

Calibration and detection limits of homemade ED-XRF system in the analysis of silver-copper alloys

Aneta Maria Gójska*, Ewelina Agnieszka Miśta-Jakubowska

National Centre for Nuclear Research, ul. A. Soltana 7, 05-400 Otwock, Poland

ARTICLE INFO

Keywords:

ED-XRF
Minimum detectable limit
Calibration method
Archaeometry

ABSTRACT

Energy dispersive X-ray fluorescence (ED-XRF) compact system was used to analyze silver-copper alloys. The X-ray tube developed at the National Centre for Nuclear Research (NCBJ) in Otwock, Poland, was used as an X-ray source and Amptek SDD spectrometer as a detector. The ESPI Metal® reference Ag-Cu alloys were used as calibration samples, allowing for estimation of a limit of detection, a limit of quantification and a minimum detectable limit. The elemental content were determined by using the fundamental parameter method (FP). The experimental data concerning the limitations for Ag and Cu detection showed that the X-ray system developed at the NCBJ with transmission type compact X-ray tube with silver anode operating up to 50 kV/30 μA and Amptek SDD spectrometer is an effective tool for chemical composition analysis of historical coins and can be successfully applied in archaeometry *in situ*. To demonstrate it two silver-copper Polish coins from 19th and early 20th centuries were examined. The elemental content was determined by using FP method, “silver peak area to copper peak area ratio (par) vs. silver concentration to copper concentration ratio (ccr)” calibration method, and Casting approximation. The obtained results showed the system designed at the NCBJ gave comparable values for determining the concentration when using the FP method and the empirical approaches.

1. Introduction

The X-ray fluorescence (XRF) is one of the most useful research methods used for elemental content determination of materials and has a wide range of applications in archaeology [1–14], medicine [15–17], environmental science [18,19] and industry [20]. The elemental content in the studied material can be identified as based on X-ray emission of specific atoms. The concentration of a specific element can be determined by using the relationship between the characteristic line intensity and the concentration of element in the sample. The determination of the elemental composition of material is one of the primary interests from the archaeological point of view. Thus, the analytical X-ray spectrometry techniques are often used in the art and cultural heritage research [6,21–23].

Since the XRF method is non-destructive, it gives among the others an opportunity to analyze the historical coin composition [1–3,5,7–11,24–31]. The analysis of elemental composition of coins can give important information about mining [1,2], minting techniques [3] and economic and political situation in the region of interest [3,4] at specific time. A lot of research has been performed using X-ray tubes [1,2,5,8–14,25], various radiation sources [3,4], as well as protons (PIXE) [26,32,33] and electrons (SEM-EDX) [7,34,35]. The X-ray tubes

[1,2], as well as radioactive sources such as americium (^{241}Am) [3,23] and plutonium (^{238}Pu) [4] were used to excite the atoms and X-ray fluorescence could then be registered.

Quantitative analysis of samples requires applying adequate theoretical methods or empirical approaches. In quantitative XRF analysis, the measured fluorescent intensities are converted into the elemental concentrations. There are several methods based on the theoretical relationship between the intensities and concentration of elements, among others: the fundamental parameters (FP) method [36–38], Casting approximation [39,40], “par-to-ccr” calibration [41,42]. These three quantitative evaluation methods were used to determine the elemental composition analysis of three Polish historical coins.

In the XRF elemental composition analysis, the possibilities and limitations of XRF system are crucial for the determination of the sample base alloys and to the verification whether the obtained results are consistent. One of the key parameters determining the lowest possible amount of the element that can be detected is the minimum detectable limit (MDL). A wide range of measurements of MDL were made by Cesareo et al. [5]. They tested MDL for Zn (the atomic number of Zn is 30 and it is close to Cu: Z = 29) and Sn (Z = 50) for detectors and X-ray tubes of different manufacturers at measurement time set to 300 s. The MDL for Zn was found to be between 100 and 300 ppm for EIS X-

* Corresponding author.

E-mail address: Aneta.Gojska@ncbj.gov.pl (A.M. Gójska).

ray tube with W and Pd anode operating at 35 kV and anode current between 0.02 mA and 0.4 mA, and with various detectors (Amptek SDD, EIS-Ketek and Rontek SDD XFlash). The MDL for Sn was found to be between 250 and 1500 ppm for these systems. The MDL for X-ray tube made by Italstructures with W anode and operating at higher voltage—60 kV—and current from 0.5 mA to 1.5 mA and Ketek SDD detector improved MDL to 50 ppm. The best result, for EIS X-ray tube operating at 40 kV and 0.2 mA and Amptek SDD detector, gave 1370 ppm for Zn. All these systems were used with collimators (2–6 mm). In Ref. [6], Guerra et al. presented the MDL for portable XRF spectrometer containing Eclipse IV Amptek X-ray tube with Rh anode (operating with 45 kV and 50 μ A) a collimator which gave 5 mm beam diameter and Amptek SDD, Amptek Si-Pin and Vortex SDD detectors. The authors presented MDL for wide range of elements for standard reference materials for acquisition time set to 1800 s. For light material like Orchard Leaves (NBS-1571) the MDL of copper was found to reach 6 ± 1 ppm for Amptek SDD and 2 ± 1 for Amptek Si-Pin detectors. For heavier material like brass (NBS-1105) it was 93 ± 9 ppm for Amptek SDD and 335 ± 24 for Amptek Si-Pin detectors.

In this paper quantitative analysis of two-component silver-copper alloys was carried out by use of ED-XRF system designed at the NCBJ. Generally, a good agreement between different analytical values of concentration was obtained, confirming accuracy of the new system. Another aim of this research was to check the utility of the novel ED-XRF system. Thus, the use of the capabilities and minimum detectable limit of Ag and Cu of the ED-XRF method is presented.

2. Experimental

2.1. Method

The ED-XRF system presented here was used to study X-ray spectra of selected historical Polish coins. Each studied sample has undergone irradiation induced by a compact X-ray tube. The X-ray radiation from the X-ray tube can lead to the ionization of K-shell of elements in a specific sample. The electron transition from higher shell (L or M) fills the hole in the K-shell and initiates the $K\alpha$ and $K\beta$ transitions that can be observed in spectra as characteristic X-ray lines. In the ED-XRF measurements, the X-ray generator designed and built at the NCBJ in Otwock-Świerk, Poland was used. The compact X-ray generator was constructed in the transmission X-ray tube technology. The generator consisted of two subassemblies: (1) electronics (power supply-control unit) and (2) X-ray tube. The power supply-control unit was powered by external power supply with 12 V DC and up to 1 A. The accelerating voltage and beam current could be smoothly adjusted. The heart of X-ray tube was an electron gun. The electron gun used in the X-ray tube had been designed and constructed at the NCBJ. It consisted of control, accelerating and focusing electrodes, anode, the output of the deflection system and electron beam (Fig. 1).

The control electrode was designed to control the intensity of the electron stream. The control took place by means of voltage supplied between the control electrode and the cathode. The negative voltage of

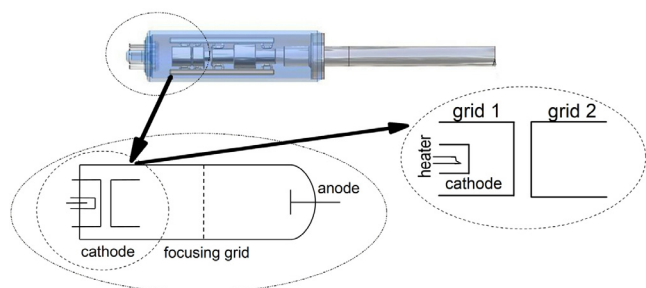


Fig. 1. Schematic drawing of the X-ray tube electrodes.

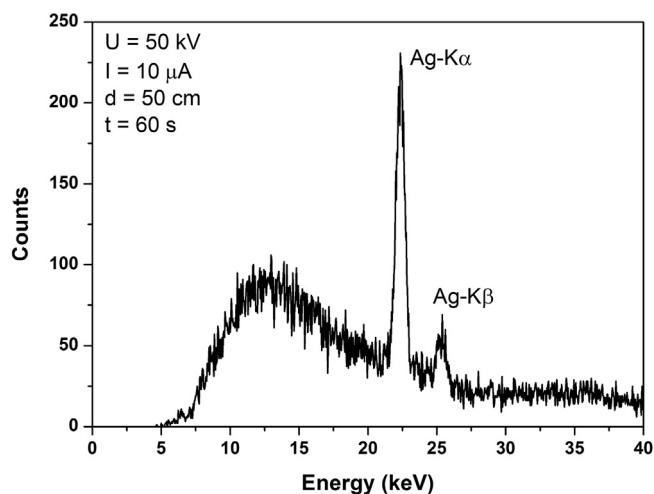


Fig. 2. Emission spectrum of the X-ray tube operating with 50 kV and 10 μ A measured during $t = 60$ s and at a distance $d = 50$ cm between X-ray source and detector.

control electrode promoted the concentration of electron tracks, thanks to which they moved towards one point. The accelerating electrode interacted with the electrons pulling them out of the space in front of the cathode and gave them higher velocity. In addition, along with the control electrode, it focused the electron tracks. The focusing electrodes work on the principle of the lens, concentrating the electron stream. The first anode was located after the accelerating electrode. High voltage of anode was applied to accelerate electrons so that the electrons moved further with higher velocity. The focused electron beam bombarded the silver anode target generating X-ray radiation (Fig. 2). The silver anode had been sputtered on beryllium. The focal spot of the beam was less than 0.5 mm. The X-ray generator was compact and weighted 0.835 kg and was 430 mm in length. Diameter of power supply-control unit was 55 mm. The anode component was 190 mm long with diameter 8 mm, while the target diameter was 5 mm.

The XRF spectrum of studied samples was induced by X-ray tube irradiation on its whole surface to obtain the average value of the elemental composition. The authors believe this may be an important advantage in comparison with other commercially available XRF systems that irradiate very small part of the studied sample. The X-ray generator was operated with anode voltage and current equal to 50 kV and 30 μ A, respectively. The fluorescence spectra of coins were registered with Amptek SDD detector. The measured energy resolution at 5.9 keV value was found to be 152.9 ± 0.3 eV. The distance between X-ray source and measured coins (SC) and between coins and detector (CD) was set to 23 cm and 24 cm, respectively (Fig. 3). The incident angle was 90° and XRF was registered at 45°. The energy spectra were analyzed by Amptek ADMCA multi-channel analyzer.

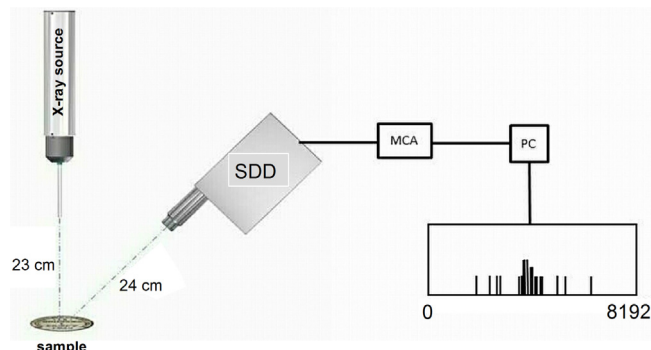


Fig. 3. Experimental setup of the XRF system.

Download English Version:

<https://daneshyari.com/en/article/8039021>

Download Persian Version:

<https://daneshyari.com/article/8039021>

[Daneshyari.com](https://daneshyari.com)