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Silver and tin plating as medieval techniques of producing counterfeit coins and their identification by means of micro-XRF

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HIGHLIGHTS

- Tiny remains of plating on the surface of coins were recognized with micro-XRF.
- More techniques of counterfeiting of coins were revealed.
- The determined low fluorescence ratio Kα/Kβ of copper was an evidence of plating.

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ABSTRACT

Archaeological surveys and metal detector prospecting yield a great amount of coins from the medieval period. Naturally, some of these are counterfeit which an experienced numismatist can determine without using chemical methods. The production of counterfeit coins in the middle ages took place in castles, caves or other remote areas where waste from this activity can still be found today – copper sheets, technical ceramics and counterfeit coins. Until recently, it has been assumed that medieval counterfeit coins are made by silver-plating copper blanks using an amalgam. However, the performed analyses reveal that there are many more techniques of counterfeiting of coins. Other techniques were based on e.g. tin amalgam plating of the blanks or alloying so-called white metal with silver-like appearance from which the coins were minted. Current chemical analyses indicate that the coins were often tinned by hot dipping with no amalgamation. Micro-X-ray fluorescence analysis has been chosen as a suitable non-destructive method to identify present chemical elements in investigated artifacts and to quantify their concentrations. In addition, a quick technique telltale the plating was applied. This technique utilizes the detected fluorescence ratio Kα/Kβ of copper, which is the main ingredient of a lot of historical metallic materials.

1. Introduction

Amalgam gold-plated metal artefacts are often objects of study in the field of cultural heritage. These artefacts are mostly found during archaeological digs or they occur as medieval or modern pieces of art. It is less known that amalgam silver-plating and tin-plating was used as well (Vlachou et al., 2002). Amalgam silver- and tin-plating can mostly be found in forgeries of medieval coins. In gold-plating (silver-, tin-plating) in fire, an amalgam of gold (silver, tin), i.e. metal dissolved in mercury, was used. Mercury evaporates by the heat and a thicker layer of gold, silver or tin forms on the surface of the metal-plated object. At present, this technique is not used due to toxicity of mercury.

Money counterfeiting workshops can mainly be found in castles, caves (the Koněprusy Caves), and possibly in other remote places in the Czech Republic. The workshop from about 1440 in the Skály Castle from where a large number of blanks and forgeries come from was the most preserved. In the second half of the 15th century, there was a workshop in the Křídlo Castle in eastern Moravia. Unique discoveries of waste from the equipment of a counterfeiting workshop in the Žampach Castle in eastern Bohemia were made also.

A fake coin can be recognized by means of a combination of elemental and microstructural analyses (Bartoli et al., 2011). X-ray fluorescence (XRF) analysis is one of the most frequently used analytical methods in investigating old metallic artefacts (Ferretti, 2014). Besides its non-destructivity, the XRF measurements and data analyses are usually quick and easy to perform (Milazzo and Cicardi, 1997). Till today, it has been successfully applied for characterization of mint and issue period of silver Roman coins

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(Gorghinian et al., 2013) or ancient and modern copper based fakes were identified (Giumlia-Mair and Lucchini, 2005). It seems that the counterfeit and original coins differ in concentrations of major and minor elements or the counterfeit coins were manufactured by means of coating of a metaling substrate. In this paper, we are dealing with the recognition of the plating of copper or copper-based alloys using XRF analysis.

There are several XRF methods/modalities available for coating identification. These include confocal XRF analysis, a method based on the internal X-ray ratios of present elements, and a depth-profiling technique based on at least two measurements performed under different experimental conditions. The depth-profiling with confocal XRF requires a special instrumentation including a micro-focus X-ray tube with focusing X-ray optics and collimating optics on the detector side of the confocal XRF setup. It is useful especially for analysis of paintings consisting of layers with different pigments (Kanngießer et al., 2004). An approximate depth distribution of an element can be also determined with its internal X-ray ratios (Kα/Kβ or Lα/Lβ) acquired with an X-ray detector (Cesareo et al., 2009). Thanks to different absorption of particular X-ray lines in a sample matrix, the deeper the element is located under the surface the more these ratios are affected. Last but not least, when two XRF measurements are performed under different conditions analysing different surface thicknesses, the coating can be identified also (Trojek et al., 2007) or (Trojek and Hložek, 2012).

2. Experimental setup and data analysis

The coins were analyzed with a micro-XRF system because some of them were damaged and only tiny remains of their plating were found. The micro-XRF device consists of a molybdenum anode X-ray tube (XOS, Power Flux PF) with polycapillary focusing optics (minimal FWHM ~15 μm for Mo-Kα line) and an SDD detector (Amptek, 25 mm^2 × 0.5 mm). The X-ray tube was operated at a maximum voltage of 50 kV and a maximum current of 1 mA. The detector was located approximately 10 mm from a sample. The geometry arrangement was 90°/45°. The acquisition time was 30 s for individual analyses and only 2 s per spot in the case of XRF scanning.

The goal of the XRF analysis was to identify present elements and to identify the coating. The approximate depth distribution of an element can be determined with its internal X-ray ratios acquired with an X-ray detector, e.g. Kα/Kβ. In this particular case, the Kα/Kβ ratio of copper, the major element in all specimens, was evaluated. This ratio is about 6–7 for most thick homogeneous copper alloys. Its value depends on attenuation of these copper K-lines in a matrix of a certain alloy. If such alloy or pure copper is plated, the ratio is reduced in most of cases. The X-ray fluorescence spectra were evaluated with the code WinAXIL that made it possible for us to determine the net peak areas of both Kα and Kβ lines independently of each other. The code MCNPX version 2.4.0 (MCNPX™ 2.4.0 user's manual, 2002) was used for calculating the Cu Kα/Kβ ratio for the given experimental conditions and the specimen composition.

3. Results

Several dozen old coins suspected to be counterfeits were analyzed with the micro-XRF system at the Czech Technical University in Prague but only three of them are discussed in detail in this article. These three coin specimens and their XRF spectra are shown in Figs. 1–6. These coins are supposed to be forgeries of the following coins:

Fig. 1. Photograph of coin #1 – forgery of the coin of Ferdinand I of Habsburg.

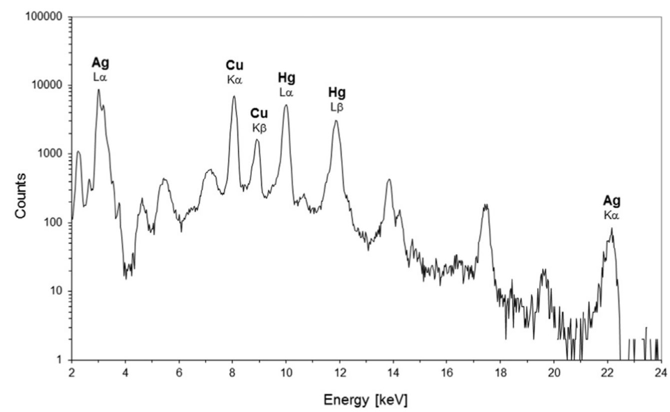

Fig. 2. XRF spectrum of coin #1; analyzed area marked in Fig. 1.

Fig. 3. Photograph of coin #2 – forgery of the pfennig of Ottokar IV of Styria.

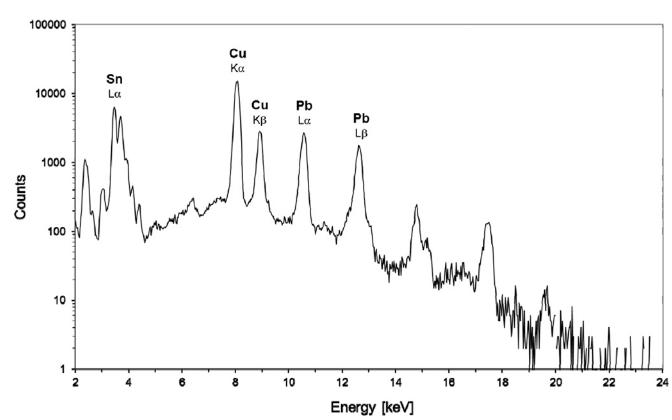

Fig. 4. XRF spectrum of coin #2; analyzed area marked in Fig. 3.

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