ICPMS implies local sampling with crater sizes of typically 10 to 300 μm, the accuracy and precision should be considered especially for heterogeneously distributed elements [4].

The chemical composition of ancient copper alloys is very often considered to be pure copper, tin and lead bronzes, although it can be variable [5–8]. The metallurgical microstructure of ancient copper artifacts strongly depends on the main components of different copper alloys [4] and is reflected in their high heterogeneity [8]. Homogeneity of investigated materials is a major prerequisite and hence crucial for spatially resolved LA-ICPMS analysis and a representativeness of obtained data. Therefore a microscopy inspection of all samples by OM was recommended by Walaszek at al. [4] to collect the information about their heterogeneity and eventual need for adaptation of the LA-ICPMS analytical procedure, depending on the sample properties. LA-ICPMS was generally proposed to be useful for the analysis of metal objects as it allows representative sampling of the different copper alloys which reduces damage of samples [4]. This procedure was used in the actual project to evaluate it with respect to the elemental composition, heterogeneity and metallographic morphology of model copper alloys originating from archeological experiments on ancient metal smelting processes.

2. Materials and methods

2.1. Instrumentation

Optical microscope (Axiovert 100A, Zeiss, Germany) with CCD camera (Leica DC500) and scanning electron microscope (Leo 1455, Zeiss, Germany) with EDX detector (Model 7353, Oxford Instruments, England) were used for metallographic analysis of the samples [4]. The SEM images were collected both in secondary electron (SE) and

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back scattered electron (BSE) modes. The obtained images were analyzed with ImageJ — Image Processing and Analysis public domain open source software (http://rsbweb.nih.gov/ij/) to characterize the dimensions and contribution of subsequent phases in the whole area of investigated alloys.

ICPMS (ELAN 6000, PerkinElmer SCIEX, Canada) was used for the determination of bulk elemental composition of samples after acid digestion. The elemental composition and distribution of major and trace elements were determined using a laser ablation system (LSX-200+, CETAC, USA) coupled to an inductively coupled plasma mass spectrometer (ELAN 9000, PerkinElmer SCIEX, Canada). An LSX-200+ system at 266 nm UV laser (Nd-YAG, solid state, Q-switched) with a maximum energy of up to 6 mJ/pulse and pulse repetition rate from 1 to 20 Hz with a viewing CCD camera system was used for laser ablation. All the instruments were tuned daily and operated in their standard modes. The operating conditions are summarized in Table 1.

2.2. Chemicals and standards

Nitric acid (65% w/w) and hydrochloric acid (30% w/w) Suprapur® quality were obtained from Merck (Merck GmbH). For ICPMS calibration the calibrating standard solutions were prepared with the multi-element standard Merck IV (Merck, Germany) and single-element stock solutions (Alfa Aesar, Germany). The solutions were diluted with 18 MΩ/cm deionized water, prepared with a high purity water device "MilliQ Gradient A" (Millipore AG, Switzerland). All chemicals used were purchased in high purity quality [4].

2.3. Reference materials

The selected reference materials (RMs) were used for the calibration of LA-ICPMS according to the recommendations given in [4]. The composition of these RMs covers the typical composition range of the most common copper alloys representative for ancient artifacts. The tin bronze RM BAM 378 (Federal Institute for Materials Research and Testing, Germany, http://www.bam.de/en/index.htm) was selected as the first standard, while lead bronze RMs: BAS 50.03-4 and BAS 50.04-4 (Bureau of Analyzed Samples Ltd, United Kingdom, http://www.basrid.co.uk/bas.htm) were selected as the second and third standards, respectively.

2.4. Model samples of ancient copper alloys

Two types of model alloys were selected for this study: SL (smelted copper) and SW (sword fragments). *SL* and *SW* originated from an experimental archeological study on ancient metal smelting processes and historical casting techniques, concerning identification of raw material influences, or specific manufacturing techniques [9]. The samples of *SL* and *SW* can be used for studies of specific corrosion or conservation experiments, because their metallographic structures and chemical composition are representative for typical ancient bronze artifacts (Fig. 1).

2.5. Sample preparation

The same samples were used for the metallographic investigations and subsequent XRF and LA-ICPMS measurements. For the investigations samples were embedded in the resin (Araldite BY 158 Epoxy resin plus Aradur 21 hardener, Huntsman International LLC, http://www.huntsman.com/advanced_materials/), grinded with the use of SiC abrasive paper and polished with the use of monocrystalline diamond suspensions (MetaDi Fluid, Buehler, USA, http://www.buehler.com/productinfo/consumables/pdfs/METADI.pdf) as described in [4]. The prepared samples were cleaned by sonification in acetone (10 min) and in ethanol (10 min), air-dried and stored in a desiccator [4].

The second set of samples was prepared for ICPMS investigations. Sample chips (with mass about 30 mg) were collected from the copper model alloys with the use of 4 mm steel drill. Samples were digested with 4 ml of *aqua regia* (30% HCl, 65% HNO_3 3:1 v/v, Merck, Germany) [10] on a hot plate for about 0.5 h and subsequently analyzed by ICPMS after cooling and filling up to 25 ml with a deionized water. Prior to analysis samples were also spiked with Rh as an internal standard. Blank digestion samples were prepared following the same procedure.

2.6. LA-ICPMS procedure

A single spot ablation ($\phi = 200$ μm) from 5 independent sampling areas was used during calibrating procedure as well as other LA-ICPMS measurements of different ancient bronze samples. Transient signals were recorded for the following isotopes: ^{57}Fe, ^{59}Co,^{61}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{109}Ag, ^{118}Sn, ^{121}Sb, ^{207}Pb and ^{209}Bi. For quantification of the total element contents, an external multi standard calibration and linear through zero calibrating curves were calculated from the averaged data collected for the following standards: BAM 378, BAS 50.03-4 and BAS 50.04-4, according to the recommendations given in [4]. The value obtained by XRF for the Cu content in each particular sample was then used for the LA-ICPMS data calculation.

3. Results and discussion

This study was carried out to validate the previously proposed LA-ICPMS procedure for the micro-invasive analysis of archeological

Table 1
Operating parameters of LA-ICPMS and ICPMS instrumentations.

Operating parameters	LA-ICPMS	ICPMS
RF power	1050 W	1300 W
Plasma Ar gas flow rate	15 L/min	13 L/min
Auxiliary Ar gas flow rate	1 L/min	1.1 L/min
Ar carrier gas flow rate	1 L/min	0.85 L/min
Sampler/skimmer cone: (Ni)	1.1 mm/0.8 mm	1.1 mm/0.8 mm
Sweeps/reading	1	30
Readings/replicate	300	1
Replicates	1	3
Dwell time	10 ms	50 ms
Mode	Peak hopping (1 point per mass)	Peak hopping (1 point per mass)
Laser operating parameters (spot mode)		
Wavelength		266 nm
Output energy		4.8 mJ
Pulse frequency		10 Hz
Beam diameter		200 μm